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A. PURE CHEMISTRY

ORGANIC CHEMISTRY AND BIOCHEMISTRY.

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1925. Vol. CXXVIII. Part I.

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## JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Bureau of Chemical Abstracts.

ABBREVIATED TITLE.	JOURNAL.
Abh. Böhm. Akad. . . .	Abhandlungen der Böhmischen Akademie.
Abh. Deut. Naturwiss. Med. Ver. Böhmen	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen.
Acta Phytochim. . . .	Acta Phytochimica.
Acta. Sci. Fennicae . . .	Acta Societatis Scientiarum Fennicae.
Agric. Bull. F. M. S. . .	Agricultural Bulletin of the Federated Malay States.
Agric. J. India . . . .	Agricultural Journal of India.
Agric. Res. Inst., Pusa, Rep. (Bull.)	Agricultural Research Institute, Pusa, Report and Bulletins.
Allgem. Z. Bierbrau. . .	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Amer. J. Bot. . . . .	American Journal of Botany.
Amer. J. Dis. Children . .	American Journal of Diseases of Children.
Amer. J. Pharm. . . . .	American Journal of Pharmacy.
Amer. J. Physiol. . . . .	American Journal of Physiology.
Amer. J. Publ. Health . .	American Journal of Public Health.
Amer. J. Sci. . . . .	American Journal of Science.
Amer. Min. . . . .	American Mineralogist.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Fís. Quím. . . . .	Anales de la Sociedad Española de Física y Química.
Analyst . . . . .	Analyst.
Annalen . . . . .	Justus Liebig's Annalen der Chemie.
Ann. Bot. . . . .	Annals of Botany.
Ann. di Bot. . . . .	Annali di Botanica.
Ann. Chim. . . . .	Annales de Chimie.
Ann. Chim. Analyt. . . .	Annales de Chimie Analytique et de Chimie Appliquée.
Annali Chim. Appl. . . .	Annali di Chimica Applicata.
Ann. Falsif. . . . .	Annales des Falsifications.
Ann. hyg. pub. méd. légale	Annales d'hygiène publique et de médecine légale.
Ann. Inst. Pasteur . . . .	Annales de l'Institut Pasteur.
Ann. Physik . . . . .	Annalen der Physik.
Ann. Physique . . . . .	Annales de Physique.
Ann. R. Staz. Chim. Agrar. Sperm.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
Ann. sci. Univ. Jassy . . .	Annales scientifiques de l'Université de Jassy.
Ann. Soc. Geol. Congo . .	Annales de la Société géologique de Belgique: Publications relatives au Congo Belge.
Apoth.-Ztg. . . . .	Apotheker-Zeitung.
Arb. Gebiet. Physik, Math., Chem.	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
Arch. Entw.-mech. Org. . .	Archiv für Entwicklungsmechanik der Organismen.
Arch. exp. Path. Pharm. . .	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Farm. sperim. Sci. aff.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Fisiol. . . . .	Archivio di Fisiologia.
Arch. Int. Med. . . . .	The Archives of Internal Medicine.
Arch. ital. Biol. . . . .	Archives italiennes de Biologie.

ABBREVIATED TITLE.	JOURNAL.
Arch. Med. Pharm. milit. .	Archives de Médecine et de Pharmacie militaires.
Arch. Néerland. . . . .	Archives Néerlandaises de sciences exactes et naturelles.
Arch. Néerland. physiol. .	Archives Néerlandaises de physiologie de l'homme et des animaux.
Arch. Pharm. . . . .	Archiv der Pharmazie.
Arch. Sci. phys. nat. . .	Archives des Sciences physiques et naturelles.
Arch. Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arkiv Kemi, Min., Geol. .	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J. . . . .	Astrophysical Journal.
Atti R. Accad. Lincei . .	Atti della Reale Accademia Nazionale dei Lincei.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Ist. Veneto Sci. .	Atti del Reale Istituto Veneto di Scienze, Lettere ed Arti.
Beitr. Min. Japan . . .	Beiträge zur Mineralogie von Japan.
Berg-Hüttenm. Rundsch. .	Berg- und Hüttenmannisches Rundschau.
Ber. . . . .	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges. . .	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges. .	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Oberhess. Ges. Natur- Heilkunde	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen.
Ber. Ohara Inst. landw. Forsch.	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
Ber. Sächs. Akad. Wiss. .	Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
Berlin. Klin. Woch. . .	Berliner Klinische Wochenschrift.
Bied. Zentr. . . . .	Biedermann's Zentralblatt.
Biochem. J. . . . .	Biochemical Journal.
Biochem. Z. . . . .	Biochemische Zeitschrift.
Bol. Acad. Nac. Ciencias, Cordoba	Boletín de la Academia Nacional des Ciencias, Cordoba.
Boll. Chim. farm. . . .	Bolletino Chimico farmaceutico.
Boll. Soc. Geol. Ital. . .	Bolletino della Società Geologica Italiana.
Boll. Soc. Med.-Chirurg. .	Bolletino della Società Medico-Chirurgica, Pavia.
Bot. Centr. . . . .	Botanisches Centralblatt.
Bot. Gaz. . . . .	Botanical Gazette.
Brass. Malt. . . . .	Brasserie et Malterie.
Brau- u. Malzind. . . .	Brau- u. Malzindustrie.
Braunkohle . . . . .	Braunkohle.
Brennstoff-Chem. . . .	Brennstoff-Chemie.
Brewers' J. . . . .	Brewers' Journal.
Brit. J. Phot. . . . .	British Journal of Photography.
Brit. Med. J. . . . .	British Medical Journal.
Buletinul Chim. . . . .	Buletinul Chimie.
Bul. Soc. Chim. România .	Buletinul Societății de Chimie din România.
Bul. Soc. Romane Stiin. .	Buletinul Societății Romane de Științe.
Bull. Acad. roy. Belg. . .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Assoc. Chim. Sucr. .	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Bureau of Standards	Bulletin of the Bureau of Standards (U.S.A.).
Bull. Com. Géol. Finlande	Bulletin de la Commission Géologique de Finlande.
Bull. Forest Exp. Stat. Meguro	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. gén. Thérap. . . .	Bulletin général de Thérapeutique médicale, chirurgicale, obstétricale.

ABBREVIATED TITLE.	JOURNAL.
Bull. Geol. d'Alsace . . .	Bulletin du Service de la Carte Geologique d'Alsace et de Lorraine.
Bull. Geol. Inst. Univ. Upsala	Bulletin of the Geological Institution of the University of Upsala.
Bull. Geol. Soc. Amer. . .	Bulletin of the Geological Society of America.
Bull. Geol. Survey, U.S.A.	Bulletin of the U.S. Geological Survey.
Bull. Geol. Survey, West Australia	Bulletin of the Geological Survey, West Australia.
Bull. Imp. Inst. . . .	Bulletin of the Imperial Institute.
Bull. Indian Ind. Lab. . .	Bulletin of Indian Industries and Labour.
Bull. Inst. Phys. Chem. Res., Japan.	Bulletin of the Institute of Physical and Chemical Research, Japan (Rikwagaku Kerkyujo Ihō).
Bull. Johns Hopkins Hospital	Bulletin of the Johns Hopkins Hospital.
Bull. School Mines and Met., Univ. Missouri . .	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. Pharmacol. . .	Bulletin des Sciences Pharmacologiques.
Bull. Soc. chim. . . .	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg. . .	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol. . .	Bulletin de la Société de Chimie biologique.
Bull. Soc. d'Encour. . . .	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
Bull. Soc. franç. Min. . .	Bulletin de la Société française de Minéralogie.
Bull. Soc. Franç. Phot. . .	Bulletin de la Société Française de Photographie.
Bull. Soc. Géol. Belg. . .	Bulletin de la Société Géologique de Belgique.
Bull. Soc. Ind. Mulhouse .	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Ind. Nord . . .	Bulletin de la Société Industrielle du Nord de la France.
Bull. Soc. Oural. Sci. Nat.	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
Bull. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. Wellcome Trop. Res. Lab.	Bulletin of the Wellcome Tropical Research Laboratory.
Cairo Sci. J. . . . .	Cairo Scientific Journal.
Canada Dept. Mines Publ. .	Canada Department of Mines Publications.
Canadian Chem. Met. . . .	Canadian Chemistry and Metallurgy.
Canadian Med. Assoc. J. . .	Canadian Medical Association Journal.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Casopis Math. Fysiky . . .	Časopis pro pěstování Matematiky a Fysiky.
Cellulosechem. . . . .	Cellulosechemie.
Centr. Min. . . . .	Centralblatt für Mineralogie, Geologie und Paläontologie.
Chem. App. . . . .	Chemische Apparatur.
Chem. Erde . . . . .	Chemie der Erde.
Chem. and Ind. . . . .	Chemistry and Industry.
Chem. Ind. . . . .	Chemische Industrie.
Chem. Listy . . . . .	Chemické Listy pro Vědu a Průmysl. Organ de la "Česká chemická Společnost pro Vědu a Průmysl."
Chem. and Met. Eng. . . .	Chemical and Metallurgical Engineering.
Chem. News . . . . .	Chemical News.
Chem. Trade J. . . . .	Chemical Trade Journal.
Chem. Umschau . . . . .	Chemische Umschau auf dem Gebiete der Fette, Oele, Wachse, und Harze.
Chem. Weekblad. . . . .	Chemisch Weekblad.
Chem.-Ztg. . . . .	Chemiker-Zeitung.
Chem. Zentr. . . . .	Chemisches Zentralblatt.
Chim. et Ind. . . . .	Chimie et Industrie.
Collegium . . . . .	Collegium.

ABBREVIATED TITLE.	JOURNAL.
Compt. rend. . . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Soc. Biol. . . . .	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Compt. rend. Trav. Lab. Carlsberg . . . . .	Comptes rendus des Travaux du Laboratoire Carlsberg.
Dept. Chem. S. Australia, Bull. . . . .	Department of Chemistry, South Australia, Bulletins.
Deut. med. Woch. . . . .	Deutsche medizinische Wochenschrift.
E.P. . . . .	English Patent.
Econ. Geol. . . . .	Economic Geology.
Econ. Proc. Roy. Dubl. Soc. . . . .	Economic Proceedings of the Royal Dublin Society.
Engineering . . . . .	Engineering.
Eng. and Min. J. . . . .	Engineering and Mining Journal.
Exper. Stat. Rec. . . . .	Experiment Station Record.
F.P. . . . .	French Patent.
Farben-Ztg. . . . .	Farben-Zeitung.
Fermentforsch. . . . .	Fermentforschung.
Feuerungstechnik . . . . .	Feuerungstechnik.
Flora . . . . .	Flora.
Földtani Közlöny . . . . .	Földtani Közlöny.
G.P. . . . .	German Patent.
Gas J. . . . .	Gas Journal.
Gas- u. Wasserfach . . . . .	Gas- und Wasserfach.
Gas World . . . . .	Gas World.
Gazzetta . . . . .	Gazzetta chimica italiana.
Geol. För. Förh. . . . .	Geologiska Föreningens i Stockholm Förhandlingar.
Geol. Mag. . . . .	Geological Magazine.
Gerber . . . . .	Gerber.
Giorn. Chim. Ind. Appl. . . . .	Giornale di Chimica Industriale ed Applicata.
Gummi-Ztg. . . . .	Gummi-Zeitung.
Handl. Vijft. Nat. . . . .	Handelingen van het Vijftende Natuur.
Hawaii Agric. Exp. Stat. Bull. . . . .	Hawaii Agricultural Experiment Station Bulletins.
Heart . . . . .	Heart.
Helv. Chim. Acta . . . . .	Helvetica Chimica Acta.
Indian J. Med. Res. . . . .	Indian Journal of Medical Research.
India-rubber J. . . . .	India-rubber Journal.
Ind. Eng. Chem. . . . .	Industrial and Engineering Chemistry.
Int. Rev. Sci. Pract. Agric. . . . .	International Review of the Science and Practice of Agriculture.
Int. Sugar J. . . . .	International Sugar Journal.
Iron Steel Inst. Carnegie Schol. Mem. . . . .	Iron and Steel Institute, Carnegie Scholarship Memoirs.
J.C.S. . . . .	Journal of the Chemical Society.
Jahrb. geol. Reichsanst. . . . .	Jahrbuch der geologischen Reichsanstalt.
Jahrb. Min. . . . .	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie.
Jahrb. Min. Beil.-Bd. . . . .	Neues Jahrbuch für Mineralogie, Geologie und Paläontologie, Beilage-Band.
Jahrb. Radioaktiv. . . . .	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot. . . . .	Jahrbuch für wissenschaftliche Botanik.
Jahresber. Ges. vaterl. Kultur . . . . .	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.
Japan. J. Med. Sci. . . . .	Japanese Journal of Medical Sciences.
Japan. J. Phys. . . . .	Japanese Journal of Physics.
Jernk. Ann. . . . .	Jernkontorets Annaler.
J. Agric. Res. . . . .	Journal of Agricultural Research.
J. Agric. Sci. . . . .	Journal of Agricultural Science.
J. Amer. Ceram. Soc. . . . .	Journal of the American Ceramic Society.

ABBREVIATED TITLE.	JOURNAL.
J. Amer. Chem. Soc. . . .	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc. . . .	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc. . . .	Journal of the American Medical Association.
J. Assoc. Off. Agric. Chem. . . .	Journal of the Association of Official Agricultural Chemists.
J. Biol. Chem. . . . .	Journal of Biological Chemistry.
J. Canad. Min. Inst. . . .	Journal of the Canadian Mining Institute.
J. Chem. Ind. Tokyo . . .	See Kōgyō-Kwagaku-Zasshi.
J. Chem. Met. Soc. S. Africa . . .	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chem. Soc. Japan. . . .	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)
J. Chim. phys. . . . .	Journal de Chimie physique.
J. Coll. Agric. Hokkaido . . .	Journal of the College of Agriculture, Hokkaido Imperial University, Japan.
J. Coll. Agric. Tokyo . . .	Journal of the College of Agriculture, Imperial University of Tokyo, Japan.
J. Coll. Eng. Tokyo . . .	Journal of the College of Engineering, Imperial University of Tokyo.
J. Coll. Sci. Tokyo . . .	Journal of the College of Science, Imperial University of Tokyo.
J. Exp. Med. . . . .	Journal of Experimental Medicine.
J. Franklin Inst. . . . .	Journal of the Franklin Institute.
J. Gen. Physiol. . . . .	Journal of General Physiology.
J. Genetics . . . . .	Journal of Genetics.
J. Geol. . . . .	Journal of Geology.
J. Geol. Soc. Tokyo . . .	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Hygiene . . . . .	Journal of Hygiene.
J. Indian Chem. Soc. . . .	Quarterly Journal of the Indian Chemical Society.
J. Indian Ind. Lab. . . . .	Journal of Indian Industries and Labour.
J. Indian Inst. Sci. . . . .	Journal of the Indian Institute of Science.
J. Ind. Hygiene . . . . .	Journal of Industrial Hygiene.
J. Inst. Brewing . . . . .	Journal of the Institute of Brewing.
J. Inst. Metals . . . . .	Journal of the Institute of Metals.
J. Inst. Petroleum Tech. . . .	Journal of the Institution of Petroleum Technologists.
J. Iron and Steel Inst. . . .	Journal of the Iron and Steel Institute.
J. Jap. Ceram. Assoc. . . .	Journal of the Japanese Ceramic Association.
J. Landw. . . . .	Journal für Landwirtschaft.
J. Marine Biol. Assoc. . . .	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res. . . . .	Journal of Medical Research.
J. Min. Agric. . . . .	Journal of the Ministry of Agriculture.
J. Path. Bact. . . . .	Journal of Pathology and Bacteriology.
J. Opt. Soc. Amer. . . . .	Journal of the Optical Society of America.
J. Pharm. Chim. . . . .	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther. . . .	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan . . .	Journal of the Pharmaceutical Society of Japan (Yakugakuzasshi).
J. Physical Chem. . . . .	Journal of Physical Chemistry.
J. Physiol. . . . .	Journal of Physiology.
J. Physiol. Path. gén. . . .	Journal de Physiologie et de Pathologie générale.
J. Phys. Radium . . . . .	Journal de Physique et le Radium.
J. pr. Chem. . . . .	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal. . .	Journal and Proceedings of the Asiatic Society of Bengal.
J. Proc. Roy. Soc. New South Wales . . .	Journal and Proceedings of the Royal Society of New South Wales.

ABBREVIATED TITLE.	JOURNAL.
J. Roy. Agric. Soc. . . .	Journal of the Royal Agricultural Society.
J. Roy. Army Med. Corps . .	Journal of the Royal Army Medical Corps.
J. Roy. Soc. West Australia	Journal of the Royal Society of West Australia.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Scot. Met. Soc. . . .	Journal of the Scottish Meteorological Society.
J. Soc. Arts . . . .	Journal of the Royal Society of Arts.
J.S.C.I. . . . .	Journal of the Society of Chemical Industry.
J. Soc. Dyers and Col. . .	Journal of the Society of Dyers and Colourists.
J. Soc. Leather Trades Chem.	Journal of the Society of Leather Trades Chemists.
J. Soc. Glass Tech. . . .	Journal of the Society of Glass Technology.
J. S. African Chem. Inst. .	Journal of the South African Chemical Institute.
J. Textile Inst. . . . .	Journal of the Textile Institute.
J. Usines Gaz . . . .	Journal des Usines à Gaz.
J. Washington Acad. Sci. .	Journal of the Washington Academy of Science.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
K. Svenska Vet. Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kentucky Exp. Stat. Bull.	Kentucky Experimental Station, Bulletin.
Keram. Rundsch. . . .	Keramisch Rundschau.
Kew Bull. . . . .	Kew Bulletin.
Kōgyō-Kwagaku-Zasshi . .	Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).
Kolloid Z. . . . .	Kolloid Zeitschrift.
Koll.-Chem. Beih. . . .	Kolloid-chemische Beihefte.
Kosmos . . . . .	Kosmos (Lemberg).
Kühn-Archiv . . . .	Kühn-Archiv.
Kunststoffe . . . .	Kunststoffe.
Lancet . . . . .	The Lancet.
Landw. Jahrb. . . . .	Landwirtschaftliche Jahrbücher.
Landw. Versuchs.-Stat. . .	Die landwirtschaftlichen Versuchs-Stationen.
Louisiana Bull. . . .	Louisiana Bulletin.
Louisiana Planter . . .	Louisiana Planter.
Lunds Univ. Arsskr. . . .	Lunds Universitets Års-skrift.
Math. és Termés. Ert. . .	Mathematikai és Természettudományi Ertesítő, Budapest.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Medd. on Grönland . . .	Meddelser on Grönland.
Med. Genees. Lab. Weltevreden	Mededeelingen uit het Geneeskundig Laboratorium te Weltevreden.
Med. Chron. . . . .	Medical Chronicle.
Med. Klinik . . . .	Medizinische Klinik.
Mem. Accad. Lincei . . .	Memorie della Reale Accademia dei Lincei.
Mem. Accad. Sci. Torino .	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Kyōtō . .	Memoirs of the College of Science, Kyōtō Imperial University.
Mem. Coll. Sci. and Eng. Kyōtō	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Dept. Agric. India .	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mem. Soc. Ing. Civ. . . .	Mémoires de la Société des Ingénieurs Civils de France.
Mem. Soc. Toscana Sci. Nat.	Memorie della Società Toscana di Scienze naturali residente in Pisa.
Mém. Poudres . . . .	Mémorial des Poudres.
Metall u. Erz . . . .	Metall und Erz.
Metallurgie . . . .	Metallurgie.



ABBREVIATED TITLE.	JOURNAL.
Metrop. Water Bd. Rep. . . . .	Metropolitan Water Board Reports.
Milch. Zentr. . . . .	Milchwirtschaftliches Zentralblatt.
Min. Mag. . . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
Mitt. Materialprüf. . . . .	Mittheilungen aus dem Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. med. Ges. Tokyo . . . . .	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Naturforsch. Ges. Halle . . . . .	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
Mitt. Path. Inst. K. Univ. Japan . . . . .	Mitteilungen aus dem pathologischen Institut der Kaiserlichen Universität zu Sendai, Japan.
Monatsh. . . . .	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Monatsh. Math. Physik . . . . .	Monatshefte für Mathematik und Physik.
Mon. Sci. . . . .	Moniteur Scientifique.
Month. Not. Roy. Astr. Soc. . . . .	Monthly Notices of the Royal Astronomical Society, London.
Münch. med. Woch. . . . .	Münchener medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen . . . . .	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Nature . . . . .	Nature.
Naturwiss. . . . .	Die Naturwissenschaften.
Naturw. Rdsch. . . . .	Naturwissenschaftliche Rundschau.
New York Agr. Expt. Sta. Bull. . . . .	New York Agricultural Experiment Station Bulletins.
New Zealand Dominion Laby. Rept. . . . .	New Zealand Dominion Laboratory Reports.
New Zealand J. Sci. Tech. . . . .	New Zealand Journal of Science and Technology.
Nippon Kwagaku Kwai Shi (J. Chem. Soc. Japan). . . . .	Nippon Kwagaku Kwa Shi (Journal of the Chemical Society of Japan).
Nova Acta Soc. Sci. . . . .	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nuovo Cim. . . . .	Il Nuovo Cimento.
Öfvers. Finska Vet.-Soc. . . . .	Öfversigt af Finska Vetenskaps-Societétens Förhandlingar, Helsingfors.
Oesterr. Chem.-Ztg. . . . .	Oesterreichische Chemiker-Zeitung.
Oversigt Danske Vid. Selsk. . . . .	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlingar.
Paper . . . . .	Paper.
Papierfabr. . . . .	Papier-Fabrikant.
Perf. and Essent. Oil Rec. . . . .	Perfumery and Essential Oil Record.
Per. spis. Sofia . . . . .	Periodicesko spisanie Sofia.
Petroleum . . . . .	Petroleum (German).
Pflüger's Archiv. . . . .	Archiv für die gesamte Physiologie des Menschen und der Thiere.
Pharm. J. . . . .	Pharmaceutical Journal.
Pharm. Weekblad . . . . .	Pharmaceutisch Weekblad.
Pharm. Zentr. . . . .	Pharmazeutische Zentralhalle.
Philippine J. Sci. . . . .	Philippine Journal of Science.
Phil. Mag. . . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans. . . . .	Philosophical Transactions of the Royal Society of London.
Phot. J. . . . .	Photographic Journal.
Phot. Korr. . . . .	Photographische Korrespondenz.
Physica . . . . .	Physica.
Physical Rev. . . . .	Physical Review.
Physikal. Z. . . . .	Physikalische Zeitschrift.
Proc. Amer. Acad. Arts Sci. . . . .	Proceedings of the American Academy of Arts and Sciences.

ABBREVIATED TITLE.	JOURNAL.
Proc. Amer. Phil. Soc. .	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc. .	Proceedings of the American Physiological Society.
Proc. Amer. Soc. Biol. Chem.	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Civ. Eng.	Proceedings of the American Society of Civil Engineers.
Proc. Amer. Soc. Testing Materials	Proceedings of American Society for Testing Materials.
Proc. Austral. Inst. Min. Met.	Proceedings of the Australasian Institute of Mining and Metallurgy.
Proc. Camb. Phil. Soc. .	Proceedings of the Cambridge Philosophical Society.
Proc. Durham Phil. Soc. .	Proceedings of the Durham Philosophical Society.
Proc. Eng. Soc. W. Pa. .	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Inst. Civ. Eng. .	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech. Eng. .	Proceedings of the Institution of Mechanical Engineers.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci. .	Proceedings of the National Academy of Sciences.
Proc. Nova Scotia Inst. Sci.	Proceedings of the Nova Scotia Institute of Science.
Proc. Phil. Soc. Glasgow .	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc. .	Proceedings of the Physical Society of London.
Proc. Physiol. Soc. .	Proceedings of the Physiological Society.
Proc. Roy. Inst. .	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad. .	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc. .	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin. .	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med. .	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania .	Proceedings of the Royal Society of Tasmania.
Proc. Sci. Assoc., Vizianagram	Proceedings of the Science Association, Maharajah's College, Vizianagram.
Proc. Soc. Exp. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine.
Proc. U.S. Nat. Mus. .	Proceedings of the United States National Museum.
Proc. verb. Soc. Toscana Sci. Nat.	Processi verbali Società Toscana di Scienze Naturali.
Pub. Fac. Sci. Univ. Masaryk.	Publications de la Faculté des Sciences de l'Université Masaryk (Spisy vydávané Přírodovědeckou Facultou Masarykovy University).
Pulp and Paper Mag. .	Pulp and Paper Magazine of Canada.
Quart. J. Geol. Soc. .	Quarterly Journal of the Geological Society.
Quart. J. Med. .	Quarterly Journal of Medicine.
Radium in Biol. Heilkunde	Radium in Biologie und Heilkunde.
Rec. Australian Mus. .	Records of the Australian Museum.
Rec. trav. bot. Néerland.	Recueil des travaux botaniques Néerlandaises.
Rec. trav. chim. .	Recueil des travaux chimiques des Pays-Bas.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett.	Rendiconti dell' Reale Istituto Lombardo di Scienze e Lettere.
Rep. Aust. Assoc. Sci. .	Report of the Australian Association for the Advancement of Science.
Rep. Brit. Assoc. .	Report of the British Association for the Advancement of Science.
Rev. chim. .	Revue chimique . . . Oficijelni organ udruženja Jugoslavenskih Kemičara.
Rev. gén. Bot. .	Revue générale de Botanique.
Rev. gén. Colloid. .	Revue générale des Colloïdes.
Rev. Gén. Mat. Col. .	Revue Générale des Matières Colorantes.

ABBREVIATED TITLE.	JOURNAL.
Rev. Mét. . . . .	Revue de Métallurgie.
Rev. Real Acad. Ciencias exact. Madrid	Revista de la Real Academia de Ciencias exactas, Fisicas y Naturales de Madrid.
Riv. Min. Crist. Ital. . . . .	Rivista di Mineralogia e Cristallografia Italiana.
Rocz. Chem. . . . .	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Sbornik Klubu Pri. . . . .	Sbornik Klubu Pfirodovědeckého (Prague).
Schweiz. Apoth. Ztg. . . . .	Schweizerische Apotheker Zeitung.
Schweiz. Chem.-Ztg. . . . .	Schweizerische Chemiker Zeitung.
Science . . . . .	Science.
Sci. Ind. Rep. Roure-Bertrand Fils	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Tôhoku Imp. Univ.	Science Reports, Tôhoku Imperial University.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Seifensied. Ztg. . . . .	Seifensieder Zeitung.
Sitzungsber. Akad. München	Sitzungsberichte der bayerischen Akademie der Wissenschaften zu München.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. Ges. Naturwiss. Marburg	Sitzungsberichte der Gesellschaft zur Beförderung der gesammten Naturwissenschaften in Marburg.
Sitzungsber. Heidelberger Akad. Wis.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Med. Naturwiss. Münster	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen Gesellschaft zu Münster-in-Westfalens.
Sitzungsber. Naturforsch. Ges. Rostock	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
Sitzungsber. phys. med. Ges. Erlangen	Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Erlangen.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Skand. Arch. Physiol. . . . .	Skandinavisches Archiv für Physiologie.
Smithsonian Miscell. Coll. . . . .	Smithsonian Miscellaneous Collections.
Soil Sci. . . . .	Soil Science.
South African J. Ind. . . . .	South African Journal of Industries.
South African J. Sci. . . . .	South African Journal of Science.
Sprechsaal . . . . .	Sprechsaal.
Stahl u. Eisen . . . . .	Stahl und Eisen.
Staz. sper. agr. ital. . . . .	Stazioni sperimentali agrarie italiane.
Strahlenther . . . . .	Strahlentherapie.
Suom. Tied. Toim. . . . .	Suomalaisen Tiedeakatemia Toimituksia.
Svensk Kem. Tidskr. . . . .	Svensk Kemisk Tidskrift.
Tech. Rep. Tôhoku Imp. Univ.	Technology Reports of the Tôhoku Imperial University, Sendai, Japan.
Tekn. Tidsk. . . . .	Teknisk Tidskrift.
Textilber. . . . .	Melliand's Textilberichte über Wissenschaft, Industrie und Handel.
Ther. Gegenw. . . . .	Die Therapie der Gegenwart.
Ther. Monatsh. . . . .	Therapeutische Half-Monatshefte.
Tonind.-Ztg. . . . .	Tonindustrie-Zeitung.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals . . . . .	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.

ABBREVIATED TITLE.	JOURNAL.
Trans. Ceram. Soc. . . .	Transactions of the Ceramic Society.
Trans. Faraday Soc. . . .	Transactions of the Faraday Society.
Trans. Inst. Min. and Met.	Transactions of the Institution of Mining and Metallurgy.
Tr. N. Eng. Inst. Min. and Met.	Transactions of the North of England Institute of Mining and Metallurgy.
Trans. New Zealand Inst. .	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Roy. Irish Acad. . .	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada . .	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin. . . .	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Soc. Sth. Africa	Transactions of the Royal Society of South Africa.
Tsch. Min. Mitt. . . . .	Tschermak's Mineralogische Mittheilungen.
U.S. Bureau of Mines, Bull. and Tech. Papers	United States Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau Plant Ind. . . .	United States Bureau of Plant Industry.
U.S. Comm. Rept. . . . .	United States Commerce Reports, Daily Consular and Trade Reports.
U.S. Dept. Agric. Bull. . . .	United States Department of Agriculture Bulletins.
U.S. Hyg. Labor. Bull. . . .	United States Hygienic Laboratory Bulletins.
U.S.P. . . . .	United States Patent.
Univ. Illinois Bull. . . . .	University of Illinois Bulletins.
Utah Agric. Coll. Exper. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Verh. Geol. Reichsanst. Wien	Verhandlungen der geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze	Verhandlungen der Gesellschaft deutscher Naturforscher und Aerzte.
Verh. Naturhist. med. Ver. Heidelberg	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
Verh. Naturhist. Rheinl. . .	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
Verh. Physiol. Ges. Berlin	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
Verh. Schweiz. Nat. Ges. . .	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
Vict. Mem. Mus. Geol. Survey, Canada	Victoria Memorial Museum Geological Survey of Canada, Bulletin.
Videnskab. Skrifter . . . .	Skrifter udgivne af Videnskabselskabet i Kristiania.
Wiener Klin. Woch. . . . .	Wiener Klinische Wochenschrift.
Wiss. Abhandl. Physikal.-Tech. Reichsanst.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Wiss. Veröff. Siemens-Konz.	Wissenschaftliche Veröffentlichungen aus dem Siemens-Konzern.
Wochbl. Papierfabr. . . . .	Wochenblatt für Papierfabrikation.
Woch. Brau. . . . .	Wochenschrift für Brauerei.
Yakugakuzasshi (J. Pharm. Soc. Japan).	Yakugakuzasshi (Journal of the Pharmaceutical Society of Japan).
Z. allg. Physiol. . . . .	Zeitschrift für allgemeine Physiologie.
Z. anal. Chem. . . . .	Zeitschrift für analytische Chemie.
Z. angew. Chem. . . . .	Zeitschrift für angewandte Chemie.
Z. anorg. Chem. . . . .	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol. . . . .	Zeitschrift für Biologie.
Z. deut. Geol. Ges. . . . .	Zeitschrift der deutschen Geologischen Gesellschaft.
Z. deut. Oel-Fett Ind. . . .	Zeitschrift der deutschen Oel- und Fett-Industrie.
Z. Elektrochem. . . . .	Zeitschrift für Elektrochemie.
Z. exp. Path. Ther. . . . .	Zeitschrift für experimentelle Pathologie und Therapie.
Z. ges. Brauw. . . . .	Zeitschrift für das gesamte Brauwesen.

ABBREVIATED TITLE.	JOURNAL.
Z. ges. exp. Med. . . .	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Schiess- u. Sprengstoffw. . . .	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. Hyg. . . .	Zeitschrift für Hygiene und Infektionskrankheiten.
Z. Immunit. . . .	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
Z. Instrument. . . .	Zeitschrift für Instrumentenkunde.
Z. Kryst. . . .	Zeitschrift für Kristallographie.
Z. Leder-Gerb.-Chem. . . .	Zeitschrift für Leder- und Gerberchemie.
Z. Metallk. . . .	Zeitschrift für Metallkunde.
Z. öffentl. Chem. . . .	Zeitschrift für öffentliche Chemie.
Z. Physik . . . .	Zeitschrift für Physik.
Z. physikal. Chem. . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Z. physikal. chem. Unterr. . . .	Zeitschrift für den physikalischen und chemischen Unterricht.
Z. physiol. Chem. . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. prakt. Geol. . . .	Zeitschrift für praktische Geologie.
Z. Sauerstoff Stickstoff Ind. . . .	Zeitschrift für Sauerstoff und Stickstoff Industrie.
Z. Spiritusind. . . .	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm. . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind. . . .	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Z. wiss. Mikrosk. . . .	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
Z. wiss. Phot. . . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie.
Z. Zuckerind. Cechoslov. . . .	Zeitschrift für Zuckerindustrie der Čechoslovakischen Republik.
Zellstoff u. Papier . . . .	Zellstoff und Papier.
Zentr. Bakt. Par. . . .	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Zentr. Zuckerind. . . .	Zentralblatt für Zuckerindustrie.

# ABSTRACTS

ISSUED BY THE

## BUREAU OF CHEMICAL ABSTRACTS.

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### A. PURE CHEMISTRY.

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#### PART I.

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#### Organic Chemistry.

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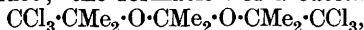
**Repetition Process for the Preparation of True Acetylenic Hydrocarbons.** M. BOURGUEL (*Compt. rend.*, 1924, **179**, 686—688).—The following method is applicable to the preparation of acetylenic hydrocarbons not obtainable by the other available methods. By treatment with sodamide, any true acetylenic hydrocarbon is converted into its sodium derivative, the sodium atom of which is replaceable by a methyl group by the action of methyl sulphate. The hydrocarbon thus obtained undergoes isomeric change when treated with sodamide:  $\text{CR}:\text{CMe} + \text{NH}_2\text{Na} = \text{CH}_2\text{R}:\text{C}:\text{CNa} + \text{NH}_3$ . The indefinite repetition of this process is limited only by the diminishing yields. By using *cyclohexylpropinene* as initial product, the author has prepared the following hydrocarbons, yields of 80—90% being obtained:  $\alpha$ -cyclohexyl- $\Delta^{\beta}$ -butinene,  $\text{C}_6\text{H}_{11} \cdot \text{CH}_2:\text{C}:\text{CMe}$ , b. p.  $79^\circ/17$  mm.;  $\alpha$ -cyclohexyl- $\Delta\gamma$ -butinene,  $\text{C}_6\text{H}_{11} \cdot [\text{CH}_2]_2:\text{C}:\text{CH}$ , b. p.  $70^\circ/17$  mm.;  $\alpha$ -cyclohexyl- $\Delta\gamma$ -pentinene, b. p.  $93^\circ/17$  mm.;  $\alpha$ -cyclohexyl- $\Delta^{\delta}$ -pentinene, b. p.  $84^\circ/16$  mm.;  $\alpha$ -cyclohexyl- $\Delta^{\delta}$ -hexinene, b. p.  $109$ — $110^\circ/17$  mm.;  $\alpha$ -cyclohexyl- $\Delta^{\epsilon}$ -hexinene, b. p.  $101^\circ/16$  mm. The substituted compounds are denser and more highly refractive than those with the  $:\text{CH}$  group; the latter give yellow precipitates with ammoniacal cuprous chloride and white, crystalline precipitates with alcoholic silver nitrate. Their sodium derivatives readily absorb carbon dioxide, giving the acids:  $\text{C}_6\text{H}_{11} \cdot [\text{CH}_2]_2:\text{C}:\text{C} \cdot \text{CO}_2\text{H}$ , m. p.  $57.5$ — $99^\circ(?)$ ;  $\text{C}_6\text{H}_{11} \cdot [\text{CH}_2]_3:\text{C}:\text{C} \cdot \text{CO}_2\text{H}$ , non-crystalline; and  $\text{C}_6\text{H}_{11} \cdot [\text{CH}_2]_4:\text{C}:\text{C} \cdot \text{CO}_2\text{H}$ , m. p.  $40$ — $41^\circ$ . T. H. P.

**Application of Röntgen Crystal Analysis to Questions of Structure of Organic Compounds.** H. MARK (*Ber.*, 1924, **57**, [B], 1820—1827).—Investigation of carbon tetraiodide shows that

the chemical molecule,  $\text{Cl}_4$ , exists in the lattice as a closed, spatially condensed group, so that in this instance the conceptions of structural organic chemistry are qualitatively confirmed and quantitatively extended by Röntgen analysis. The cubic modification of carbon tetrabromide, stable above  $46.91^\circ$ , likewise contains the chemical molecule as a spatially enclosed group in the lattice with the tetrahedral symmetry predicted from structural chemistry, whereas the occurrence of a double molecule,  $\text{C}_2\text{Br}_8$ , is observed in the lattice of the monoclinic-prismatic variety; the feeble bond between the molecules becomes ruptured above  $46.91^\circ$ , with the formation of two tetrahedral, symmetrical  $\text{CBr}_4$  molecules, which form a cubic lattice. Pentaerythritol exhibits less symmetry in its lattice than is expected from stereochemical considerations, but does not give any indication of the association of chemical molecules in the crystal. Analysis of carbamide shows the difference in magnitude of the main and subsidiary valencies, and indicates that the latter join the oxygen atoms of the different molecules. The presence of methyl groups in methyl- and *s*-dimethyl-carbamide weakens these subsidiary valencies in such a manner that they become less active as crystallisation forces. In the crystallisation of metaldehyde, 4 mols. of acetaldehyde unite to a symmetrical complex which is the unit of the crystal lattice. In acetaldehyde-ammonia, the largest group in the lattice consists of six chemical molecules, which assume the form of a hexagon. Analysis of hexamethylene-tetramine confirms quantitatively the structural formula of the substance. The chemical molecule forms an isolated group in the lattice; the directions of the main valencies are those demanded by stereochemistry. In benzene, hexachlorobenzene, and hexabromobenzene the benzene ring in the lattice appears to have only centric symmetry, instead of hexagonal symmetry required by structural chemistry; only the diagonally situated carbon atoms are therefore equivalent to one another, so that three types of carbon atoms are to be distinguished in the molecule. H. W.

**Electron Displacement in Carbon Compounds. I. Electron Displacement versus Alternate Polarity in Aliphatic Compounds.** H. J. LUCAS and A. Y. JAMESON (*J. Amer. Chem. Soc.*, 1924, 46, 2475—2482).— $\alpha$ -Bromobutane is converted completely and irreversibly into  $\beta$ -bromobutane in 80 hours at  $248^\circ$  (cf. Cuy, A., 1920, i, 361). The mechanism of this reaction, as well as that of the addition of hydrogen halides to unsaturated compounds, is discussed. It is concluded that electron displacement, rather than alternate polarities of carbon atoms, offers the better explanation of such reactions. F. G. W.

**tert.-Trichlorobutyl Alcohol and its Esters.** M. TAFKE (*Roczniki Farmacji*, 1924, 2, 99—107; from *Chem. Zentr.*, 1924, ii, 304).—Chloroform condenses readily with acetone in presence of potassium hydroxide at  $2-3^\circ$ . Orthoformic acid is formed as an intermediate product; the formation of a substance,



b. p.  $171^\circ$ , was detected. Trichlorobutyl alcohol was also obtained

conveniently by the Butlerow-Grignard reaction; the following derivatives were prepared: *acetate*, b. p. 190—191°; *benzoate* as an oil.

F. A. M.

**Primary  $\gamma$ - and  $\delta$ -Methylhexanols.** A. DEWAELE and A. WECKERING (*Bull. Soc. chim. Belg.*, 1924, **33**, 495—504).— $\beta$ -Bromopentane was condensed with ethyl sodiomalonate to *ethyl  $\alpha$ -methylbutylmalonate*, b. p. 244—246°/757 mm.,  $d_4^{20}$  0.9713,  $n_D^{20}$  1.4263. It was hydrolysed to  *$\alpha$ -methylbutylmalonic acid*, m. p. 88—89°, which lost carbon dioxide at 120°, giving  *$\beta$ -methylhexoic acid*, b. p. 212—213°/755 mm.,  $d_4^{20}$  0.9187,  $n_D^{20}$  1.4222; (*ethyl ester*, b. p. 176—177°/756 mm.,  $d_4^{20}$  0.8679,  $n_D^{20}$  1.4119) (cf. Ciamician and Silber, A., 1908, i, 277; 1913, i, 1356). The action of phosphorus trichloride on the acid produced  *$\beta$ -methylhexoyl chloride*, b. p. 163—164°/751 mm.,  $d_4^{20}$  0.967, which with excess of ammonia formed the *amide*, m. p. 97°, which was converted by phosphoric oxide into the *nitrile*, b. p. 171—172°/749 mm.,  $d_4^{20}$  0.8109,  $n_D^{20}$  1.4143. The latter substance was reduced with sodium and alcohol to  *$\beta$ -methylhexylamine*, b. p. 148—149°/756 mm.,  $d_4^{20}$  0.7787,  $n_D^{20}$  1.4257; its *oxamide*, m. p. 91—92°, and *phenylthiocarbamide* derivative, m. p. 42—43°, are described. Bouveault's method of reduction converted the ethyl  $\beta$ -methylhexoate into  *$\gamma$ -methylhexanol*, b. p. 168—169°/754 mm.,  $d_4^{20}$  0.8258,  $n_D^{20}$  1.4245; *naphthylurethane* derivative, m. p. 45—47°; *acetate*, b. p. 183—184°/754 mm.,  $d_4^{20}$  0.8743,  $n_D^{20}$  1.4156. By heating at 100° with hydrogen chloride under pressure, the alcohol was converted into  *$\alpha$ -chloro- $\gamma$ -methylhexane*, b. p. 150—152°/758 mm.,  $d_4^{20}$  0.8766,  $n_D^{20}$  1.4274;  *$\alpha$ -bromo- $\gamma$ -methylhexane* has b. p. 168—170°/758 mm. The alcohol was oxidised by chromic acid to  *$\beta$ -methylhexaldehyde*, b. p. 142—143°/755 mm.,  $d_4^{20}$  0.8203,  $n_D^{20}$  1.4122; *semicarbazone*, m. p. 108—109°.

$\beta$ -Bromobutane was converted into  $\beta$ -methylbutyl alcohol (yield 50%) by the method of Freundler and Damond (A., 1906, i, 2); methylene diisoamyl ether and  $\gamma\delta$ -dimethylhexane were formed as by-products. The alcohol was transformed by hydrogen bromide into  *$\alpha$ -bromo- $\beta$ -methylbutane*, which with ethyl sodiomalonate produced impure ethyl  $\beta$ -methylbutylmalonate, b. p. 250°/761 mm.,  $d_4^{20}$  0.9757,  $n_D^{20}$  1.42059, and this, treated with potassium hydroxide, gave  *$\beta$ -methylbutylmalonic acid*, m. p. 78°, and ethyl di- $\beta$ -methylbutylmalonate, b. p. 292°,  $d_4^{20}$  0.9426. By dry distillation of  $\beta$ -methylbutylmalonic acid there was obtained  *$\gamma$ -methylhexoic acid* (cf. Ciamician and Silber, *loc. cit.*), b. p. 217—218°/754 mm.,  $d_4^{20}$  0.9194,  $n_D^{20}$  1.4211; (*ethyl ester*, b. p. 183°/750 mm.,  $d_4^{20}$  0.8708,  $n_D^{20}$  1.40514; *chloride*, b. p. 167—168°/767 mm.,  $d_4^{20}$  0.9677; *amide*, m. p. 98°; *anilide*, m. p. 76.5°; *nitrile*, b. p. 180°/740 mm.,  $d_4^{20}$  0.8141,  $n_D^{20}$  1.41436. The nitrile was reduced to  *$\delta$ -methylhexylamine*, b. p. 152—153°/750 mm.,  $d_4^{20}$  0.7802,  $n_D^{20}$  1.42383; its *oxamide*, m. p. 73.5°, *phenylthiocarbamide*, m. p. 81°, and *naphthylcarbamide* derivatives, m. p. 110°, are described. Reduction of the ethyl  $\gamma$ -methylhexoate gave  *$\delta$ -methylhexanol*, b. p. 173°/761 mm.,  $d_4^{20}$  0.8239,  $n_D^{20}$  1.4219; *acetate*, b. p. 190°/757 mm.,  $d_4^{20}$  0.8740,  $n_D^{20}$  1.4186; *naphthylurethane* derivative, m. p. 50°.

F. M. H.



**Unsaponifiable Constituents (Higher Alcohols) of Shark and Ray Liver Oils.** IV. Y. TOYAMA (*Chem. Umschau*, 1924, **31**, 153—155; cf. A., 1924, i, 604).—The unsaponifiable constituents of the liver oils from *Chimaera mitsukurii* (Dean) consist chiefly of butyl, chimyl, and selachyl alcohols. The oils from *C. phantasma* (Jordan and Snyder) and *Squalus japonicus* (Ishikawi) yielded similar products. The unsaponifiable product from the oil from *S. wakiyae* (Tanaka) consists chiefly of selachyl and chimyl alcohols, with apparently traces of more highly unsaturated substances. The liver-oil of *Prionace glauca* (Linné) yields cholesterol in an almost pure state. None of the oils here mentioned contain any squalene. P. M.

**Carbonates of Ethylene Glycol and Related Compounds.** C. F. ALLPRESS and W. MAW (*J. Chem. Soc.*, 1924, **125**, 2259—2264).—*Dicarbomethoxyglycol*, b. p. 101°/3 mm., and *dicarbethoxyglycol*,  $\text{CO}_2\text{R}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}_2\text{R}$ , b. p. 249—250°/760 mm., 116—117°/2 mm., are obtained from glycol (1 mol.) and methyl or ethyl chloroformate (3 mols.) in chloroform solution, in presence of pyridine (3 mols.). On hydrolysis, both compounds yield ethylene glycol.

*Tricarbomethoxyglycerol*, b. p. 152°/1.5 mm., and *tricarbethoxyglycerol*, b. p. 168—169°/0.2 mm., are produced in an analogous manner, using 4 instead of 3 mols. of pyridine and chloroformic ester. Partial hydrolysis of tricarbethoxyglycerol by means of barium hydroxide leads to the formation of *dicarbethoxyglycerol*, b. p. 162—163°/0.5 mm.; further hydrolysis yields glycerol, but no indication of a monocarbethoxy compound. *Monocarbomethoxyglycerol carbonate*,  $\begin{array}{c} \text{CO}—\text{O} \\ | \quad \diagup \\ \text{O}—\text{CH}_2 \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}_2\text{Me}$ , m. p. 88°, is

produced when sodium hydroxide is employed instead of pyridine. The same substance can be obtained by the action of methyl chloroformate on the sodium derivative of glycerol, and this method is employed for the preparation of *monocarbethoxyglycerol carbonate*, b. p. 304—306°.

Ethyl tartrate, ethyl chloroformate, and pyridine yield *diethyl dicarbethoxytartrate*, b. p. 173—174°/0.4 mm.,  $[\alpha]_D + 14.9^\circ$  in alcohol. If sodium is used in place of pyridine, an inactive product, b. p. 174—175°/0.6 mm., is produced. C. J. S.

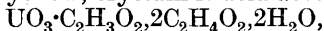
**Organic Polysulphides. II. Action of Anhydrous Potassium Pentasulphide on Allyl Iodide and on some Aromatic Halogen Compounds.** J. S. THOMAS and R. W. RIDING (*J. Chem. Soc.*, 1924, **125**, 2214—2219).—The crude product obtained by the interaction of allyl iodide and anhydrous potassium pentasulphide by the method previously used (T., 1923, **123**, 3271), when heated in a vacuum or preserved in a vacuum desiccator for several days, yields *diallyl pentasulphide*,  $d^{18}$  1.249, which does not form additive compounds with silver nitrate or mercuric iodide, but slowly reacts with mercuric chloride to form insoluble products. Diallyl pentasulphide reacts, in chloroform solution, with iodine to give a *tetraiodide*,  $\text{C}_6\text{H}_{10}\text{I}_4\text{S}_5$ , m. p. about 92°. Bromine reacts with diallyl

pentasulphide under similar conditions to give diallyl disulphide tetrabromide and an oily liquid believed to be a *tribromo* derivative,  $C_6H_{10}Br_3S_5$ . The latter substance, when treated with piperidine in benzene solution, loses hydrogen bromide, with the formation of a double compound of uncertain composition. Diallyl pentasulphide and piperidine interact in ethereal solution, yielding a red oil from which *diallyl pentasulphide tripiperidine*,  $C_6H_{10}S_5 \cdot 3C_5H_{11}N$ , is obtained as an uncrystallisable oil. *Dibenzyl pentasulphide*,  $C_{14}H_{14}S_5$ , the most stable pentasulphide so far obtained, is a dense, oily liquid resulting from the action of potassium pentasulphide on benzyl chloride in anhydrous ether; with piperidine, it forms a red, oily *tripiperidine* compound, which oxidises in air to form benzoylpiperidine.

The product resulting from the interaction of potassium pentasulphide and *p*-bromonitrobenzene when purified with alcohol yields a *potassium* salt,  $(C_6H_4 \cdot NO_2)_2S_2 \cdot 2C_2H_5OK$ , from which a disulphide containing alcohol, m. p.  $74^\circ$ , is obtained by the action of hydrochloric acid in concentrated aqueous solution. The alcohol is readily expelled, and a *disulphide*, m. p.  $178-180^\circ$ , obtained.

C. J. S.

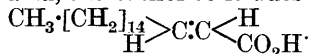
**Acid Uranyl Acetate.** A. COLANI (*Bull. Soc. chim.*, 1924, [iv], 35, 1305—1307).—By dissolving uranyl oxide,  $UO_3 \cdot H_2O$ , in boiling glacial acetic acid, a yellow, crystalline acid acetate,



was obtained. Its formation was confirmed by allowing finely divided uranyl acetate dihydrate to absorb acetic acid vapour at the ordinary temperature. Exposed to the air, this salt evolves acetic acid, becoming converted at the ordinary temperature into the normal acetate in 72 hours.

H. T.

**Configuration of  $\Delta^a$ -Oleic Acid.** G. B. SEMERIA (*Atti R. Accad. Sci. Torino*, 1924, 59, 360—364).—Since cryometric measurements show that stearic acid forms solid solutions with  $\Delta^a$ -oleic acid, the author concludes that the latter has the *trans*-configuration,



T. H. P.

**$\gamma$ -Hydroxystearic Acid.** P. W. CLUTTERBUCK (*J. Chem. Soc.*, 1924, 125, 2330—2333).—An almost quantitative yield of  *$\gamma$ -hydroxystearic acid*, m. p.  $89^\circ$  (slow decomp.), is obtained by heating stearylactone with water and excess of alkali for  $\frac{1}{2}$  hour and acidifying. The acid is more stable than  *$\gamma$ -hydroxybutyric acid*, and does not, under ordinary conditions, exhibit a tendency to pass into the lactone; when heated at  $100^\circ$ , the lactone is formed.

The conversion of stearylactone into sodium  *$\gamma$ -hydroxystearate* is bimolecular, and the conversion of the acid into lactone unimolecular.

C. J. S.

**Walden Inversion. III. Oxidation of Optically Active Thiolsuccinic Acid and Thiolsuccinamic Acid to the Corresponding Sulpho Acids.** P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1924, 60, 685—692).—Continuing previous work

(A., 1924, i, 940), it has been found that both *d*-thiolsuccinic acid and *d*-thiolsuccinamic acid, which differ from one another in the polarity of one of the terminal carbon atoms, undergo oxidation to the corresponding sulphonic acid without change in the sign of rotation. The following series of reactions was carried out: *l*-bromosuccinic acid,  $[\alpha]_D^{20} -73.62^\circ \rightarrow$  *d*-xanthosuccinic acid,  $[\alpha]_D^{20} +62.43^\circ \rightarrow$  *d*-thiolsuccinic acid, m. p.  $138^\circ$ ,  $[\alpha]_D^{20} +68.43^\circ \rightarrow$  *d*-sulphosuccinic acid (isolated in different experiments as *barium*, *sodium*, and *potassium* salts which had  $[\alpha]_D^{20} +7.54^\circ$ ,  $+15.87^\circ$ , and  $+13.34^\circ$ , respectively, in 10% hydrochloric acid); *l*-bromosuccinamic acid  $\rightarrow$  *d*-xanthosuccinamic acid, m. p.  $138^\circ$ ,  $[\alpha]_D^{20} +73.07^\circ \rightarrow$  *d*-thiolsuccinamic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{SH})\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $133^\circ$ ,  $[\alpha]_D^{20} +59.80^\circ \rightarrow$  *d*-sulphosuccinmonoamide (isolated as *barium* salt, which had  $[\alpha]_D^{20} +5.85^\circ$  in 10% hydrochloric acid). E. S.

**Diffraction of X-Rays by Polymerised Liquids.** J. DE SMEDT (*Bull. Acad. roy. Belg.*, 1924, [v], 10, 366—372).—X-Ray diffraction figures have been investigated for the two groups of polymeric compounds: (1) acetaldehyde, ethyl acetate, butyric acid, and paraldehyde, and (2) benzaldehyde and benzyl benzoate. The results obtained show that, with ethyl acetate, butyric acid, benzyl benzoate, and paraldehyde, the first diffraction ring is due, not to the molecule, but to a part thereof, acting as diffraction centre. The acetaldehyde molecule must be regarded as forming a compact group and acting as a single diffraction centre, whereas the ethyl acetate molecule appears to be resolved into two analogous groups,  $\text{CH}_3\cdot\text{CO}\cdot$  and  $\cdot\text{OEt}$ , and the benzyl benzoate molecule into  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot$  and  $\cdot\text{O}\cdot\text{CH}_2\text{Ph}$ ; for butyric acid, the mode of scission is not evident. A second diffraction ring is observed only with butyric acid, benzaldehyde, and benzyl benzoate, the last compound showing also a third ring. T. H. P.

**Mechanism of Grignard's Reaction.** H. RHEINBOLDT and H. ROLEFF (*Ber.*, 1924, 57, [B], 1921—1925).—If the correctness of the formulation,  $\text{CR}_2\text{R}'\cdot\text{OMgX}$ , for the "individual" Grignard's reagents be assumed, the compounds derived from  $\text{CRPh}\cdot\text{O}$  and  $\text{MgR}'\text{X}$  and from  $\text{CRR}'\cdot\text{O}$  and  $\text{MgPhX}$  must be identical. This point has been tested in the case in which  $\text{R}'$  is a radical which can give rise to an olefine. Whereas, however, reduction occurs with magnesium *isobutyl* bromide and benzaldehyde or benzophenone, it is not observed with *isovaleraldehyde* and magnesium phenyl bromide, benzophenone and magnesium *cyclohexyl* chloride, phenyl *cyclohexyl* ketone and magnesium phenyl bromide, or phenyl *isobutyl* ketone and magnesium phenyl bromide. Since, further, reduction or elimination of an olefinic hydrocarbon is not observed when the bromomagnesium alkoxides of phenyl-*isobutylcarbinol*, phenyl-*cyclohexylcarbinol* and diphenyl-*cyclohexylcarbinol* are heated, it follows that this conception of the constitution of the "individual" compounds is inadequate. More probably addition of Grignard's reagents to carbonyl compounds occurs primarily in such a manner that molecular compounds,

$\text{CRR}_2\text{:O}\cdots\text{MgR}'\cdot\text{X}$ , are produced which resemble the products of the addition of metallic salts to the carbonyl oxygen atom.

H. W.

**Hydroxyaldehydes. VII.** B. HELFERICH and W. SCHÄFER (*Ber.*, 1924, 57, [B], 1911—1917).—Extension of previous work (A., 1923, i, 1177) to hydroxyaldehydes in which the hydroxy and aldehydic groups are far removed from one another shows that these substances are also capable of existing in cyclic forms, although the formation of a ten-membered ring is involved.

Ethyl oleate is reduced to the corresponding primary alcohol, which is ozonised in glacial acetic acid solution; reduction of the ozonide with zinc dust yields nonaldehyde and *α*-hydroxynonaldehyde,  $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}_2]_7\cdot\text{CHO}$ , m. p.  $58^\circ$ . Similarly, *oleyl acetate*, b. p.  $216\text{--}220^\circ/14$  mm.,  $d_4^{18.5}$  0.8757,  $n_D^{18.5}$  1.4511, is transformed into *α*-acetoxynonaldehyde, b. p.  $163^\circ/14$  mm.,  $d_4^{20}$  0.9268,  $n_D^{18.5}$  1.4391, and *oleyl benzoate*, b. p.  $273\text{--}275^\circ/15$  mm.,  $d_4^{19}$  0.9439,  $n_D^{19.3}$  1.4918, into *α*-benzoyloxynonaldehyde, b. p.  $215\text{--}217^\circ/14$  mm.,  $d_4^{19}$  1.0571,  $n_D^{19.3}$  1.4994. Methyl and ethyl oleates yield similarly *methyl η*-aldehydo-octoate,  $d_4^{18.7}$  0.9938,  $n_D^{18.7}$  1.4426, and *ethyl η*-aldehydo-octoate,  $d_4^{18.5}$  0.9961,  $n_D^{18.5}$  1.4418. Nonaldehyde is converted by methyl-alcoholic hydrogen chloride into the corresponding *dimethylacetal*, b. p.  $96\text{--}98^\circ/15$  mm.,  $d_4^{18}$  0.8733,  $n_D^{18.5}$  1.4246; *α*-benzoyloxynonaldehyde *dimethylacetal*, b. p.  $234\text{--}235^\circ/15$  mm.,  $d_4^{19}$  1.0096,  $n_D^{19}$  1.4862, and *methyl η*-aldehydo-octoate *dimethylacetal*, b. p.  $148\text{--}150^\circ/14$  mm.,  $d_4^{19}$  0.9379,  $n_D^{18.5}$  1.4312, are prepared in like manner. On the other hand, *α*-hydroxynonaldehyde is transformed under similar conditions into the *methyl semiacetal*,  $\text{CH}_2\cdot[\text{CH}_2]_7\cdot\text{CH}\cdot\text{OMe}$ ,  $\text{---O---}$ , b. p.  $125\text{--}130^\circ/15$  mm.,  $d_4^{18.5}$  0.8892,  $n_D^{18.5}$  1.4306; *α*-hydroxynonaldehyde *dimethylacetal*, b. p.  $158\text{--}160^\circ/14$  mm.,  $d_4^{19}$  0.9329,  $n_D^{18.5}$  1.4441, is prepared by the action of alcoholic potassium hydroxide solution on the corresponding benzoyl compound. A substance,  $\text{C}_{18}\text{H}_{34}\text{O}_3$ , b. p.  $210\text{--}220^\circ/15$  mm., is obtained as by-product in the preparation of the semiacetal. The carbonyl group appears to be in the free form in *α*-hydroxynonaldehyde, since the substance is converted by magnesium ethyl bromide into *n*-undecane- $\alpha$ -*α*-diol, b. p.  $175^\circ/14$  mm.,  $d_4^{18}$  0.9273.

$\Delta^8$ -Pentenol, b. p.  $142^\circ$ , is obtained by the reduction of ethyl allylmalonate with sodium. It is converted by treatment with ozone into *γ*-hydroxy-*n*-butyraldehyde,  $d_4^{18}$  1.0447,  $n_D^{18}$  1.4291, which appears to exist mainly in the cyclic form [2-hydroxytetrahydrofuran].

H. W.

**Condensation of *n*-Butaldehyde with Methyl Ethyl Ketone.** S. G. POWELL (*J. Amer. Chem. Soc.*, 1924, 46, 2514—2517).—*n*-Butaldehyde condenses with methyl ethyl ketone in presence of solid or alcoholic potassium hydroxide with formation of *δ*-hydroxy-*γ*-methylheptan- $\beta$ -one, b. p.  $110^\circ/16$  mm.,  $n_D^{20}$  1.442,  $d_4^{20}$  0.9238, and *γ*-methyl- $\Delta^8$ -hepten- $\beta$ -one,  $\text{C}_8\text{H}_{14}\cdot\text{CH}(\text{OH})\cdot\text{CHMe}\cdot\text{COMe}$ , b. p.  $170\text{--}176^\circ/760$  mm.,  $n_D^{19}$  1.451,  $d_4^{19}$  0.8613 (*semicarbazone*, m. p.  $164^\circ$ ;

*oxime*, b. p. 119—120°/20 mm.), the unsaturated product being also obtained by heating the above heptanone with iodine. The heptanone is reduced by hydrogen in presence of nickel at 180° to  $\gamma$ -methylheptan- $\beta$ -one, b. p. 162°/760 mm.,  $n_D^{20}$  1.415,  $d_4^{20}$  0.8175 (semicarbazone, lustrous plates, m. p. 82°), which is further reduced by the action of sodium in moist ether in presence of sodium hydrogen carbonate to  $\gamma$ -methylheptan- $\beta$ -ol, b. p. 172—173°/760 mm.,  $n_D^{13}$  1.436,  $d_4^{13}$  0.8272 (acetate, b. p. 185°,  $n_D^{21}$  1.418,  $d_4^{21}$  0.8545). *Ethyl methyl-n-butylacetoacetate*, b. p. 118—122°/10 mm.,  $n_D^{20}$  1.4320,  $d_4^{20}$  0.9460, obtained by methylating ethyl *n*-butylacetoacetate, is hydrolysed by boiling with aqueous potassium hydroxide to the above  $\gamma$ -methylheptan- $\beta$ -ol. F. G. W.

**Hydroxyglyoximes.** G. PONZIO (*Atti R. Accad. Sci. Torino*, 1924, 59, 348—352).—Methyl- and phenyl-hydroxyglyoximes,  $\text{NOH}\cdot\text{CR}\cdot\text{C}(\text{OH})\cdot\text{NOH}$ , may be readily obtained in almost theoretical yields by treating the corresponding chloro compounds,  $\text{NOH}\cdot\text{CR}\cdot\text{CCl}\cdot\text{NOH}$  (cf. A., 1923, i, 472), with sodium acetate in presence of dilute acetic acid. By the same method, dichloroglyoximes may be converted into dihydroxyglyoximes, chloroaldoximes into hydroxamic acids, and chloro-oximinoketones into acylformhydroxamic acids. The new compound, acetylformhydroxamic or pyruvhydroxamic acid,  $\text{NOH}\cdot\text{CAc}\cdot\text{OH}$ , prepared in this way from chloro-oximinoacetone, is to be described later.

T. H. P.

**Relations between Rotatory Power and Structure in the Sugar Group. V. Chloro- and Bromo-acetyl Derivatives of Arabinose. Nomenclature of Alpha and Beta Forms in the Sugar Group. Some Derivatives of 1:6-Bromoacetylglucose, -gentiobiose, and -maltose.** C. S. HUDSON and E. P. PHELPS (*J. Amer. Chem. Soc.*, 1924, 46, 2591—2604).—The specific rotations of  $\beta$ -chloro- and  $\beta$ -bromo-acetyl-*d*- and -*l*-arabinoses in chloroform are  $[\alpha]_D^{20}$   $\mp 244^\circ$  and  $\mp 288^\circ$ , respectively (cf. Chavanne, A., 1902, i, 346; Brauns, A., 1924, i, 837). Whilst the rotation of fluoroacetyl arabinose (Brauns, *loc. cit.*) agrees with the calculated value, that of  $\beta$ -iodoacetyl arabinose is  $36^\circ$  larger than that calculated from iodoacetylglucose, probably indicating a new type of ring structure in the arabinose derivative. The known halogenacetyl derivatives of arabinose should be classed as  $\beta$ -compounds from their rotatory power. Hudson's system of nomenclature (A., 1909, i, 135) is discussed in relation to suggestions of Svanberg and Josephson (A., 1924, i, 370) and of Kuhn (A., 1923, i, 589). The calculated rotations of twelve acyl derivatives of maltose and gentiobiose are in good agreement with such observed values as have been recorded. F. G. W.

**Mutarotation. IV. Solution Volume and Refraction Constants of  $\alpha$ - and  $\beta$ -Methylglucoside.** C. N. RIIBER (*Ber.*, 1924, 57, [B], 1797—1799; cf. A., 1924, ii, 806).—The molecular solution volume and molecular refraction of  $\alpha$ -methylglucoside, m. p. 166°,  $[\alpha]_D^{20}$   $+158.9^\circ$ , are respectively 132.61 ml. and 70.17,

whereas the corresponding figures for  $\beta$ -methylglucoside are 133.26 and 70.55. Comparison of these data with those found previously for dextrose (*loc. cit.*) confirms the relationship of the  $\alpha$ - and  $\beta$ -methylglucosides to the  $\alpha$ - and  $\beta$ -forms of the parent sugar (cf. Armstrong, T., 1903, 83, 1307). H. W.

**Influence of Catalysts on Carbonisation.** R. LESSING and M. A. L. BANKS (*J. Chem. Soc.*, 1924, 125, 2344—2356).—With a view to trace the influence of the typical ash on the peculiar behaviour of the four main constituents of coal, experiments were conducted to determine the yield of coke formed when sucrose and cellulose are carbonised in the presence of small quantities of various compounds. Forty different compounds were used, and applied to the carbohydrate either as an aqueous solution, or by precipitation. In the case of sucrose, the yield of coke varies from 18.74% with sulphuric acid as catalyst, to 5.02% with nickel oxide; the yield of coke from cellulose varies from 20.36% with sulphuric acid, to 5.16% with oxalic acid.

In general, salts of strong acids and weak bases cause the highest yields of coke, and oxides of copper, nickel, calcium, and magnesium have the least effect. Sodium carbonate, hydroxide, and silicate have a greater influence on the coking of cellulose than of sucrose.

Considerable differences are noticeable in the appearance and structure of the cokes obtained from sucrose, variation in the swelling property being very marked, and these are classified as compact, swelled, or flaky. The majority of catalysts producing high or medium coke yields cause production of swelled cokes when sucrose is carbonised with its own weight of water, and compact cokes when dry sugar and catalyst are used. Flaky coke is obtained from pure sucrose or sucrose mixed with catalysts not causing an increase in yield of coke. The velocity of carbonisation of sucrose is greater than that of cellulose.

Experiments were also conducted with a specially prepared coal consisting mainly of clarain, with a little vitrain, separated from the other coal constituents by physical methods. The ash content was reduced to 0.86% by extraction with hydrochloric acid. The coal was carbonised in an electric coking oven and the yields of coke, tar, and gas were determined. The effect of the catalysts is a distribution between the solid and liquid carbonisation products, the yield of gas being a function of the temperature of carbonisation. The order of the influence of the various catalysts is approximately the same as in the sucrose and cellulose experiments, untreated coal giving the lowest yield of coke. C. J. S.

**Synthesis of a Disaccharide-Glucoside.** B. HELFERICH and J. BECKER (*Annalen*, 1924, 440, 1—18).—The reaction between triphenylmethyl chloride and alcohols previously studied (A., 1923, i, 331) yields, in the case of  $\alpha$ -methyl-*D*-glucoside, a well-crystallised ether in which one hydroxyl group (probably the primary group) is etherified, and this ether has been utilised for the synthesis



with 10% hydrochloric acid, 6(?) *-methyl-d-glucose*, yellow syrup,  $[\alpha]_D^{21} + 80.1^\circ$  (in water), falling to  $+66.3^\circ$  in 46 hours; *osazone*,  $C_{19}H_{24}O_4N_4$ , m. p.  $177^\circ$ ,  $[\alpha]_D^{25} - 70.3^\circ$ , falling to  $-46.9^\circ$  in 20 hours (in alcohol). 6(?) *-Tribenzoyl-p-toluenesulphonyl- $\alpha$ -methyl-d-glucoside*, m. p.  $166^\circ$ ,  $[\alpha]_D^{20} + 89.7^\circ$ ,  $[\alpha]_D^{25} + 90.1^\circ$  in pyridine, on hydrolysis with ammonia in methyl alcohol, yields 6(?) *-p-toluenesulphonyl- $\alpha$ -methyl-d-glucoside* ( $+2\frac{1}{2}H_2O$ ), m. p.  $55-58^\circ$  (sintering at  $50^\circ$ ),  $[\alpha]_D^{22} + 98.1^\circ$  in pyridine,  $[\alpha]_D^{20} + 69.7^\circ$  in water. Tribenzoyl- $\alpha$ -methyl-d-glucoside and acetobromoglucose in carbon tetrachloride in the presence of silver oxide give, in 28.6% yield, 6(?) *-(tetra-acetyl- $\beta$ -glucosido)-tribenzoyl- $\alpha$ -methyl-d-glucoside*, lustrous needles, sintering at  $142^\circ$ , m. p.  $152^\circ$ ,  $[\alpha]_D^{24} + 50.5^\circ$ ,  $[\alpha]_D^{22} + 50.7^\circ$  in pyridine, which with dry ammonia in methyl alcohol is converted into 6(?) *-( $\beta$ -d-glucosido)- $\alpha$ -methyl-d-glucoside* ( $+1EtOH$ ), sintering about  $100^\circ$ , m. p.  $102^\circ$  (decomp.). The dry substance has m. p.  $120^\circ$  (decomp.),  $[\alpha]_D^{24} + 59.4^\circ$ ; dried at  $142^\circ$ , the substance has  $[\alpha]_D^{23} + 61.8^\circ$ .

[With H. WIEGAND.]—Hepta-acetylmethylmaltoside, obtained by Fischer's method (A., 1910, i, 716), with dry ammonia in methyl alcohol, gives in 70% yield  $\beta$ -methylmaltoside ( $+1H_2O$ ), m. p.  $110^\circ$ ,  $[\alpha]_D^{19} + 76^\circ$ ,  $+74.6^\circ$  in water; the anhydrous substance sinters at  $105^\circ$  and has m. p.  $155^\circ$  (decomp.),  $[\alpha]_D^{19} + 78.8^\circ$  in water.

R. B.

**Constitution of Starch and Different Modes of Action of the Amylases.** R. KUHN (*Ber.*, 1924, 57, [B], 1965—1968).—Examination of the hydrolysis of soluble starch, amylose, and amylopectin with malt amylase by polarimetric and reductometric measurements confirms the observations of Brown and Heron (T., 1879, 35, 596) and Brown and Morris (T., 1885, 47, 527; 1895, 67, 309) according to which maltose is liberated entirely in the  $\beta$ -form. If, however, maltase-free pancreas or taka-diastase is used, the nascent maltose has the  $\alpha$ -structure. Degradation of starch can occur in three distinct ways, which are characterised by the different course of transformation of an oxide ring stable only in amylose and amylopectin. Thus malt amylase causes isomerisation in the reducing half of the generated maltose, whereas intraglicosidic transformation in the non-reducing half of a dissaccharide molecule is effected by pancreas amylase. Finally, interglucosidic isomerisations may occur, such as the conversion of  $\alpha$ - into  $\beta$ -polyamyloses and certain other reactions which may lead to the anhydrides of trisaccharides.

H. W.

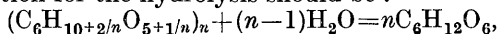
**Hydrolysis of Starch by Salts. IV. Hydrolysis by Blood Pigments and Plant Peroxydases.** W. BIEDERMANN and C. JERNAKOFF (*Biochem. Z.*, 1924, 150, 477—491).—Hæmoglobin accelerates the hydrolysis of starch by salts and itself hydrolyses amyloses even in considerable dilution. The former result is obtained after boiling the hæmoglobin, and is also given by solutions of hæmin and hæmatin. The peroxydase content and amyolytic activity of potato and horse-radish extracts are parallel to one another. (Cf. A., 1924, i, 1288.)

J. P.



**Selective Photochemical Action of Polarised Light. I. Hydrolysis of Starch.** E. C. C. BALY and E. S. SEMMENS (*Proc. Roy. Soc.*, 1924, **B**, **97**, 250—253).—Plane-polarised light exerts a powerful acceleration of the diastatic hydrolysis of starch from potatoes, wheat, and maize. O. O.

**Molecular Weight of Glycogen.** W. FEARON (*Nature*, 1924, **114**, 752).—In the complete hydrolysis of raffinose or stachyose, only  $(n-1)$  molecules of water are required to produce  $n$  molecules of hexose. Application to the hydrolysis of a higher polysaccharide such as glycogen suggests that either (a) the latter exists in some stage of the hydrolysis as a cyclic compound requiring the addition of 2 mols. of water in order to produce two derivative mols., or (b) the equation for the hydrolysis should be :



the value of  $n$  being obtained by calculating the difference between the observed and theoretical values for the hydrogen.

A. A. E.

**Action of Aqueous and Aqueous-alcoholic Solutions of Sodium Hydroxide on Cellulose.** W. VIEWEG (*Ber.*, 1924, **57**, [B], 1917—1921).—Cellulose was immersed in aqueous-alcoholic solutions of sodium hydroxide containing varying amounts of alkali and 10, 35, and 50% of alcohol; the quantity of sodium hydroxide removed by the cellulose was measured by titration before and after immersion of the sample. The curves which are obtained do not indicate the existence of a compound of cellulose and sodium hydroxide stable under these conditions. The influence of alcohol on the adsorption of alkali hydroxide by cellulose is more pronounced in concentrated than in dilute solutions of alkali, whilst also the adsorption is greater when the concentration of alcohol is greater. The experiments show the impossibility of isolating the compound,  $(\text{C}_6\text{H}_{10}\text{O}_5)_2\text{NaOH}$  (formed from its components in the presence of water), if the latter is washed with alcohol (cf. Rassow and Wadewitz, A., 1924, i, 374). Repetition of previous experiments (A., 1907, i, 893) confirms the stability of the compound in alkali solutions of medium strength; the breaks in the curves which indicate the formation of the compound occur at different concentrations of alkali hydroxide with different varieties of cellulose. H. W.

**Ethers of Polysaccharides with Hydroxy-acids.** W. WELTZIEN (*Biochem. Z.*, 1924, **150**, 476).—A correction of Chowdhury (cf. A., 1924, i, 1029) in regard to citations of previous work on the methylation of hydrocellulose. J. P.

**Strength of Trimethylamine Oxide and Trimethylalkoxy-ammonium Hydroxides as Bases. Structure of Ammonium Compounds.** T. D. STEWART and S. MAESER (*J. Amer. Chem. Soc.*, 1924, **46**, 2583—2590).—The hydrolysis of salts of trimethylamine oxide measured colorimetrically by means of methyl-violet and methyl-orange showed that this base has a dissociation

constant of about  $4 \times 10^{-10}$ . The conductivities of solutions of trimethylethoxyammonium iodide, trimethylmethoxyammonium iodide, and of mixtures of these with sodium hydroxide showed that the trimethylalkoxyammonium hydroxides are strong bases. The results are discussed in relation to the Lewis theory of atomic structure, with which they are in agreement. Pure trimethylethoxyammonium iodide decomposes sharply at 135–136°. F. G. W.

**Catalytic Action of Traces of Iron on the Oxidation of Cysteine and Glutathione.** D. C. HARRISON (*Biochem. J.*, 1924, **18**, 1009–1022).—The rates of atmospheric oxidation of both cysteine and glutathione are very greatly reduced by the removal of iron impurities. The addition of very minute quantities of iron produces a marked increase on the rate of oxidation of cysteine and glutathione from which iron has previously been removed. Inhibition by hydrogen cyanide of oxidation of the above substances is due to interaction of the latter with the catalytic iron. The velocities of absorption of oxygen in the case of the purified compounds alone and in the case of the unpurified compounds in the presence of cyanide are linear. Iron in hæmatin can catalyse these oxidations. S. S. Z.

**Preparation of (Iodo-)Esters of Carbamic Acid and of Acylated Carbamic Acids (Allophanic Acid, Acetylcarbamic Acid, etc.).** CHINOIN FABRIK CHEMISCH-PHARMAZEUTISCHER PRODUKTE A.-G. VON KERESTY UND WOLF (D.R.-P. 387963; from *Chem. Zentr.*, 1924, ii, 403).—The corresponding esters of chloroalcohols are treated with a metallic iodide preferably in presence of a suitable solvent such as acetone; thus  $\beta$ -chloroethylurethane, m. p. 76° (from  $\beta$ -chloroethyl chloroformate and ammonia), on heating with sodium iodide in absolute acetone at 80–90° affords  $\beta$ -iodoethylurethane, m. p. 93–94°.  $\alpha\alpha'$ -Dichloroisopropylurethane, m. p. 82°, affords  $\alpha\alpha'$ -di-iodoisopropylurethane.  $\beta$ -Chloroethyl chloroformate on heating with carbamide forms  $\beta$ -chloroethyl allophanate, m. p. 181–182°, which affords  $\beta$ -iodoethyl allophanate, m. p. 192°, on heating with sodium iodide in acetone.  $\beta$ -Chloroethylacetylurethane, m. p. 76.5° (from  $\beta$ -chloroethylurethane and acetyl chloride), gives analogously  $\beta$ -iodoethylacetylurethane, m. p. 76°. The products have a therapeutic action, especially on the nervous system. F. A. M.

**New Hydroxamic Acids of Hydroxy- and Alkoxy-fatty Acids.** L. W. JONES and D. H. POWERS (*J. Amer. Chem. Soc.*, 1924, **46**, 2518–2533).—*Hydroxyacethydroxamic acid*,  
 $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$ ,

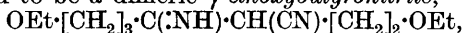
m. p. 85°, was obtained by the action of hydroxylamine on ethyl glycolate. The *acetyl* derivative, m. p. 64.5°, the *benzoyl* derivative, m. p. 160.4°, and their *silver* and *potassium* salts, are described. The potassium salt of the benzoyl derivative, decomp. 125°, undergoes rearrangement, when heated with ethyl or *isoamyl* alcohol, into formaldehyde, potassium benzoate, and ethyl or

isoamyl allophanate. *Methoxyacetylhydroxamic acid*, m. p.  $85.5^\circ$ , yields an *acetyl* derivative, m. p.  $82^\circ$ , and a *benzoyl* derivative, m. p.  $84.5^\circ$ , the *potassium* salt of which decomposes at  $100^\circ$  into carbon dioxide, potassium benzoate, formaldehyde, and *methoxymethylcarbimide*, a lachrymatory oil, b. p.  $87.5^\circ$ , which is decomposed by water into carbon dioxide, ammonia, methyl alcohol, and formaldehyde, and polymerises when kept to a white, vitreous solid. *Ethoxyacetylhydroxamic acid*, m. p.  $74-76^\circ$ , its *acetyl* derivative, needles, m. p.  $84^\circ$ , and *benzoyl* derivative, m. p.  $156^\circ$ , are described. The *potassium* salt of the latter, decomp.  $115^\circ$ , is decomposed in boiling water with formation of carbon dioxide, alcohol, ammonia, formaldehyde, and potassium benzoate. *Ethoxymethylcarbimide*, a lachrymatory oil, b. p.  $105-106^\circ$ , is decomposed by water. Methyl  $\beta$ -methoxypropionate (cf. Purdie and Marshall, T., 1891, 59, 474) has b. p.  $144-145^\circ/760$  mm.;  $\beta$ -methoxypropionic acid, b. p.  $126^\circ/30$  mm., and  $\beta$ -methoxypropionyl chloride, b. p.  $135-136^\circ/758$  mm., were also prepared.  $\beta$ -Methoxypropionhydroxamic acid, m. p.  $93-95^\circ$ , its *acetyl* derivative, m. p.  $86^\circ$ , and *benzoyl* derivative, m. p.  $148^\circ$ , are described. The *potassium* salt of the latter, decomp.  $110^\circ$ , yields, when boiled with water,  $\beta$ -methoxyethylcarbimide, b. p.  $123-124^\circ$ , which was also obtained by the action of silver cyanate on  $\beta$ -methoxyethyl iodide in ether at  $130^\circ$ .

F. G. W.

**Abnormal Reaction of Propylene Chlorohydrin.** A. DEWAELE (*Bull. Soc. chim. Belg.*, 1924, 33, 504-507).— $\beta$ -Chloropropyl alcohol, b. p.  $133-134^\circ/761$  mm., obtained as a by-product in the preparation of allyl chloride from allyl alcohol and hydrogen chloride, is converted by potassium cyanide, with a little sodium iodide, in aqueous-alcoholic solution into  $\beta$ -hydroxybutyronitrile (yield 60%), b. p.  $214-215^\circ$ ,  $d_{20}^{20}$  0.9938, together with the two crotononitriles (cf. Bruylants, A., 1922, i, 817). The identity of the cyanohydrin was established since phosphorus pentachloride changed it into  $\beta$ -chlorobutyronitrile, and dehydration with phosphoric oxide gave crotononitrile. The cyanohydrin with sodium hydroxide gave crystals of its *sodium* derivative ( $+H_2O$ ), and with sodium ethoxide and ethyl iodide gave  $\beta$ -ethoxybutyronitrile. F. M. H.

**Action of Organo-magnesium Compounds on Nitriles.**  
 **$\gamma$ -Ethoxybutyronitrile.** R. BRECKPOT (*Bull. Soc. chim. Belg.*, 1924, 33, 490-494).— $\gamma$ -Ethoxybutyronitrile, b. p.  $180-182^\circ/744$  mm., was prepared by the action of sodium ethoxide on  $\gamma$ -chlorobutyronitrile; by-products were identified as the nitrile and amide of trimethylenecarboxylic acid. By the action of magnesium ethyl bromide on  $\gamma$ -ethoxybutyronitrile, gas was evolved; the product was separated into three fractions: (1) b. p.  $185-200^\circ$ , forming a *semicarbazone*, m. p.  $87^\circ$ , probably ethyl  $\gamma$ -ethoxypropyl ketone or the ketimine, (2) b. p.  $206-208^\circ/16$  mm.,  $d_{20}^{20}$  0.9939,  $n_D^{20}$  1.4971, was concluded to be a dimeric  $\gamma$ -ethoxybutyronitrile,



(3) b. p.  $225-230^\circ$ , was not identified.

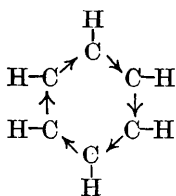
F. M. H.

**Action of Organo-magnesium Compounds on Nitriles.**

**Ethyl Cyanoformate.** P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1924, [v], 10, 392—395; cf. A., 1924, i, 984).—The action of magnesium ethyl bromide on ethyl cyanoformate proceeds mainly in accordance with the equation:  $\text{CN}\cdot\text{CO}_2\text{Et} + \text{MgRX} = \text{MgX}\cdot\text{CN} + \text{R}\cdot\text{CO}_2\text{Et}$ , and yields finally triethylcarbinol. At the same time, a secondary reaction takes place, giving  $\gamma$ -hydroxy- $\gamma$ -ethylhexan- $\delta$ -one (cf. Blaise and Maire, A., 1909, i, 85), b. p. 189—191° (*semi-carbazone*, m. p. 175—177°). T. H. P.

**Applications of Röntgen Crystal Analysis to Questions of Structure of Organic Compounds.** H. MARK.—(See i, 1).

**Structure of the Benzene Nucleus.** M. DOMINIKIEWICZ (*Roczniki Chemji*, 1923, 3, 326—349).—An attempt is made to account for the peculiar properties of benzene and its derivatives by a structural formula in which the carbon atoms are assumed to be mobile, the whole structure being kept together by the mutual attraction of the component atoms. It is assumed that true



benzene derivatives possess no double linkings as such, although the linkings differ from those in ordinary saturated compounds; in the appended diagram two valencies of one atom satisfy one valency of a neighbouring one, and this accounts for the "aromatic" character of the compound. In a space model, the carbon atoms are represented by the usual tetrahedra, the apex of one touching the edge of the next one between two apices. In this way, the six carbon atoms are in the same plane in accordance with stereochemical requirements.

The entrance of substituents which are capable of acting as auxochromes affects the character of the nucleus, its saturated nature being less pronounced and the structure being more prone to tautomeric change (*e.g.*, quinonoid change). It is held that in these cases the nucleus assumes a bridged or Dewar phase with two double bonds; whilst whenever three double linkings are produced the nucleus immediately reverts to the original structure. In the bridged formula, the faces of the tetrahedra representing the para carbon atoms are completely in contact, also those of the ortho and meta carbon atoms on each side, so that there is no longer a ring.

The molecule is, moreover, assumed to be rotating about an axis passing through the two para carbons; this is the case whether the ring is in its original "benzenoid" or the modified "D" condition. The frequent occurrence of *p*-substituted derivatives is held to support this assumption, because the para position is stationary and thus more readily attacked; this accounts for the formation of 1:4-dihydro derivatives on hydrogenation, quinones from phenols, etc. The nucleus in the quinonoid condition has again a different structure, the tetrahedra representing the para atoms being in contact along one edge, whilst the other atoms retain the position they occupied in the "D" condition;

this explains the ready passage from phenols to quinones and *vice versa*. A similar arrangement also applies to the ortho-quinonoid condition.

The structures of naphthalene and anthracene are discussed from the point of view of the theory, but it is impossible to summarise briefly the author's arguments. G. A. R. K.

**Photochemical Action of Iodine on Moist *p*-Chlorotoluene.**

O. SILBERRAD (*J. Chem. Soc.*, 1924, 125, 2196—2197).—A mixture of *p*-chlorotoluene (100 g.), water (75 g.), and iodine (0.1 g.) exposed to sunlight for a period of 2 years yielded, on distillation, 85.5 g. of unaltered *p*-chlorotoluene, together with the following products: toluene, 1.86 g.; *p*-chlorobenzoic acid, 1.35 g.; *s*-4 : 4'-dichlorodiphenylethane, 0.2 g.; hydrogen chloride, 0.82 g. The following equations indicate the course of the reactions: (i)  $C_6H_4Cl \cdot CH_3 + I_2 = C_6H_4Cl \cdot CH_2I + HI$ ; (ii)  $2C_6H_4Cl \cdot CH_2I = C_6H_4Cl \cdot CH_2 \cdot CH_2 \cdot C_6H_4Cl + I_2$ ; (iii)  $C_6H_4Cl \cdot CH_2I + 4I + 2H_2O = C_6H_4Cl \cdot CO_2H + 5HI$ ; (iv)  $C_6H_4Cl \cdot CH_3 + 2HI = C_6H_5 \cdot CH_3 + I_2 + HCl$ . A. C.

**Reactions of the Unsymmetrical Trinitrotoluenes.** O. L. BRADY, S. W. HEWETSON, and L. KLEIN (*J. Chem. Soc.*, 1924, 125, 2400—2404).—Aqueous sodium sulphite readily acts on the unsymmetrical trinitrotoluenes, giving sodium dinitrotoluenesulphonates, which are converted by methylamine into dinitromethyltoluidines, whence the sulphonic acid group can be located. Thus 2 : 3 : 4-, 3 : 4 : 6-, 3 : 4 : 5-, and 2 : 3 : 5-trinitrotoluenes yield, respectively, sodium 2 : 4-dinitrotoluene-3-sulphonate, 4 : 6-dinitrotoluene-3-sulphonate, 3 : 5-dinitrotoluene-4-sulphonate, and 3 : 5-dinitrotoluene-2-sulphonate. On heating with crystalline sodium acetate, the trinitrotoluenes give, respectively, 2 : 4-dinitro-*m*-cresol, 4 : 6-dinitro-*m*-cresol, m. p. 73°, 3 : 5-dinitro-*p*-cresol, and 3 : 5-dinitro-*o*-cresol. The trinitrotoluenes react with toluidine or naphthylamine in hot alcoholic solution: 2 : 3 : 4-trinitrotoluene with *m*-toluidine and  $\beta$ -naphthylamine forms 2 : 6-dinitrodi-*m*-tolylamine, m. p. 110°, and 2 : 6-dinitro-*m*-tolyl- $\beta$ -naphthylamine, m. p. 166°. 3 : 4 : 6-Trinitrotoluene with *m*- and *o*-toluidine and  $\alpha$ - and  $\beta$ -naphthylamine forms 4 : 6-dinitrodi-*m*-tolylamine, m. p. 135°; 4 : 6-dinitro-*m*-tolyl-*o*-tolylamine, m. p. 99°; 4 : 6-dinitro-*m*-tolyl- $\alpha$ -naphthylamine, m. p. 182°; 4 : 6-dinitro-*m*-tolyl- $\beta$ -naphthylamine, m. p. 211°. 2 : 3 : 5-Trinitrotoluene with *o*-toluidine forms 4 : 6-dinitrodi-*o*-tolylamine, m. p. 109°. 2 : 4 : 6 : 2' : 4' : 6'-Hexanitrodi-*m*-tolylamine, m. p. 60°, is produced in 20% yield on warming 4 : 6-dinitrodi-*m*-tolylamine with nitric acid, but the 2 : 6-dinitro compound gives only a trace of it. Phenyl-2 : 6-dinitro-*m*-tolylamine is reduced by ammonium sulphide to phenyl-2(6 ?)-nitro-6(2 ?)-amino-*m*-tolylamine, m. p. 139°, which on diazotisation yields 7-nitro-1-phenyl-4(or 6)-methyl-1 : 2 : 3-benzotriazole, m. p. 147°; this is not converted by heat into the nitromethylcarbazole. [Cf. *B.*, Jan. 23.] F. M. H.

**Polarity Effects in the Isomeric  $\omega$ -Bromoxylenes and Isomeric Iodotoluenes.** J. B. SHOESMITH and R. H. SLATER (*J. Chem. Soc.*, 1924, 125, 2278—2283).—According to the theory

of induced alternate polarities (cf. T., 1922, **121**, 1392; 1923, **123**, 2838; A., 1924, i, 842), the order of ease of hydrolysis of the isomeric  $\omega$ -bromoxylenes should be  $p$  and  $o > m$ , and of reduction by hydrogen iodide  $m > o$  and  $p$ , whilst the order of reduction of the iodotoluenes should be  $o$  and  $p > m$ . These predictions are confirmed experimentally. The complete order of hydrolysis of the  $\omega$ -bromoxylenes is found to be  $p > o > m$ , whilst all are more easily hydrolysed than benzyl bromide, and  $\omega$ -bromo- $p$ -xylene more readily than  $\omega$ -iodo- $p$ -xylene. The order of reduction is  $m > o > p$ , with the unsubstituted compound intermediate between  $o$  and  $p$ , and the order of ease of reduction of the iodotoluenes is  $o > p > m$ .  
F. M. H.

**Molecular Coefficients of Refraction.** F. EISENLOHR and L. SCHULZ (*Ber.*, 1924, **57**, [B], 1808—1820; cf. A., 1920, ii, 717; 1921, ii, 229).—In consequence of the recent criticisms of the authors' work by von Auwers and Kolligs (A., 1922, ii, 174; 1923, i, 99), the optical constants of a large series of benzenoid hydrocarbons have been redetermined. The decomposition of well-defined semicarbazones of aldehydes and ketones by sodium ethoxide yields the "standard" hydrocarbons with which the constants of the substances prepared by the reduction of the requisite styrenes by Paal's method and by sodium and alcohol are compared. Hydrocarbons prepared by Clemmensen's process are generally unsatisfactory; Fittig's method frequently, but not invariably, yields homogeneous products. Examination of the data thus obtained confirms the validity of the regularities observed previously (*loc. cit.*) with the simpler hydrocarbons and establishes the possibility of calculating the index of refraction of any benzenoid hydrocarbon when the influences of substitution are taken into account as described previously.

The following data are recorded for "standard" hydrocarbons: ethylbenzene, b. p. 135—136°,  $d_4^{20 \text{ vac.}}$  0.8667,  $n_{\text{He}}^{20}$  1.49477;  $n$ -heptylbenzene, b. p. 145.0—145.2°,  $d_4^{20 \text{ vac.}}$  0.8604,  $n_{\text{He}}^{20}$  1.48640;  $n$ -octylbenzene, b. p. 264—265°,  $d_4^{20 \text{ vac.}}$  0.8583,  $n_{\text{He}}^{20}$  1.48534; cetylbenzene (prepared by Fittig's method), b. p. 235—237°/16 mm.,  $n_D^{21.8}$  1.47986;  $o$ -ethyltoluene, b. p. 163.7—163.9°/753 mm.,  $d_4^{20 \text{ vac.}}$  0.8747,  $n_{\text{He}}^{20}$  1.50219;  $m$ -ethyltoluene, b. p. 159.2—159.8°,  $d_4^{20 \text{ vac.}}$  0.8615,  $n_{\text{He}}^{20}$  1.49654;  $p$ -ethyltoluene, b. p. 159.5—160°/763 mm.,  $d_4^{20 \text{ vac.}}$  0.8584,  $n_{\text{He}}^{20}$  1.49483;  $o$ -propyltoluene, b. p. 180.5—181.5°,  $d_4^{20 \text{ vac.}}$  0.8740,  $n_{\text{He}}^{20}$  1.49909;  $m$ -propyltoluene, b. p. 176.5—177.5°,  $d_4^{20 \text{ vac.}}$  0.8625,  $n_{\text{He}}^{20}$  1.49398;  $p$ -propyltoluene, b. p. 179.5—180°,  $d_4^{20 \text{ vac.}}$  0.8570,  $n_{\text{He}}^{20}$  1.49197;  $o$ -isopropyltoluene, b. p. 174.5—175.5°,  $d_4^{20 \text{ vac.}}$  0.8741,  $n_{\text{He}}^{20}$  1.49862;  $m$ -isopropyltoluene, b. p. 174.5—175.5°,  $d_4^{20 \text{ vac.}}$  0.86193,  $n_{\text{He}}^{20}$  1.49396;  $p$ -isopropyltoluene, b. p. 176.0—176.5°/762 mm.,  $d_4^{20 \text{ vac.}}$  0.8580;  $n_{\text{He}}^{20}$  1.49141,  $o$ -heptyltoluene, b. p. 263—263.2°,  $d_4^{20 \text{ vac.}}$  0.8717,  $n_{\text{He}}^{20}$  1.49521;  $m$ -heptyltoluene, b. p. 260.0—260.8°,  $d_4^{20 \text{ vac.}}$  0.8615,  $n_{\text{He}}^{20}$  1.49140;  $p$ -heptyltoluene, b. p. 265.0—265.2°,  $d_4^{20 \text{ vac.}}$  0.8560,  $n_{\text{He}}^{20}$  1.48968. Physical constants are recorded for the following hydrocarbons prepared by hydrogenation of the requisite styrenes:  $o$ -ethyltoluene,  $p$ -ethyltoluene,

*o*-propyltoluene and *o*-, *m*-, and *p*-isopropyltoluenes. The values for  $n_a^{20}$ ,  $n_\beta^{20}$ , and  $n_\gamma^{20}$ , are also recorded. H. W.

**Mechanism of Substitution Reactions in the Aromatic Nucleus.** I. E. DE B. BARNETT and M. A. MATTHEWS (*Rec. trav. chim.*, 1924, **43**, 530—541).—The decomposition of additive compounds formed between chloroanthracenes and bromine or nitric acid by combination with the *meso*-carbon atoms has been studied. The presence of nuclear chlorine atoms favours loss of bromine instead of hydrogen bromide from the chloroanthracene 9 : 10-dibromide when the "bridge" is re-established (cf. T., 1921, **119**, 901). An explanation based on geometrical isomerism is elaborated (cf. A., 1924, i, 1292).

1-Chloroanthracene combines with bromine in carbon tetrachloride, giving its *dibromide*, which when boiled with xylene, gives 1-chloroanthracene and 1-chloro-9(or 10)-bromoanthracene, m. p. 150° (cf. Fischer and Ziegler, A., 1912, i, 754); with cold pyridine 1-chloroanthracene *dibromide* gives 1-*chloro*-9 : 10-*dihydroanthraquinyl*-9 : 10-*dipyridinium dibromide*, turning yellow at 135—140°, m. p. 150°. 2-Chloroanthracene, m. p. 223°, forms an unstable *dibromide*, yielding 2-*chloro*-9 : 10-*dihydroanthraquinyl*-9 : 10-*dipyridinium dibromide*, turning yellow at 165°, m. p. 180°. The *dibromide* of 1 : 5-dichloroanthracene is converted by boiling xylene into 1 : 5-dichloroanthracene and by pyridine at 40° into its *dipyridinium* salt, decomp. 195°, which with ammonia forms 1 : 5-*dichloroanthranilpyridinium bromide*, unmelted at 325°. The *dibromide* of 1 : 8-dichloroanthracene is changed by boiling xylene into a compound of indefinite m. p. and by pyridine into its *dipyridinium* salt (unstable).

Nitric acid forms additive compounds with the chloroanthracenes in boiling acetic acid solution. The product from 1-chloroanthracene was converted by pyridine into 1-*chloro*-9(or 10)-*nitroanthracene*, m. p. 196°. Similarly, 2-*chloro*-9(or 10)-*nitroanthracene*, m. p. 185°, was prepared and 1 : 5-*dichloro*-9-*nitroanthracene*, m. p. 208° (from an additive compound, m. p. 201°). From 1 : 8-dichloroanthracene there was isolated 1 : 8-*dichloro*-9(or 10)-*nitrodihydroanthranol*, m. p. 201°; heating this with hydriodic and acetic acids removed nitric acid, leaving 1 : 8-dichloroanthracene; with cold pyridine, by loss of water, 1 : 8-*dichloro*-9(or 10)-*nitroanthracene*, m. p. 203°, was formed but 12.6% of the additive compound had lost nitrous acid to re-establish the bridge.

Reduction of 1 : 5-dichloroanthraquinone with zinc dust and more dilute ammonia than that used by Liebermann and Beudet (A., 1914, i, 514) gave a eutectic mixture, m. p. 202°, of the quinone with 1 : 5-dichloroanthracene. Once only, 1 : 5-*dichloro*-9-*hydroxyanthrone*, turning yellow at 190°, m. p. 196—197°, was produced.

F. M. H.

**Mechanism of Substitution Reactions in the Aromatic Nucleus.** H. J. PRINS (*Rec. trav. chim.*, 1924, **43**, 685—686; cf. A., 1924, i, 1292, also preceding abstract).—Barnett and his collaborators have tried to prove the suggestion of Holleman

concerning this problem by contesting, in the first place, the validity of van der Linden's objection. Whether this is possible is shown on several grounds to be doubtful.

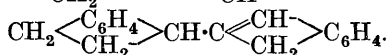
W. E. E.

**Synthesis of 9-Methylphenanthrene.** A. WINDAUS, H. JENSEN, and A. SCHRAMME (*Ber.*, 1924, 57, [B], 1875—1877).—Acetophenone condenses with oxindole in the presence of piperidine at 180° to give 3- $\alpha$ -phenylethylideneoxindole,  $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{C} \begin{smallmatrix} \text{CO} \\ \text{---} \end{smallmatrix}$ :CPhMe, m. p. 193—194°, which is hydrogenated with considerable difficulty to  $\alpha$ -phenylethylloxindole, m. p. 130°. The latter compound is converted by the method of Windaus and Eickel (this vol., i, 32) into 9-methyl-9:10-dihydrophenanthrene-10-carboxylic acid, m. p. 190°; methyl ester, m. p. 64°. The latter compound is transformed through the hydrazide, azide, and urethane (which have not been isolated) into 9-methylphenanthrene (*picrate*, m. p. 152—153°). The hydrocarbon appears to be identical with that obtained by Windaus (*A.*, 1924, i, 1090) from colchicine, but an exhaustive comparison of the two products was not possible on account of the small amount of available material.

H. W.

**Polymerides of Indene.** H. STOBBE and E. FÄRBER (*Ber.*, 1924, 57, [B], 1838—1851).—Di-indene, b. p. 235—245°/16 mm., m. p. 51° (cf. Weissgerber, *A.*, 1911, i, 623), is obtained by the action of glacial acetic, phosphoric, dilute sulphuric, or hydrochloric acid on indene; the reaction is not due entirely to hydrogen ions, since it is also effected by solutions of aluminium or zinc chloride. It is converted by recrystallisation from slightly aqueous acetic acid or alcohol into a substance, m. p. 57—58°; it is uncertain whether this material is an isomeride of that of lower melting point or a more homogeneous product. Contrary to the observations of Weissgerber, di-indene (m. p. 57—58°) is an unsaturated substance, since it combines with bromine without loss of hydrogen bromide to yield a *dibromide*,  $\text{C}_{18}\text{H}_{16}\text{Br}_2$ , m. p. 120—121°, which loses the halogen completely when distilled under diminished pressure or in the presence of alkali, whilst it is oxidised by chromic acid to  $\alpha$ -hydrindone. Di-indene must therefore contain a hydrindene nucleus substituted in the  $\alpha$ -position. Since the absorption spectrum of the compound does not resemble that of stilbene, the constitution  $\text{CH}_2 \langle \text{C}_6\text{H}_4 \rangle \text{C} \begin{smallmatrix} \text{C} \\ \text{---} \end{smallmatrix} \langle \text{C}_6\text{H}_4 \rangle \text{CH}_2$  is excluded, and the choice

rests between  $\text{CH}_2 \langle \text{C}_6\text{H}_4 \rangle \text{CH} \cdot \text{C} \begin{smallmatrix} \text{C} \\ \text{---} \end{smallmatrix} \langle \text{C}_6\text{H}_4 \rangle \text{CH}_2$  and



Di-indene is reduced by sodium and alcohol to *dihydrodi-indene*, b. p. 225—226°/20 mm., 239—241°/50 mm. It is polymerised by concentrated sulphuric acid or hydrogen bromide to amorphous, saturated substances of varying melting point.

A saturated *di-indene*,  $\text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2$ , m. p. 116° (cf. Zschoch,  $\text{CH}_2 \text{---} \text{CH} \cdot \text{CH} \cdot \text{C}_6\text{H}_4$



*Diss.*, Leipzig, 1921), is obtained by the reduction of truxone by Clemmensen's method; the constitution assigned to it has been put forward by Weissgerber for di-indene.

Indene is converted by sulphuric acid (95%) or more slowly by the chlorides of aluminium, calcium, or zinc into polymerides which, in spite of varying complexity,  $(C_9H_8)_{16}$  to  $(C_9H_8)_{22}$ , and differing m. p., 220—280°, are considered sufficiently characteristic to be grouped together under the name "*metaindene*." The material is scarcely affected when heated at 200° under atmospheric pressure, but largely decomposed in sealed tubes at this temperature. At 350°, depolymerisation occurs with production of indene and di-indene.

As judged by the increase in the refractive index of the product, the photopolymerisation of pure indene in an atmosphere of nitrogen follows a normal, non-autocatalytic course, which is preceded by an induction period. After exposure to sunlight during a year, small amounts of the polymerides,  $(C_9H_8)_8$  and  $(C_9H_8)_{16}$ , are produced, the latter being identical with metaindene. If a trace of air is present in the nitrogen, similar polymerides are formed in greater quantity, whilst in the presence of air indene rapidly becomes yellow and deposits crystals.

Indene undergoes little change when heated at 115—118° in the dark in an atmosphere of nitrogen, whereas at 190—200° it is transformed after 96 hours into a colophony-like mass which contains little unchanged indene, some truxene, and mainly a mixture of polymerides including the substances  $(C_9H_8)_8$  and  $(C_9H_8)_{12}$ . It is therefore not so highly polymerised in the dark at 200° as in the light at 20° or by concentrated sulphuric acid. The formation of paraindene,  $(?) (C_9H_8)_4$  (cf. Weger and Billmann, A., 1903, i, 332), could not be established.

Indene is converted by a solution of iodine in aqueous potassium iodide (cf. Meyer, A., 1912, i, 525) into polymerides of high molecular weight; partial iodination also occurs. The isolation of *iodododecaindene*,  $C_{108}H_{95}I$ , m. p. 200—210° (decomp.), is described; the halogen is very firmly retained.

The action of sunlight on solutions of indene and iodine in benzene leads to the formation of resins containing iodine and, possibly, indene di-iodide.  
H. W.

**Preparation of Triphenylmethane and the Action of Heat on the Ethers and Esters Derived from Triphenylcarbinol.** J. F. NORRIS and R. C. YOUNG (*J. Amer. Chem. Soc.*, 1924, 46, 2580—2583).—Triphenylmethyl chloride is converted into triphenylmethane by *n*-butyl ether and by alcohol in presence of aluminium chloride. Triphenylmethane is also formed by the action of aluminium chloride on triphenylcarbinol, or on triphenylmethyl ethyl ether, in ethereal solution. In carbon disulphide solution, aluminium chloride converts triphenylmethyl ethyl ether into triphenylmethyl chloride. Triphenylmethyl ethyl ether decomposes at 300° into triphenylmethane and acetaldehyde; the *iso*-propyl ether yields similarly triphenylmethane and acetone, and

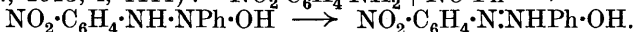
the *n*-butyl ether yields triphenylmethane and butaldehyde. Benzophenone is obtained by the action of aluminium chloride on dichlorodiphenylmethane in ether. A method is described by which triphenylmethane can be prepared simply from carbon tetrachloride, benzene, ether, and aluminium chloride, in 64% of the theoretical yield.

F. G. W.

**Preparation of Perylene.** COMPAGNIE NATIONALE DE MATIÈRES COLORANTES ET DE PRODUITS CHIMIQUES (Brit. Pat. 208721).—Perylene is obtained by distilling a mixture of  $\beta$ -dinaphthol, or its phosphoric or chlorophosphoric esters, with a metallic salt (*e.g.*, zinc chloride, ferric or ferrous chloride) and a metallic reducing agent (*e.g.*, zinc dust or reduced iron). The reaction may take place in the presence of water vapour (in the case of  $\beta$ -dinaphthol itself) or of an inert or a reducing gas (*e.g.*, hydrogen).

W. T. K. B.

**Action of Nitrosobenzene on *o*-Nitroaniline.** G. CHARRIER and A. BERETTA (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 170—173).—The action of nitrosobenzene on either *m*- or *p*-nitroaniline results in the formation of the corresponding nitroazo compound (cf. A., 1913, i, 1111):  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 + \text{NO} \cdot \text{Ph} \longrightarrow$



With *o*-nitroaniline, however, the action of nitrosobenzene yields *o*-nitro-*p'*-nitrosodiphenylamine. This may be the result of dehydrogenation by the excess of nitrosobenzene, but may be due to the fact that the initial additive compound undergoes parasemidinic transposition of the  $\cdot\text{NPh} \cdot \text{OH}$  group, with loss of hydrogen:  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NPh} \cdot \text{OH} \longrightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{C}_6\text{H}_4 \cdot \text{NOH}$ . In view of its intense colour and its solubility in alkali solution, the product is probably the oximino derivative. Oxidation by means of hydrogen peroxide in acetic acid solution converts it completely into *op'*-dinitrodiphenylamine, whilst the action of nitric acid on it gives *opp'*-trinitrodiphenylamine, which is obtainable also by transposition of the corresponding nitrosoamine.

*o*-Nitro-*p'*-nitrosodiphenylamine (*o*-nitrophenylimino-*p*-benzoquinonemonoxime) forms silky, garnet-red needles, m. p. 175°.

T. H. P.

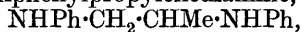
**Derivatives of Aniline Disulphoxide.** C. M. BERE and S. SMILES (*J. Chem. Soc.*, 1924, **125**, 2359—2363; cf. A., 1924, i, 275).—*Acetanilide-p-sulphinic acid*, m. p. 180° (decomp.), is reduced by dilute hydrogen iodide in presence of sulphurous acid to di-*p*-acetamidophenyl disulphoxide (yield 90%); the colourless crystals, m. p. 218—219° (decomp.), obtained from acetic acid, retain solvent, but, after drying at 130° melt at 235° (cf. Hinsberg, A., 1909, i, 374). The disulphoxide is phototropic, becoming yellow in the light and fading in the dark. On reduction, it yields  $\beta$ -di-*p*-acetamidophenyl disulphide, m. p. 182°, which could not be converted into the  $\alpha$ -form (cf. Hinsberg, *loc. cit.*), whilst with *p*-acetamidophenyl mercaptan it gives the disulphide and acetanilide-*p*-sulphinic acid; on hydrolysis, it forms di-*p*-aminophenyl disulph-

oxide in 80% yield, m. p. 175° (decomp.); its colour is yellow, deepening in the light.

5 : 5'-*Diacetamido-2 : 2'-ditolyl disulphoxide*, m. p. 180°, and 4 : 4'-*dihydroxy-3 : 3'-dicarboxydiphenyl disulphoxide*, m. p. 206—208° (decomp.), are colourless and unaffected by light. Benz-anilide-*p*-sulphonyl chloride is obtained in 90% yield from benz-anilide and chlorosulphonic acid and is reduced to benzanilide-*p*-sulphinic acid, m. p. 206° (decomp.), which is reduced further to *di-p*-benzamidophenyl *disulphoxide*, decomp. 220°; this is colourless, slowly becoming yellow in the light. F. M. H.

**Chlorination of *p*-Xylidine, and certain New Azo Dyes.** A. S. WHEELER and M. MORSE (*J. Amer. Chem. Soc.*, 1924, **46**, 2572—2576).—5-*Chloroaceto-p-2-xylidide*, m. p. 176° (cf. Kluge, A., 1885, 1208), was prepared by the action of chlorine on aceto-*p*-xylidide in glacial acetic acid at 16°. Further action of chlorine yields a *dichloroaceto-p-2-xylidide*, m. p. 167°. 5-*Chloro-p-2-xylidine hydrochloride* forms white, silky needles, which sublime when heated. Dyes obtained by coupling diazotised 5-chloro-*p*-xylidine with phenol (brownish-yellow, m. p. 223°), resorcinol (orange-red, m. p. 200—220°), thymol (dull brown, m. p. 290°),  $\alpha$ -naphthol (dark red, m. p. 163—164°),  $\beta$ -naphthol (scarlet-red, m. p. 165°), 2-naphthol-6-sulphonic acid (red, m. p. above 360°), 1-naphthol-5-sulphonic acid (brownish-red, m. p. above 360°), and 1 : 8-dihydroxy-naphthalene-3 : 6-disulphonic acid (purplish-red, m. p. above 360°) are described. F. G. W.

**Resolution of *dl*-Diphenylpropylenediamine and *dl*-1 : 4-Diphenyl-2-methylpiperazine.** F. B. KIPPING and W. J. POPE (*J. Chem. Soc.*, 1924, **125**, 2396—2399).—From the *d*-camphor- $\beta$ -sulphonate of *dl*-diphenylpropylenediamine,



m. p. 28—29° (cf. Trapesonanzjan, A., 1893, i, 79), was isolated 1-*diphenylpropylenediamine d-camphor- $\beta$ -sulphonate*, m. p. 173°,  $[\alpha]_{\text{Hg green}}^{15} + 22.7^\circ$ , giving the *l*-base, m. p. 44—45°,  $[\alpha]_{\text{Hg green}}^{20} - 23.7^\circ$ ; the base from the residues was converted into the 1-*camphor- $\beta$ -sulphonate* and the *d*-base thus isolated, m. p. 44—45°,  $[\alpha]_{\text{Hg green}}^{20} + 24.4^\circ$ ; the rotatory powers of the enantiomorphs diminish considerably with increasing concentration. From the different bases were prepared : *d*- and 1-*diacetyldiphenylpropylenediamine*, m. p. 101—102°,  $[\alpha]_{\text{Hg green}}^{20} + 142^\circ$  and  $-138^\circ$ ; *dl*-*dibenzoyldiphenylpropylenediamine*, m. p. 140—141°, *d*- and 1-*dibenzoyl* derivatives, m. p. 144°,  $[\alpha]_{\text{Hg green}}^{20} - 218^\circ$  and  $+221^\circ$ ; *dl*-*benzenesulphonyldiphenylpropylenediamine*, m. p. 151—152° (*hydrochloride*, m. p. 212—213°), *d*- and 1-*benzenesulphonyl* derivatives, m. p. 161—162° (*hydrochloride*, m. p. 228°),  $[\alpha]_{\text{Hg green}}^{20} - 39.6^\circ$  and  $+38.9^\circ$ .

*dl*-1 : 4-Diphenyl-2-methylpiperazine, m. p. 102—103°, was prepared by Trapesonanzjan's method (*loc. cit.*) and the *d*- and 1-*isomerides*, m. p. 96°, similarly; their rotations,  $[\alpha]_{\text{Hg green}}^{20} - 25.2^\circ$  and  $+24.5^\circ$ , are of opposite sign to those of the parent diphenylpropylenediamines. That no racemisation occurs during formation of the piperazines was proved by resolution of the *dl*-piperazine,

when from 1:1:4-*diphenyl-2-methylpiperazine d-camphor- $\beta$ -sulphonate*, m. p. 175°,  $[\alpha]_{\text{Hg green}}^{20} +32.9^\circ$ , the liberated base gave  $[\alpha]_{\text{Hg green}}^{20} +24.95^\circ$ . The rotations measured are in alcoholic solution. F. M. H.

**Action of Organo-magnesium Compounds on Nitriles.  $\alpha$ -Aminonitriles.** A. CHRISTIAEN (*Bull. Soc. chim. Belg.*, 1924, **33**, 483—490).—Organo-magnesium compounds replace the cyano group of  $\alpha$ -piperidino- $\alpha$ -phenylacetone nitrile by alkyl, and with anilinophenylacetone nitrile form  $\alpha\beta$ -dianilino- $\alpha\beta$ -diphenylethane, reactions analogous to those described by Bruylants (A., 1924, i, 984). Under certain conditions, hydrogen cyanide is eliminated from the nitrile molecule.

Piperidinophenylacetone nitrile was prepared by the action of potassium cyanide and benzaldehyde on piperidine hydrochloride (cf. A., 1904, i, 989). With magnesium ethyl bromide, it gives  $\alpha$ -piperidino- $\alpha$ -phenyl-*n*-propane (yield 80%), b. p. 134°/12 mm., 268°/761 mm.;  $d_4^{20}$  0.9544; *hydrochloride*, m. p. 179°. With magnesium phenyl bromide, it gives piperidinodiphenylmethane, m. p. 75°, b. p. 175—190°/15 mm., purified through its *hydrochloride*, m. p. 249—250°. With magnesium benzyl bromide, it forms piperidinophenylbenzylmethane (yield 60%), b. p. 198—200°/18 mm.; *hydrochloride*, m. p. 120°.

Anilinophenylacetone nitrile, m. p. 85°, was prepared (yield 60%) by interaction of benzaldehyde, sodium hydrogen sulphite, aniline, and potassium cyanide (equimolecular quantities) in concentrated solution. The action of magnesium ethyl bromide or of magnesium phenyl bromide gives two products, *s*-dianilinodiphenylethane, m. p. 139°, b. p. 185—200°/18 mm. (cf. A., 1908, i, 259), in 25—30% of the theoretical yield, and benzyldeneaniline. F. M. H.

**Action of Nitrous Acid on *o*- and *p*-Phenolsulphonic Acids.** W. RODIONOW and W. MATWEEW.—(See i, 83.)

**Action of Sodium on the Acetates of *o*- and *p*-Cresol.** R. I. E. HALL (*J. Chem. Soc.*, 1924, **125**, 2266—2268).—The action of sodium on *o*- and *p*-tolyl acetates is analogous to that on phenyl acetate (cf. Perkin and Hodgkinson, T., 1880, **37**, 487; Perkin, T., 1921, **119**, 1284). Thus from *o*-tolyl acetate there are obtained 2:8-dimethylchromone, b. p. 170—185°/12 mm., m. p. 110°; 1-hydroxy-3:5-dimethylxanthone, b. p. 225—228°/10 mm., m. p. 145°; a little *o*-hydroxytoluic acid, and acetone, ethyl acetate, acetic acid, and *o*-cresol. *p*-Tolyl acetate yields 2:6-dimethylchromone, b. p. 155—160°/10 mm., m. p. 101.5°, and 1-hydroxy-3:7-dimethylxanthone, b. p. 215—220°/12 mm., m. p. 165°, together with *p*-hydroxytoluic acid and *p*-cresol. F. M. H.

**Additive Compounds of Quinol with Aliphatic Amines.** R. N. HARGER (*J. Amer. Chem. Soc.*, 1924, **46**, 2536—2539).—The following additive compounds of quinol with aliphatic amines were obtained by adding the respective amine to a solution of quinol in ether or benzene: quinol-diethylamine,  $[\text{C}_6\text{H}_4(\text{OH})_2]_2\text{NHEt}_2$ , m. p. 134°, stable in the dry state, completely dissociated in aqueous

solution, in which oxidation rapidly sets in; *quinol-dimethylamine*,  $C_6H_4(OH)_2.NHMe_2$ , m. p.  $127^\circ$ , with an odour of methylamine, methylamine being lost on exposure to air; *quinol-ethylamine*,  $C_6H_4(OH)_2.NH_2Et$ , m. p.  $87-90^\circ$ , very readily oxidised in air; and *quinol-benzylamine*,  $C_6H_4(OH)_2.CH_2Ph.NH_2$ , m. p.  $71^\circ$ .  
F. G. W.

**Colorimetric Dissociation Constants of the Mono- and Di-nitroquinols.** E. B. R. PRIDEAUX and G. R. NUNN (*J. Chem. Soc.*, 1924, 125, 2110—2116).—Dinitroquinol, m. p.  $134-136^\circ$ , prepared by Nietzki's method (A., 1883, 466), is 2 : 6-dinitroquinol, as stated by Bader (A., 1891, 257), not the 2 : 5-compound, as stated by Beilstein. On treatment with buffer solutions of various acidities it develops colours agreeing with those described by Henderson and Forbes (A., 1910, ii, 541). The  $M/20$  solution in alcohol gives complete absorption from  $\lambda 0.475 \mu$  downwards. Distinct bands, with a portion of the violet end of the spectrum visible, are shown in neutral and alkaline solutions. The colorimetric constants,  $k_1$ ,  $k_2$ ,  $k_3$ , of the yellow, orange, and violet forms (cf. equations of Noyes and others, A., 1910, ii, 746) were investigated by means of the colour comparator (or by Nessler glasses). The first tinge of orange showed at  $p_H$  3.0 and deepened as  $p_H$  increased; the first violet tint showed at  $p_H$  8.0, fully developed at  $p_H$  9.5 to 10; the tube at  $p_H$  2.5 was the last to show a pure yellow shade. The fractions transformed at different values of  $p_H$  were found by comparison with an alkaline solution of dinitrophenol which, it was assumed, would have at corresponding concentrations a yellow colour identical with that which would be shown by the dinitroquinol if it could be completely changed into the yellow form without any further change into the orange (cf. Salm, A., 1906, ii, 218; Gillespie, A., 1920, ii, 382; Michaelis and Gyemant, A., 1921, ii, 56; Kolthoff, A., 1921, ii, 409). The values obtained,  $p_{k_1} = 2.8$ ,  $p_{k_2} = 5.2$ ,  $p_{k_3} = 9.05$ , were checked by the buffer solution method. Mononitroquinol prepared by Elb's method (A., 1893, i, 640) showed similar absorption spectra and had the constants  $p_{k_1} = 3.25$ ,  $p_{k_2} = 7.6$ ,  $p_{k_3} = 10.2$ . It is considered that in the case of acids consisting of *aci*- and *pseudo*-tautomerides in equilibrium, the electrometric ( $k_e$ ) and colorimetric ( $k_c$ ) constants are mainly controlled by the *aci*-tautomeride. Comparison of their constants shows that the nitroquinols are (as expected) stronger acids than the nitrophenols. A. C.

**Oxidation of Quinol in Presence of Aliphatic Amines. Formation of Bisalkylaminobenzoquinones.** R. N. HARGER (*J. Amer. Chem. Soc.*, 1924, 46, 2540—2551).—When an aqueous or alcoholic solution containing quinol and a primary or secondary amine is exposed to air or oxygen, the latter is absorbed and a bisalkylaminobenzoquinone is produced. The amount of oxygen absorbed is greater than that required for the formation of the above derivative, due probably to oxidation of the uncondensed quinol. Hydrogen peroxide is not a product of the reaction. *Bismethylaminobenzoquinone* forms red plates, m. p.  $270^\circ$ ; *bisdimethylaminobenzoquinone*, red needles, m. p.  $171^\circ$  (cf. Mylius, A., 1885,

803); *bisethylaminobenzoquinone*, red plates, m. p.  $212^{\circ}$ ; *bisisobutylaminobenzoquinone*, red plates, m. p.  $196^{\circ}$ ; *bis-sec.-butylaminobenzoquinone*, dark needles, m. p.  $160^{\circ}$ ; *bisamylaminobenzoquinone*, flat, purple crystals, m. p.  $170^{\circ}$ ; *bisallylaminobenzoquinone*, brilliant red crystals, m. p.  $195^{\circ}$ ; and *bisbenzylaminobenzoquinone*, bright red crystals, m. p.  $246^{\circ}$ . A solution of quinol in 10*N*-aqueous ammonia absorbs oxygen and gradually sets to a stiff black jelly; in presence of 10*N*-sodium hydroxide, quinol absorbs 3.7 equivalents of oxygen, and the solution deposits brown needles. When alcoholic methylamine is mixed with benzoquinone in an atmosphere of hydrogen, heat is evolved, the liquid darkens, but no product is deposited; in contact with air or oxygen, the above bismethylaminobenzoquinone separates in an impure condition. The same compound is obtained by the action of hydrogen peroxide on quinol and methylamine.

F. G. W.

**Synthesis of Divarinol.** F. MAUTHNER (*J. pr. Chem.*, 1924, [ii], 108, 275—277; cf. A., 1924, i, 524).—3 : 5-Dimethoxyphenyl ethyl ketone on reduction by Clemmensen's method gives 3 : 5-dimethoxy-*n*-propylbenzene, b. p.  $126$ — $127^{\circ}/10$  mm. By demethylation with hydriodic acid in acetic acid solution, 3 : 5-dihydroxy-*n*-propylbenzene, m. p.  $83$ — $84^{\circ}$ , is produced, identical with the divarinol obtained by Hesse from *Evernia divaricata* (A., 1911, i, 208).

A. E. C.

**Oxidation-reduction. VI. Indophenols. (A) Dibromo-Substitution Products of Phenolindophenol. (B) Substituted Indophenols of the *o*-Type. (C) Miscellaneous.** B. COHEN, H. D. GIBBS, and W. M. CLARK (*U.S. Public Health Reports*, 1924, 39, 804—823).—A study of the equilibrium potentials found with mixtures of the oxidant and reductant of the following compounds: *o*-cresolindo-2 : 6-dibromophenol, *m*-cresolindo-2 : 6-dibromophenol, thymolindo-2 : 6-dibromophenol, guaiacolindo-2 : 6-dibromophenol, *o*-bromophenolindo-2 : 6-dibromophenol, *m*-bromophenolindo-2 : 6-dibromophenol, *o*-chlorophenolindo-2 : 6-dibromophenol, phenol-*o*-indophenol, *o*-bromophenol-*o*-indophenol, guaiacolindophenol, 1-naphtholindophenol, and 1-naphtholindo-*o*-cresol-2-sulphonate. Tables are given showing the potentials at various concentrations, and curves are given showing the effects of successive bromine substitution among them, which is an increase of the acid dissociation constant in the oxidised state. A distinct but slight shift to more positive potentials is observed in *m*-cresol-*o*-indophenol as compared with the corresponding *p*-compound.

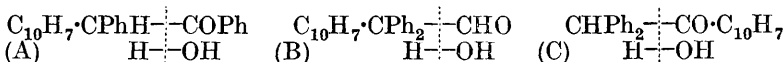
CHEMICAL ABSTRACTS.

**Dehydration of the Optically Active Methyl- and Ethylhydrobenzoins.** A. MCKENZIE and R. ROGER (*J. Chem. Soc.*, 1924, 125, 2148—2155; cf. A., 1924, i, 650).—*r*- $\alpha\beta$ -Dihydroxy- $\alpha\beta$ -diphenylpropane (*r*-methylhydrobenzoin) was dehydrated by boiling with a mixture of equal parts of concentrated sulphuric acid and water. The products formed were the *r*-diethylenic oxide, m. p.

171—172° (cf. Lévy, A., 1921, i, 860), and diphenylmethylacetaldehyde (cf. Tiffeneau and Dorlencourt, A., 1906, i, 724), which gave a semicarbazone, m. p. 194—195°, and an oxime, m. p. 121—122°. Phosphoric anhydride gave a similar result. The diethylenic oxide forms no amino-alcohol with ammonia and does not react with magnesium methyl iodide. *l*-Methylhydrobenzoin,  $[\alpha]_D^{25} + 34^\circ$ , prepared by the method of McKenzie and Wren (cf. T., 1910, 97, 473), formed a brown, pasty mass with dilute sulphuric acid (*d* 1.55) from which *l*-di-diphenylmethylethylene oxide,  $\left(\begin{array}{c} \text{CPhMe}\cdot\text{CHPh} \\ \text{---O---} \end{array}\right)_2$ , m. p. 183—184°, was isolated, having  $[\alpha]_D^{25} - 76.8^\circ$  in chloroform and  $[\alpha]_D^{25} - 76.2^\circ$  in benzene. The rotatory power was not altered on keeping with alcoholic potassium ethoxide. The semicarbazone of diphenylmethylacetaldehyde was obtained from the oil remaining after the removal of the oxide. Dehydration of *l*-methylhydrobenzoin by concentrated sulphuric acid gave inactive methyldeoxybenzoin. The *l*-diethylene oxide also yielded *r*-methyldeoxybenzoin under like treatment. The semicarbazone (m. p. 193—194°) isolated by Neuberg and Ohle (A., 1922, i, 480), and believed by them to be that of methyldeoxybenzoin, is probably the semicarbazone of diphenylmethylacetaldehyde. *r*-Ethylhydrobenzoin with dilute sulphuric acid yields the diethylenic oxide, m. p. 137—138°, and diphenylbutanone, the semicarbazone of which has m. p. 194—195° (Orékhov gives 191—192°). Concentrated sulphuric acid converts the oxide into ethyldeoxybenzoin and some diphenylbutanone. *l*-Di-diphenylethylethylene oxide,  $\left(\begin{array}{c} \text{CPhEt}\cdot\text{CHPh} \\ \text{---O---} \end{array}\right)_2$ , m. p. 167—168°, was obtained by the action of diluted sulphuric acid on the *l*-ethylhydroxybenzoin. It had  $[\alpha]_D^{25} - 91.5^\circ$  in chloroform and  $[\alpha]_D^{25} - 106.9^\circ$  in benzene. Treatment with concentrated sulphuric acid converted it into the inactive ethyldeoxybenzoin. The consistency of this with the mechanism of vinyl dehydration advanced by Tiffeneau and Orékhov (A., 1920, i, 673) is pointed out. It is considered that dehydration with concentrated acid involves the intermediate formation of the laevorotatory diethylenic oxide, which then undergoes inactivation in its conversion into the *r*-alkyldeoxybenzoin. A. C.

**Elimination of the Amino Group of Tertiary Amino-Alcohols. II. The Semipinacolinic Deamination of  $\beta$ -Hydroxy- $\alpha\beta$ -diphenyl- $\beta$ -naphthylethylamine.** A. MCKENZIE and W. S. DENNLER (*J. Chem. Soc.*, 1924, 125, 2105—2110).— $\alpha$ -Naphthylhydrobenzoin,  $\text{C}_{10}\text{H}_7\cdot\text{CPh}(\text{OH})\cdot\text{CHPh}\cdot\text{OH}$  (the expected product of the action of nitrous acid on  $\beta$ -hydroxy- $\alpha\beta$ -diphenyl- $\beta$ -naphthylethylamine, cf. T., 1923, 123, 79), has been dehydrated by means of sulphuric acid and the following isomeric products have been identified: diphenylnaphthylacetaldehyde,  $\text{C}_{10}\text{H}_7\cdot\text{CPh}_2\cdot\text{CHO}$  (I), (semihydrobenzoin transformation); naphthyldeoxybenzoin,  $\text{C}_{10}\text{H}_7\cdot\text{CHPh}\cdot\text{COPh}$  (II), (vinyl dehydration or semipinacolinic transformation); diphenylacetone,  $\text{CHPh}_2\cdot\text{CO}\cdot\text{C}_{10}\text{H}_7$ , (III) (semipinacolinic transformation); and

diphenylnaphthylethylene oxide,  $\text{C}_{10}\text{H}_7\cdot\text{CPh}\cdot\text{CHPh}$  (IV), or  $\text{C}_{10}\text{H}_7\cdot\text{CH}\cdot\text{CPh}_2$  (V) (oxidic dehydration). Contrary to the views of Elbs (cf. A., 1887, 940), the migrational tendency of the phenyl group is considered to be greater than that of the naphthyl group.  $\alpha$ -Naphthylhydrobenzoin when boiled with sulphuric acid and water yields a viscous oil from the benzene solution of which ethyl alcohol precipitates (IV) (or V), m. p. 180—181°. This ethylenic oxide is unimolecular in benzene solution.  $\alpha$ -Naphthyldeoxybenzoin (II), m. p. 109—110°, differing from the isomeride, m. p. 108—109° (cf. McKenzie and Richardson, T., 1923, 123, 79), in the coloration which it gives with concentrated sulphuric acid, together with an amorphous solid, were isolated from the benzene mother-liquors. Hydrolysis of the amorphous solid with boiling alcoholic potassium ethoxide resulted in the isolation of (i) diphenylnaphthylmethane (B) indicating the presence of diphenylnaphthylacetaldehyde, and (ii) phenylnaphthylmethane (A) confirming the presence of (II), whilst both benzoic and formic acids were found in the alkaline solution.



The isomeride, m. p. 108—109°, obtained by dehydration with concentrated sulphuric acid is diphenylacetone (III), since it yields  $\alpha$ -naphthoic acid (C) with alcoholic potassium hydroxide and benzophenone on oxidation with chromic acid. Diphenylacetone was synthesised by the action of naphthalene and aluminium chloride, and also of magnesium  $\alpha$ -naphthyl bromide on diphenylacetyl chloride.

A. C.

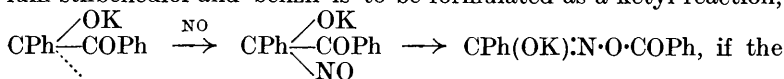
**Potassium Stilbenediol.** G. SCHEUING and A. HENSLE (*Annalen*, 1924, 440, 72—88).—The red dipotassium salt of stilbenediol obtained by Staudinger and Binkert (A., 1922, i, 1016) is more readily obtained by the action of potassium ethoxide on benzoin in boiling benzene, the reaction constituting a general method for the preparation of such compounds. The potassium salt undergoes considerable alcoholysis in alcoholic solution, and, in contrast with the colourless monosodium derivative (Meisenheimer, A., 1905, i, 291), which with acetic anhydride or benzoyl chloride is converted into the monoacyl derivative of benzoin, yields *isobenzil* with benzoyl chloride and the diacetate of stilbenediol with acetic anhydride (cf. Nef, A., 1900, i, 20). Benzyl chloride converts the potassium salt into benzylbenzoin, m. p. 119° (*urethane*, m. p. 221°), identical with the product obtained from benzil and magnesium benzyl chloride (García Banús, A., 1922, i, 734), the benzyl group being thus linked to carbon.

The reactions of potassium stilbenediol have been further studied with a view to obtain evidence of the nature of the reddish-brown colouring matter produced in the action of potassium ethoxide on an alcoholic solution of benzoin. The autoxidation of this solution

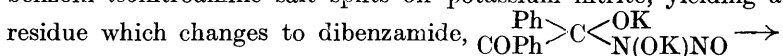


yields potassium benzoate and benzil, whereas autoxidation of the potassium stilbenediol yields mainly benzoic acid (cf. Staudinger, *loc. cit.*). Nitric oxide (2 mols.) reacts readily with potassium stilbenediol (1 mol.) in alcoholic solution, with formation of dibenzhydroxamic acid (yield 40%), nitrous oxide, and benzil (yield 55%). An intermediate additive compound comparable with the products obtained by Traube (A., 1898, i, 349) is probably first formed, which undergoes the change  $\text{COPh} \cdot \text{CPh} \begin{smallmatrix} \text{OK} \\ \text{N(NO)OK} \end{smallmatrix} \longrightarrow \text{COPh} \cdot \text{CO} \cdot \text{Ph} + \text{K}_2\text{O} + \text{H}_2\text{O}$ .

Dibenzhydroxamic acid is formed directly by the action of nitric oxide on benzil in presence of alkali. Pyruvic acid and phenylpyruvic acid on treatment with nitroxyl undergo similar transformation into hydroxamic and benzhydroxamic acids. It is also possible, however, that the formation of dibenzhydroxamic acid from potassium stilbenediol and benzil is to be formulated as a ketyl reaction,



violet-red solution obtained from potassium and benzil in benzene solution contains the ketyl of benzil (cf. Schlenk, A., 1913, i, 1205), but the highest yields of dibenzhydroxamic acid (96%) were obtained by the action of nitric oxide on a benzene solution of benzoin (1 mol.), benzil (3 mols.), and potassium ethoxide (2 mols.) containing very little alcohol, which is more in harmony with Nef's view of the violet-red substance as a quinonoid compound of potassium stilbenediol and benzil. In the presence of *pp'*-dibromobenzil, nitric oxide reacts with potassium stilbenediol in alcohol to give *pp'*-dibromodibenzhydroxamic acid,  $\text{C}_{14}\text{H}_9\text{O}_3\text{NBr}_2$ , m. p.  $173^\circ$ , benzoic acid, *p*-bromobenzoic acid, benzhydroxamic acid, ethyl benzoate, and benzil, a little *pp'*-dibromobenzil being also isolated. The action of nitric oxide on pure potassium stilbenediol in ethereal suspension at the ordinary temperature gives dibenzamide (35% yield), some benzoic acid, and a little dibenzhydroxamic acid (9%). In the cold, these proportions are approximately reversed; hydroxamic acid is formed in 30% yield, dibenzamide in only 10% yield, together with a mixture of benzoic and benzoic acids. It is suggested that the benzoin isonitroamine salt splits off potassium nitrite, yielding a



$\text{Ph} \cdot \text{C(OK):N} \cdot \text{COPh} + \text{KNO}_2$ , a mechanism which finds some support in the formation of nitrite in the reaction. In view of the above results, the Angeli-Rimini reaction (A., 1912, i, 117, 626) loses its value as a specific reagent for aldehydes. R. B.

**1 : 3-Dimethylcyclopentane-3-carboxylic Acid.** N. ZELINSKI and E. RJACHINA (*Ber.*, 1924, **57**, [B], 1931).— $\beta$ -Methyladipic acid is converted by passage over thorium oxide at  $360\text{--}380^\circ$  into the corresponding ketone, which, with magnesium methyl iodide, yields 1 : 3-dimethylcyclopentan-3-ol, b. p.  $70^\circ/20$  mm. The latter substance is converted by hydrogen chloride into the corresponding chloride, b. p.  $134\text{--}136^\circ$ , which, with magnesium and carbon

dioxide, yields 1 : 3-dimethylcyclopentane-3-carboxylic acid, b. p. 226—227°/746 mm.,  $d_4^{20}$  0.9899,  $n_D^{20}$  1.4479. The amide, m. p. 95°, and the copper salt are described. The boiling point of the acid is much lower than that of the isomeric heptanaphthenecarboxylic acid. H. W.

**Influence of Substituents on Chemical and Physical Properties : the Velocity of Reaction between Substituted Benzoic Anhydrides and an Aliphatic Alcohol.** H. G. RULE and T. R. PATERSON (*J. Chem. Soc.*, 1924, 125, 2155—2163).—The influence of the groups NO<sub>2</sub>, Cl, OMe, and Me on the reactivity of benzoic anhydride has been determined, using (a) an excess of ethyl alcohol at 60°, or (b) a molecular proportion of cetyl alcohol in benzene solution. Comparative figures for the substituents Me, OMe, and H were obtained by method (a), the velocity coefficient ( $k$ ) being calculated from the usual expression for a unimolecular reaction. Owing to high reactivity and low solubility of the nitro and chloro derivatives, the effects of the groups NO<sub>2</sub> and Cl as compared with H were determined by method (b), and the velocity coefficients calculated from  $k' = 1/a \cdot 1/t \cdot x/(a-x)$ , where  $a$  is the original concentration of anhydride and of cetyl alcohol, and  $x$  is the number of gram-mols. converted in  $t$  hours. The concentration used was 0.02*N*. The mean values of  $k$  were :— $o$ -Cl, 0.142;  $m$ -NO<sub>2</sub>, 0.81;  $o$ -OMe, 0.0078;  $m$ -OMe, 0.029;  $p$ -OMe, 0.006;  $o$ -Me, 0.0086;  $m$ -Me, 0.0143;  $p$ -Me, 0.0109; for  $k'$  :  $o$ -NO<sub>2</sub>, 0.103;  $m$ -NO<sub>2</sub>, 0.51;  $p$ -NO<sub>2</sub>, 0.89;  $o$ -Cl, 0.12;  $m$ -Cl, 0.55;  $p$ -Cl, 0.49. Contrary to the results of Michael and Oechslin (cf. A., 1909, ii, 220) with the esterification of the free acids in excess of methyl alcohol at 135°, the anhydride reaction is highly sensitive to the influence of substituents, the effect being in the order NO<sub>2</sub> > Cl > (H, OMe) > Me (in both cases), although if the  $o$ -,  $m$ -, and  $p$ -derivatives are considered separately the positions of Cl and OMe vary slightly according to the isomerides compared. A table is given showing the influence of the same (and other) substituents on the reactivity of benzene determined by other methods, and the agreement of these results is pointed out (cf. Rule, A., 1924, ii, 645; Kellas, A., 1898, i, 86; Olivier, A., 1923, i, 769). Except in the case of certain of the  $o$ -anhydrides, there is a definite "alternate effect" observable in the influence of a substituent in the  $o$ -,  $m$ -, and  $p$ -positions, respectively. Thus  $k_m > k_p$  or  $k_o$  for the negative substituents Me, OMe, and Cl, whilst for the positive nitro group  $k_m < k_p$ . In the esterification of the free acids, Michael and Oechslin (*loc. cit.*) find the reverse of this order (cf. Kailan, A., 1907, ii, 242).

The following new compounds are described :  $p$ -chlorobenzoic anhydride, m. p. 194.8°, obtained in 50% yield by heating the acid chloride with the sodium salt of the acid;  $m$ -chlorobenzoic anhydride, m. p. 95.5°, by oxidation of  $m$ -chlorobenzaldehyde and dehydration with phosphoric oxide;  $o$ -chlorobenzoic anhydride, m. p. 79.6°;  $o$ -methoxybenzoic anhydride, m. p. 72.4°, by the action of sodium carbonate and pyridine on  $o$ -methoxybenzoyl chloride;  $m$ -methoxybenzoic anhydride, m. p. 66.6°. A. C.

**Action of Benzoyl Peroxide on Chloroform and on Carbon Tetrachloride.** (A New Synthesis of  $\omega$ -Trichlorotoluic Acids.) J. BOËSEKEN and H. GELISSEN (*Rec. trav. chim.*, 1924, **43**, 869—871).—When boiled with excess of carbon tetrachloride on the water-bath, benzoyl peroxide is converted into  $\omega$ -trichloro-*p*-toluic acid (Perkin and Davis, T., 1922, **121**, 2202), whilst small quantities of hexachloroethane, chlorobenzene, and phthalic acid are formed, with evolution of carbon dioxide and carbonyl chloride. Similarly, with chloroform,  $\omega$ -trichloro-*p*-toluic acid and benzene are the principal products, a little hexachloroethane and diphenyl being produced, whilst carbon dioxide and carbonyl chloride are evolved. The reaction probably follows the course  $(\text{Ph}\cdot\text{CO})_2\text{O}_2 + \text{CCl}_4 \longrightarrow \text{Ph}\cdot\text{CO}_2\text{CCl}_3 + \text{PhCl} + \text{CO}_2 \longrightarrow \text{C}_6\text{H}_4(\text{COCl})_2 + \text{HCl}$  or  $\text{CCl}_3\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ .

By the action of dry benzene on benzoyl peroxide, benzoic acid, carbon dioxide, and diphenyl are produced. Since, with *p*-chlorobenzoyl and *m*-nitrobenzoyl peroxides, *pp'*-dichlorodiphenyl and *mm'*-dinitrodiphenyl are not produced, but only mono-substituted diphenyl derivatives, the reaction is probably to be represented:  $(\text{Ph}\cdot\text{CO})_2\text{O}_2 + \text{C}_6\text{H}_6 \longrightarrow \text{Ph}\cdot\text{CO}_2\text{H} + \text{Ph}\cdot\text{Ph} + \text{CO}_2$ ;  $(\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2)_2\text{O}_2 + \text{C}_6\text{H}_6 = \text{X}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H} + \text{Ph}\cdot\text{C}_6\text{H}_4\text{X} + \text{CO}_2$ . R. B.

**Electrolytic Reduction of 2:6-Dibromobenzoic Acid.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1924, **43**, 872—873).—2:6-Dibromobenzoic acid, m. p. 151—152° (cf. Sudborough, T., 1895, **67**, 602), on reduction by the usual electrolytic method (Mettler, A., 1905, i, 436; Olivier, A., 1922, i, 646) yields the *o*-bromobenzyl alcohol obtained by Mettler (A., 1906, i, 851) by the electrolytic reduction of *o*-bromobenzoic acid, the introduction of a second ortho bromine atom thus increasing the mobility of the first. Sodium amalgam in acid solution does not reduce 2:6-dibromobenzoic acid; in alkaline solution hydrogenation of the ring occurs.

R. B.

**Reduction Products of Arylidenecyanoacetic Acids.** W. BAKER and A. LAPWORTH (*J. Chem. Soc.*, 1924, **125**, 2333—2338).—Arylidenecyanoacetic acids, unlike the corresponding alkylidene compounds, are readily reduced by sodium amalgam and water to the corresponding saturated acids. Benzylidene-, anisylidene-, salicylidene-, piperonylidene-, *m*-hydroxybenzylidene-, and 2:4-dihydroxybenzylidene-cyanoacetic acids have been reduced by this method with good yields.  $\alpha$ -Cyano- $\beta$ -anisylpropionic acid has m. p. 82.5°,  $\alpha$ -cyano- $\beta$ -salicylpropionic acid, m. p. 138°,  $\alpha$ -cyano- $\beta$ -*m*-tolylpropionic acid, m. p. 105—106°.  $\alpha$ -Cyano- $\beta$ -2:4-dihydroxyphenylpropionic acid, m. p. 135—140°, was not obtained in the pure state, owing to the extreme difficulty of recrystallisation. The saturated acids are readily hydrolysed by alkali hydroxide to the corresponding malonic acids; treatment with copper powder generally leads to the formation of the nitrile. Whilst bromination of  $\alpha$ -cyano- $\beta$ -phenylpropionic acid in water results in partial hydrolysis of the nitrile group, in benzene evolution of carbon dioxide occurs and

$\alpha$ -bromo- $\beta$ -phenylpropionitrile, b. p. 137—138°/9—10 mm.,  $d_{17}^{25}$  1.438, is formed. This substance is hydrolysed by aqueous sodium hydroxide to sodium cinnamate.  $\alpha$ -Bromo- $\beta$ -phenylpropionamide, m. p. 128.5°, is prepared from the nitrile by means of a warm alkaline solution of hydrogen peroxide. It may also be obtained by solution of the nitrile in 95% sulphuric acid and, after maintaining at 25° for 40 hours, diluting with water. Hydrolysis with alkalis yields cinnamic acid. C. J. S.

**Internally Complex Borates.** A. ROSENHEIM (*Ber.*, 1924, 57, [B], 1828).—In their recent communication (Rosenheim and Vermehren, A., 1924, i, 1194), the authors have overlooked the possibility of a spiran-like, molecular asymmetry as an explanation of the optical isomerism of the salicylic acid borates. The hypothesis that the boron atom has the co-ordination number 4 in complex anions is not, however, weakened. H. W.

**Alkylamino Esters of Tropic and Acyltropic Acids.** CHEMISCHE WERKE GRENZACH AKT.-GES. (D.R.-P. 382137; Swiss Pats. 98917, 99208, and 99209; from *Chem. Zentr.*, 1924, i, 1105).—The following compounds are described:  $\beta$ -dimethylaminoethyl tropate hydrochloride,  $\text{NMe}_2 \cdot [\text{CH}_2]_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{OH} \cdot \text{HCl}$ , a colourless oil;  $\beta$ -piperidinoethyl tropate,  $\text{C}_5\text{H}_{10}\text{N} \cdot [\text{CH}_2]_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{OH}$ , an oil;  $\beta$ -piperidinoethyl acetyltropate hydrochloride,  $\text{C}_5\text{H}_{10}\text{N} \cdot [\text{CH}_2]_2 \cdot \text{O} \cdot \text{CO} \cdot \text{CHPh} \cdot \text{CH}_2 \cdot \text{OAc} \cdot \text{HCl}$ , m. p. 164°. G. W. R.

**Walden Inversion. VIII. Influence of the Solvent on the Sign of the Product in the Conversion of  $\beta$ -Hydroxy- $\beta$ -phenylpropionic Acids into  $\beta$ -Bromo- $\beta$ -phenylpropionic Acids.** G. SENTER and A. M. WARD (*J. Chem. Soc.*, 1924, 125, 2137—2144).—The influence of the solvent on the sign of rotation in the conversion of the  $\beta$ -hydroxy- $\beta$ -phenylpropionic acids into the  $\beta$ -bromo-acids by means of hydrogen bromide has been investigated in eleven different solvents, including formic, acetic, and propionic acids; a reversal of sign occurs in each case. The activity of the resulting bromo-acid varies with the experimental conditions and with the solvent. The yield of bromo-acid obtained in the same solvent increases with rise in temperature, whilst the activity decreases. The best conditions for the conversion of the hydroxy-acid into the bromo-acid in glacial acetic acid solution were found to be at 25° in a 10% solution (previously saturated with hydrogen bromide) when a 74% yield of bromo-acid having  $[\alpha] +51.6^\circ$  was obtained. C. J. S.

**Refractivity of *o*-Phthalaldehydic Acid. (A Correction.)** L. SEEKLES (*Rec. trav. chim.*, 1924, 43, 550).—Calculation of the refractivity of *o*-phthalaldehydic acid in alcoholic solution by means of Auwers' constants (A., 1915, ii, 297) showed that it occurs in the aldehydic acid form and not the lactonic (cf. A., 1924, i, 642).

F. M. H.

**Influence of Substituents on the Formation of Derivatives of 1-Hydrindone from  $\beta$ -Phenylpropionic Acids.** E. A. SPEIGHT, A. STEVENSON, and J. F. THORPE (*J. Chem. Soc.*, 1924, **125**, 2185—2192; cf. T., 1923, **123**, 1755).— $\beta$ -Phenylpropionic acids with the substituent groups  $\text{CH}_2\cdot\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{H}$ , Me, and Et (with or without a carboxyl group in addition), respectively, have been treated with concentrated sulphuric acid (*a*) at the ordinary temperature, (*b*) at  $100^\circ$ , and the products of reaction investigated.  $\beta$ -Phenylglutaric acid,  $\text{CHPh}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , obtained by a modification of Michael's method (cf. A., 1887, 672), is unchanged at the ordinary temperature, but at  $100^\circ$  forms 1-ketohydrindene-3-acetic acid,  $\text{C}_6\text{H}_4\langle\text{CH}(\text{CH}_2\text{CO}_2\text{H})\rangle\text{CH}_2$ , m. p.  $154\cdot5^\circ$ ; semicarbazone, m. p.  $249^\circ$  (decomp.). Hot alkaline permanganate oxidises it to phthalic acid. Ethyl  $\beta$ -phenylglutarate, b. p.  $174\text{—}175^\circ/9\text{ mm.}$  gives the same hydrindone with concentrated sulphuric acid at  $100^\circ$ , and so does the anhydride of the acid, which is evidence of intermediate anhydride formation in these condensations (cf. T., 1923, **123**, 1755). With benzylsuccinic acid (a  $\beta$ -phenylpropionic acid with  $-\text{CH}_2\cdot\text{CO}_2\text{H}$  in the  $\alpha$ -position), ring closure appears to take place with formation of a tetrahydronaphthalene derivative. Phenylsuccinic acid shows no change under (*a*), but at  $100^\circ$  forms 1-ketohydrindene-3-carboxylic acid, m. p.  $84^\circ$ , which in a vacuum forms an anhydride, m. p.  $120^\circ$ ; semicarbazone, m. p.  $231^\circ$  (decomp.). This acid forms a tar with hot alkaline permanganate, but is oxidised to phthalic acid by chromic acid. Benzylmalonic acid,  $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{CO}_2\text{H})_2$ , and phenylpyruvic acid are decomposed by sulphuric acid at both temperatures. Ethyl benzoylmalonate forms benzoylactic acid at the ordinary temperature and at  $100^\circ$  yields benzoic acid, without any ring formation. Both  $\alpha$ -benzylpropionic and benzylmethylmalonic acids at  $100^\circ$  form 1-keto-2-methylhydrindene; semicarbazone, m. p.  $198^\circ$  (cf. Miller and Rohde, A., 1890, 1139). Both  $\alpha$ -benzylbutyric and benzylethylmalonic acids at  $100^\circ$  give 1-keto-2-ethylhydrindene, having a faint, pleasant odour, b. p.  $143\text{—}144^\circ/22\text{ mm.}$ ; semicarbazone, m. p.  $202^\circ$  (decomp.).  $\beta$ -Phenylbutyric acid yields 1-keto-3-methylhydrindene at both temperatures; the m. p. of the semicarbazone is  $208^\circ$ , not  $190^\circ$  (cf. Mitchell and Thorpe, T., 1910, **97**, 2275). Phenylmethylis succinic acid shows unusual behaviour, giving malonic acid at the ordinary temperature and completely decomposing at  $100^\circ$ . The simplest acid capable of undergoing hydrindone formation,  $\beta$ -phenylpropionic acid, shows no change at  $100^\circ$ , but at  $130^\circ$  a 10% yield of 1-ketohydrindene is obtained. The above reactions show (i) that neither a second carboxyl group nor a  $\beta$ -substituent is necessary for ring-closure, (ii) that an  $\alpha$ -carboxyl group appears to hinder whilst a  $\beta$ -carboxyl group appears to assist ring formation, and (iii) that an alkyl group in either position has a powerful positive effect. A. C.

**Synthesis of certain Dihydrophenanthrene Derivatives.** A. WINDAUS and W. EICKEL (*Ber.*, 1924, **57**, [B], 1871—1875).—In continuation of previous work (Kirchner, A., 1923, i, 913),

3-*p*-methoxybenzylideneoxindole is reduced by hydrogen in the presence of spongy palladium to 3-*p*-methoxybenzyloxindole, m. p. 114°. Fission of the lactam ring is effected with barium hydroxide at 170—180°, and the amino-acid thus produced is diazotised and the solution treated with copper powder, whereby 3-methoxy-9 : 10-dihydrophenanthrene-9-carboxylic acid, m. p. 155°, is produced. The methyl ester, m. p. 98°, is converted into the hydrazide, m. p. 152—153°, which yields successively the corresponding azide, decomp. about 72° when rapidly heated, and the urethane, m. p. 124—125°; the latter compound is converted by hydrochloric acid into 3-methoxyphenanthrene, m. p. 60°. The following compounds are prepared by a similar series of changes starting from piperonal and oxindole : 3-(3' : 4'-methylenedioxybenzyl)oxindole, m. p. 138—139°; 3 : 4(2 : 3)-methylenedioxy-9 : 10-dihydrophenanthrene-9-carboxylic acid, m. p. 192—193° (methyl ester, m. p. 107—108°; hydrazide, m. p. 187—189°; azide, decomp. about 95°; corresponding urethane, m. p. 150—152°).  
H. W.

**Derivatives of 1 : 8-Naphthalic Acid. II. Preparation and Properties of 8-Benzoyl- $\alpha$ -naphthoic Acid and its Derivatives.** F. A. MASON (*J. Chem. Soc.*, 1924, 125, 2119—2123).—8-Benzoyl- $\alpha$ -naphthoic acid, m. p. 110—112° (decomp.), is prepared in 72% yield by adding a mixture of aluminium chloride in tetrachloroethane and dry benzene to a cooled solution of 1 : 8-naphthalyl chloride in tetrachloroethane (cf. Copisarow, T., 1917, 111, 10). It differs from benzoylbenzoic acid in its instability when heated (it decomposes even at 100°) and in not forming a diketone, with ring closure, when heated with concentrated sulphuric acid or other condensing agents. When heated with thionyl chloride, it gives 8-benzoyl- $\alpha$ -naphthoyl chloride, m. p. 125—127°, rhombic crystals which fume in air with hydrolysis. Treatment with aluminium chloride does not result in ring closure. The ethyl ester has m. p. 166—167°. Toluoyl and xyloyl derivatives were prepared from 1 : 8-naphthalyl chloride in a similar way to the benzoyl compound. 8-Toluoyl- $\alpha$ -naphthoic acid has m. p. 135—137°, then solidifying and remelting at 175—177° (heated slowly). 8-o-Xyloyl- $\alpha$ -naphthoic acid has m. p. 147—149°; 8-m-xyloyl- $\alpha$ -naphthoic acid, m. p. 214—215°; 8-p-xyloyl- $\alpha$ -naphthoic acid, m. p. 158—159°. In the preparation of the toluoylnaphthoic acid, a substance,  $C_{28}H_{20}O_2$ , m. p. 234°, which is either ditolyl-naphthalide,  $C_{10}H_6 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{C}(C_7H_7)_2 \end{smallmatrix} O$ , or 1 : 8-ditoluoylnaphthalene,  $C_{10}H_6(CO \cdot C_7H_7)_2$ , was obtained. Attempts to prepare the corresponding compound from benzene were unsuccessful.  
A. C.

**Resolution of *trans*-cycloButane-1 : 2-dicarboxylic Acid.** L. J. GOLDSWORTHY (*J. Chem. Soc.*, 1924, 125, 2012—2013).—*trans*-cycloButane-1 : 2-dicarboxylic acid has been resolved by fractional crystallisation of the quinine salt from water. The quinine salt of the *l*-acid,  $(C_{20}H_{24}O_2N_2)_2 \cdot C_6H_8O_4 \cdot 8H_2O$ , when dehydrated at 120° has  $[\alpha]_D -192.9^\circ$  in alcohol. The *l*-acid, m. p. 105°, has  $[\alpha]_D^{20} -124.3^\circ$  in water. The *d*-acid, m. p. 105°, has

$[\alpha]_D^{30} +123.3^\circ$  in water (*ethyl* ester, b. p.  $236^\circ/761$  mm.,  $[\alpha]_D^{30} +77.9^\circ$  in acetone).  
C. J. S.

**Action of Diazomethane on some Aromatic Acyl Chlorides.**

**II. Synthesis of Fisetol.** M. NIERENSTEIN, D. G. WANG, and J. C. WARR (*J. Amer. Chem. Soc.*, 1924, **46**, 2551—2555).—Diacetyl- $\beta$ -resorcoyl chloride (2:4-diacetoxybenzoyl chloride), obtained by the action of excess of thionyl chloride on diacetyl- $\beta$ -resorcylic acid in chloroform, has m. p.  $37^\circ$  (cf. Pacsu, A., 1923, i, 339). When treated with diazomethane in ether, the above chloride yields *o*-chloro-2:4-diacetoxyacetophenone, m. p.  $73^\circ$ , which, when boiled with acetic anhydride and sodium acetate, affords *o*:2:4-triacetoxyacetophenone, needles, m. p.  $129^\circ$ , and this is converted into fisetol (*o*:2:4-trihydroxyacetophenone) when treated with cold methyl-alcoholic ammonia. 2:4-Dimethylfisetol, m. p.  $131^\circ$ , obtained from fisetol by the action of diazomethane (cf. Slater and Stephen, T., 1920, **117**, 316), yields *o*:2:4-trimethylfisetol, m. p.  $61$ — $62^\circ$ , when treated with methyl iodide and silver oxide. Trimethylfisetol is also obtained by methylating *o*:4-dimethylfisetol, prepared by the hydrolysis of tetramethylfisetin. On oxidation with alkaline permanganate, 2:4-dimethylfisetol yields 2:4-dimethoxybenzoic acid.  
F. G. W.

**Derivatives of 1:8-Naphthalic Acid. I. Preparation and Properties of 1:8-Naphthalyl Chloride.** F. A. MASON (*J. Chem. Soc.*, 1924, **125**, 2116—2119).—1:8-Naphthalyl chloride, m. p. about  $84$ — $86^\circ$ , is obtained in 70—75% yield by heating naphthalic anhydride in phosphoryl chloride with a large excess of phosphorus pentachloride under reflux with exclusion of moisture. The crystals fume strongly and are immediately decomposed by water, with re-formation of the anhydride. They decompose completely on distillation even under reduced pressure. The chloride reacts vigorously with phenol to give phenolnaphthalein (cf. Joubert, A., 1893, i, 477), with resorcinol to give naphthafluorescein (cf. Terrisse, A., 1885, 667) and with mono- and di-alkylated *m*-aminophenols to form *naphtharhodamines*, which possess similar crimson colours to the ordinary rhodamines. With alcohols, mixtures of normal di-esters and naphthalic anhydride are obtained. The *diethyl*, m. p.  $58$ — $60^\circ$ ; *dimethyl*, m. p.  $101$ — $102^\circ$ , and *di-n-butyl* esters, m. p.  $52$ — $53^\circ$ , were prepared. Attempts to prepare the dibenzyl ester were unsuccessful.  
A. C.

**Preparation of Diphenic Acid.** G. CHARRIER and A. BERETTA (*Gazzetta*, 1924, **54**, 765—769).—The authors are unable to obtain the high yields of diphenic acid which Bischoff and Adkins (A., 1923, i, 578) claim are obtainable by oxidising phenanthraquinone with chromic acid mixture. As much as 44% of the theoretical yield of diphenic acid is, however, rapidly formed when phenanthraquinone is oxidised by means of alkaline permanganate solution; the crude phenanthraquinone obtained by treating phenanthrene with chromic acid mixture can be used. If the alkali is omitted, smaller yields of diphenic acid result, whilst calcium permanganate

gives a number of products, including a white *compound*, m. p. 228°, which is free from carboxyl, and is being investigated. Small proportions of diphenic acid are furnished by the action of alkaline permanganate solution on either phenanthrene or the oily product obtained by reducing this with sodium and amyl alcohol.

T. H. P.

**Interaction between Ethyl Ethylidenemalonate and Anilino-phenylacetoneitrile.** L. HIGGINBOTHAM, A. LAPWORTH, and C. SIMPSON (*J. Chem. Soc.*, 1924, 125, 2339—2344; cf. T., 1907, 91, 694).—Interaction of aqueous-alcoholic anilinophenylacetoneitrile, ethyl ethylidenemalonate, and potassium hydroxide yielded

(i) a *potassio* derivative (possibly of  $\begin{matrix} \text{CPh(CN)·NHPH} \\ \text{CHMe·CH(CO}_2\text{Et)}_2 \end{matrix}$ ), m. p.

108—111°, which on heating (a) with alkali gave cyanide, aniline, and  $\alpha$ [ $\alpha$ -benzoyl-ethyl]malonic acid and (b) with aqueous acetone or acetic acid gave *ethyl 5-cyano-2-keto-1:5-diphenyl-4-methylpyrrolidine-3-carboxylate*,

$\begin{matrix} \text{CPh(CN)——NPh} \\ \text{CHMe·CH(CO}_2\text{Et)} \end{matrix} > \text{CO}$ , m. p. 99°; (ii)

the second product was the *acid* corresponding with this ester, m. p. 40—65°. With alkali the acid formed cyanide, aniline, and  $\alpha$ [ $\alpha$ -benzoyl-ethyl]malonic acid, and with boiling hydrochloric acid formed *5-cyano-2-keto-1:5-diphenyl-4-methylpyrrolidine*, m. p. 111°, which was converted by alcoholic potassium hydroxide into  $\beta$ -benzoylbutyric acid, and by sulphuric acid at 100° into *2-keto-1:5-diphenyl-4-methylpyrrolidine-5-carboxylamide*, m. p. 193—194°. By a modification, interaction of anilinophenylacetoneitrile, ethyl ethylidenemalonate, and potassium hydroxide produced  $\alpha$ [ $\alpha$ -benzoyl-ethyl]malonic acid, which at 160° was converted into  $\beta$ -benzoylbutyric acid, m. p. 59—60° (*semicarbazone*, m. p. 177—178°);  $\alpha$ [ $\alpha$ -benzoyl-ethyl]malonic acid was synthesised from phenyl  $\alpha$ -bromoethyl ketone and ethyl *potassio*(or *sodio*)malonate. With alkali, *N*-methylanilinophenylacetoneitrile forms a *substance*, m. p. 126—128°, giving a *hydrochloride*, m. p. 242—244° (decomp. from 230°).  
F. M. H.

**isoPhenolphthalein and some of its Derivatives.** W. R. ORNDORFF and W. R. BARRETT (*J. Amer. Chem. Soc.*, 1924, 46, 2483—2497).—*isoPhenolphthalein* (op-dihydroxydiphenylphthalide) is formed, together with fluoran, as a by-product in the preparation of phenolphthalein, and can be synthesised by the condensation of phenol with *o*-hydroxybenzoyl-*o*-benzoic acid in presence of stannic chloride at 100—110°. It forms a *monohydrate*, monoclinic needles, which yield the anhydrous substance, triclinic crystals, m. p. 200°, when heated at 120°. The solubility of the latter (g. per 100 c.c. of solvent) at 21° is as follows: alcohol (95%), 20·02; methyl alcohol, 20·26; acetone, 47·26; benzene, 0·77; and glacial acetic acid, 1·13. In dilute alkali,  $p_H$  8·4, it is pale yellow, changing to a purple, of bluer tint than that of phenolphthalein, at  $p_H$  12·0. The colour fades on keeping, or on addition of strong alkalis, but is restored when the solution is warmed.

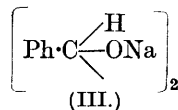
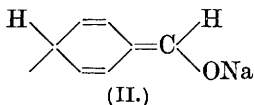
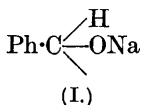




**Alkylidenebenzoylpyruvic Esters.** H. GAULT and A. FUNKE (*Compt. rend.*, 1924, **179**, 535—537).—Diethyl benzoylpyruvate (2 mols.) condenses with 1 mol. of formaldehyde, yielding, almost quantitatively, *diethyl methylenebenzoylpyruvate* (*ethyl βδ-dibenzoyl-αε-diketo-n-pimelate*),  $(\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CHBz})_2\text{CH}_2$ , *monohydrate*, m. p. 95°; *diphenylhydrazone*, m. p. 100°. The ester is hydrolysed by dilute mineral acids with formation of oxalic acid and αε-diphenylpentane-αε-dione, whence its constitution is inferred. Attempts to prepare the anhydrous ester were unsuccessful, but after prolonged contact with concentrated sulphuric acid two compounds were isolated, an ester and an acid, which correspond with the above diethyl ester and its acid each dehydrated to the extent of 2 mols. of water. Acetaldehyde and cænanthol also condense with diethyl benzoylpyruvate.

H. J. E.

**Reaction between Metallic Sodium and Aromatic Aldehydes, Ketones, and Esters. I. Aldehydes.** F. F. BLICKE (*J. Amer. Chem. Soc.*, 1924, **46**, 2560—2571).—When benzaldehyde is treated in ethereal solution with one molecular proportion of metallic sodium, in an atmosphere of nitrogen, a colourless, flocculent precipitate (due to adventitious oxygen) first separates; the reaction mixture then turns brownish-green, and finally an intense green precipitate of the monosodium derivative (I) is formed. On dilution in a mixture of acetic acid and ice, still with exclusion of air, the green colour is immediately discharged, and the ethereal extract, on distillation, yields benzaldehyde, benzyl alcohol, benzoic acid, benzyl ether, and benzyl benzoate, whilst benzoin was identified in the residue. The green colour is attributed to the quinonoid (tautomeric) form (II) of the sodium compound, whilst the polymeride (III) is probably also present. The action of water



on (I) proceeds according to the scheme  $\text{CHPh}\cdot\text{ONa} \rightarrow \text{CHPh}\cdot\text{OH} \rightarrow \text{CH}_2\text{Ph}\cdot\text{OH} + \text{CHPhO}$  (cf. Schlenk and Weickel, A., 1911, i, 545). Further, (I) reduces benzaldehyde to benzyl alcohol, being itself transformed into  $\text{CPh}(\text{ONa})\cdot\text{CPh}(\text{ONa})$ . The last yields the corresponding unsaturated glycol on hydrolysis, and this immediately rearranges to benzoin (cf. Lachmann, A., 1924, i, 649). The benzyl benzoate is formed by the action of sodium benzoate on benzaldehyde (cf. Claisen, A., 1887, 574; Kohn and Trantom, T., 1899, 75, 1161), in which reaction benzyl ether appears as a by-product (cf. O. Kamm and W. F. Kamm, *J. Amer. Pharm. Assoc.*, 1922, **11**, 599).

When two molecular proportions of sodium are added to benzaldehyde under similar conditions, a deep green, insoluble product is obtained, which yields, on hydrolysis, benzyl alcohol and hydrobenzoin. The disodium derivative,  $\text{CHPhNa}(\text{ONa})$ , probably reduces the benzaldehyde with formation of (III), from which the hydrobenzoin is obtained on hydrolysis.

In the reaction between benzaldehyde, bromobenzene, and sodium, the disodium derivative of benzaldehyde is first formed. This reacts with bromobenzene, by virtue of the reactivity of the sodium atom attached to carbon, to form the sodium salt of benzhydrol. This reduces benzaldehyde to benzyl alcohol, being itself oxidised to the free radical,  $\text{CPh}_2(\text{ONa})$  (cf. Schlenk and Weickel, *loc. cit.*). This then forms the disodium derivative  $\text{CPh}_2\text{Na}(\text{ONa})$ , which reacts further with bromobenzene to form the sodium salt of triphenylcarbinol. The products isolated corresponded in quantity with the equation  $3\text{CHPhO} + 7\text{Na} + 4\text{PhBr} = 2\text{CPh}_3\cdot\text{ONa} + \text{CH}_2\text{Ph}\cdot\text{ONa} + 4\text{NaBr} + \text{H}$ . When *p*-bromotoluene was used in the above reaction, diphenyl-*p*-tolylcarbinol could not be isolated from the reaction mixture, but by oxidation of the crude product, triphenylcarbinol-4-carboxylic acid was obtained. With 1-bromonaphthalene, the diphenyl-1-naphthylcarbinol was identified by conversion into phenylchrysofluorene (Ullmann and Mourawiew-Winigradoff, A., 1905, i, 642).  
F. G. W.

**Schiff's Bases from 3 : 5-Dibromosalicylaldehyde.** C. M. BREWSTER (*J. Amer. Chem. Soc.*, 1924, **46**, 2463—2468).—Whilst the Schiff's bases derived from salicylaldehyde are always obtained in the colourless (phenolic) form (cf. Manchot and Furlong, A., 1909, i, 805), those from 3 : 5-dibromosalicylaldehyde yield first the deeply coloured quinonoid compounds which can in some cases be transformed into the paler phenolic modifications. The following compounds, none of which is phototropic, but some of which are thermotropic, are described : 3 : 5-dibromosalicylidene-aniline, orange-red, m. p.  $91^\circ$ ; -*o*-toluidine, orange needles, m. p.  $120$ — $121^\circ$ ; -*p*-toluidine, orange-red needles, m. p.  $130^\circ$ ; - $\alpha$ -naphthylamine, pale orange-yellow, m. p.  $138^\circ$ ; - $\beta$ -naphthylamine, orange-red, m. p.  $171^\circ$  after sintering at  $168^\circ$ ; bis-3 : 5-dibromosalicylidene-*m*-phenylenediamine, salmon-coloured, m. p.  $225^\circ$  to a red liquid, becoming paler on cooling; bis-3 : 5-dibromosalicylidene-*p*-phenylenediamine, deep red (from nitrobenzene) or yellow (from toluene or amyl alcohol), m. p.  $310^\circ$  (decomp.); bis-3 : 5-dibromosalicylidene-benzidine, scarlet, m. p. not below  $300^\circ$  : a yellow form is obtained, which reverts to the red form on keeping, on acidifying a solution of the compound in alcoholic sodium hydroxide; bis-3 : 5-dibromosalicylidenedianisidine, maroon-red, rhomboid crystals, m. p.  $305^\circ$  (decomp.); 3 : 5-dibromosalicylidene-*p*-phenylenediamine, orange-brown crystals, m. p.  $191^\circ$ ; -*p*-bromoaniline, brilliant crimson leaflets (from alcohol) or a cream-coloured precipitate, changing on keeping to orange, and at  $120^\circ$  to crimson (from glacial acetic acid), m. p.  $160^\circ$ ; -*p*-phenetidine, orange-yellow, rhomboid crystals, turning crimson at about  $100^\circ$ , m. p.  $133^\circ$ ; bis-3 : 5-dibromosalicylidene-*o*-toluidine, scarlet crystals, m. p.  $302^\circ$  : a yellow form, which quickly turns red, is obtained on neutralising a solution of the substance in alcoholic sodium hydroxide. 3 : 5-Dibromosalicylaldehyde-*p*-bromophenylhydrazone, yellow needles, has m. p.  $224^\circ$  (decomp.).  
F. G. W.

**Condensation of Diphenylformamidine with Phenols. II.**

**General Nature of the Reaction.** J. B. SHOESMITH and J. HALDANE (*J. Chem. Soc.*, 1924, **125**, 2405—2407; cf. *ibid.*, 1923, **123**, 2704).—When phenols are condensed with diphenylformamidine at carefully regulated temperatures, an aldehydo group enters in the *o*-position to a hydroxyl group; in two cases, the intermediate product, a Schiff's base, has been isolated. After heating diphenylformamidine and  $\beta$ -naphthol at 130° for 6 hours, hydrolysis yields 2-hydroxy-1-naphthaldehyde (separated through its Schiff's base) in 60% yield; the intermediate product is 2-hydroxy-1-naphthylideneaniline. Similarly, the condensation product from  $\alpha$ -naphthol on hydrolysis gives a sodium salt, from which 1-hydroxy-2-naphthaldehyde is liberated. From resorcinol monomethyl ether (2 hours at 183—184°) is obtained 2-hydroxy-4-methoxybenzaldehyde (yield 20%); the intermediate product from resorcinol and diphenylformamidine is 4:6-dihydroxyisophthalylidenebisaniline, m. p. 202—203°. Guaiacol yields 2-hydroxy-3-methoxybenzaldehyde and pyrogallol yields 2:3:4-trihydroxybenzaldehyde. *o*-Cresol gives 2-hydroxy-3-methylbenzaldehyde, *m*-cresol gives 2-hydroxy-4-methylbenzaldehyde, *p*-cresol 2-hydroxy-5-methylbenzaldehyde, and phenol gives salicylaldehyde (yield 10%). At 250° diphenylformamidine decomposes into aniline and phenylcarbylamine; this occurs also in presence of certain phenols, whilst others render it stable. F. M. H.

**Nitration of 2:3-Dimethoxybenzaldehyde.** W. H. PERKIN, jun., R. ROBINSON, and F. W. STOYLE (*J. Chem. Soc.*, 1924, **125**, 2355—2358).—The supposed mononitro-*o*-veratraldehyde, m. p. 88° (cf. T., 1914, **105**, 2389; 1923, **123**, 1584), consists of the isomeric 5- and 6-nitro-2:3-dimethoxybenzaldehydes; the formation of the latter is attributed to depression by the aldehydo group of the reactivity of the *o*-methoxyl group.

The nitration product gives, with *p*-toluidine, two substances. One is 5-nitro-2:3-dimethoxybenzylidene-*p*-toluidine, m. p. 143°; hydrolysis of it, or of 5-nitro-2:3-dimethoxybenzylideneaniline, m. p. 122° (*hydrochloride* reddens at 180°, m. p. 200°), yields 5-nitro-2:3-dimethoxybenzaldehyde, m. p. 115°; *dimethylacetal*, m. p. 89°; *phenylhydrazone*, m. p. 179°; *semicarbazone*, m. p. 210°; *oxime*, m. p. 155°; the aldehyde is oxidised to 5-nitro-2:3-dimethoxybenzoic acid. The other is 6-nitro-2:3-dimethoxybenzylidene-*p*-toluidine, m. p. 104°; hydrolysis of this, or of 6-nitro-2:3-dimethoxybenzylideneaniline, m. p. 84° (*hydrochloride*, m. p. 156° [decomp.]), forms 6-nitro-2:3-dimethoxybenzaldehyde, m. p. 110°; *dimethylacetal*, m. p. 72°; *phenylhydrazone*, m. p. 138°; *semicarbazone*, m. p. 227—228°; *oxime*, m. p. 130°; the aldehyde is oxidised to 6-nitro-2:3-dimethoxybenzoic acid, m. p. 183°.

F. M. H.

**Conversion of Naphthenic Acids into Ketones with the Aid of Catalysts.** N. ZELINSKY and E. RJACHINA (*Ber.*, 1924, **57**, [B], 1932—1937).—Naphthenic acids appear generally to be

converted readily into the corresponding methyl ketones by catalytic methods, differing thus from unsaturated fatty acids. The raw material used in the investigation was a mixture of naphthenic acids obtained from petroleum from Balachany (Caucasus), which, mixed with a considerable excess of acetic acid, was passed over a mixture of manganous and zinc oxides at 410–420°. The product was a mixture of acetone, ketones derived from naphthenic and acetic acids and ketones produced from the naphthenic acids. It was submitted to fractional distillation, after which the separate fractions were treated with sodium hydrogen sulphite. The ketones regenerated from the bisulphite compounds were analytically pure mixtures of isomerides derived from the naphthenic acids,  $C_5H_9 \cdot CO_2H$ ,  $C_7H_{13} \cdot CO_2H$ , and  $C_8H_{15} \cdot CO_2H$ . The following substances are described: the *ketone*,  $C_7H_{12}O$ , b. p. 177–184° (*semicarbazone*, m. p. 105–107°); *ketones*,  $C_9H_{16}O$ , b. p. 184–190°,  $d_4^{15}$  0.8836,  $n_D^{15}$  1.8353 (*semicarbazone*, m. p. 135°), and b. p. 204–207°,  $d_4^{15}$  0.8921,  $n_D^{15}$  1.4429 (*semicarbazone*, m. p. 142°); the *ketone*,  $C_{10}H_{18}O$ , b. p. 210–212°,  $d_4^{21}$  0.8861,  $n_D^{21}$  1.4441 (*semicarbazone*, m. p. 140°). With the object of gaining further insight into the nature of the ring of the naphthenic acids, the ketone fractions, b. p. 210–212° and 212–215°, have been converted through the secondary alcohols and iodides into the corresponding decanaphthenes; comparison of the physical properties of these substances with those of menthane shows that they cannot possibly contain a hexahydro-aromatic nucleus. The ketones which do not yield compounds with sodium hydrogen sulphite were separated by distillation into a series of fractions each consisting of a large number of isomerides; ketones, b. p. 190–207°, are derived from the naphthenic acids,  $C_7H_{13} \cdot CO_2H$ , whereas those of b. p. 207–210°, 212–215°, and 220–235° correspond with the acids  $C_8H_{15} \cdot CO_2H$ ,  $C_9H_{17} \cdot CO_2H$ , and  $C_{10}H_{19} \cdot CO_2H$ . The ketones, b. p. above 235°, have not yet been investigated.

H. W.

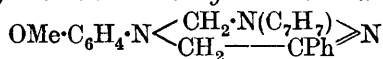
**Isomerism of Hydrazones. Isomeric Hydrazones of Phenacylamines and the Determination of their Configuration.** M. BUSCH, G. FRIEDENBERGER, and W. TISCHBEIN (*Ber.*, 1924, 55, [B], 1783–1792; cf. Busch and Hefele, A., 1911, i, 582). —Isomeric hydrazones may be prepared by the action of phenacylanilines on arylhydrazines in alcoholic suspension in the presence of acetic acid at the atmospheric temperature; occasionally, the condensation may be facilitated by somewhat increasing the temperature, but, in this case, the formation of the isomerides of lower melting point ( $\beta$  forms) may be suppressed. The forms are remarkably stable and show little tendency to pass into an equilibrium mixture in the molten state, in solution, or in the presence of acids. Hydrogen sulphide smoothly transforms the  $\beta$  varieties into the  $\alpha$  forms of higher melting point. Both varieties are converted in solution by atmospheric oxygen or by mercuric oxide into the corresponding azo derivatives, which are readily reduced to the  $\alpha$ -hydrazones, thus affording a second mode of transition from the  $\beta$  to the  $\alpha$  forms. The configuration of the hydrazones is elucidated

from the observation that the  $\alpha$  forms (I) condense with aliphatic aldehydes to triazine derivatives, whereas the  $\beta$  forms (II) only



yield similar products as a consequence of partial isomerisation, whilst viscous oils are mainly formed. In certain cases, crystalline substances have been isolated from the  $\beta$  forms; these are shown to be additive compounds of aldol-like structure.

The following substances are described:  $\omega$ -*p*-Anisidinoacetophenone-*o*-tolylhydrazone,  $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{N} : \text{CPh} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ ,  $\alpha$  form, m. p. 145—146°;  $\beta$  form, m. p. 95—96°, and the corresponding *azo* derivative,  $\text{C}_{22}\text{H}_{21}\text{ON}_3$ , m. p. 138—139°; 5-phenyl-3-*o*-tolyl-1-*p*-anisyl-1 : 2 : 3 : 6-tetrahydro-1 : 3 : 4-triazine,



(from the  $\alpha$ -hydrazone and formaldehyde), m. p. 143—144°; 5-phenyl-3-*o*-tolyl-1-*p*-anisyl-2-methyl-1 : 2 : 3 : 6-tetrahydro-1 : 3 : 4-triazine, m. p. 127—128°; 2 : 5-diphenyl-3-*o*-tolyl-1-*p*-anisyl-1 : 2 : 3 : 6-tetrahydro-1 : 3 : 4-triazine, m. p. 170°; 5-phenyl-3-*o*-tolyl-1-*p*-anisyl-2-*p*-chlorophenyl-1 : 2 : 3 : 6-tetrahydro-1 : 3 : 4-triazine, m. p. 139—140°; 5-phenyl-3-*o*-tolyl-1 : 2-di-*p*-anisyl-1 : 2 : 3 : 6-tetrahydro-1 : 3 : 4-triazine, m. p. 166°; 5-phenyl-3-*o*-tolyl-1-*p*-anisyl-2-*p*-dimethylaminophenyl-1 : 2 : 3 : 6-tetrahydro-1 : 3 : 4-triazine, m. p. 158°. The  $\beta$ -hydrazone is converted by *p*-chlorobenzaldehyde into the additive product,

$\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{N}(\text{C}_7\text{H}_7) \cdot \text{N} : \text{CPh} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , m. p. 123—124°; similarly constituted products, m. p. 152° and 118°, respectively, are prepared from anisaldehyde and *p*-dimethylaminobenzaldehyde.

The following hydrazones have been prepared:  $\omega$ -anilinoacetophenonephenylhydrazone, m. p. 106.5°;  $\omega$ -*p*-toluidinoacetophenonephenylhydrazone,  $\alpha$  form, m. p. 140°;  $\beta$  form, m. p. 95°;  $\omega$ -*p*-toluidinoacetophenone-*o*-tolylhydrazone,  $\alpha$  form, m. p. 160—162°,  $\beta$  form, m. p. 96—97°;  $\omega$ -anilinoacetophenone-*o*-tolylhydrazone,  $\alpha$  form, m. p. 148.5°,  $\beta$  form, m. p. 95—96°;  $\omega$ -*o*-toluidinoacetophenone-*o*-tolylhydrazone,  $\alpha$  form, m. p. 147—148°;  $\omega$ -*o*-anisidinoacetophenone-*o*-tolylhydrazone,  $\alpha$  form, m. p. 127—128°,  $\beta$  form, m. p. 115—117°;  $\omega$ -*p*-chloroanilinoacetophenone-*o*-tolylhydrazone,  $\alpha$  form, m. p. 102—104°;  $\omega$ -*as*-*m*-xylidinoacetophenone-*o*-tolylhydrazone,  $\alpha$  form, m. p. 137—138°,  $\beta$  form, m. p. 75—77°;  $\omega$ -*p*-toluidinoacetophenone-*as*-*m*-xylidylhydrazone,  $\alpha$  form, m. p. 149—150°;  $\omega$ -*o*-toluidinoacetophenone-*as*-*m*-xylidylhydrazone,  $\alpha$  form, m. p. 118—120°;  $\omega$ -*p*-toluidinoacetophenone-*o*-anisylhydrazone,  $\alpha$  form, m. p. 136—137°;  $\omega$ -*p*-toluidinoacetophenone-*o*-chlorophenylhydrazone,  $\alpha$  form, m. p. 142°,  $\beta$  form, m. p. 96°;  $\omega$ -*p*-toluidinoacetophenone-*m*-chlorophenylhydrazone,  $\alpha$  form, m. p. 92°;  $\omega$ -*p*-toluidinoacetophenone-*p*-chlorophenylhydrazone,  $\alpha$  form, m. p. 138°;  $\omega$ -*p*-toluidino-*o*-acetophenone- $\alpha$ -naphthylhydrazone,  $\alpha$  form, m. p. 147—158°,  $\beta$  form, m. p. 84°.

H. W.  
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**Action of Hydrazines on Semicarbazones. I.** (MISS) M. M. J. SUTHERLAND and F. J. WILSON (*J. Chem. Soc.*, 1924, **125**, 2145—2148).—The semicarbazones of acetophenone and benzophenone react with phenylhydrazine, when heated in toluene solution, to form  $\delta$ -anilinosemicarbazones with evolution of ammonia according to the scheme  $\text{CRR}'\text{:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 + \text{NH}_2\cdot\text{NHPh} = \text{NH}_3 + \text{CRR}'\text{:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$ , the reaction being similar to that between semicarbazones and arylamines (cf. Borsche, A., 1902, i, 186; 1904, i, 945; 1905, i, 305). Dilute hydrochloric acid hydrolyses the anilinosemicarbazone, giving the ketone and  $\delta$ -anilinosemicarbazide hydrochloride. *Acetophenone- $\delta$ -anilinosemicarbazone*, m. p.  $210^\circ$ , yields  *$\delta$ -anilinosemicarbazide hydrochloride*, m. p.  $193^\circ$  (decomp.), on hydrolysis. The *benzylidene* derivative of the latter has m. p.  $206^\circ$ .  *$\delta$ -Anilinosemicarbazide*, m. p.  $151^\circ$ , synthesised by heating  $\beta$ -carbethoxyphenylhydrazine with hydrazine hydrate (cf. Heller, A., 1891, 1212), yielded the same hydrochloride. *Benzophenone- $\delta$ -anilinosemicarbazone* had m. p.  $161^\circ$ , and was accompanied by a small quantity of benzophenonephenylhydrazone. Corresponding products were formed on hydrolysis with dilute hydrochloric acid, but with excess of 12% acid, complete hydrolysis into benzophenone, hydrazine and phenylhydrazine hydrochlorides, and carbon dioxide took place. Acetonesemicarbazone behaved differently with phenylhydrazine, the reaction being mainly one of displacement, with formation of acetonephenylhydrazone and semicarbazide (or its decomposition products). The toluene mother-liquors yielded a small quantity of *acetone- $\delta$ -anilinosemicarbazone*, m. p.  $169^\circ$ , but however the conditions were varied the reaction did not proceed more than 10% in this direction. A. C.

**Oxidation of Acetomesitylene with Permanganate.** W. H. PERKIN, jun., and R. B. TAPLEY (*J. Chem. Soc.*, 1924, **125**, 2428—2437).—Mesitylgyoxylic acid, dimethylterephthalonic acid, 4 : 6-dimethylphthalonic acid, and carboxymethylphthalonic acid have been isolated from the products of the oxidation of acetomesitylene with permanganate.

Mesitylgyoxylic acid yields trimethylmandelic acid when reduced with an excess of sodium amalgam, and when oxidised by permanganate gives dimethylterephthalonic acid (*phenylhydrazone*, m. p.  $213^\circ$  [decomp.]) as the main product. The *dimethyl* ester of dimethylterephthalonic acid, m. p.  $85^\circ$ , has been obtained by direct esterification as well as by the action of methyl alcohol on the acid chloride. 2 : 6-Dimethylterephthalic acid is formed when the corresponding terephthalonic acid is oxidised by permanganate. Reduction of dimethylterephthalonic acid with excess of sodium amalgam, below  $15^\circ$ , gives 4-carboxy-2 : 6-dimethylmandelic acid, m. p.  $243$ — $244^\circ$  after softening at  $230^\circ$ . When the reduction is conducted at the boil in sodium carbonate solution with excess of sodium amalgam there is produced 4-carboxy-2 : 6-dimethylphenylacetic acid, m. p. about  $285^\circ$ ; *dimethyl* ester, m. p.  $78^\circ$ .

When dimethylterephthalonic acid is treated with aniline there is formed the *aniline* salt of *anilodimethylterephthalonic acid*, m. p.

168°, which by elimination of aniline and carbon dioxide when boiled with water or with xylene, is converted into 2 : 6-dimethylbenzaldehydeanil-4-carboxylic acid, m. p. 185—186°, giving 2 : 6-dimethylbenzaldehyde-4-carboxylic acid, m. p. 211—212° (*phenylhydrazone*, m. p. about 228°), when boiled with hydrochloric acid.

4 : 6-Dimethylphthalonic acid is obtained in the *anhydrous* form, m. p. 178°, from dilute hydrochloric acid, or as the *monohydrate*, m. p. 86—87°, from water. The *dimethyl* ester melts at 76—79°. When the acid is treated with sulphuric acid, 4 : 6-dimethylphthalic anhydride is produced. 4 : 6-Dimethylbenzaldehydeanil-2-carboxyanilide, m. p. 213°, is obtained by the action of aniline on dimethylphthalonic acid, and this substance when heated with hydrochloric acid yields the 4 : 6-dimethylbenzaldehyde-2-carboxyanilide, m. p. 174°.

4(6?)-Carboxy-6(4?)-methylphthalonic acid is very deliquescent and when dried at 100° has m. p. about 218° (decomp.). By esterification of the impure acid with methyl alcohol, there were obtained two substances which are believed to be the dimethyl ester, m. p. 155—156°, and the trimethyl ester, b. p. 210—214°/15 mm. Reduction of the acid with a large excess of sodium amalgam gave dicarboxymethylmandelic acid, m. p. 228°. C. J. S.

**Isomerism of the Oximes. XX. Isomeric *p*-Nitrobenzophenoneoximes and their Four Methyl Esters.** O. L. BRADY and R. P. MEHTA (*J. Chem. Soc.*, 1924, 125, 2297—2304).—Four crystalline ethers of benzophenoneoxime are isolated, thus supporting the Hantzsch-Werner hypothesis, which demands the existence of an oxygen and a nitrogen ether corresponding with each of the two isomeric oximes.

After oximation of *p*-nitrobenzophenone, a *sodium* salt sparingly soluble in 2*N*-sodium hydroxide is isolated, from which carbon dioxide liberates anti-*p*-nitrobenzophenoneoxime, m. p. 158°, whilst syn-*p*-nitrobenzophenoneoxime, m. p. 115° after many recrystallisations, is liberated from the mother-liquors; their configuration is established by the Beckmann change, when the former yields *p*-nitrobenzanilide, m. p. 214°, and the latter a crude amide, which is hydrolysed to aniline and *p*-nitroaniline. When methyl sulphate acts on an aqueous methyl-alcoholic solution of the *anti*-oxime in presence of sodium hydroxide at 0°, the product less soluble in ether proves to be the *N*-methyl ether of the *anti*-oxime, m. p. 147°, converted by hydrogen iodide into methylamine, whilst the more soluble is the *O*-methyl ether of the *anti*-oxime, m. p. 93°. Methylation of the *syn*-oxime gives equal amounts of the *N*-methyl ether of the *syn*-oxime, m. p. 176°, and that of the *anti*-oxime (which is attributed to isomerisation at the moment of formation) together with the *O*-methyl ether of the *syn*-oxime, m. p. 96°. The *N*-methyl ethers are not readily interconvertible, but are decomposed by acids to the ketone; the stability of the *O*-methyl ethers makes it improbable that they are structural isomerides. Acetic anhydride converts either the *anti*- or *syn*-oxime into *acetyl*-anti-*p*-nitrobenzophenoneoxime, m. p. 178°. Phenylcarbimide converts the *anti*-



oxime into *carbanilino*-anti-*p*-nitrobenzophenone oxime, m. p. 181° (decomp.), whilst the *syn*-oxime yields the same product, in an impure form. F. M. H.

**Replacement of the Benzoyl Group by the Nitro Group.** L. ELION (*Rec. trav. chim.*, 1924, 43, 867—868).—The replacement of an acetyl group by a nitro group previously observed in the transformation of 3 : 5-dibromo-4-aminoacetophenone into 2 : 6-dibromo-4-nitrophenylnitroamine (A., 1923, i, 390) now finds a parallel in the replacement of the benzoyl by the nitro group, fuming nitric acid converting 3 : 5-dibromo-4-aminobenzophenone into the same 2 : 6-dibromo-4-nitrophenylnitroamine. R. B.

**Benzilic Acid Transformation.** G. SCHEUING (*Ber.*, 1924, 57, [B], 1963—1965).—The conversion of benzil into benzilic acid by alcoholic alkali hydroxide in the presence of ether (Schönberg and Keller, A., 1923, i, 928) has been described previously by the author (A., 1923, i, 231). The action of the ether (cf. Lachman, A., 1924, i, 653) depends on its ability to repress the dissociation of the additive compound of potassium hydroxide and benzil. The evidence adduced by Schönberg in favour of the view that only one molecular proportion of alkali hydroxide is necessary for the change is inconclusive, since the alkali is regenerated in part during the transformation. The statement that alkoxide is more effective than hydroxide in causing the benzilic acid transformation is erroneous (cf. Lachman, *loc. cit.*). H. W.

**Blue Adsorption Compounds of Iodine. IV.** G. BARGER and F. J. EATON (*J. Chem. Soc.*, 1924, 125, 2407—2414).—Certain constitutive and ionic influences are discussed. It is concluded that a crossed conjugated double bond is insufficient to ensure adsorption of iodine, since 2-benzylidene-1 : 3-indanedione, the *o*-hydroxybenzylidene derivative, 1 : 2-diketohydrindene, its 2-methyl derivative, ethyl 1 : 3-diketohydrindenecarboxylate, and the sodium derivative of 2-propionyl-1 : 3-diketohydrindene do not give a blue compound, whilst the sodium derivative of ethyl 1 : 3-diketohydrindenecarboxylate and disodium salt of 1 : 3-diketohydrindenecarboxylic acid do. Although *o*-hydroxybenzylideneacetophenone does, its dibenzoyl derivative does not. Of compounds possessing a bridge oxygen atom, a negative result is given by ethylenephthalide, ethylenediphthalide, fluorenephthalide, and diphenylphthalide, whilst benzylidenephthalide gives a positive result which is attributed to the colloidal nature of its solutions. The following derivatives of 7-hydroxy-4-methylcoumarin all give a blue compound, but at varying iodine concentrations, and none so readily as the benzoyl derivative : carbethoxy-, phenylacetyl-, cinnamoyl-,  $\beta$ -naphthoyl-,  $\alpha$ -chlorobenzoyl-, *m*-nitrobenzoyl-, *p*-nitrobenzoyl-, phenylcarbimido- (cf. T., 1915, 107, 417). Experiments with benzoyl-*p*-methylumbelliferone,  $\alpha$ -naphthaflavone, and indeno-flavone, in which disodium hydrogen phosphate and phosphoric acid were present in addition to iodine and potassium iodide, show that neither the rate of development of the blue colour nor its

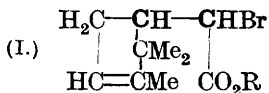
intensity is affected by variations in the phosphate-ion concentration. Study of the effect of various salts in the case of benzoyl- $\beta$ -methylumbelliferone shows that the colour develops most rapidly in presence of iodide. A precipitate appears on addition of potassium iodide to a solution of thalious chloride and iodine. When the iodine compound of coumarin (as also of acetocoumarin and benzoyl- $\beta$ -methylumbelliferone) is precipitated by different concentrations of iodine, the crystals show high iodine concentrations, but are of variable composition. F. M. H.

**Decomposition of Anthraquinone by Heat.** H. F. LEWIS and S. SHAFFER (*Ind. Eng. Chem.*, 1924, **16**, 717—718).—The decomposition of anthraquinone begins appreciably at 450°; a red and a brown substance, both soluble in aqueous alkali, are present amongst the products. [See also *B.*, 1924, 667.] D. F. T.

**Methylisopropylantraquinone.** M. PHILLIPS (*J. Amer. Chem. Soc.*, 1924, **46**, 2533—2536).—Phthalic anhydride condenses with *p*-cymene in presence of aluminium chloride to form *o*-2:5-methylisopropylbenzoylbenzoic acid, m. p. 124°, which yields 1:4-methylisopropylantraquinone, yellow needles, m. p. 113.8°, when heated with fuming sulphuric acid. Methylisopropylanthrane picrate, brown needles, m. p. 131°, was obtained by heating the above quinone with ammonia and zinc dust, and adding picric acid to the alcoholic extract of the solid reaction product obtained. Dinitromethylisopropylantraquinone, yellow needles, m. p. 232° (decomp.), is described. F. G. W.

**New Halogen Derivatives of Camphor. IV. Action of Hydroxylamine on  $\alpha$ - and  $\alpha'$ -Chlorocamphor and Bromocamphor. V. Action of Sodium Methoxide and Ethoxide on  $\alpha\beta$ -Dibromocamphor. Formation of Esters of  $\alpha$ -Bromocampholenic Acid.** H. BURGESS (*J. Chem. Soc.*, 1924, **125**, 2375—2381).—IV.  $\beta$ -Camphorquinonedioxime, m. p. 240°, is prepared by the action of hydroxylamine on  $\alpha$ -bromocamphor (cf. Angelico, A., 1900, i, 675),  $\alpha$ -chlorocamphor, and the  $\alpha'$ -chloro- and  $\alpha'$ -bromo-camphors.

V (cf. Kachler and Spitzer, A., 1882, **42**, 864; 1883, **44**, 1008; Forster, T., 1902, **81**, 265).—The by-product in the preparation of  $\alpha\beta$ -dibromocamphor by the action of sodium ethoxide on  $\alpha\beta$ -dibromocamphor (cf. T., 1923, **123**, 1867) is ethyl  $\alpha$ -bromocampholenate (I), b. p. 140°/15 mm.,  $d_4^{25}$  1.235,  $[\alpha]_{5461}^{20}$  —82° in benzene. Similarly, methyl  $\alpha$ -bromocampholenate, b. p. 134°/14 mm.,  $[\alpha]_{5461}^{20}$  —19° in benzene, is obtained, or it may be prepared in 86%



yield by addition of sodium methoxide to a methyl-alcoholic solution of  $\alpha\beta$ -dibromocamphor. Either ester is converted by boiling aqueous potassium hydroxide into  $\alpha$ -hydroxycampholenic acid, m. p. 103°,  $[\alpha]_{5461}^{20}$  —50° in chloroform (its copper salt chars at 195°, m. p. 197—198° [decomp.]), together with oily unsaturated acids. With ammonia, the methyl ester yields (i)  $\alpha$ -bromocampholenamide,

m. p. 110—111°,  $[\alpha]_{5461} -32^\circ$  in alcohol; (ii) an *isomeride* which is regarded as  $\alpha'$ -bromocampholenamide, m. p. 112.5°,  $[\alpha]_{5461} +52^\circ$  in alcohol, and (iii) a product, m. p. 123°. Rotations for other values of  $\lambda$  are given and a table of rotations for the esters shows that the simple dispersion law is obeyed.

F. M. H.

**Studies of Dynamic Isomerism. XVI. The Mutarotation of Beryllium Benzoylcamphor. Formation of an Additive Compound with Chloroform. The Optical Activity of Beryllium.** H. BURGESS and T. M. LOWRY (*J. Chem. Soc.*, 1924, 125, 2081—2096; cf. T., 1923, 123, 822, 2111).—To investigate the dynamic isomerism of benzoylcamphor, several of its metallic derivatives were prepared and examined as to how far they possessed the typical properties of co-ordination compounds. *Beryllium benzoylcamphor*,  $(C_{17}H_{19}O_2)_2Be$ , forms circular, transparent plates (usually), m. p. 208°, and also tetragonal crystals,  $a:c=1:1.7324$ ; it is prepared in 97% yield by adding piperidine and hydrated beryllium sulphate to a hot aqueous alcoholic solution of benzoylcamphor. Both the parent substance and the beryllium compound show mutarotation, the latter in spite of the fact that all the mobile hydrogen has been replaced by the metal. The rotatory power of beryllium benzoylcamphor is very high; tables are given showing its values at different temperatures and concentrations, for solutions in benzene, chloroform, acetone, alcohol, heptane, and *cyclohexane*. In benzene,  $[\alpha]$  is some 50° higher than in the other liquids. The mutarotation is slow, but reversible in benzene. The solid obtained from a slowly evaporated benzene solution of which the rotatory power had reached a steady value when redissolved in the same volume of benzene showed the original high value. Mutarotation was shown in all the above solvents, proving that the phenomenon is definitely characteristic of the solute. The change in rotatory power does not result in any change of molecular weight, hence like that of nitrocamphor is due to reversible isomeric change (T., 1899, 75, 217). Observations of freezing point show that the stable and labile forms of the compound are isomeric, and measurements of the solubility in heptane and *cyclohexane* show that they are present in approximately equal proportions when equilibrium is reached. The probable rotatory power of the labile isomeride in heptane is estimated as  $[\alpha]_{5461} 292^\circ$ ,  $[\alpha]_{5780} 246^\circ$ , and the partial specific rotation of the beryllium complex is 78°. Crystallised from a mixture of chloroform and acetone, beryllium benzoylcamphor separates in tough, glassy, anorthic prisms, m. p. 204°, containing 2 mols. of chloroform. These prisms, dissolved in acetone or benzene, show a much more rapid mutarotation than the ordinary tabular crystals. Contrary to its behaviour when used as a solvent for nitrocamphor, chloroform acts as a catalyst for beryllium benzoylcamphor and promotes the chemical change giving rise to the mutarotation (T., 1899, 75, 211). This is attributed to the formation of an unstable additive compound,

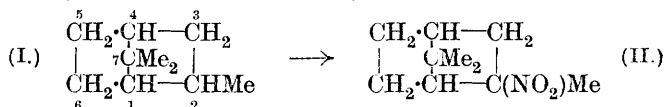
$$C_8H_{14} \begin{array}{c} \diagup C: CPh-O \\ \diagdown CO \end{array} Be \begin{array}{c} \diagdown CHCl_3 \quad OC \\ \diagup O-CPh:C \end{array} C_8H_{14}.$$

The mutarotation in

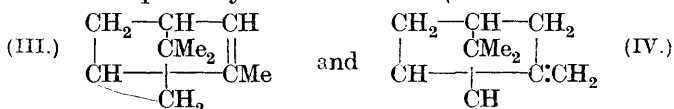
benzene is greatly increased by the presence of benzoic acid or piperidine in the solvent. Less than 1 part in 1000 parts of piperidine increases the velocity of change about seventy-fold. In chloroform, the rate of change is about 250 times as great as in benzene, whilst acetone is a still more active catalyst. From these and other facts, it is inferred that the origin of the mutarotation of beryllium benzoylcampbor is fundamentally different from that of nitrocamphor and the sugars, although there are many points of analogy. The chloroform compound, the rotatory power of which does not differ much from that of the equilibrium mixture, is regarded as an intermediate phase in the isomeric change when brought about by this catalyst. A. C.

**Permanganic Oxidation of Nopinene.** G. BRUS (*Compt. rend.*, 1924, **179**, 501—503).—The oxidation technique was similar to that used by Dupont and Brus in the case of pinene (A., 1923, i, 934). The primary product is nopinene glycol, which is subsequently converted into nopinic acid and finally into nopinone. The product consists of a mixture of these substances, and the proportion of nopinic acid becomes smaller when the reaction is carried out rapidly and at a high temperature. Oxidation of this acid by lead dioxide in presence of acetic acid or of its sodium salt by potassium permanganate gives nopinone. H. J. E.

**isoBornylane and some of its Derivatives.** S. NAMETKIN (*Annalen*, 1924, **440**, 60—72).—The nitration method previously used in studying the structure of fenchane (A., 1916, i, 269) has now been applied to the investigation of the structure of *isobornylane*, the dihydrofenchene obtained by Zelinsky (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 770) by catalytic hydrogenation of *dl*-fenchene. Dilute nitric acid (*d* 1.075) at 130—135° converts *isobornylane* mainly into a tertiary nitro compound, showing that *isobornylane* contains a -CHMe group, since the third methyl group cannot be attached to the carbon atom common to both ring systems; *apocamphoric* acid is found in the acid layer. These facts establish the structure of *isobornylane* as 2 : 7 : 7-trimethyl-[1 : 7 : 4]-*bicyclohexane* (I).



The tertiary nitro compound on reduction and treatment with nitrous acid is converted into a tertiary alcohol, 2 : 7 : 7-trimethyl-[1 : 7 : 4]-*bicyclohexan-2-ol*, which is not identical with the tertiary alcohol of the same constitution obtained by Komppa and Roschier from magnesium methyl iodide and *apocamphor* (A., 1917, i, 466). The new alcohol on dehydration under the influence of mineral acid yields a mixture probably of *D-d*-fenchenes (Wallach's nomenclature)



Besides the tertiary nitro compound, a secondary nitro compound (V) and a ketone are also produced in the action of nitric acid on *isobornylane*. Since *apocamphoric acid* is the only dibasic acid produced and the further action of nitric acid on the tertiary nitro-*isobornylane* yields no *apocamphoric acid*, the nitro group in the secondary nitro compound must occupy the 3-position. The new ketone, *isobornylone*, possesses a structure (VI) identical with that



assigned to fenchone. The preponderating formation of the tertiary over the secondary nitro compound is in harmony with Konovalov's rule.

[With L. ABAKUMOWSKY and A. SELIVANOV.]—*dl*-Fenchene is converted by Sabatier and Senderens' method (temperature 160—165°) into *isobornylane*, b. p. 163.5—164.5°/753 mm.,  $d_4^{20}$  0.8579,  $n_{20}$  1.4590,  $[\alpha]_D$  -12.36, which in contrast with fenchane is rapidly attacked by fuming nitric acid. Dilute nitric acid also attacks *isobornylane* more readily than fenchane, giving a *tert.*-nitro-*isobornylane*, b. p. 112—113°/12 mm.,  $d_4^{20}$  1.0575,  $n_{20}$  1.4813,  $[\alpha]_D$  -26.72° (in alcohol), which is not readily attacked by nitric acid. Reduction with tin and hydrochloric acid converts the nitro compound into *tert.*-amino-*isobornylane*, b. p. 199—199.5°/756 mm.,  $d_4^{20}$  0.9171,  $n_{20}$  1.4800,  $[\alpha]_D$  -6.24° (alcohol) (*benzoyl* derivative, m. p. 134—135°), which with nitrous acid yields a *tert.*-*isobornylol*, m. p. 46—48°, and an unsaturated *hydrocarbon*,  $\text{C}_{10}\text{H}_{16}$ , b. p. 150—155°/749 mm.,  $d_4^{20}$  0.8628,  $n_{20}$  1.4665,  $[\alpha]_D$  +0.7°, yielding on hydrogenation at 160—165° a saturated *hydrocarbon*,  $\text{C}_{10}\text{H}_{18}$ ,  $d_4^{20}$  0.8541,  $n_{20}$  1.4567,  $[\alpha]_D$  +1.99°, which is not identical with *isobornylane*, showing that isomerisation has taken place during the dehydration. *isoBornylone*, b. p. 197.5—198°/762 mm.,  $d_4^{20}$  0.9681,  $n_{20}$  1.4694, has a camphor-like odour, resembling also camphenilone, and yields a *semicarbazone*, m. p. 174—175°. *sec.*-Nitro-*isobornylane*, a pale yellow oil, b. p. 89—90°/1.2 mm.,  $d_4^{20}$  1.0466,  $n_{20}$  1.4805, is completely soluble in water. The *apocamphoric acid*, m. p. 205—206°, was identified as the *cis*-form by its reaction with acetyl chloride. R. B.

**Structure of Dicyclic Terpenes.** K. SŁAWIŃSKI (*Roczniki Chemji*, 1923, 3, 378—382).—The views of Dupont (A., 1922, i, 1042) on the structure of dicyclic terpenes are criticised and contrasted with the author's conjugation theory (A., 1924, i, 865). It is pointed out that both the theories outlined by Dupont—that of free valencies and that involving the oscillation of valencies—fail to account for existing facts and lead to predictions which are not realised experimentally. G. A. R. K.

**Resolution of  $\alpha$ -Terpineol.** A. T. FULLER and J. KENYON (*J. Chem. Soc.*, 1924, 125, 2304—2316).—The isolation of both optically active *terpineols* by resolution of *dl*- $\alpha$ -terpineol is recorded. The potassium derivative of *dl*- $\alpha$ -terpineol, with phthalic anhydride

in benzene solution, forms  $\alpha$ -terpinyl hydrogen phthalate (yield 80%), m. p. 117—118°; similarly, it forms dl- $\alpha$ -terpinyl hydrogen d-camphorate, m. p. 127—128°, which with *d*- $\alpha$ -phenylethylamine gives a salt, m. p. 115—117°. Repeated recrystallisation of the *brucine* salt of the above phthalate, m. p. 150°, from methyl alcohol produced *l*-brucine *l*- $\alpha$ -terpinyl phthalate,  $[\alpha]_D^{17} -16.2^\circ$  in ethyl alcohol, giving *l*-terpinyl hydrogen phthalate,  $[\alpha]_D -36.7^\circ$  in ethyl alcohol; the *l*-strychnine *l*-ester melts at 207°,  $[\alpha]_D^{17} -41.8^\circ$  in chloroform. The ester liberated from the mother-liquors of the brucine salt was converted into its *morphine* salt, m. p. 142°, which by recrystallisation gave the *l*-morphine *d*-ester, whence *d*- $\alpha$ -terpinyl hydrogen phthalate was liberated. The *l*-cinchonidine *d*-ester was prepared: thus samples of the ester,  $[\alpha]_D \pm 36.7^\circ$ , were obtained by crystallisation of four different alkaloidal salts. The *l*-brucine *d*-ester has  $[\alpha]_D^{17} +7.8^\circ$  in ethyl alcohol.

Hydrolysis of the *d*- and *l*-esters with alcoholic potassium hydroxide yielded the *d*- and *l*- $\alpha$ -terpineols, b. p. 104°/15 mm.,  $[\alpha]_D^{20} \pm 100.5^\circ$ ; *d*-terpineol melts at 36.9°,  $n_D$  1.4819,  $d_4^{15} 0.9475$ ; *l*-terpineol melts at 37°,  $d_4^{15} 0.9402$ ; simple rotatory dispersion is exhibited. The *phenylurethane* of *d*- $\alpha$ -terpineol melts at 109.5°,  $[\alpha]_D^{20} +40.9^\circ$  in chloroform; the *nitrosochloride* melts at 107—108°,  $[\alpha]_D^{20} +256.5^\circ$  in ethyl alcohol. *d*-Terpineol with the mixed formic acetic anhydride gave *d*- $\alpha$ -terpinyl formate,  $d_4^{27} 0.9889$ ,  $n_D$  1.4712,  $[\alpha]_D +88.32^\circ$ ; with magnesium ethyl chloride it gave  $C_{10}H_{17}OMgCl$ , which with acetic anhydride yielded *d*- $\alpha$ -terpinyl acetate,  $d_4^{20} 0.9659$ ,  $n_D$  1.4657,  $[\alpha]_D +79.92^\circ$ ; similarly, the propionate,  $d_4^{22} 0.9525$ ,  $n_D$  1.4641,  $[\alpha]_D +75.12^\circ$ , the *n*-butyrate,  $d_4^{18.5} 0.9455$ ,  $n_D$  1.4632,  $[\alpha]_D +70.36^\circ$ , and the *n*-valerate,  $d_4^{16} 0.9424$ ,  $n_D$  1.4633,  $[\alpha]_D +65.20^\circ$ , were prepared. The densities at different temperatures, and refractive indices for various wave-lengths, are quoted. The values of the physical constants show a smooth progression as the length of the ester chain increases. The  $[\alpha]_\lambda$ -mol.wt. curve is smooth, with a slight irregularity at the propionate; the alcohol itself also lies on this curve.

Steam-distillation of *d*-terpinyl hydrogen phthalate with sodium hydroxide gave *d*- $\alpha$ -terpineol and, by dehydration, *d*-limonene,  $[\alpha]_D^{20} +107.8^\circ$ .

Tables are given showing  $[\alpha]_\lambda$  for different values of  $\lambda$  and, with the more important substances, for different solvents. F. M. H.

**Two Homologues of Diprene.** O. ASCHAN [with I. F. M. KROHN] (*Ber.*, 1924, 57, [B], 1959—1962).—A further sample of diprene (cf. A., 1924, i, 1212) has been obtained from the by-products of the technical preparation of isoprene-caoutchouc having b. p. 171.5—173°/752 mm., 68.5—69°/16 mm.,  $d_4^{20} 0.8481$ ,  $n_D^{23.4} 1.49660$ . The constants are in harmony with those determined previously (*loc. cit.*), except that the present density is somewhat lower. *Dibutadiene*,  $C_8H_{12}$ , b. p. 126—127°/745 mm., 60—60.5°/74 mm.,  $d_4^{20} 0.8319$ ,  $n_D^{20.4} 1.46228$ , and *dimethyldiprene*,  $C_{12}H_{20}$ , b. p. 200.5—201.5°/758 mm., 88—88.5°/12 mm.,  $d_4^{21} 0.8535$ ,  $n_D^{20} 1.47915$ , are obtained as by-products in the technical condensation of

butadiene and  $\beta\gamma$ -dimethylbutadiene, respectively. As judged from their physical constants the hydrocarbons are monocyclic terpenes containing two double linkings. H. W.

**Saponins and Related Substances. XI, XII, XIII.** A. W. VAN DER HAAR (*Rec. trav. chim.*, 1924, **43**, 542—549).—Prunol (cf. Power and Moore, T., 1910, **97**, 1099), urson, and a mixture of the two melt at 279—280°; the methyl, acetylmethyl, and acetyl derivatives of prunol have the same m. p. (and the last, the same rotation) as the corresponding urson derivatives; prunol, like urson, contains a carboxyl group. Prunol and urson are therefore considered to be identical. Power and Moore's preparation of a diacetylprunol (hydrolysed to the monoacetyl derivative) could not be repeated, but the monoacetyl compound (hydrolysable to prunol) was obtained. Since urson (prunol) must be  $C_{30}H_{48}(OH)\cdot CO_2H$ , the name ursolic acid is proposed. When distilled with zinc dust in a current of hydrogen, oleanol behaves like ursolic acid, losing carbon dioxide and forming an oil. Contrary to the view of Power and Tutin (T., 1908, **93**, 891), it is therefore regarded as  $C_{30}H_{48}(OH)\cdot CO_2H$ , and the name oleanolic acid is proposed. The m. p. of malol and its methyl and acetylmethyl derivatives as given by Sando (A., 1923, i, 990) are compared with those of ursolic acid and corresponding derivatives. It is concluded that malol is identical with ursolic acid and that Sando's "diacetyl-malol" is in reality a monoacetyl derivative. F. M. H.

**Colouring Matters of Fungi. I. Atromentin.** F. KÖGL and J. J. POSTOWSKY (*Annalen*, 1924, **440**, 19—35).—The colouring-matter present in *Agaricus atrotomentosus* can be isolated in yields of about 2% of the dried fungus by extraction with 2% sodium hydroxide solution, followed by precipitation of the dye with dilute acid, extraction with chloroform, and crystallisation from alcohol, whilst by Thörner's method (A., 1878, 575; 1880, 47) exhaustive extraction gave only 0.6% of the dye, for which the name atromentin is proposed. Atromentin,  $C_{20}H_{14}O_7$ , crystallises from acetic acid in small plates with a bronze or chocolate-brown lustre, containing  $1\frac{1}{2}$  mols. of solvent which is lost at 136° in a vacuum. It does not melt, sublimes with difficulty, and shows no characteristic absorption spectrum. It dyes dull tobacco-brown shades on wool, green shades on chrome-mordanted wool. A solution of atromentin in acetic acid mixed with excess of bromine produces an intense bluish-green stain on the skin or other albuminous substances. Its solution in sulphuric acid becomes deep green on the addition of boric acid. Molecular weight determinations in alcohol agree with the molecular formula  $(C_{20}H_{14}O_7)_2$ . It gives a *diammonium* salt (cf. Thörner, *loc. cit.*); with sodium hydrogen carbonate, a violet *monosodium* salt,  $C_{20}H_{13}O_7Na$ , and with sodium ethoxide, a green *trisodium* salt,  $C_{20}H_{11}O_7Na_3$ , is obtained, which on treatment with alcoholic hydrogen chloride yield only the original dye. Acetylation with sodium acetate and acetic anhydride by Thörner's method gives a *penta-acetyl* derivative, yellow plates, m. p. 240—241°, in 80—90% of the theoretical

yield, not a diacetyl derivative, as Thörner supposed. The addition of a little zinc dust to the acetylation mixture gives a nearly quantitative yield of *hepta-acetyl-leuco-atromentin*,  $C_{34}H_{30}O_{14}$ , m. p. 235—236°, which on hydrolysis readily undergoes oxidation, yielding the original dye. This behaviour indicates that two of the oxygen atoms are present in a quinone ring constituting the chromophore, and not in a pyrone ring, as the sensitiveness of the dye to alkali at first suggests. Methylation with methyl sulphate yields an indefinite red substance, whilst diazomethane yields a *dimethyl ether*,  $C_{22}H_{18}O_7$ , bluish-brown needles, m. p. above 270°. Atromentin is slowly attacked even by 5% sodium hydroxide. Decomposition with 50% potassium hydroxide at 140—165° yields a mixture of two well-crystallised isomeric *hydroxy-acids*,  $C_{11}H_{10}O_3$ , m. p. 183° and 164°, the higher-melting acid preponderating. On bromination in ethereal solution, the acids yield a product, m. p. 100° (decomp.); further bromination of the acid, m. p. 183°, yields a substance losing hydrogen bromide in the air, which shows the characteristic atromentin reaction on skin. Both acids yield the same *monoacetyl* derivative,  $C_{11}H_9O_3Ac$ , m. p. 141°. Decomposition with 30% potassium hydroxide yields a yellow and a colourless product which have not yet been further investigated. On distillation with zinc dust, atromentin yields a *hydrocarbon*,  $C_{15}H_{12}$ , m. p. 202—203°, which is not 2-methyl- or 1:3-dimethyl-anthracene, but may be the hitherto unknown 4-methylphenanthrene. A micro-method for the determination of acetyl groups is described, in which the procedure of Meyer (A., 1906, ii, 58) is adapted to the apparatus for the steam-distillation of small quantities of substances described by Pozzi-Escot (A., 1904, ii, 554).

R. B.

**Tannins and Similar Substances. XVII. Hamameli-tannin. III.** K. FREUDENBERG and F. BLÜMMEL (*Annalen*, 1924, 440, 45—59).—By means of an improved technique (due to E. Vollbrecht) involving extraction with cold acetone, removal of resins and fats by benzene extraction, and a further extraction of the tannin with ethyl acetate, the tannin is obtained on pouring the extract into water as a gelatinous substance, which on further purification with talc and lead acetate followed by fractional precipitation from acetone with benzene, crystallises from water in long, colourless needles,  $C_{20}H_{20}O_{14} \cdot 6H_2O$ , which lose water of crystallisation at 100°/12 mm.,  $[\alpha]_{D}^{21} +35.7^\circ$  (in water). The composition thus agrees with that previously deduced (A., 1919, i, 215; 1920, i, 562), and since the tannin behaves towards the magenta-sulphurous acid reagent exactly as dextrose, the carbonyl group of the hexose must be present in the digalloylhexose. Further study of the hydrolysis with tannase (A., 1922, i, 285) shows that gallic acid and the hexose are obtained in exactly the proportions required for a digalloylhexose. After removal of the gallic acid, the sugar solution is concentrated, freed from tannase by extraction with alcohol and treatment of the alcoholic solution with alumina, and purified by treating the aqueous solution with calcium carbonate.



The hexose,  $[\alpha]_{578}^{21} -7.1^\circ$  (in water), forms no osazone and yielded no furfuraldehyde, lævulic, mucic, or saccharic acids. With *p*-nitrophenylhydrazine in alcoholic solution it gives (yield 45%) a bright yellow *p*-nitrophenylhydrazone,  $C_{12}H_{17}O_7N_3$ , m. p. 165—166°,  $[\alpha]_{578}^{20} +144^\circ$  (in pyridine). *p*-Toluenesulphonylhydrazine, m. p. 112° (acetyl derivative, m. p. 151°), obtained from *p*-toluenesulphonyl chloride and hydrazine hydrate in benzene, gives a colourless *p*-toluenesulphonylhydrazone of the hexose,  $C_{13}H_{20}O_7N_2S$ , m. p. 155°,  $[\alpha]_{578}^{21} +76.1^\circ$  (in pyridine), which on heating with benzaldehyde in alcoholic solution is decomposed, yielding benzaldehyde-*p*-toluenesulphonylhydrazone, m. p. 127—128°. Dextrose-*p*-toluenesulphonylhydrazone, m. p. 179°,  $[\alpha]_{578}^{22} -9.59^\circ$  (in aqueous pyridine, 1:4), is similarly decomposed. On oxidation with mercuric oxide in the presence of calcium carbonate (cf. Blanchetière, A., 1923, i, 539) the hamameli hexose is converted into an encrystallisable calcium salt from which a syrupy hexonic acid was obtained. The ammonium salt of this acid,  $C_6H_{15}O_7N$ , has m. p. 152°,  $[\alpha]_{578}^{22} -3.9^\circ$  (in water). The hexonic acid yields a phenylhydrazide, m. p. 202—203°,  $[\alpha]_{578}^{22} +35.2^\circ$  (in 25% water, 25% acetic acid, 50% pyridine), which is not identical with gluconylphenylhydrazide, and a *p*-toluenesulphonylhydrazide, m. p. 173° (decomp.),  $[\alpha]_{578}^{22} +11.3^\circ$  (in pyridine). The *p*-toluenesulphonylhydrazide of gluconic acid has m. p. 184°,  $[\alpha]_{578}^{22} +40.5^\circ$  (in pyridine). The hexonic acid is also formed in the oxidation of the sugar with nitric acid, oxalic acid being also produced and, in one experiment, another acid, yielding a triamide,  $C_6H_{11}O_6N_3$ , needles, darkening at 210°, m. p. 235°, a triphenylhydrazide,  $C_{24}H_{26}O_6N_6$ , m. p. 187°, and a tri-*p*-toluenesulphonylhydrazide, m. p. 71°, which is possibly a dihydroxycitric acid,  $CO_2H \cdot CH(OH) \cdot C(OH)(CO_2H) \cdot CH(OH) \cdot CO_2H$ . In view of these results, the branched hexose structure,  $CH_2(OH) \cdot CH(OH) \cdot C(OH)(CHO) \cdot CH(OH) \cdot CH_2 \cdot OH$ , is suggested for the sugar, which on oxidation would yield the hexonic acid,  $CH_2(OH) \cdot CH(OH) \cdot C(OH)(CO_2H) \cdot CH(OH) \cdot CH_2 \cdot OH$ , the further oxidation of which should yield the dihydroxycitric acid and finally oxalic acid. It remains undetermined whether the galloyl groups in the tannin are attached to the primary or secondary hydroxyl groups of the sugar.

R. B.

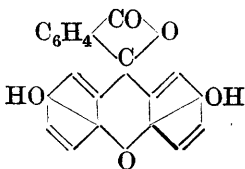
**Chroman Series.** A. I. M. KAHIL and M. NIERENSTEIN (*J. Amer. Chem. Soc.*, 1924, 46, 2556—2560).—2-Methoxydiphenylcarbinol was converted into 2-methoxydiphenylmethyl chloride, needles, m. p. 73°, by the action of thionyl chloride in chloroform, and this, on treatment with activated magnesium and carbon dioxide, yielded 2-methoxydiphenylacetic acid, silky needles, m. p. 176—177°. The latter was converted into 2-methoxydiphenylacetyl chloride, needles, m. p. 67°, by the action of phosphorus pentachloride in chloroform, from which, by the action of diazomethane, 2-methoxydiphenylmethyl chloromethyl ketone,  $OMe \cdot C_6H_4 \cdot CHPh \cdot CO \cdot CH_2Cl$ , plates, m. p. 107°, was obtained. This ketone is converted, by the action of aluminium chloride in benzene, into 3-phenylchroman-2-one, plates, m. p. 76° (phenylhydrazone, yellow needles, m. p. 127—

128°), which yields *2-hydroxy-3-phenylchroman*, needles, m. p. 87° (*acetyl* derivative, needles, m. p. 117°), on reduction with zinc dust and acetic anhydride. *3-Bromo-2-hydroxy-3-phenylchroman*, needles, m. p. 157—158°, obtained from the above hydroxyphenylchroman by the action of bromine in chloroform, yields *2-hydroxy-3-methoxy-3-phenylchroman*, needles, m. p. 127° (*acetyl* derivative, m. p. 167—168°), when boiled with methyl alcohol. *2-Chloro-3-methoxy-3-phenylchroman*, needles, m. p. 84°, is obtained from the latter by the action of thionyl chloride, and yields *3-methoxy-3-phenylchroman*, needles, m. p. 41°, when treated with magnesium in ether, and this, when treated with acetyl chloride in benzene, yields *3-hydroxy-3-phenylchroman*, needles, m. p. 101—102° (*acetyl* derivative, needles, m. p. 124—125°). F. G. W.

**2-Chloromethylfuran from 2-Furylcarbinol.** H. GILMAN and C. C. VERNON (*J. Amer. Chem. Soc.*, 1924, **46**, 2576—2579).—2-Chloromethylfuran was obtained by the action of thionyl chloride on a cooled dilute ethereal solution of 2-furylcarbinol, and also by the action of hydrogen chloride in ethereal solution, preferably in presence of calcium carbide. It could not be distilled and was identified by conversion into 2-ethoxymethylfuran, b. p. 148—150°,  $d_4^{20}$  0.9888,  $n_D^{20}$  1.4316. F. G. W.

**Structure of Fluoran and Phthalophenone Derivatives.** M. DOMINIKIEWICZ (*Roczniki Chemji*, 1923, **3**, 350—361).—Although quinolphthalein cannot be represented by an ortho- or para-quinonoid formula like other phthaleins, it forms highly coloured salts. On the other hand, although analogous to fluorescein, it is not fluorescent in alkaline solution and possesses no affinity for animal fibres. When nitrated in acetic acid solution, however, it forms a 1 : 8-dinitro compound (needles), which dyes wool and silk a brilliant orange. The corresponding *diamino* compound is readily obtained and possesses the properties of a rhodamine, dyeing animal fibres from an acid bath. In the presence of an excess of alkali, however, both this property and the fluorescence of the amino compound disappear, the substance behaving in a manner analogous to Liebermann's 2 : 3 : 6 : 7-tetrahydroxyfluoran (A., 1901, i, 595).

It is clearly the amino groups which exert an auxochromic effect and enable a quinonoid change to take place without disturbing the fluoran skeleton of the substance. On adding alkali, however, the fluoran ring is opened and fluorescence disappears, whilst a new quinonoid form appears involving the hydroxyl groups. These phenomena are explained by assuming the annexed structure for quinolphthalein, from which it is clear that the formation of a coloured, quinonoid form must involve the rupture of the fluoran ring. The fluorescence of the 1 : 8-diamino compound in acid solution is due to an ortho-quinonoid form.



A fundamental distinction is made between derivatives of phthalo-

phenone which are non-fluorescent and phthaleins proper; the former are derivatives of diphenylphthalide from which an ortho- or a para-quinonoid derivative can be obtained, according to the position of the hydroxyl groups; an ortho-quinonoid arrangement occurs only when the substance is unable to form a true phthalein.

G. A. R. K.

**Action of Sodium on the Acetates of *o*- and *p*-Cresol.** R. I. E. HALL.—(See i, 23.)

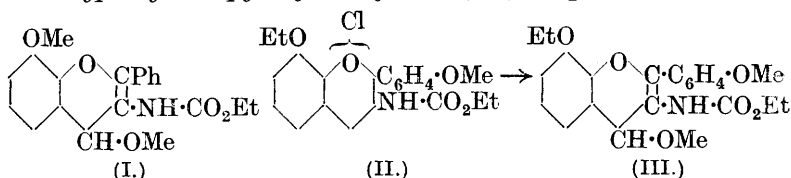
**Syntheses of Pelargonidin and Cyanidin.** R. WILLSTÄTTER, L. ZECHMEISTER, and W. KINDLER (*Ber.*, 1924, **57**, [B], 1938—1944).—The synthesis of pelargonidin has been recorded previously (cf. A., 1920, i, 561). 3:5:7-Trimethoxycoumarin is converted by magnesium 3:4-dimethoxyphenyl iodide and subsequent treatment of the product with hydrochloric acid into 3:5:7-trimethoxy-2-3':4'-dimethoxyphenylbenzopyrylium chloride, which is demethylated with hydriodic acid and converted into 3:5:7-trihydroxy-2-3':4'-dihydroxyphenylbenzopyrylium chloride, identical with the cyanidin chloride from cornflowers and roses (cf. A., 1913, i, 1372). H. W.

**Synthesis of New Anthocyanidins.** R. WILLSTÄTTER and O. T. SCHMIDT (*Ber.*, 1924, **57**, [B], 1945—1950).—In continuation of previous work (A., 1920, i, 561; preceding abstract), 3:5:7-trimethoxycoumarin has been converted by magnesium 2:4-dimethoxyphenyl iodide and treatment of the product with hydrochloric acid into 3:5:7-trimethoxy-2-(2':4'-dimethoxyphenyl)benzopyrylium chloride, from which, after demethylation, 3:5:7-trihydroxy-2-(2':4'-dihydroxyphenyl)benzopyrylium chloride (*morinidin chloride*) is prepared as the mono-, di-, and tri-hydrate. Similarly, 3:5:7-trimethoxycoumarin and magnesium phenyl bromide yield successively 3:5:7-trimethoxy-2-phenylbenzopyrylium chloride, (?)  $C_{18}H_{18}O_4Cl_2$ , and 3:5:7-trihydroxy-2-phenylbenzopyrylium chloride (*galanginidin chloride*), which exists as the *mono*-, *di*-, and *tetra-hydrates* (cf. Pratt and Robinson, T., 1924, **125**, 188). Morinidin is isomeric with cyanidin, but, in colour, it appears more closely related to pelargonidin, so that the entry of a second hydroxyl group into the molecule of the latter has far less influence when it occurs in the meta than in the ortho position. Galanginidin is scarlet-yellow in acid aqueous, orange-yellow in alcoholic solution; the colour of the anthocyanins appears, therefore, to be conditioned by the presence of at least one hydroxyl group in the phenyl nucleus.

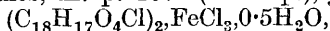
H. W.

**New Route to the 3-Hydroxybenzopyrylium Salts.** L. R. RIDGWAY and R. ROBINSON (*J. Chem. Soc.*, 1924, **125**, 2240—2244).—2-Hydroxy-3-ethoxybenzaldehyde condenses with  $\omega$ -carbethoxyaminoacetophenones yielding products which on hydrolysis with hydrochloric acid give 3-hydroxybenzopyrylium salts, the latter substances being also obtained from  $\omega$ -acetoxyacetophenones. *o*-Vanillin and  $\omega$ -carbethoxyaminoacetophenone condense in glacial acetic acid in the presence of hydrogen chloride, yielding 3-carbethoxyamino-8-methoxy-2-phenylbenzopyranyl methyl ether (I). m. p.

101°. The *ethyl ether*, m. p. 111°, is analogously prepared. Similarly, *ω*-carbethoxyamino-*p*-methoxyacetophenone, m. p. 76°, from *ω*-amino-*p*-methoxyacetophenone stannichloride and ethyl chloroformate in the presence of sodium carbonate, condenses with 2-hydroxy-3-ethoxybenzaldehyde, yielding 3-carbethoxyamino-8-ethoxy-2-*p*-methoxyphenylbenzopyrylium chloride (II), a dark red oil which could not be readily crystallised, and on treatment with water yields the pseudo base from which 3-carbethoxyamino-8-ethoxy-2-*p*-methoxyphenylbenzopyranyl methyl ether (III), m. p. 104°, is obtained

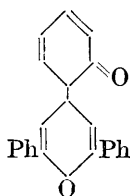


on boiling with methyl alcohol. Hydrolysis of the pyrylium chloride (II) with 20% hydrochloric acid yields 3-*hydroxy*-8-ethoxy-2-*p*-methoxyphenylbenzopyrylium chloride, crimson needles, m. p. 176° [bromide, red needles, m. p. 197° (decomp.), ferrichloride,



orange-red plates, m. p. 196°], the same product being obtained by condensation of 2-hydroxy-3-ethoxybenzaldehyde with *ω*-acetoxy-*p*-methoxyacetophenone in dry ether, followed by crystallisation of the product from hydrochloric acid. 2-Hydroxy-3-ethoxybenzaldehyde and *ω*-*p*-dimethoxyacetophenone in dry ether with hydrogen chloride similarly yield 3-methoxy-8-ethoxy-2-*p*-methoxyphenylbenzopyrylium chloride,  $\text{C}_{19}\text{H}_{19}\text{O}_4\text{Cl} + 3.5\text{H}_2\text{O}$ , red needles, m. p. 160° (decomp.), which could not be hydrolysed to the 3-hydroxybenzopyrylium derivative previously described. The corresponding bromide, maroon needles, m. p. 135–138° (decomp.), is demethylated with respect to the *p*-methoxy group when heated with acetic acid saturated with hydrogen bromide, yielding a bromide, red needles, m. p. 155° (decomp.). 3-Methoxy-8-ethoxy-2-*p*-methoxyphenylpyrylium ferrichloride, red needles, has m. p. 166°. R. B.

**Arylated Pyrylium Compounds and their Relations to the Benzopyrylium Compounds.** XIV. W. DILTHEY and E. FLORET (*Annalen*, 1924, **440**, 89–96).—With the object of obtaining an *o*-violone of the  $\gamma$ -series (annexed formula), the methyl ether



of *o*-hydroxybenzylidene diacetophenone was condensed to the corresponding pyrylium salt from which on demethylation a 2:6-diphenyl-4-*o*-hydroxyphenylpyrylium salt was obtained, and this on treatment with pyridine yielded a blue anhydro-base. This could not be crystallised and changed spontaneously to the yellow phenacylidene flavene obtained by Feuerstein and Kostanecki (*A.*, 1898, i, 370). The mechanism of this change of an arylated pyrylium to a benzopyrylium compound involves the intermediate form-

ation of a pyranol which may have one of several alternative structures, but the formula  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \begin{array}{l} \text{CH:CPh} \cdot \text{OH} \\ \text{CH:CPh} \end{array}$  most

probably represents the final stage in the transition, since from this by loss of water the phenacylidene-flavone is readily formed. These relations are in harmony with the previously expressed conception of the pseudo-bases (pyranols) derived from pyrylium salts as the enolic forms of 1:5-diketones (cf. A., 1920, i, 62; 1921, i, 188; 1922, i, 668). The pseudo-base has not been isolated, but its phenolic acetate has been obtained by the action of alkali on the acetylated pyrylium salt. Since both the anhydro-pyrylium base and the benzopyrylium derivative are formed by loss of water from the enolic 1:5-diketone, these results show that the benzopyrylium ring is the more easily formed, a fact which may explain the non-occurrence of the arylated pyryliums in nature. The synthesis of arylated pyryliums from 1:5-diketones is parallel to the formation of benzopyrylium salts by condensation of *o*-hydroxychalkones (Decker and Fellenberg, A., 1907, i, 1064; 1909, i, 116), whilst the recently described synthesis of pyrylium salts from acetophenone and 1:3-diketones (A., 1924, i, 1332), similarly corresponds with Bülow's method for benzopyrylium compounds (A., 1901, i, 440, 559, 603; 1902, i, 112), the differences in the methods consisting chiefly in the more powerful condensing agents required for the pyrylium salt formation. The present work, however, shows that the presence of acetic anhydride is not essential in the latter case.

*2-Methoxybenzylidenediacetophenone*, m. p. 115°, from *o*-methoxybenzaldehyde (1 mol.) and acetophenone (2 mols.), or from 2-methoxychalkone (1 mol.) and acetophenone (1 mol.), with ferric chloride in acetic anhydride solution (cf. Kostanecki and Roszbach, A., 1896, i, 556), yields 2:6-diphenyl-4-*o*-methoxyphenylpyrylium ferrichloride,  $\text{C}_{24}\text{H}_{13}\text{O}_2\text{Cl}_4\text{Fe}$ , m. p. 154—155°, which with hydrogen bromide in alcoholic or acetic acid solution is converted into 2:6-diphenyl-4-*o*-methoxyphenylpyrylium bromide,  $\text{C}_{24}\text{H}_{20}\text{O}_2\text{Br}_2 \cdot \text{H}_2\text{O}$ , golden-yellow needles, melting first at 80° and then at 197°. Alcoholic ammonia converts the pyrylium bromide into 2:6-diphenyl-4-*o*-methoxyphenylpyridine, needles, m. p. 122°, which with hydrochloric acid at 150—160° yields 2:6-diphenyl-4-*o*-hydroxyphenylpyridine, needles, m. p. 178° (hydrochloride, yellow, effervescent at 139°, m. p. 220°). Hydrobromic acid, alone or with acetic acid, converts the pyrylium bromide into 2:6-diphenyl-4-*o*-hydroxyphenylpyrylium bromide, reddish-violet, m. p. 245—246°; the chloride has m. p. 227—228°, the picrate has m. p. 238°. The chloride on treatment with acetic anhydride followed by perchloric acid yields 2:6-diphenyl-4-*o*-acetoxyphenylpyrylium perchlorate, yellow needles, m. p. 191—194°, from which by treatment with sodium acetate the free, colourless acetate of the pseudo-base,  $\text{C}_{25}\text{H}_{20}\text{O}_4$ , m. p. 112—113°, is obtained. Treatment of the pyrylium chloride in alcoholic solution with aqueous pyridine, ammonia, or alkalis, yields phenacylidene-flavone, m. p. 131°, from which flavone was

obtained by oxidation with potassium permanganate in alcoholic solution, together with benzoic acid and traces of *o*-hydroxyacetophenone or salicylic acid. R. B.

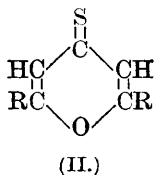
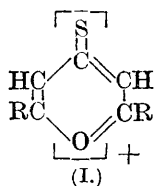
**Heterocyclic Ring Systems.** R. SEKA (*Ber.*, 1924, 57, [B], 1861—1867).—Attempts are described to obtain substances containing the ring system  $X \begin{array}{c} \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \\ \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \end{array} X$ , in which X is an atom

other than carbon. Ethyl 2:5-dimethylfuran-3:4-dicarboxylate is converted by liquid ammonia under pressure at 50° into the corresponding *diamide*, m. p. 243—244° (decomp.) after softening at 240°, from which the imide could not be prepared. The ester is converted by an ethereal solution of magnesium phenyl bromide into 2:5-dimethylfuro-2:2':5:5'-tetraphenyltetrahydrofuran,

$O \begin{array}{c} \diagup \text{CMe} \diagdown \\ \diagdown \text{C} \diagup \\ \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \end{array} O$ , m. p. 199° after softening, and by magnesium methyl iodide into 2:5-dimethylfuro-2:2':5:5'-tetramethyltetrahydrofuran, b. p. 107—109°/9 mm. Ethyl 2:5-dimethylpyrrole-3:4-dicarboxylate is transformed by magnesium phenyl bromide into ethyl 2:5-dimethyl-3-diphenylhydroxymethylpyrrole-4-carboxylate,  $\begin{array}{c} \text{C}(\text{CPh}_2\text{OH})\text{CMe} \\ \diagup \quad \diagdown \\ \text{C}(\text{CO}_2\text{Et})=\text{CMe} \end{array} \text{NH}$ , m. p. 189° (decomp.) after darkening at

185°; the second carbethoxy group is not affected, even when a large excess of the reagent is used. Ethyl 2:5-dimethyl-1-phenylpyrrole-3:4-dicarboxylate and magnesium phenyl bromide yield (?) 3:4-dibenzoyl-1-phenyl-2:5-dimethylpyrrole, m. p. 206—207°, whereas with magnesium methyl iodide 2:5-dimethyl-1-phenylpyrrolo-2:2':5:5'-tetramethyltetrahydrofuran,  $\text{PhN} \begin{array}{c} \diagup \text{CMe} \diagdown \\ \diagdown \text{C} \diagup \\ \diagup \text{C} \diagdown \\ \diagdown \text{C} \diagup \end{array} O$ , b. p. 145°/10 mm., is produced. H. W.

**Dipyrroles and the Relationships of the Linkings in Pyrone Ring Systems.** F. ARNDT, E. SCHOLZ, and P. NACHTWEY (*Ber.*, 1924, 57, [B], 1903—1911).—4-Thio-2:6-diphenylpyrone resembles ethyl thiochelidonate (A., 1924, i, 199) in its ability to form a dipyrrole derivative, whereas this property does not appear to be possessed by 4-thiopyrone or 4-thio-2:6-dimethylpyrone. In explanation of this difference the conceptions of Collie with regard to the constitution of pyrones are revived in a somewhat modified form. In thiopyrone and 4-thio-2:6-dimethylthiopyrone, the basic function of the oxygen within the molecule



is engaged by the acidic, mercaptan function of the sulphur (I), so that the product is not a true thioketone. In proportion, however, as the basic function is diminished by the introduction of acidic groups in the 2 and 6 positions, the compound tends to acquire more or less completely the constitution (II) and to behave therefore as a thioketone. Confirmation of this view is found in the colour of various

pyrone derivatives, in the ability of those only which contain negative groups in the 2 and 6 positions to react with the usual reagents for ketones, and in the behaviour of the compounds towards bromine.

4-*Thiopyrone*, m. p. 49°, either remains unchanged or yields brown, oily decomposition products when heated with or without copper at 150—200°. 4-*Thio-2 : 6-diphenylpyrone*, m. p. 173°, prepared from diphenylpyrone and phosphorus pentasulphide in the presence of boiling benzene, passes at 220—230° into 2 : 6 : 2' : 6'-*tetraphenyl-4 : 4'-dipyrylene*,  $O \langle \begin{smallmatrix} \text{CPh:CH} \\ \text{CPh:CH} \end{smallmatrix} \rangle \text{C:C} \langle \begin{smallmatrix} \text{CH:CPh} \\ \text{CH:CPh} \end{smallmatrix} \rangle O$ , m. p. 313°, which is converted by bromine in chloroform solution into *tetraphenyl-dipyrroxonium perbromide*,  $\text{C}_{34}\text{H}_{24}\text{O}_2\text{Br}_6$ , m. p. 275—280° (decomp.). Diphenylpyrone is converted by bromine into a very unstable (?) tetrabromide, which, when preserved, passes into the compound,  $(\text{C}_{17}\text{H}_{12}\text{O}_2)_2\text{HBr.Br}_2$ , m. p. 174—175°. Ethyl 4-thiochelidonate is converted by semicarbazide into the semicarbazone of *ethyl chelidonate*, m. p. 201° (decomp.), which is transformed by dilute alkali hydroxide into the monosemicarbazone of ethyl acetonedioxalate, m. p. 275°, thus showing that the pyrone ring remains intact in the original semicarbazone. 4-*Thio-2 : 6-diphenylpyrone* is converted by hydroxylamine into 2 : 6-*diphenylpyroneoxime*, m. p. 196—197°.

H. W.

**Condensation of Acetylene and Hydrogen Sulphide in Presence of Catalysts.** (Miss) M. G. TOMKINSON (*J. Chem. Soc.*, 1924, 125, 2264—2266).—The reaction between acetylene and hydrogen sulphide is catalysed by metallic sulphides (cf. Sabatier and Mailhe, A., 1910, i, 536; Tomkinson, A., 1923, ii, 66), and the catalytic effect of metallic oxides is due to the prior conversion of the oxide into sulphide, with formation of water. With ferric oxide, the liquid produced yielded on distillation a volatile fraction containing acetaldehyde, 30—40% of thiophen, and a less volatile fraction, b. p. about 200°, which probably contains the thiophen homologues found by Steinkopf (A., 1914, i, 425; 1922, i, 850). Ferrous sulphide, nickel oxide and sulphide, cobalt sulphide, cupric oxide and sulphide, vanadium pentoxide, and manganese dioxide gave similar results. Contrary to the observations of Tschitschibabin (A., 1915, i, 638), no condensation took place below 450° with pure alumina; above this temperature, decomposition takes place with formation of a carbonaceous deposit. Lead monoxide and sulphide and silica gel behave similarly and aluminium sulphide gives only a slight effect. Molybdenum oxide,  $\text{MoO}_3$ , and to a less extent zinc oxide or sulphide, cadmium sulphide, or thoria, at 300—400° gives a minute quantity of a brilliant blue, purple, and red distillate, and these substances do not promote the formation of thiophen.

R. B.

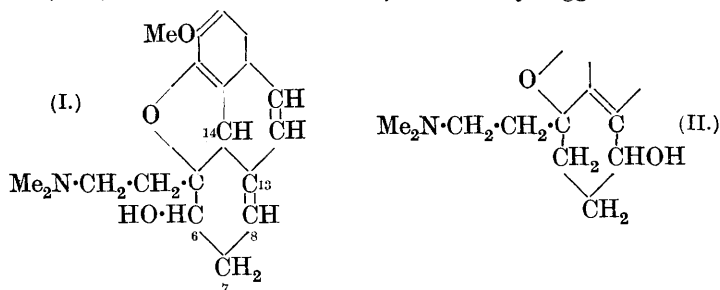
**[Action of Alkali on Ethyl Alcohol and the "Nitric Oxide Reaction" of W. Traube.]** K. HESS (*Ber.*, 1924, 57, [B], 1930).—The recent observations of Stechow (A., 1924, i, 1157) on Traube's reaction have no bearing on the results of the application of this reaction to the constitution of cuskhygrine (Hess and Fink,

A., 1920, i, 497), since the experimental conditions in the two cases are entirely different.

H. W.

**$\alpha$ -Methylmorphimethine and its Isomerides.** E. SPEYER and K. KOULEN (*Annalen*, 1924, 438, 34—57).—Six methylmorphimethines have been described. The  $\alpha$ -compound was prepared by Grimaux (A., 1882, 218) and by Hess (A., 1884, 613) by boiling codeine methiodide with alkali and is converted into the  $\beta$ -isomeride by hot alcoholic potassium hydroxide (Knorr, A., 1902, i, 817).  $\gamma$ - and  $\delta$ -Methylmorphimethines are similarly derived from *iso*-codeine (Schryver and Lees, T., 1901, 79, 563; Knorr, A., 1902, i, 818), whilst the  $\epsilon$ -base is obtained from  $\psi$ -codeine (Knorr, A., 1907, i, 151) and the  $\zeta$ -base from *allo*- $\psi$ -codeine (Knorr, A., 1907, i, 956). The relations between these three pairs of isomerides are now further elucidated and structural formulæ assigned to them.

Assuming Knorr and Hörlein's structure for codeine,  $\alpha$ -methylmorphimethine should have the formula (I), whilst the  $\gamma$ -base is a stereoisomeride differing in the configuration of the  $\cdot\text{CH}(\text{OH})\cdot$  group. In the same way, (II) represents the stereoisomeric  $\epsilon$ - and  $\zeta$ -bases. Knorr (*Ber.*, 1907, 40, 3347, footnote) has already suggested that the

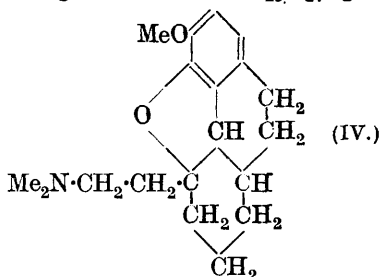
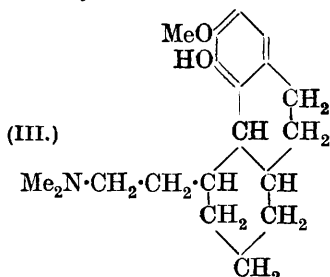


$\beta$ -base is formed from the  $\alpha$ -base by wandering of the double bond from the 8:13 to the 13:14 position. This is confirmed by the production of the same tetrahydro- $\alpha$ -methylmorphimethine by hydrogenation of either base in the presence of palladium. A similar wandering of the double bond accounts for the conversion of the  $\gamma$ - into the  $\delta$ -base.

Treatment of tetrahydro- $\alpha$ -methylmorphimethine with phosphorus pentachloride gives chlorotetrahydro- $\alpha$ -methylmorphimethine (*hydrochloride*, m. p. 267°; *hydrobromide*, m. p. 236°), the methiodide of which is found to be identical with the compound obtained by Freund and Melber (A., 1920, i, 757) from chlorodihydrocodide. The chlorotetrahydro base is unusually stable to hot water, and hot dilute acids or alkalis, probably because aliphatic double bonds are absent. The chlorine is removed by sodium and alcohol, the product being *dihydrodeoxytetrahydro- $\alpha$ -methylmorphimethine* (III), m. p. 163—164° (*methiodide*, m. p. 248°). The reduction of the oxygen bridge linking with formation of a phenolic hydroxyl group is shown by methylation to *methylidihydrodeoxytetrahydro- $\alpha$ -methylmorphimethine methiodide*,  $\text{C}_{20}\text{H}_{31}\text{O}_2\text{N}\cdot\text{MeI}$ , m. p. 210—212°. The base (III) is converted by Hofmann's method into a nitrogen-free product,  $\text{C}_{15}\text{H}_{18}\text{O}_2$ , m. p. 77—78°, and trimethylamine. An attempt



to obtain the base (III) directly from chloro- $\alpha$ -methylmorphimethine (= I, Cl in place of OH) by hydrogenation in the presence of palladium yielded, instead, two new halogen-free bases,  $C_{19}H_{27}O_2N$ ,

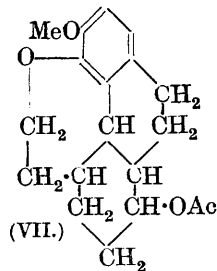
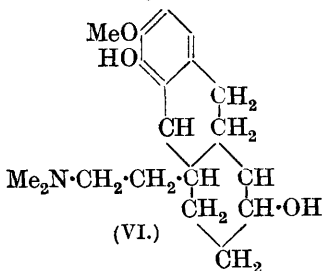
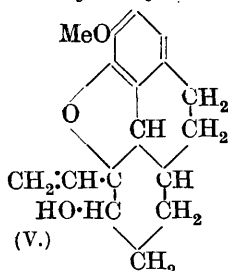


(a) crystalline *deoxytetrahydro- $\alpha$ -methylmorphimethine*, m. p.  $156^\circ$  (*methiodide*, m. p.  $235^\circ$ ), and (b) oily *deoxytetrahydro- $\alpha$ -methylmorphimethine (hydrobromide)*, decomp.  $215-220^\circ$ ; *hydriodide*, m. p.  $208-210^\circ$ ; *methiodide*, decomp.  $272-273^\circ$ ). To both bases the structure (IV) is assigned, the difference being possibly stereoisomeric. From the crystalline base a nitrogen-free compound,  $C_{17}H_{20}O_2$ , m. p.  $94^\circ$ , is prepared, but no degradation product can be obtained from the oily base.

By hydrogen peroxide,  $\alpha$ -methylmorphimethine is converted into an *N-oxide*,  $C_{19}H_{23}O_4N \cdot H_2O$ , decomp.  $188^\circ$ . The *N-oxide*,  $C_{19}H_{27}O_4N \cdot 1\frac{1}{2}H_2O$ , from tetrahydro- $\alpha$ -methylmorphimethine melts at  $94^\circ$ . The former gives no *N-oxide-sulphonic acid* by treatment with sulphoacetic acid (cf. Freund and Speyer, A., 1911, i, 909), but from the tetrahydro-*N-oxide* were obtained "*ordinary*" and " *$\alpha$* " *tetrahydro- $\alpha$ -methylmorphimethine-N-oxide-sulphonic acids*,  $C_{19}H_{27}O_7NS$ , the former being sparingly soluble in water.

$\alpha$ - and  $\gamma$ -Methylmorphimethines are converted by phosphorus pentachloride into the same chloro- $\alpha$ -methylmorphimethine hydrochloride. This is not a complete proof that they are stereoisomerides, for codeine and  $\psi$ -codeine, although they are structural isomerides, similarly give a single  $\alpha$ -chlorocodeine.

*Tetrahydro- $\gamma$ -methylmorphimethine*, m. p.  $115^\circ$ ,  $[\alpha]_D^{18} -29.2^\circ$  (*sulphate*, *hydrochloride*, *hydriodide*, and *methiodide* described), forms an oily *acetyl* derivative, the *hydriodide* of which melts at  $220^\circ$ .



By Hofmann degradation, tetrahydro- $\gamma$ -methylmorphimethine yields trimethylamine and a compound,  $C_{17}H_{20}O_3$  (V), b. p.  $190-200^\circ/13$  mm.

$\delta$ -Methylmorphimethine gives a tetrahydro derivative identical with that from the  $\gamma$ -compound, as shown by mixed m. p. of the tetrahydro-bases and of their acetyl derivatives.

Hydrogenation of  $\epsilon$ - and  $\zeta$ -methylmorphimethines in the presence of palladium yields hexahydro compounds, the oxygen bridge being broken. *Hexahydro- $\epsilon$ -methylmorphimethine*,  $C_{19}H_{29}O_3N$ , (VI), m. p.  $155^\circ$ , is apparently optically inactive, is easily soluble in sodium hydroxide, and is reprecipitated by ammonium chloride. The *hydrochloride*, m. p.  $213^\circ$ , the oily *diacetyl* derivative, and the *methiodide* of the latter, m. p.  $170$ — $185^\circ$ , are described. From this methiodide by boiling with concentrated aqueous potassium hydroxide are obtained trimethylamine and a nitrogen-free, alkali-insoluble, deep yellow oil,  $C_{19}H_{24}O_4$  (VII), b. p.  $245$ — $253^\circ/15$  mm., setting to a glassy mass.

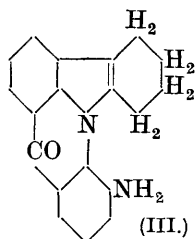
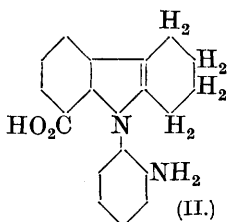
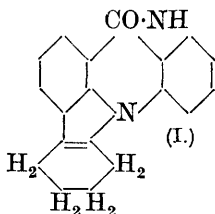
*Hexahydro- $\zeta$ -methylmorphimethine*,  $C_{19}H_{29}O_3N$  (VI), m. p.  $174$ — $175^\circ$ , optically inactive, gives no crystalline methiodide or acetyl derivative. The *hydriodide* decomposes slowly at  $245^\circ$ . C. H.

**Strychnos Alkaloids. XLIV. The Hydrazone of Brucinonic Acid.** H. LEUCHS and S. KANAO (*Ber.*, 1924, 57, [B], 1799—1802; cf. A., 1923, i, 941).—*Brucinonic acid hydrazone*,  $C_{23}H_{26}O_7N_4 \cdot 3H_2O$ , m. p.  $203^\circ$  (decomp.), is converted by ethyl alcohol and hydrogen chloride into a mixture of isomeric *ethyl* esters, m. p.  $178$ — $182^\circ$  (decomp.), and m. p.  $248$ — $250^\circ$ ,  $[\alpha]_D^{25}$ — $171^\circ$  in glacial acetic acid solution, respectively. The ester of lower m. p. is transformed by hydrazine hydrate into the *hydrazide* of brucinonic acid hydrazone,  $C_{23}H_{28}O_6N_6$ , m. p.  $210^\circ$  (decomp.), after softening at  $188^\circ$ ; this is converted by nitrous acid into brucinonic acid and a crystalline substance,  $C_{21}H_{22}O_6N_2$ , incipient decomp.  $270^\circ$ ,  $[\alpha]_D^{25} + 8.1^\circ$  in glacial acetic acid; this is probably a hydrate of the ketone,  $C_{21}H_{20}O_5N_2$  (cf. *loc. cit.*). H. W.

**New Lupine Alkaloid, Spathulatine, isolated from *Lupinus spathulatus* (Rydb.).** J. F. COUCH (*J. Amer. Chem. Soc.*, 1924, 46, 2507—2514).—The isolation and purification, from the pods and seeds of *Lupinus spathulatus* (Rydb.), of a new alkaloid, *spathulatine*,  $C_{33}H_{64}O_5N_4$ , prismatic crystals, m. p.  $227^\circ$ , is described. The alkaloid is faintly alkaline to litmus, but titration with acids does not give a sharp end-point. It has  $[\alpha]_D - 1.88^\circ$  in chloroform at  $27^\circ$ ,  $-2.32^\circ$  in alcohol at  $28.5^\circ$ , and  $-2.44^\circ$  in water at  $27.5^\circ$ . It crystallises from water in rhombic prisms of a *dihydrate*, and forms a characteristic *mercuric iodide additive* compound,  $C_{33}H_{64}O_5N_4 \cdot 3HgI_2$ , rhombic prisms resembling dodecahedra, m. p.  $164^\circ$ . Alkyloxy determinations gave negative results, and no reaction was observed with pure chloroform (cf. Bergh, *Arch. Pharm.*, 1904, 242, 416). The alkaloid is rapidly resinified by dilute sulphuric acid. Its salts are extremely soluble in water. [Cf. B., 1924, 1028.] F. G. W.

**Stereochemistry of Saturated Tervalent Nitrogen. VI. Attempts to Prepare Optically Active Compounds of Tervalent Nitrogen.** J. MEISENHEIMER, L. ANGERMANN, O. FINN and E. VIEWEG.—(See A., 1924, i, 1299.)

**Derivatives of Acridone and Tetrahydrocarbazole.** W. H. LINNELL and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1924, **125**, 2451—2460).—Attempts to prepare 6-carboxy-2'-nitrodiphenylamine-*N*-acetic acid by condensing phenylglycine-*o*-carboxylic acid with *o*-chloronitrobenzene yielded 2'-nitrodiphenylamine-6-carboxylic acid, elimination of acetic acid taking place during the condensation. The reaction is analogous to the decomposition of brucinolic acid into glycollic acid and brucinolone (Leuchs and Weber, A., 1909, i, 253), and of the conversion of the nitroso derivative of acridone-9-aminoacetic ester into 5-keto-5 : 10 : 16 : 17 : 18 : 19-hexahydroacridindoline (Clemo, Perkin, and Robinson, A., 1924, i, 1337), but is not due to the combined weights of the groups attached to the nitrogen atom, since the half-ester, ethyl 6-carboxy-2'-nitrodiphenylamine-*N*-acetate, is obtained by the action of ethyl bromoacetate on 2'-nitrodiphenylamine-6-carboxylic acid. On hydrolysis, or on reduction followed by hydrolysis of the acetamido derivative, or on dehydration, the acetic acid residue is again eliminated from the half-ester, dehydration of the amino ester giving a like result. Heating alone under reduced pressure converts the amino ester, ethyl 6-carboxy-2'-aminodiphenylamine-*N*-acetate, into glycollic acid and anhydro-2'-aminodiphenylamine-6-carboxylic acid. The nitroso derivative of the latter substance, on reduction with zinc and acetic acid in the presence of *cyclohexanone*, is converted into a tetrahydrocarbazole derivative to which the structure (I) is assigned for the following reasons. Alcoholic potassium hydroxide



hydrolyses the anhydro linking,  $-\text{NH}\cdot\text{CO}-$ , yielding 2'-amino-9-phenyl-1 : 2 : 3 : 4-tetrahydrocarbazole-8-carboxylic acid (II), which on treatment with sulphuric acid is converted into the acridone (III) by ring closure. The parent substance, 9-phenyltetrahydrocarbazole, resembles 9-benzoyltetrahydrocarbazole (Perkin and Plant, T., 1923, **123**, 675) in its behaviour with nitric acid, being partly nitrated, giving (5 ?)-nitro-9-phenyltetrahydrocarbazole, but mainly adding on  $-\text{OH}$  and  $-\text{NO}_2$  at the double bond in the tetrahydro ring, yielding 11-nitro-10-hydroxy-9-phenylhexahydrocarbazole, which with potassium hydroxide is decomposed, giving *o*-anilinobenzoylvaleric acid, analogous to the decomposition of 11-nitro-9-benzoyl-10-hexahydrocarbazole (Perkin and Plant, *loc. cit.*).

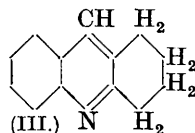
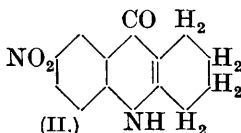
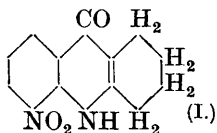
Phenylglycine-*o*-carboxylic acid and *o*-chloronitrobenzene in the presence of copper-bronze powder and potassium carbonate, alone or in amyl alcohol, toluene, or benzene, yielded only 2'-nitrodiphenyl-

amine-6-carboxylic acid, which with ethyl bromoacetate in alcohol yields *ethyl 2'-nitro-6-carboxydiphenylamine-N-acetate*, orange prisms, m. p.  $74.5^{\circ}$ , which on hydrolysis with aqueous or methyl-alcoholic potassium hydroxide gives 2'-nitrodiphenylamine-6-carboxylic acid. Heating with sulphuric acid, or with phosphoryl chloride in toluene, or with thionyl chloride and then with aluminium chloride in toluene converted the nitro ester into 9-nitroacridone, whilst on reduction with stannous chloride and hydrogen chloride in ether it yields *ethyl 2'-amino-6-carboxydiphenylamine-N-acetate*, an oil (*acetyl* derivative, m. p.  $121^{\circ}$ ), hydrolysed to 2'-aminodiphenylamine-6-carboxylic acid by aqueous or methyl-alcoholic potassium hydroxide. Heating with sulphuric acid or treatment with thionyl chloride and then aluminium chloride in toluene converts the amino ester into 9-aminoacridone, whilst on treatment with methyl alcoholic hydrogen chloride it yields methyl 2'-aminodiphenylamine-6-carboxylate. Attempts to obtain ethyl 2'-amino-6-carboxydiphenylamine-N-acetate in a crystalline form by distillation under diminished pressure yielded anhydro-2'-aminodiphenylamine-6-carboxylic acid, the nitroso derivative of which with *cyclohexanone*, zinc dust, and acetic acid yields an *anhydro-tetrahydrocarbazole* derivative,  $C_{19}H_{16}ON_2$ , m. p.  $204^{\circ}$ . 2'-Amino-9-phenyl-1:2:3:4-tetrahydrocarbazole-8-carboxylic acid, m. p.  $168^{\circ}$ , obtained from this by hydrolysis with sulphuric acid, is converted into a primary amine, m. p.  $262^{\circ}$ , isomeric with the anhydro derivative, m. p.  $204^{\circ}$ .

9-Phenyltetrahydrocarbazole, m. p.  $86^{\circ}$ , obtained by reducing nitrosodiphenylamine with zinc dust and acetic acid in the presence of *cyclohexanone*, with nitric acid and glacial acetic acid at  $40^{\circ}$  yields 5(?) -nitro-9-phenyltetrahydrocarbazole, yellow plates, m. p.  $120^{\circ}$ , and 11-nitro-10-hydroxy-9-phenylhexahydrocarbazole, colourless needles, m. p.  $145^{\circ}$  (decomp.), hydrolysed by aqueous alcoholic potassium hydroxide to o-anilinobenzoylvaleric acid, m. p.  $92^{\circ}$ .

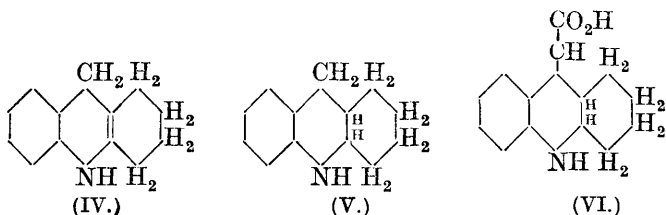
R. B.

**Tetrahydroacridine, Octahydroacridine and their Derivatives.** W. H. PERKIN, jun., and W. G. SEDGWICK (*J. Chem. Soc.*, 1924, **125**, 2437—2451).—With a view to study the general behaviour of the reduced acridine skeleton, a number of tetra- and octa-hydroacridine derivatives have been examined. Tetrahydroacridine, unlike tetrahydrocarbazole (cf. Perkin and Plant, T., 1923, **123**, 678), does not form an additive derivative with nitric acid. In the presence of sulphuric acid, two mononitro derivatives (I) and (II) are formed; these have been synthesised.



These nitro derivatives and the 2- and 4-isomerides are bright yellow substances giving red solutions in aqueous or alcoholic potassium hydroxide. On reduction, they yield aminotetrahydroacridones, without addition of hydrogen to the double bond,

and the amino derivatives diazotise normally. Similarly, no additive compound with nitric acid was obtained from tetrahydroacridine, whilst in the presence of sulphuric acid a nitrotetrahydroacridine was obtained which is probably the 4-nitro derivative, although this could not be reduced to the known 4-amino-octahydroacridine. Attempts to reduce tetrahydroacridine to hexahydroacridine (IV) were unsuccessful, the product being always octahydro-



acridine (V), unchanged tetrahydroacridine being present when insufficient reducing agent for complete reduction was used. This behaviour supports the formula (III) for tetrahydroacridine. The octahydroacridine thus obtained is a mixture of two isomerides, (A) m. p. 82° (mainly), and (B) m. p. 72°. These are presumably the two racemic modifications arising from the presence of two asymmetric carbon atoms, but their resolution has not yet been attempted. The same kind of isomerism has been observed with octahydroacridinecarboxylic acid (VI), and is possible with hexahydrocarbazole (Perkin and Plant, A., 1924, i, 1104), although in this case only one modification has been isolated. The octahydroacridines are very stable, the reduced system appearing to enhance the stability of the attached benzene nucleus, since attempts at further reduction to tesserakaidecahydroacridine were unsuccessful (cf. Willstätter, A., 1923, i, 771). Tetrahydroacridone, obtained by Tiedtke's method (A., 1909, i, 255), with aqueous nitric acid or in glacial acetic acid, yields the *nitrate*, C<sub>13</sub>H<sub>13</sub>ON.HNO<sub>3</sub>, which when gradually heated yields a sublimate of nitrotetrahydroacridone. 6(?8)-*Methyltetrahydroacridone*, m. p. 342°, was similarly obtained from 1-methylcyclohexan-3-one and anthranilic acid, 3-methylcyclohexylideneanthranilic acid, m. p. 140°, being formed intermediately. *Methyl 3-methylcyclohexylideneanthranilate* (?), yellow syrup, from methyl anthranilate and cyclohexanone, on hydrolysis yields anthranilic acid and cyclohexanone. With sulphuric acid and potassium nitrate at -15 to -10°, tetrahydroacridone yields 3-nitrotetrahydroacridone, m. p. 336° (decomp.), and 1-nitrotetrahydroacridone, m. p. 227°. The 3-nitro derivative was synthesised by heating 5-nitroanthranilic acid (obtained by hydrolysing the acetyl derivative with alcoholic hydrochloric acid or with acetic and sulphuric acids) with cyclohexanone at 120°, the temperature being subsequently raised to 220° to dehydrate the cyclohexylidene-5-nitroanthranilic acid, red needles, m. p. 271° (decomp.), first formed. Similarly, 3-nitroanthranilic acid, obtained quantitatively by treating 3-nitrophthalamidic acid with sodium hypochlorite (cf. Kahn, A., 1903, i, 93), is converted into 1-nitrotetrahydroacridone. 4-Nitro-

anthranilic acid, obtained quantitatively by a modification of Wheeler's method (A., 1898, i, 368), in the same way yields cyclohexylidene-4-nitroanthranilic acid, yellow needles, m. p. 269° (decomp.), and 2-nitrotetrahydroacridone, m. p. 332°. 4-Nitrotetrahydroacridone, m. p. 270°, was similarly synthesised from 6-nitroanthranilic acid. cyclohexylidene-6-nitroanthranilic acid, m. p. 214° (decomp.), is decomposed on boiling with water, alcohol, or dilute acids into 6-nitroanthranilic acid and cyclohexanone. 3-Nitrotetrahydroacridone, on reduction with zinc dust and alcoholic hydrochloric acid, is converted into 3-aminotetrahydroacridone, m. p. 322° (darkens) (hydrochloride, m. p. 310°, acetyl derivative, m. p. 344°). 1-Aminotetrahydroacridone has m. p. 255°, and 2-aminotetrahydroacridone, m. p. 320° (hydrochloride, acetyl derivative, m. p. 336°). Hexahydroanthranilic acid and cyclohexanone at 130° and then at 260° give decahydroacridone, m. p. 275° (darkens), a strong base, which does not form a characteristic picrate, and on electrolytic reduction yielded a substance, m. p. 179—180°,  $C_{13}H_{21}ON$  (?).

Tetrahydroacridine, obtained by Borsche's method (A., 1908, i, 682), yields a sulphate, m. p. 220°, a nitrate, yellow plates, m. p. 160°, a picrate, m. p. 208° (decomp.), and a methiodide, m. p. 202—204°. With phosphorus pentachloride and oxychloride it is converted into 5-chlorotetrahydroacridine, m. p. 226°, which with dilute acids is slowly converted into tetrahydroacridone. Nitration with nitric acid and glacial acetic acid, or sulphuric acid and potassium nitrate, yields 4(?)-nitrotetrahydroacridine, orange-brown needles, m. p. 110°, which on reduction with stannous chloride and alcoholic hydrochloric acid is converted into 4(?)-aminotetrahydroacridine, m. p. 160° [hydrochloride, orange needles, m. p. 242°, nitrate, yellow; picrate, red prisms, m. p. 236° (decomp.), acetyl derivative, m. p. 204°]. Reduction of nitrotetrahydroacridine with tin and hydrochloric acid gives a readily oxidisable base (acetyl derivative,  $C_{15}H_{20}ON_2$ , m. p. 195°, hydrochloride, m. p. 235°), which is possibly 4(?)-amino-octahydroacridine.

Reduction of tetrahydroacridine with tin and alcoholic hydrochloric acid yields a mixture of octahydroacridines (A) and (B), which are separated by means of their sulphates or picrates, the sulphate and picrate of (A) separating first. Octahydroacridine (A), m. p. 82° (picrate, m. p. 195°; methiodide, yellow, m. p. 212°, acetyl derivative) is also obtained on reducing tetrahydroacridone with sodium amalgam in neutral solution. Methylation with methyl sulphate yields 10-methyloctahydroacridine (A), oil, b. p. 140° (picrate, m. p. 160°), which is also formed on reduction of tetrahydroacridine methiodide with sodium amalgam. Octahydroacridine (A) cannot be nitrated directly; the acetyl derivative with sulphuric acid and potassium nitrate gives a yellow product which when boiled with hydrochloric acid yields 4(?)-nitro-octahydroacridine hydrochloride, m. p. 198°. Nitro-octahydroacridine (A), red needles, has m. p. 104°; the mother-liquor contains an isomeride, yellow needles, m. p. 180°. Octahydroacridine (B) (picrate, m. p. 175°; methiodide, yellow prisms, m. p. 217°; acetyl derivative, m. p. 136°) has m. p. 72°. Reduction of tetrahydroacridinecarboxylic

acid (Borsche, *loc. cit.*) with sodium amalgam in neutral solution yields a mixture of octahydroacridinecarboxylic acids (A) and (B) which are separated by crystallisation from alcohol, *octahydroacridinecarboxylic acid* (A), m. p. 180°, separating first. *Octahydroacridinecarboxylic acid* (B) has m. p. 221°. Both acids on heating at 260° afford carbon dioxide and the corresponding octahydroacridine.

R. B.

**2-Pyridone-1-acetic Acid.** A. KIRPAL (*Ber.*, 1924, 57, [B], 1954—1955; cf. SPÄTH and KOLLER, *A.*, 1923, i, 595).—2-Hydroxypyridine is converted by chloroacetic acid in warm alcoholic solution into 1-chloro-2-hydroxypyridine-1-acetic acid, m. p. 98°, in which the halogen atom is not ionised and is so firmly united that it cannot be removed by moist silver oxide. The acid is transformed by boiling concentrated alkali hydroxide solution into 2-pyridone-1-acetic acid, m. p. 222°, which is also obtained from the chloro compound at 200°, whereas at higher temperatures 1-methyl-2-pyridone is produced. The *silver* salt, *methyl* ester, m. p. 45°, and *amide*, m. p. 228°, of 2-pyridone-1-acetic acid are described.

H. W.

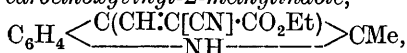
**Preparation of O-O-Diacyl Derivatives of Diphenolisatin and its Products of Substitution in the Phenol and Isatin Groups.** F. HOFFMANN-LA ROCHE UND CO. A.-G. (Brit. Pat. 221976).—Diphenolisatin (or its substitution products) is treated with an acylating agent at a temperature not considerably exceeding 100°. Details are given of the preparation of the following: *diacetyldiphenolisatin*, fine, crystalline powder, m. p. 242°; *diphenylacetyldiguaiacolisatin*, shining, white crystals, m. p. 169—170°; *O-O-dibenzoyldiphenolisatin*, coarse prisms, m. p. 221—222°; *O-O-di-p-toluenesulphonyldiphenolisatin*, white crystals, m. p. 219—220°; *dicarbethoxydiphenolisatin*, white needles, m. p. 156—157°; *dicinnamoyldiguaiacolisatin*, fine, white crystals, m. p. 230—231°; *dicarbethoxydiguaiacolisatin*, fine needles, m. p. 119—120°; *dibenzoyldi-o-cresolisatin*, fine, white crystals, m. p. 210—211°; *O-O-diacetyldi-o-cresolisatin*, coarse, white crystals, m. p. 180—181°. The products possess laxative properties and are very moderately toxic. They are insoluble in water, but mostly soluble in organic solvents.

W. T. K. B.

**Action of Halogens on Pyrrole to give Coloured Solutions.** G. E. K. BRANCH and H. E. H. BRANCH (*J. Amer. Chem. Soc.*, 1924, 46, 2469—2474).—When iodine is added to a suspension of potassium pyrrole in absolute ether, or to a mixture of sodium ethoxide, alcohol, and pyrrole, a blue solution is obtained which contains, in addition to tetraiodopyrrole, the compound  $(C_4H_7N_2I)_n$ , which readily absorbs oxygen with formation of a black powder  $(C_4H_7O_2N_2I)_n$ . Coloured ethereal solutions are also obtained by the action of iodine and bromine on magnesium pyrrol iodide, or on the mercury-pyrrole compound obtained by the action of magnesium pyrrol iodide on mercuric chloride, or by the action of aqueous sodium hypobromite on pyrrole. When a suspension of mercuric iodide in a

moist ethereal solution of pyrrole (1 mol.) is treated with iodine (1 atom) in ether, the mercuric iodide dissolves to a green solution. Further addition of iodine causes precipitation of a black solid, unless sodium ethoxide is added, when 2-3 more equivalents of iodine may be made to react, before the green solution deposits the black solid, which contains mercury and iodine. F. G. W.

**Substituted Indole Derivatives. II.** R. SEKA (*Ber.*, 1924, 57, [B], 1868—1871; cf. A., 1923, i, 1125).—2-Methyl-3-aldehydoindole is converted by nitromethane in alkaline solution into 3-*ω*-nitrovinyl-2-methylindole,  $C_6H_4 \left\langle \begin{array}{c} C(CH:CHNO_2) \\ NH \end{array} \right\rangle CMe$ , m. p. 191.5° (decomp.), and by ethyl cyanoacetate under similar conditions into 3-*ω*-cyano-*ω*-carbethoxyvinyl-2-methylindole,



m. p. 246—247°. 3-*ω*-Cyano-*ω*-phenylvinyl-2-methylindole, prepared from 2-methyl-3-aldehydoindole and phenylacetonitrile in the presence of sodium ethoxide and alcohol, has m. p. 179.5°. 3-Cyano-1-acetyl-2-methylindole, m. p. 116°, is prepared by the action of acetic anhydride and sodium acetate on the oxime of 3-aldehydo-2-methylindole. When treated with ethyl cyanoacetate and sodium ethoxide at 120°, it unexpectedly yields 3-cyano-2-methylindole, m. p. 209—210°, which is also obtained under similar conditions in the absence of the cyano ester. With phenylacetonitrile it gives a compound,  $(C_7H_6N)_4$ , m. p. 102—103°, the constitution of which has not been elucidated. H. W.

**Syntheses in the Indole Group. I.** W. O. KERMACK (*J. Chem. Soc.*, 1924, 125, 2285—2291).—The introduction of a positive cyano group into the benzene ring of indolecarboxylic acid appears to lower the reactivity of the hydrogen atoms in the pyrrole nucleus, since the condensation product with aminoacetal yields neither an indole-diazine nor a carboline with alcoholic hydrogen chloride (cf. Kermack, Perkin, and Robinson, T., 1921, 119, 1602; 1922, 121, 1872; Blaikie and Perkin, A., 1924, i, 547). Attempts to prepare 6-carbethoxyindole-2-carboxylic acid from ethyl 2-nitro-*p*-toluate and ethyl oxalate were unsuccessful. With the exception of 6-cyanoindole and indole-6-carboxylic acid, the indole derivatives described in this paper only react with Ehrlich's reagent on prolonged boiling in presence of additional concentrated hydrochloric acid.

Ethyl 2-nitro-*p*-toluate and ethyl oxalate condense in alcoholic sodium ethoxide solution, giving ethyl 2-nitro-4-carbethoxyphenylpyruvate, faintly yellow needles, m. p. 88—89°, the partial hydrolysis of which to the carbethoxypyruvic acid could not be accomplished. Reduction with zinc dust and acetic acid yields ethyl indole-2 : 6-dicarboxylate, yellow needles, m. p. 132°; the free acid (+0.5AcOH) has m. p. above 310°. Similarly, 2-nitro-*p*-toluonitrile and ethyl oxalate, etc., afford ethyl 2-nitro-4-cyanophenylpyruvate, yellow needles, m. p. 107°, which on reduction yields ethyl 6-cyanoindole-2-carboxylate, greenish-yellow needles, m. p. 171°. The free acid,



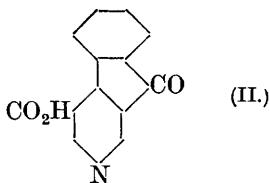
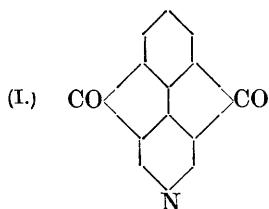
m. p. 290—295° (decomp.) after sintering at 280°, on treatment with acetyl chloride and phosphorus pentachloride, is converted into its chloride, which with aminodimethylacetal (2 mols.) yields 6-cyano-indole-2-carboxydimethylacetalylamide, yellow needles, m. p. 215°, from which no crystalline compound was obtained with alcoholic hydrogen chloride. 6-Cyanoindole 2-carboxylic acid on distillation with quicklime yields 6-cyanoindole, flat needles, m. p. 129—130°, which appears to be much more stable towards acids than indole itself, and on hydrolysis with methyl-alcoholic potassium hydroxide yields indole-6-carboxylic acid, m. p. 243—244°. R. B.

**Transformation of Iodoantimonates of Nitrogenated Organic Bases into Crystalline Iodomercurates.** E. CAILLE and E. VIEL (*Compt. rend.*, 1924, 179, 689—690).—When hydrochloric acid solutions of the iodoantimonates (cf. A., 1923, ii, 443, 585) are boiled with mercury, the corresponding iodomercurates (cf. François and Blanc, A., 1922, i, 851) are formed, and after removal of the precipitated mercurous iodide and antimony by filtration may be obtained crystalline. The pyridine compound,  $\text{HgI}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ , forms lemon-yellow needles, and is obtained in 45% yield, being partly decomposed into mercurous iodide and pyridine hydriodide by the excess of mercury. The iodomercurates of aniline, quinoline, piperazine, theobromine, and nicotine were also prepared. T. H. P.

**2:6-Distyrylpyridine and its Derivatives.** B. D. SHAW (*J. Chem. Soc.*, 1924, 125, 2363—2365).—The base, m. p. 164°, obtained as a by-product in the action of benzaldehyde on  $\alpha$ -picoline, and regarded by Ladenburg (A., 1903, i, 275) as diphenylpyridylcyclopropane, is the 2:6-distyrylpyridine previously obtained by Schuster (A., 1892, 1360). The hydrochloride, golden-yellow needles, has m. p. 215° in a sealed tube. On bromination in warm carbon disulphide solution, the base yields 2:6-distyrylpyridine dibromide,  $\text{C}_{21}\text{H}_{17}\text{NBr}_2$ , m. p. 214—215° (decomp.), and not the tetrabromide claimed by Schuster (*loc. cit.*); the latter compound, m. p. 179° (decomp.), is obtained by boiling the base with excess of bromine in carbon tetrachloride. The dichloride, m. p. 213°, is obtained by the action of chlorine in carbon tetrachloride solution. Reduction of the base with sodium and amyl alcohol yields 2:6-di- $\beta$ -phenylethylpiperidine, oil, b. p. 290—295°/20 mm. The oxalate, m. p. 179°, hydrochloride, m. p. 183°, and nitrate, m. p. 167—170°, are colourless. R. B.

**Pyridofluorene and some of its Derivatives.** W. H. MILLS, W. H. PALMER, and (MISS) M. G. TOMKINSON (*J. Chem. Soc.*, 1924, 125, 2365—2370).—With the object of throwing light on the isomerism of certain 9-substituted derivatives of fluorene (Schmidt and Mezger, A., 1907, i, 43; Schmidt and Stützel, A., 1908, i, 415), pyridofluorene and some of its derivatives have been prepared and examined. Since dimethylpyridofluorenecarboxylic acid, like fluorenecarboxylic acid, does not undergo further condensation

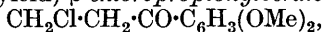
under the influence of dehydrating agents to a compound of the type (I), it is possible that the formation of the five-membered ring



in the fluorenone increases the distance between the 5-carboxyl group and the 4-hydrogen atom (cf. II), a supposition which favours the non-coplanar configuration for the fluorene molecule required to explain the existence of isomeric 9-derivatives of fluorene as stereoisomerides. Such a configuration necessitates molecular asymmetry in the unsymmetrically substituted derivatives, but attempts to resolve fluorenonecarboxylic acid with alkaloids, and 1 : 3-dimethylpyridofluorene and 1 : 3-dimethylpyridofluorenone with camphor-sulphonic acids, yielded no positive results.

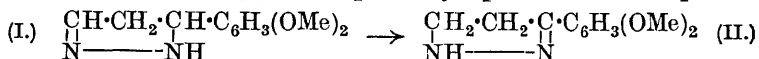
4-Phenyl-lutidinedicarboxylic acid, m. p. 296° (decomp.), obtained by hydrolysis of its ethyl ester with alcoholic sodium hydroxide (cf. Kirchner, A., 1892, 1486), with sulphuric acid at 100° yields 1 : 3-dimethylpyridofluorenone-4-carboxylic acid, yellow crystals, m. p. 280·5° (decomp.) [sulphate, yellow prisms (+3H<sub>2</sub>O), m. p. 275—276°], which on oxidation with alkaline potassium permanganate yields pyridofluorenone-1 : 3 : 4-tricarboxylic acid, yellow plates, m. p. 203° (decomp.), resolidifying and melting again at 255°, which is also obtained by elimination of water from phenylpyridinetetracarboxylic acid with fuming sulphuric acid. Reduction with hydriodic acid at 130° yields pyridofluorene-1 : 3 : 4-tricarboxylic acid, m. p. 255°, the calcium salt of which, with soda-lime in a current of hydrogen under reduced pressure, yields pyridofluorene, m. p. 78°. 1 : 3-Dimethylpyridofluorenone, m. p. 158°, obtained by distillation of its 4-carboxylic acid, on reduction with hydriodic acid (*d* 1·7) similarly yields 1 : 3-dimethylpyridofluorene, m. p. 87·5° (yellow hydriodide). Pyridofluorenone-tricarboxylic acid on distillation under diminished pressure yields a substance, m. p. 130°, probably pyridofluorenone. R. B.

**The 3 : 4-Dimethoxyphenylpyrazoline obtained from Catechin.** K. FREUDENBERG and H. FIKENTSCHER (*Annalen*, 1924, 440, 36—38).—The action of  $\beta$ -chloropropionyl chloride on veratrole in carbon disulphide solution in the presence of aluminium chloride gives (70% yield)  $\beta$ -chloropropionylveratole,



pale yellow, m. p. 114°, which with hydrazine is converted into the 3-*mp*-dimethoxyphenylpyrazoline, colourless needles, m. p. 138°(?) [sulphate, m. p. 202° (decomp.), nitroso derivative, m. p. 187°], previously obtained from catechin and from 3 : 4-dimethoxycinnamaldehyde (A., 1924, i, 660), a synthesis which confirms the

structure previously assigned to the pyrazoline as against the alternative structure (I), which probably represents the first product



of the action of hydrazine on dimethoxycinnamaldehyde and subsequently isomerises to the stable form (II). R. B.

**Isomeric C-Substituted Pyrazolines.** K. FREUDENBERG and W. STOLL (*Annalen*, 1924, 440, 38—45).—The conversion of a catechin derivative into a pyrazoline derivative (A., 1924, i, 660) has induced further investigations on the constitution of pyrazoline derivatives with a view to determine the possibility of  $\Delta$ -isomerism among such compounds through the different positions of the double bond. Such isomerism has already been observed by Buchner and Heide in the case of the methyl ethyl 4-phenylpyrazoline-3:5-dicarboxylates, but, as in the case of the recently described 3-*mp*-dimethoxyphenylpyrazoline (cf. preceding abstract), only one 3-phenylpyrazoline could be obtained by methods which would be expected to give  $\Delta$ -isomerides, and the 3-arylpyrazolines appear to be capable of existence only in the one form. With the 3:5-diarylpyrazolines the isomerism is possible, and two 3:5-anisylphenylpyrazolines and their 4-hydroxy derivatives have been obtained. Similarly, two 3:5-phenylmethylpyrazolines and 3- and 5-methylpyrazolines have been obtained, but attempts to prepare pyrazolines containing the double linking between carbon atoms 3 and 4 or 4 and 5 ended in failure, phenylphenylacetylenecarbinol (Moureu and Desmot, A., 1902, i, 289) yielding on heating with hydrazine only the ordinary 3:5-diphenylpyrazoline. Such  $\Delta$ -isomerism is not observed among the pyrazoles, the two 4-hydroxy-3:5-anisylphenylpyrazolines yielding the same 3-phenyl-5-anisylpyrazole.

3-Phenylpyrazoline, b. p. 150°/13 mm., from cinnamaldehyde and hydrazine hydrate (Kishner, A., 1913, i, 1164) or from phenyl vinyl ketone and hydrazine hydrate, gives a *picrate*, m. p. 117—118° (decomp.), and a *nitroso* derivative, m. p. 150°. *p*-Anisylideneacetophenone and hydrazine yield 3-phenyl-5-anisylpyrazoline, which is unstable and is isolated as its *acetyl* derivative, m. p. 109°. Similarly, benzylidene-*p*-methoxyacetophenone yields 1-*acetyl*-5-phenyl-3-anisylpyrazoline, m. p. 134—135°.  $\alpha$ -Anisyl- $\beta$ -benzoyl-ethylene oxide, prepared by the action of anisaldehyde on bromoacetophenone in the presence of sodium ethoxide, similarly yields 4-hydroxy-3-phenyl-5-anisylpyrazoline, m. p. 174—175° (decomp.). 4-Hydroxy-5-phenyl-3-anisylpyrazoline, similarly obtained from phenylanisylethylene oxide, has m. p. 176—177°. 3:5-Diphenylpyrazoline, from benzylideneacetophenone (Kishner, A., 1915, i, 952) or  $\alpha\gamma$ -diphenylpropin- $\gamma$ -ol, gives a 1-*acetyl* derivative, m. p. 125°, and with *p*-toluenesulphonyl chloride in pyridine 1(*p*-toluenesulphonyl)-3:5-diphenylpyrazoline, m. p. 187°. 5-Phenyl-3-methylpyrazoline, prepared by Kishner's method, gives a *benzoyl* derivative, m. p. 137—138°, and a *phenylcarbamide*, m. p. 135°. 3-Phenyl-5-

*methylpyrazoline*, b. p. 158—159°/13 mm., *phenylcarbamide*, m. p. 126°, *benzoyl* derivative, m. p. 214°, was similarly obtained from phenyl  $\alpha$ -propenyl ketone, b. p. 126—128°/13 mm. (cf. Auwers, A., 1921, i, 466). 5-Methylpyrazoline (*picrate*, m. p. 126°, *phenylcarbamide*, m. p. 127°) and 3-methylpyrazoline (*picrate*, m. p. 153°, *phenylcarbamide*, m. p. 109°) were similarly prepared from crotonaldehyde and  $\beta$ -chloroethyl methyl ketone, respectively. Chalkone dibromide on boiling with hydrazine in methyl-alcoholic solution yields 3:5-diphenylpyrazole; with smaller quantities of alcohol, the corresponding 3:5-pyrazoline is formed. R. B.

**Halogen-substituted 1-Arylpyrazolones.** F. D. CHATTAWAY and C. R. N. STROUTS (*J. Chem. Soc.*, 1924, 125, 2423—2427).—Neither the position of the halogen substituent nor its accumulation in the phenyl residue appears to affect the reactivity of the methylene group in the 1-chlorophenyl-3-methyl-5-pyrazolones, which all react with methyl iodide, yielding chloro-substituted 1-phenyl-2:3-dimethyl-5-pyrazolones, distinguished from antipyrine by the extremely bitter taste of their aqueous solutions.

The *o*-chlorophenylhydrazone of ethyl acetoacetate when heated at 150—170° yields 1-*o*-chlorophenyl-3-methyl-5-pyrazolone, m. p. 199° (*hydrochloride*, m. p. 154°, decomp. at 172° into pyrazolone and hydrogen chloride; 4-*oximino* derivative, golden-brown prisms, m. p. 174°; 4-*benzylidene* derivative, orange prisms, m. p. 159°), which with methyl iodide and methyl alcohol at 100—120° yields 1-*o*-chlorophenyl-2:3-dimethyl-5-pyrazolone (*o*-chloroantipyrine), m. p. 113°. 1-*o*-Chlorophenyl-3-methyl-5-pyrazolone-4-azo-*o*-chlorobenzene, golden-yellow prisms, has m. p. 212°. 1-*m*-Chlorophenyl-3-methyl-5-pyrazolone, m. p. 131° [*hydrochloride*, m. p. 184° (decomp.)], yields a 4-*oximino* derivative, orange needles, m. p. 173° (decomp.), a 4-*benzylidene* derivative, red needles, m. p. 128°, and with boiling acetone a 4-*isopropylidene* derivative, sulphur-yellow needles, m. p. 110°. 1-*m*-Chlorophenyl-3-methyl-5-pyrazolone-4-azo-2':4'-dichlorobenzene, golden-brown needles, has m. p. 190° and 1-*m*-chlorophenyl-2:3-dimethyl-5-pyrazolone (*m*-chloroantipyrine), m. p. 89—90°. 1-*m*-Chlorophenyl-3-methyl-5-pyrazolone and phenylhydrazine yield bis-1-*m*-chlorophenyl-3-methyl-5-pyrazolone, which with ferric chloride or with excess of nitrous acid yields *m*-chloro-pyrazole-blue,  $C_6H_4Cl \cdot N < \begin{array}{c} N=CMe \\ CO \cdot C \end{array} \begin{array}{c} CMe \cdot N \\ =C-CO \end{array} > N \cdot C_6H_4Cl$ , crystalline

powder, m. p. 209° (decomp.). The other chlorophenylmethylpyrazolones do not yield pyrazole-blues when boiled with ferric chloride. 1-*p*-Chlorophenyl-3-methyl-5-pyrazolone gives a *hydrochloride*, m. p. 194—195° (decomp.), a 4-*oximino* derivative, m. p. 180° (decomp.), orange needles and brick-red prisms, and a *benzylidene* derivative, scarlet prisms, m. p. 156°. 1-*p*-Chlorophenyl-3-methyl-5-pyrazolone-4-azo-*p*-chlorobenzene, orange-red needles, has m. p. 232°, 1-*p*-chlorophenyl-2:3-dimethyl-5-pyrazolone (*p*-chloroantipyrine), m. p. 126°. Bis-1-*p*-chlorophenyl-3-methyl-5-pyrazolone,  $C_6H_4Cl \cdot N < \begin{array}{c} N=CMe \\ CO \cdot CH \end{array} \begin{array}{c} CMe \cdot N \\ =CH-CO \end{array} > N \cdot C_6H_4Cl$ , decomp. without melting;

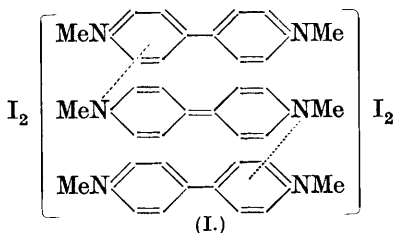
*p*-chloropyrazole-blue, blue needles, decomp. at about 300°. 1(2': 4'-Dichlorophenyl)-3-methyl-5-pyrazolone, m. p. 178°, yields a *hydrochloride*, m. p. 153°, decomp. at 170°, a 4-oximino derivative, canary-yellow needles, m. p. 166—168° (decomp.), and a 4-benzylidene derivative, orange, m. p. 131°. 1(2': 4'-Dichlorophenyl)-3-methyl-5-pyrazolone-4-azobenzene, orange needles, has m. p. 137—138°, and 1(2': 4'-dichlorophenyl)-2: 3-dimethyl-5-pyrazolone, m. p. 143°. R. B.

**Action of Sodamide on 3-Methylpyridine.** O. SEIDE (*Ber.*, 1924, 57, [B], 1802—1808; cf. A., 1924, i, 767).—3-Methylpyridine is converted by sodamide in the presence of xylene at 135—140° into 2-amino-3-methylpyridine, m. p. 24°, b. p. 222°/748 mm., 95°/8 mm. (the isomeric 6-amino-3-methylpyridine does not appear to be formed). The *hydrochloride*, *chloroplatinate* (+H<sub>2</sub>O), m. p. 209° (decomp.), and *picrate*, m. p. 229°, are described. The *acetyl* derivative, m. p. 64°, and the *benzoyl* compound, m. p. 220°, have been prepared. The base is converted by concentrated sulphuric acid and nitric acid (*d* 1.4) into 2-nitroamino-3-methylpyridine, m. p. 159° (decomp.), which is isomerised by sulphuric acid to 5-nitro-2-amino-3-methylpyridine, m. p. 255°. The position of the amino group in 2-amino-3-methylpyridine is deduced from the conversion of the substance by the usual methods successively into 2-hydroxy-3-methylpyridine, b. p. 288—290°/752 mm., m. p. 140°, 2-chloro-3-methylpyridine, b. p. 192—193°/751 mm. [*chloroplatinate* (+H<sub>2</sub>O), m. p. 208°], and 2-chloropyridine-3-carboxylic acid, m. p. 193°. H. W.

**Attempted Preparation of 1: 8-Naphthyridine Derivatives.** O. SEIDE (*Ber.*, 1924, 57, [B], 1806—1808).—The *anhydride* of 2-aminopyridine-3-carboxylic acid, C<sub>5</sub>H<sub>5</sub>N<CO·NH>C<sub>5</sub>H<sub>5</sub>N, m. p. 390° (corr. decomp.), was obtained in an attempt to prepare 2: 4-dihydroxy-1: 8-naphthyridine, C<sub>5</sub>H<sub>5</sub>N<C(OH):CH>N=C·OH, by the action of sodium ethoxide on *methyl 2-acetamidopyridine-3-carboxylate*, m. p. 88°. The constitution of the product is established by its transformation by concentrated potassium hydroxide solution into 2-aminopyridine-3-carboxylic acid. H. W.

#### Quinhydrone-like Compounds of Dihydro-4: 4'-dipyridyl.

B. EMMERT, G. JUNGCK, and H. HÄFFNER (*Ber.*, 1924, 57, [B], 1792—1797). — Reduction of dipyridyl dimethiodide by 1: 1'-dimethyltetrahydro-4: 4'-dicollidyl (cf. A., 1922, i, 1064; 1923, i, 1134) leads to the formation of *hexamethyldipyridyl-blue iodide* (I) which is stable towards air when dry, but is oxidised quantitatively in glacial acetic acid solution by oxygen to dipyridyl dimethiodide. It differs from the dipyridyl-violet halides described



previously (*loc. cit.*) in the relative proportions of benzenoid and quinonoid components of its molecule.

Meriquinonoid *dihydro-4 : 4'-dipyridyl*, an unstable, dark green substance, is prepared by the reduction of 4 : 4'-dipyridyl hydrate dissolved in methyl alcohol with sodium amalgam. It is converted by dilute hydrochloric acid into dipyridyl-violet chloride (Dimroth and Frister, A., 1923, i, 150).

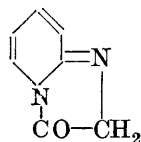
[With R. KUHN.]—Mainly as a result of determinations of the mol. weight of tetrabenzylidipyridyl-violet chloride in boiling methyl alcohol, Weitz, König, and von Wistinghausen (A., 1924, i, 425) have been led to discard the meriquinonoid conception of these compounds in favour of a radical structure. Repetition of these experiments under somewhat modified conditions has furnished considerably higher results which harmonise better with the meriquinonoid structure, but doubts are expressed with regard to the validity of the method in general for the present purpose.

H. W.

**Indigoid Dyes of the Pyridine Series.** H. FINGER and F. KRAFT (*Ber.*, 1924, 57, [B], 1950—1953).—Doubts are cast on the constitution of pyridoxyl obtained by Reindel (A., 1924, i, 1235) by the action of boiling sodium hydroxide solution on pyridylglycine; it is suggested that ring closure takes place at the pyridine nitrogen atom with production of a glyoxaline ring.

Pyridylglycine yields a *monohydrate*. 2-Aminopyridine is converted by chloroacetyl chloride in the presence of benzene into 1-*chloroacetylpyrid-2-imine hydrochloride*,  $\text{NH}\cdot\text{C}_5\text{H}_4\text{N}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}\cdot\text{HCl}$ , m. p. 157°; the corresponding *base*, m. p. 123°, and its *picrate*, m. p. 155—157° (decomp.), are described. The base is rapidly converted when heated by itself or in the presence of solvents of high boiling point into a compound, m. p. 245°, which is identical with “pyridoxyl hydrochloride” (cf. Reindel, *loc. cit.*), and to which the annexed constitution is now assigned. It is converted (as is also pyridylglycine) by sodium acetate and acetic anhydride into an acetyl derivative which is hydrolysed by hydrochloric acid to an isomeric *hydrochloride*,  $\text{C}_7\text{H}_6\text{ON}_2\cdot\text{HCl}$ , m. p. about 295° (corresponding *picrate*, m. p. 211°), which, like pyridoxyl hydrochloride, is oxidised by potassium ferricyanide in alkaline solution to Reindel's red dye. The nature of the isomerism is not explained.

H. W.



**Alkylated and Halogenated Indazoles.** K. VON AUWERS and A. LOHR (*J. pr. Chem.*, 1924, [ii], 108, 297—320).—(I) Methylindazoles.—5-Methylindazole with methyl iodide and sodium methoxide yields 1 : 5-dimethylindazole, but if the methyl iodide be in large excess, 2 : 5-dimethylindazole is also formed. With ethyl bromide at 100°, 5-methyl-2-ethylindazole is formed as a pale yellow oil, b. p. 151°/15 mm.; the *picrate* forms yellow prisms, m. p. 160—161°. Ethyl bromide and alcoholic sodium ethoxide give a mixture of 5-methyl-2-ethylindazole and 5-methyl-1-ethylindazole, a yellow oil, b. p. 125—126°/12 mm. (*picrate*, m. p. 146—  
d\*

147°). 5-Methyl-2-allylindazole, formed by the action of allyl bromide as above, is a pale yellow oil, b. p. 146—147°/12 mm.; the *picrate* has m. p. 137·5—138·5°. By the second method, a mixture of 5-methyl-2-allylindazole and 5-methyl-1-allylindazole (viscous oil, b. p. 137—138°/12 mm.) is produced (*picrate*, m. p. 115—116°). 2-Benzyl-5-methylindazole (by the action of benzyl chloride below 100°) forms crystals, m. p. 41·5—42·5°, b. p. 214—215°/15 mm.; the *picrate* has m. p. 151—152°. A mixture of the 2-benzyl and 1-benzyl derivatives results if alcoholic sodium ethoxide is present. 1-Benzyl-5-methylindazole forms small plates, m. p. 52—53°; the *picrate* forms yellow needles, m. p. 99—100°. By heating 5-methylindazole and benzyl chloride at 170°, a mixture of the two isomerides is usually produced, although sometimes the product is almost wholly the 1- or the 2-benzyl derivative.

Methyl 5-methylindazole-2-carboxylate, produced by the interaction of 3-methylindazole and methyl chloroformate below 100°, forms plates, m. p. 65—66°, and when heated under diminished pressure gives a mixture of 1 : 5- and 2 : 5-dimethylindazoles with much resinification. The corresponding *ethyl* ester (white needles, m. p. 67—68°) behaves similarly.

3-Methylindazole reacts with benzyl chloride below 100° to form 2-benzyl-3-methylindazole (white needles, m. p. 85—86°); the *picrate* has m. p. 224—225°. The reaction at 170° sometimes gives a mixture of the 2-benzyl compound and 1-benzyl-3-methylindazole (needles, m. p. 58—59°). 2-Benzyl-3-methylindazole gives, with methyl iodide at 100°, 1 : 3-dimethyl-2-benzylindazolium iodide (needles, m. p. 187°), which is also produced by the interaction of 1 : 3-dimethylindazole and benzyl iodide under identical conditions, and, on heating under diminished pressure, gives 1 : 3-dimethylindazole.

2 : 3-Dimethyl-1-benzylindazolium iodide, from 1-benzyl-3-methylindazole and methyl iodide, forms prisms, m. p. 197°; when heated under diminished pressure, it gives a mixture of 2 : 3-dimethylindazole and 1-benzyl-3-methylindazole.

(II) Labile and Stable Isomeric Nitrobenzoylindazoles.—By heating a mixture of 3-methylindazole and *o*-nitrobenzoyl chloride at the m. p., the stable *o*-nitrobenzoyl-3-methylindazole (small plates, m. p. 175—176°) results. The labile *isomeride* (yellow prisms, m. p. 139°) is formed in alcoholic solution, or by the action of the acid chloride on the *silver* salt; this gradually changes to the stable *isomeride*. The stable *m*-nitrobenzoyl derivative forms prisms, m. p. 141—142°; the labile form could not be isolated. The stable *p*-nitrobenzoyl derivative forms fine, white needles, m. p. 131—132°; the labile *isomeride* (from the indazole and acid chloride in cold ether) forms yellow prisms, m. p. 143·5—144·5°, not readily converted to the stable form. Stable *o*-nitrobenzoyl-3-bromoindazole, needles, m. p. 182—183°, is formed by all the usual methods (including the reaction between the acid chloride and the *silver* salt).

(III) Halogenated Indazoles.—3-Chloroindazole (m. p. 147—148°) and 3-bromoindazole (m. p. 141—142°) are formed by the

action of alkaline sodium hypochlorite or hypobromite on indazole. 3-Iodoindazole (m. p.  $142^{\circ}$ ), is formed by the gradual addition of iodine to an alkaline solution of indazole. 3-Bromoindazole with methyl sulphate and sodium hydroxide gives a mixture of 3-bromo-1-methylindazole and 3-bromo-2-methylindazole. By the interaction of 3:5-dibromoindazole and methyl bromide at  $120^{\circ}$ , 3:5-dibromo-1:2-dimethylindazolium bromide is formed as fine, white needles, m. p.  $216^{\circ}$ . This on heating above its m. p. yields 3:5-dibromo-1-methylindazole (m. p.  $104-106^{\circ}$ ). By the action of nitrous fumes on 3:5-dibromo-o-acetotoluidide (white prisms, m. p.  $201-202^{\circ}$ ), the nitroso derivative, yellow crystals, m. p. (crude)  $56-57^{\circ}$ , is formed. This on warming in benzene solution gives 5:7-dibromoindazole (fine needles, m. p.  $197-198^{\circ}$ ). The 2-methyl derivative forms needles, m. p.  $123^{\circ}$ ; by the action of methyl bromide in excess, 5:7-dibromo-1:2-dimethylindazolium bromide is formed as white needles, m. p.  $228^{\circ}$  (decomp.). 5:7-Dibromoindazole gives with alkaline sodium hypobromite, 3:5:7-tribromoindazole, white needles, m. p.  $205-206^{\circ}$ , which on methylation with methyl bromide yields 3:5:7-tribromo-2-methylindazole as needles, m. p.  $173^{\circ}$ ; this may also be obtained by the bromination of 5:7-dibromo-2-methylindazole in acetic acid solution.

3-Iodo-2-methylindazole (stout prisms, or plates, m. p.  $150-151^{\circ}$ ) is obtained by the action of methyl iodide and sodium methoxide on 3-iodoindazole in methyl-alcoholic solution; on reduction, 2-methylindazole is produced, with some 3-iodo-1-methylindazole. Methyl iodide converts 3-iodo-2-methylindazole into 3-iodo-1:2-dimethylindazolium iodide, m. p.  $220^{\circ}$ ; on dry distillation, 3-iodo-1-methylindazole is produced (impure). 3-Bromo-5-methylindazole with methyl sulphate and alkali yields 3-bromo-2:5-dimethylindazole, white needles, m. p.  $127-128^{\circ}$ , forming a picrate, m. p.  $153-154^{\circ}$ . The isomeric 3-bromo-1:5-dimethylindazole was not isolated. By the action of methyl iodide on the 2:5-dimethyl derivative at  $100^{\circ}$ , 3-bromo-1:2:5-trimethylindazolium iodide is formed as needles, m. p.  $221^{\circ}$  (decomp.). On heating above its m. p., it yields 3-bromo-2:5-dimethylindazole and probably some 3-bromo-1:5-dimethylindazole. The latter could not be prepared by the direct bromination of 1:5-dimethylindazole.

A. E. C.

**C( $\alpha$ -Pyridyl)-1-methylpyrrole. II.** J. P. WIBAUT and A. COPPENS (*Rec. trav. chim.*, 1924, **43**, 526-529).—The potassium derivative of the C-(2'-pyridyl)pyrrole, m. p.  $132^{\circ}$ , of Wibaut and Dingemanse (A., 1923, i, 1232) was boiled with excess of methyl iodide and ether. After removal of the solvent from the filtrate, the residue was divided into two parts by treatment with ether: (a) was purified through its picrate (yield 20%), m. p.  $193-194^{\circ}$  (cf. *loc. cit.*), from which ammonia liberated C-(2'-pyridyl)-1-methylpyrrole, m. p.  $43.5-44.5^{\circ}$ ; (b) its methiodide was obtained pure after many recrystallisations, m. p.  $146.2-146.6^{\circ}$  (yield 6%), and also prepared by the action of methyl iodide on C-(2'-pyridyl)-1-methylpyrrole.

F. M. H.

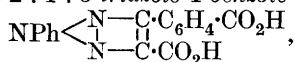
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**Solvent Action of Trialkyltrimethylenetriamines on Uric Acid.** J. GRAYMORE (*J. Chem. Soc.*, 1924, **125**, 2283—2285).—Some cyclic triamines of the type  $(\text{CH}_2\text{NR})_3$  have been prepared. Trimethyl- and triethyl-trimethylenetriamine yield urates having a solubility in water of 1 part in 11 parts and 1 part in 9 parts, respectively, but hypodermic injection of the triethyl compound produces symptoms of irritation and toxic indications. *Trimethyltrimethylenetriamine urate*, obtained by heating the base and uric acid in aqueous solution, decomposes without melting. *Trimethyltrimethylenetriamine dibromide*,  $(\text{CH}_2\text{NMe})_3\text{Br}_2$ , light yellow needles, has m. p.  $97^\circ$ . *Triethyltrimethylenetriamine urate* decomposes without melting. The *hydrochloride*,  $(\text{CH}_2\text{NEt})_3\text{HCl}$ , and the *dibromide*, colourless needles, m. p.  $144\text{--}145^\circ$ , are described. R. B.

**So-called vic.-2 : N-Aryltriazolephthalonic Acids.** G. CHARRIER (*Gazzetta*, 1924, **54**, 647—658).—Oxidation of the 2-phenyl- $\alpha\beta$ -naphthatriazolequinones (A., 1924, i, 1351) by means of alkaline permanganate yields the acids previously described as vic.-2 : N-aryltriazolephthalonic acids (A., 1924, i, 329) but now shown to be 5-carboxy-2-aryl-2 : 1 : 3-triazole-4-benzoic acids. Hence, both the structural and empirical formulæ of these acids and their derivatives require alteration as follows.

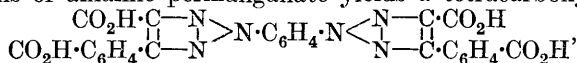
*5-Carboxy-2-phenyl-2 : 1 : 3-triazole-4-benzoic acid*,



not vic.-2-phenyltriazolephthalonic acid, has m. p.  $242^\circ$ . The sodium salt,  $\text{C}_{16}\text{H}_{10}\text{O}_4\text{N}_3\text{Na} \cdot 4\text{H}_2\text{O}$ ; barium salt ( $+4\text{H}_2\text{O}$  and  $+5\text{H}_2\text{O}$ ); strontium salt ( $+4\frac{1}{2}\text{H}_2\text{O}$ ); methyl ester; methyl hydrogen ester; ethyl ester and the diamide,  $\text{C}_{14}\text{H}_9\text{N}_3(\text{CONH}_2)_2$ , have the properties previously given.

*5-Carboxy-2-p-chlorophenyl-2 : 1 : 3-triazole-4-benzoic acid* (not vic.-2-*p*-chlorophenyltriazolephthalonic acid),  $\text{C}_{16}\text{H}_{10}\text{O}_4\text{N}_3\text{Cl}$ , has m. p.  $264\text{--}265^\circ$ . The corresponding bromophenyl and carboxyphenyl derivatives have m. p.  $270^\circ$  and  $287\text{--}288^\circ$ , respectively.

Oxidation of *p*-phenylene-1 : 2-dinaphthaditriazole (A., 1924, i, 334) or of 1 : 2-naphthatriazole-2-*p*-benzeneazo-2-naphthylamine by means of alkaline permanganate yields a tetracarboxylic acid,



which forms white needles, m. p.  $322\text{--}323^\circ$  (slight decomp.). T. H. P.

**Tripyrrylmethanes.** II. H. FISCHER and M. HEYSE (*Annalen*, 1924, **439**, 246—264; cf. Fischer and Ammann, A., 1924, i, 78).—In the presence of potassium hydrogen sulphate, pyrrole-2- and -3-aldehydes condense readily with two mol. proportions of trisubstituted pyrroles to form well-crystalline tripyrrylmethanes, the constitution of which is proved by mol. weight determinations and by their almost quantitative fission by hydrochloric acid into the corresponding dipyrpyrlylmethene and the tri-

substituted pyrrole. Tri-(3-acetyl-2 : 4-dimethylpyrrol)methane crystallises with 1 mol. of ethyl alcohol (not 0.5 mol. as previously reported), m. p. 265°, or with 0.5 mol. (not 1 mol.) of acetic acid, m. p. 187°. Hydrochloric acid in hot alcohol removes 1 mol. of acetyldimethylpyrrole, leaving Piloty's bis-(3-acetyl-2 : 4-dimethylpyrrol)methene hydrochloride, m. p. 203° (free base, m. p. 219°).

3-Acetyl-2 : 4-dimethylpyrroldi-(3-carbethoxy-2 : 4-dimethylpyrrol)-methane, m. p. 219° (+1EtOH, m. p. 146°), is prepared from 3-acetyl-2 : 4-dimethylpyrrole-5-aldehyde by condensation with ethyl 2 : 4-dimethylpyrrole-3-carboxylate.

3-Carbethoxy-2 : 5-dimethylpyrroldi-(3-acetyl-2 : 4-dimethylpyrrol)-methane, m. p. 231° (decomp.), undergoes fission by hydrochloric acid into ethyl 2 : 5-dimethylpyrrole-3-carboxylate and bis-(3-acetyl-2 : 4-dimethylpyrrol)methene; i.e., the pyrrole liberated is that which was attached to the methane carbon atom in the 3-position.

3-Carbethoxy-2 : 5-dimethylpyrroldi-(3-carbethoxy-2 : 4-dimethylpyrrol)methane, m. p. 184°, results from the condensation of ethyl 2 : 5-dimethylpyrrole-4-aldehyde-3-carboxylate with ethyl 2 : 4-dimethylpyrrole-3-carboxylate.

Tri-(3-carbethoxy-2 : 4-dimethylpyrrol)methane, m. p. 194°, previously prepared by the chloroform method, is now obtained in 80% yield from ethyl 2 : 4-dimethylpyrrole-5-aldehyde-3-carboxylate and ethyl 2 : 4-dimethylpyrrole-3-carboxylate. The fission into methene and pyrrole by hydrochloric acid may also be brought about by boiling ferric chloride solution.

The condensation of ethyl 2 : 4-dimethylpyrrole-5-aldehyde-3-carboxylate with ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate gives no tripyrrylmethane, but only the corresponding methene.

5-Carbethoxy-2 : 4-dimethylpyrroldi-(3-acetyl-2 : 4-dimethylpyrrol)-methane, m. p. 247°, and 5-carbethoxy-2 : 4-dimethylpyrroldi-(3-carbethoxy-2 : 4-dimethylpyrrol)methane, m. p. 201°, are prepared by condensing ethyl 2 : 4-dimethylpyrrole-3-aldehyde-5-carboxylate with 3-acetyl- and 3-carbethoxy-2 : 4-dimethylpyrroles respectively. In the fission of the latter tripyrrylmethane (m. p. 201°) the 3-linking is again broken in preference to a 2-linking, the products being ethyl 2 : 4-dimethylpyrrole-5-carboxylate and bis-(3-carbethoxy-2 : 4-dimethylpyrrol)methene hydrochloride, m. p. 213°.

(3-Acetyl-2 : 4-dimethylpyrrol)(4-hydroxy-3-carbethoxy-2-methylpyrrolenyl)methene, m. p. 253° (hydrochloride, m. p. 203°), is formed when hydrogen chloride is passed into an alcoholic solution of equimolecular proportions of 3-acetyl-2 : 4-dimethylpyrrole-5-aldehyde and ethyl 4-hydroxy-2-methylpyrrole-3-carboxylate. The isomeric (3-acetyl-2 : 4-dimethylpyrrolenyl)(4-hydroxy-3-carbethoxy-2-methylpyrrol)methene, m. p. 245° (hydrochloride, m. p. 195°), is analogously prepared.

The looseness of a carbon-carbon linking in the 3-position is further illustrated by the easy hydrolysis of 2 : 4 : 5-trimethylpyrrole-3-aldehyde by concentrated hydrochloric acid into formic acid and trimethylpyrrole, the reaction being complete in 3 minutes at the b. p.

The condensation of  $\omega$ -ethoxymethylfurfuraldehyde with 3-acetyl-

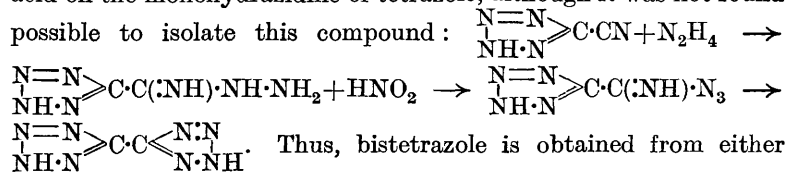
and 3-carbethoxy-2:4-dimethylpyrroles yields the corresponding furfuryldipyrrolymethanes, *ω*-ethoxymethylfurfuryl-bis-(3-acetyl-2:4-dimethylpyrroly)methane, m. p. 196.5°, and *ω*-ethoxymethylfurfuryl-bis-(3-carbethoxy-2:4-dimethylpyrroly)methane, m. p. 99°. Trimethylpyrrole-3-aldehyde condenses similarly with the acetyl- and carbethoxy-dimethylpyrroles to form 2:3:4-trimethylpyrroly-bis-(3-acetyl-2:4-dimethylpyrroly)methane, m. p. 191°, and 2:3:4-trimethylpyrroly-bis-(3-carbethoxy-2:4-dimethylpyrroly)methane, m. p. 246°. These undergo the usual fission with hydrochloric acid into trimethylpyrrole and bis-(3-acetyl- or 3-carbethoxy-2:4-dimethylpyrroly)methene hydrochloride, m. p. 213°.

Benary's ethyl 3-hydroxy-5:5'-dimethyl-2:3'-dipyrrole-4:4'-dicarboxylate (A., 1913, i, 651, but V, not I as there given) is prepared by a simplified method in 63% yield. Its acetyl derivative, m. p. 169—170°, couples with diazobenzene to form a brown azo compound, C<sub>24</sub>H<sub>26</sub>O<sub>6</sub>N<sub>4</sub>, m. p. 176°. From the acetyl derivative, ethyl 3-acetoxy-5:5'-dimethyl-2'-aldehydo-2:3'-dipyrrole-4:4'-dicarboxylate, m. p. 206.5°, is obtained by Gattermann's hydrocyanic acid method; the *p*-nitrophenylhydrazone melts at 262°.

The dipyrrole itself condenses with benzaldehyde to give phenyl-bis-(3-hydroxy-4:4'-dicarbethoxy-5:5'-dimethyl-2:3'-dipyrroly)methane, m. p. 208° (blackening). The corresponding nitro compound, from *p*-nitrobenzaldehyde, melts at 173°. By the Gattermann method, the dipyrrole may be condensed with hydrocyanic acid to form the 2'-aldehydo derivative, m. p. 200° (decomp.) (*p*-nitrophenylhydrazone, brown needles), or with chloroacetonitrile to form the 2'-chloroacetyl derivative, C<sub>18</sub>H<sub>21</sub>O<sub>6</sub>N<sub>2</sub>Cl, m. p. 183°. Acetylation of the 2'-aldehydo compound yields the above acetoxy-aldehyde of m. p. 206.5°. These experiments are a confirmation of Benary's structure for the dipyrrole, which must contain only one free 2-position.

C. H.

**Action of Hydrazine on Cyanotetrazole.** E. OLIVERI-MANDALÀ (*Gazzetta*, 1924, 54, 774—777).—That the cyanotetrazole used by Curtius, Darapsky, and Müller (A., 1916, i, 84) contained bistetrazole as impurity is confirmed by addition of hydrazine to alcoholic solutions of cyanotetrazole and bistetrazole, respectively, the former giving no precipitate and the latter the bishydrazonium salt of bistetrazole. Bistetrazole is, however, also obtained if the crude product of the interaction of cyanotetrazole and hydrazine is treated with nitrous acid, probably owing to the action of this acid on the monohydrazidine of tetrazole, although it was not found possible to isolate this compound:



Thus, bistetrazole is obtained from either cyanogen or cyanotetrazole by treatment either with azoimide or with hydrazine and nitrous acid in succession (cf. Angeli, A., 1894, i, 149).

T. H. P.

**Dibenzoylglyoxime Peroxide.** G. RUGGERI (*Atti R. Accad. Sci. Torino*, 1924, **59**, 365—372).—The action of nitrogen peroxide converts oximinoacetophenone into benzoylmethylnitrolic acid, which undergoes condensation with elimination of nitrous acid and formation of dibenzoylglyoxime peroxide:  $2\text{NO}_2 \cdot \text{CBz} \cdot \text{NOH} \rightarrow \text{C}_2\text{O}_2\text{N}_2\text{Bz}_2 + 2\text{HNO}_2$ . The direct product of the reaction between dibenzoylglyoxime and phenylhydrazine (cf. Klingemann, A., 1892, 995) is *benzoylphenylhydrazinoglyoxime*, yellow prisms, m. p.  $138^\circ$  (decomp.):  $\text{C}_2\text{O}_2\text{N}_2\text{Bz}_2 + 2\text{NHPh} \cdot \text{NH}_2 \rightarrow \text{NHBz} \cdot \text{NHPh} + \text{NOH} \cdot \text{CBz} \cdot \text{C}(\text{NOH}) \cdot \text{NH} \cdot \text{NHPh}$ . This compound is unstable and readily loses water with formation of 4-nitroso-3-phenylhydrazino-5-phenylisooxazole, an orange-yellow compound, m. p.  $106^\circ$  (decomp.), which, when heated with certain organic solvents, undergoes isomerisation into 3-benzoyl-5-phenylhydrazinofuro(ab<sub>1</sub>)-diazole: 
$$\begin{array}{c} \text{O} \\ \parallel \\ \text{N} : \text{C}(\text{NH} \cdot \text{NHPh}) \end{array} \begin{array}{c} \text{CPh} \\ \searrow \end{array} \text{NO} \rightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{N} : \text{C}(\text{NH} \cdot \text{NHPh}) \end{array} \begin{array}{c} \text{CBz} \\ \searrow \end{array} \text{N}.$$
 Thus, phenylhydrazine behaves towards dibenzoylglyoxime in the same way as aniline, that is, as a base.

Although benzoylphenylhydrazinoglyoxime is obtainable pure, neither Böseken (A., 1898, i, 696) nor Wieland and Gmelin (A., 1910, i, 784) was able to isolate benzoylphenylaminoglyoxime, its anhydro derivative, 4-nitroso-3-anilino-5-phenylisooxazole, being obtained.

Diacetylglyoxime peroxide behaves differently from dibenzoylglyoxime peroxide, since with phenylhydrazine it gives first the phenylhydrazone and then the phenylosazone (cf. Mills, *Chem. News*, 1903, **88**, 228).

The benzoyl derivative of benzoylmethylnitrolic acid,  $\text{NO}_2 \cdot \text{CBz} \cdot \text{NOBz}$ ,

forms pale yellow prisms, m. p.  $138^\circ$ .

4-Amino-3-phenylhydrazino-5-phenylisooxazole,  $\text{C}_{15}\text{H}_{14}\text{ON}_4$ , forms nacreous scales, m. p.  $132^\circ$  (decomp.), and 3-benzoyl-5-phenylhydrazinofuro(ab<sub>1</sub>)-diazole, yellow needles, m. p.  $172^\circ$ . T. H. P.

**Peroxides of Dioximes of Diacetylglyoximes.** G. PONZIO and V. BERNARDI (*Atti R. Accad. Sci. Torino*, 1924, **59**, 353—359).—The dioxime of diacetylglyoxime peroxide (A., 1924, i, 56) behaves differently from the compound obtained by Behrend and Tryller (A., 1895, i, 201), so that the constitution given by these authors is erroneous.

Chloro-oximinoacetonephenylhydrazone, m. p.  $127^\circ$  (decomp.) (not  $123^\circ$ , as given previously), gives, when treated in ethereal solution with aqueous 5% sodium carbonate solution, the phenylosazone of diacetylglyoxime peroxide, m. p.  $176^\circ$  (cf. Mills, *Chem. News*, 1903, **88**, 228).

The peroxide of the dioxime of diacetylglyoxime peroxide,  $\text{O} \cdot \text{N} : \text{C} \cdot \text{CMe} : \text{N} \cdot \text{O}$   
 $\text{O} \cdot \text{N} : \text{C} \cdot \text{CMe} : \text{N} \cdot \text{O}$ , prepared by treating the dioxime of diacetylglyoxime peroxide (1) in ethereal solution with nitrogen peroxide, or (2) with nitric acid (1 : 1), or (3) with potassium permanganate, forms lustrous, yellow laminae, m. p.  $187^\circ$  (decomp.), has the normal

*M* in naphthalene, and gives with concentrated sulphuric acid a yellow coloration turned green by addition of phenol. When boiled for a short time with dilute hydrochloric or sulphuric acid, it yields ammonia, hydrocyanic and oxalic acids, and a compound,  $C_6H_6O_7N_4$ , m. p.  $75^\circ$ .

The peroxide of the dioxime of dibenzoylglyoxime peroxide,  $C_{16}H_{10}O_4N_4$ , similarly obtained, has m. p.  $162-168^\circ$ , according to the method of heating, and dissolves in cold concentrated sulphuric acid, giving an orange-yellow coloration which turns brown on addition of phenol.

T. H. P.

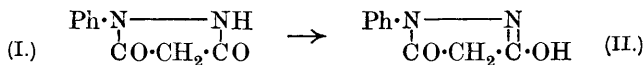
**New Group of Dyes from Poison Gases through the 2-Aminothiazoles as Intermediates. Preparation of Thiazole Dyes of Doebner-violet Type.** M. T. BOGERT and M. CHERTCOFF (*Proc. Nat. Acad. Sci.*, 1924, 10, 418-420).—A preliminary communication. 2-Amino-4-methyl- and 2-amino-4-phenyl-thiazole, obtained by condensing thiocarbamide with chloroacetone or  $\omega$ -chloroacetophenone, respectively, both interact with aromatic aldehydes (benzaldehyde, its *p*-chloro, *o*-, *m*-, and *p*-nitro, *o*- and *p*-hydroxy, and *p*-dimethylamino derivatives, and piperonal) to yield, in opposition to what has been stated hitherto, *aryldithiazolylmethanes*, the condensation taking place in the 5-position. The products are readily oxidised to dark red *carbinols*, which afford dark green *salts* and dye silk, wool, or tannin-mordanted cotton in green shades, bluer and duller than malachite-green. Azo dyes also may be obtained, *viz.*, by interaction of aryldiazonium compounds with the above thiazoles, "coupling" taking place in the 5-position.

W. A. S.

**Chlorination of *p*-Xylidine and certain New Azo Dyes.** A. S. WHEELER and M. MORSE.—(See i, 22.)

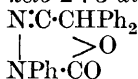
**Action of Ketens on Hydrazine Derivatives.** J. VAN ALPHEN (*Rec. trav. chim.*, 1924, 43, 823-866).—Aromatic and aliphatic keto- and aldo-ketens combine in ethereal solution with phenylhydrazine and nuclear substituted phenylhydrazines, yielding exclusively  $\beta$ -acylated phenylhydrazides, the position and nature of the nuclear substituent affecting only the velocity of reaction. Addition to the  $\alpha$ -nitrogen atom was not observed, even at  $-80^\circ$  or in the presence of acid (cf. Marckwald, A., 1893, i, 26; 1899, i, 503; Busch, A., 1903, i, 537; 1910, i, 75), but the  $\beta$ -acylated phenylhydrazides can combine (although much more slowly) with a second mol. of keten on the less basic  $\alpha$ -nitrogen atom.  $\alpha$ -Diphenylacetyl- $\beta$ -acetylphenylhydrazide obtained in this way yields on hydrolysis  $\alpha$ -diphenylacetylphenylhydrazide, which, in contrast to 2:4-diphenyl-semicarbazide and -thiosemicarbazide, is not transformed into the  $\beta$ -acylhydrazide either by boiling with acids in alcoholic solution or by heating at  $180^\circ$ . With methylhydrazine, in which the  $\alpha$ - and  $\beta$ -nitrogen atoms are more nearly equal in basicity,  $\alpha\beta$ -diacyl derivatives are immediately formed by addition of 2 mols. of keten, and monoacyl derivatives could not be isolated, the velocity of addition to the  $\alpha$ - and  $\beta$ -nitrogen atoms being approxi-

mately equal. Carbon suboxide (1 mol.) combines with phenylhydrazine (1 mol.) in ethereal solution, giving an unstable compound (I) which is converted on keeping into the tautomeric 1-phenyl-3:5-diketopyrazolidine (II), the additive compound (m. p. 164°) of which with phenylhydrazine was previously obtained



by Michaelis (A., 1892, 1004), and named in error as the derivative of 1-phenyl-3:5-pyrazolidone. Analogous compounds are produced from carbon suboxide (1 mol.) and nuclear substituted phenylhydrazines (2 mols.), the second mol. of substituted phenylhydrazine being attached to the substituted 1-phenyl-3:5-diketopyrazolidine by the primary or secondary valencies of the  $\beta$ -nitrogen atom in the phenylhydrazine, since all these compounds reduce yellow mercuric oxide in alcoholic solution and yield no condensation product on heating with benzaldehyde. Keten in ethereal solution (cf. Schmidlin and Bergmann, A., 1910, i, 816) has been used to acetylate *p*- and *m*-nitroaniline, tribromoaniline, anthranilic acid, and methylaniline. The introduction of negative groups into the aniline molecule hinders such acetylations. Tribromoaniline is only acetylated slowly and picramide not at all, these results agreeing with Staudinger's acylations, using diphenylketen. *o*-Nitroaniline is only acetylated by keten in the presence of hydrogen chloride; this is possibly due to the formation of acetyl chloride, a stronger acetylating agent. Diphenylamine, cetyl alcohol, phenol, and dextrose are not acetylated by keten. Carbon suboxide combines with *o*-, *m*-, and *p*-phenylenediamines, forming white, insoluble compounds of the general formula  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CH}_2$ . The compound formed from the *o*-diamine agrees in properties with *o*-phenylenemalonamide (R. Meyer, A., 1906, i, 765).

Diphenylketen and phenylhydrazine in ethereal solution give  $\beta$ -diphenylacetylphenylhydrazide, m. p. 168° (Staudinger, A., 1905, i, 444). The diphenylacetyldiazobenzene produced is unstable and could not be isolated. Acetic anhydride converts it into  $\alpha$ -acetyl- $\beta$ -diphenylacetylphenylhydrazide, m. p. 134—135°, from which  $\beta$ -diphenylacetylphenylhydrazide is regenerated on hydrolysis with alcoholic sulphuric acid. With carbonyl chloride in benzene solution a colourless compound, m. p. 113°, is produced. In view of Freund's work (A., 1890, i, 1440; 1892, i, 508; 1894, i, 96), this is probably 3-phenyl-5-diphenylmethyl-2-keto-2:3-dihydrofuro-3:4-diazole,



Attempts to obtain  $\alpha$ -diphenylacetylphenylhydrazide by partial hydrolysis of  $\alpha$ -diphenylacetyl- $\beta$ -benzylidenephénylhydrazone, m. p. 182—183°, were unsuccessful, but hydrolysis of  $\alpha$ -diphenylacetyl- $\beta$ -acetylphenylhydrazide, m. p. 158—159° (from diphenylketen and  $\beta$ -acetylphenylhydrazide) yielded  $\alpha$ -diphenylacetylphenylhydrazide, light yellow flocks, m. p. 80—82°. This yields diphenylacetanilide

with nitrous acid, the *benzylidene* derivative, m. p. 182—183° with benzaldehyde,  $\alpha$ -diphenylacetyl- $\beta$ -acetylphenylhydrazide with acetic anhydride, and a white *hydrochloride*, decomposed by water, with hydrogen chloride in dry ether. With carbonyl chloride, a substance is formed which sinters at 105°, melts at 120°, does not combine with

aniline, and probably has the structure 
$$\begin{array}{c} \text{NH}-\text{CO} \\ | \\ \text{NPh}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{CPh}_2 \end{array} \end{array}$$
 Diphenyl-

keten reacts more readily with  $\alpha$ -diphenylacetylphenylhydrazide than with the  $\beta$ -compound, the product in either case being  $\alpha\beta$ -*didiphenylacetylphenylhydrazide*, sintering at 83°. Diphenylketen and *o*-tolylhydrazine yield  $\beta$ -*diphenylacetyl-o-tolylhydrazide*, colourless needles, m. p. 175°.  $\beta$ -*Diphenylacetyl-m-tolylhydrazide*, m. p. 143—144°;  $\beta$ -*diphenylacetyl-p-tolylhydrazide*, m. p. 177°;  $\beta$ -*diphenylacetyl-p-nitrophenylhydrazide*, reddish-brown needles, m. p. 218—219°;  $\beta$ -*diphenylacetyl-p-bromophenylhydrazide*, colourless needles, m. p. 182.5° (decomp.), and  $\beta$ -*diphenylacetyl-o-nitrophenylhydrazide*, light yellow needles, m. p. 174—175°, were similarly obtained. The *o*-nitrophenylhydrazide, unlike the remaining hydrazides, does not reduce mercuric oxide in alcoholic solution, probably on account of the *o*-nitro group, but its  $\beta$ -structure is shown by the absence of a condensation product with benzaldehyde and production of the characteristic deep violet colour in alkali hydroxide solution (cf. Mattaar, A., 1922, i, 251).  $\alpha\beta$ -*Didiphenylacetylmethylhydrazide*, m. p. 183°, could not be hydrolysed with alcoholic sulphuric acid.

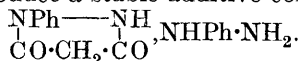
*iso*Butyryl bromide and phenylhydrazine in ethereal solution yield  $\alpha\beta$ -*diisobutyrylphenylhydrazide*, m. p. 160°, whilst in pyridine solution the  $\beta$ -*isobutyrylphenylhydrazide* is also formed. The pure  $\beta$ -*isobutyrylphenylhydrazide*, however, is prepared from *isobutyric acid* (Bölsing and Tafel, A., 1892, 981). The following hydrazides were similarly prepared, using *isobutyryl bromide* in pyridine solution or *isobutyric acid* alone:  $\beta$ -*isobutyryl-o-tolylhydrazide*, m. p. 99—100°;  $\beta$ -*isobutyryl-m-tolylhydrazide*, m. p. 143°;  $\beta$ -*isobutyryl-p-tolylhydrazide*, m. p. 153°;  $\beta$ -*isobutyryl-p-nitrophenylhydrazide*, light brown, m. p. 185°;  $\beta$ -*isobutyryl-p-bromophenylhydrazide*, m. p. 159.5° (decomp.) (m. p. 164°, from *isobutyric acid*), and  $\beta$ -*isobutyryl-o-nitrophenylhydrazide*, m. p. 151°, which gives a violet solution in alkali, whereas  $\alpha\beta$ -*diisobutyryl-o-nitrophenylhydrazide* gives an almost colourless solution. These  $\beta$ -*isobutyrylhydrazides* were also obtained by the action of dimethylketen on the corresponding hydrazine. Methylhydrazine and dimethylketen yield a liquid which is probably  $\alpha\beta$ -*diisobutyrylmethylhydrazide*.

Keten and phenylhydrazine hydrochloride do not react in acetone solution. With  $\beta$ -acetylphenylhydrazide in benzene, keten yields a mass which probably contains  $\alpha\beta$ -*diacetylphenylhydrazide*.  $\beta$ -*Acetyl-o-nitrophenylhydrazide*,  $\beta$ -*acetyl-p-nitrophenylhydrazide*, and  $\beta$ -*acetyl-p-bromophenylhydrazide*, m. p. 161° (decomp.), were obtained from keten and an ethereal solution of the corresponding hydrazine. Methylhydrazine and keten similarly yield  $\alpha\beta$ -*diacetylmethylhydrazide*, b. p. 280°.

Carbon suboxide and excess of phenylhydrazine in dry ether yield the substance, m. p.  $164^{\circ}$ , obtained by Michaelis (*loc. cit.*). With equimolecular quantities of phenylhydrazine and carbon suboxide, a white substance, isomeric with 1-phenyl-3:5-diketopyrazolidine, is produced, the structure (I) of which is shown by the following reactions. On keeping, the substance slowly changes into (II), more rapidly on heating. When boiled with water or alcohol, it dissolves, giving an acid reaction, and on cooling the compound of m. p.  $164^{\circ}$  crystallises out, the reaction being due to hydrolysis:

$$\begin{array}{c} \text{NPh} \text{---} \text{NH} \\ | \quad | \\ \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \end{array} + \text{H}_2\text{O} \rightarrow \text{NPh} \cdot \text{NH}_2 + \text{CH}_2(\text{CO}_2\text{H})_2,$$

the phenylhydrazine produced then combining with a fresh mol. of the substance to produce a stable additive compound,



This formula is supported by the fact that (I) combines much more readily with phenylhydrazine than does (II), and by the decomposition of the additive compound by dilute alkali hydroxide, or by boiling with phenylhydrazine, into 1-phenyl-3:5-diketopyrazolidine and phenylhydrazine, or by heating with benzaldehyde, which converts it into 1-phenyl-4-benzylidene-3:5-diketopyrazolidine, m. p.  $266^{\circ}$ . Carbon suboxide yields the following analogous products with excess of the corresponding hydrazines: *o*-tolylhydrazine derivative of 1-*o*-tolyl-3:5-diketopyrazolidine, m. p.  $168^{\circ}$ ; *m*-tolylhydrazine derivative of 1-*m*-tolyl-3:5-diketopyrazolidine, m. p.  $192^{\circ}$ ; *p*-tolylhydrazine derivative of 1-*p*-tolyl-3:5-diketopyrazolidine, m. p.  $198\text{--}200^{\circ}$ , which with benzaldehyde yields 1-*p*-tolyl-4-benzylidene-3:5-diketopyrazolidine; *o*-nitrophenylhydrazine derivative of 1-*o*-nitrophenyl-3:5-diketopyrazolidine, yellow needles, m. p.  $241^{\circ}$  (decomp.); and *p*-nitrophenylhydrazine derivative of 1-*p*-nitrophenyl-3:5-diketopyrazolidine, yellow needles, m. p.  $271^{\circ}$  (decomp.). Carbon suboxide and excess of methylhydrazine yield a thick oil, which is probably 1-methyl-3:5-diketopyrazolidine. With excess of carbon suboxide, a white substance is formed, turning liquid on exposure to the air.

Diphenylketen and methylamine in light petroleum yield *N*-methyl-diphenylacetamide,  $\text{NHMe} \cdot \text{CO} \cdot \text{CHPh}_2$ , m. p.  $166.5^{\circ}$ . *N*-*o*-Nitrophenyl-diphenylacetamide, light yellow crystals, m. p.  $188^{\circ}$ , was similarly obtained, but diphenylketen and picramide do not react. *Diphenylacetyl*-2:4:6-tribromoaniline, m. p.  $226\text{--}277^{\circ}$  (?), was similarly obtained.

Whilst carbon suboxide readily yields malonanilide with aniline (Staudinger, A., 1909, i, 83), with *o*- and *m*-nitroanilines, yellow, crystalline products are formed slowly; with piperidine a white precipitate is formed and with carbamide, a white, amorphous substance, probably barbituric acid.

R. B.

**Products of the Action of Nitrous Acid on *o*- and *p*-Phenol-sulphonic Acids.** I. W. RODIONOW and W. MATWEEV (*Ber.*, 1924, 57, [B], 1711—1715).—The presence of nitrous acid is necessary for the induction of the nitration of phenol-*p*-sulphonic



acid (cf. Martinsen, A., 1905, ii, 149). Attempts to isolate the primary product of the action of nitrous acid on technical phenol-*p*-sulphonic acid yield a small proportion of 4-diazophenol-2-sulphonic acid,  $\text{OH}\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{SO}_3\text{H}$ , the formation of which is due to the presence of phenol-*o*-sulphonic acid, from which it can be derived in 75–85% yield. The compound is identical with that prepared by Bennewitz by the diazotisation of 4-aminophenol-2-sulphonic acid; its constitution, however, cannot be regarded as established. Under similar conditions, phenol-*p*-sulphonic acid appears to yield 2-diazophenol-4-sulphonic acid. H. W.

#### Action of Normal Sodium Arsenite on Azido Compounds.

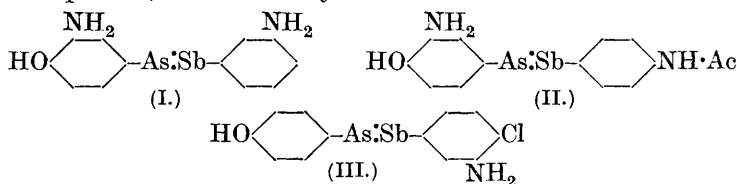
A. GUTMANN (*Ber.*, 1924, 57, [B], 1956–1958).—The azides of sodium, barium, and lead do not react with normal sodium arsenite, which gives a silver mirror with ammoniacal solutions of silver azide, due solely to the reducing action of the arsenite on the silver salt. Chloroazoimide (cf. Raschig, A., 1909, ii, 41) and sodium arsenite yield sodium azide, arsenate, and chloride; iodoazoimide behaves similarly. The permanence of the azido groups in inorganic compounds appears most readily explicable on the basis of the Curtius formula. Benzylazoimide, benzoylazoimide, phenylazoimide, and phenylhydrazine-*p*-azoiminobenzene-*p*-sulphonate behave differently, since, although oxidation of arsenite to arsenate occurs, the azido group is also broken down into nitrogen and amine or ammonia; this behaviour is in harmony with Thiele's conception,  $\text{R}\cdot\text{N}:\text{N}:\text{N}:$ . Alkylazoimides are very stable towards alkali hydroxide solutions, whereas acylazoimides are hydrolysed to the alkali azide and the salt of the acid. H. W.

**Preparation of Arsinic Acids from the corresponding Chloroarsines.** H. BURTON and C. S. GIBSON (*J. Chem. Soc.*, 1924, 125, 2275–2278).—Arsinic acids are conveniently obtained by oxidising the corresponding tertiary chloroarsine (1 mol.) in acetone solution or suspension with a 10% aqueous solution of sodium toluene-*p*-sulphonchloroamide ("chloramine-*T*"). The method is analogous to the formation of sulphilimines and arsylimines from alkyl sulphides and tertiary arsines (Mann and Pope, T., 1922, 121, 1052, 1754) and avoids both the formation of the colouring matter produced in Wieland and Rheinheimer's method (A., 1921, i, 371) and the troublesome separation of the sodium salt of the arsinic acid from sodium chloride and bromide in Quick and Adams' method (A., 1922, i, 600). In this way, the following arsinic acids have been prepared: *n*-butylarsinic acid, m. p.  $160^\circ$  (yield 74%); *o*-tolylarsinic acid, m. p.  $163$ – $164^\circ$  (yield quantitative); diphenylarsinic acid, m. p.  $169$ – $170^\circ$  (75% yield), and phenarsazinic acid (yield 92%). The amphoteric nature of phenarsazinic acid is further demonstrated by the preparation of the *hydrochloride*, m. p.  $200$ – $205^\circ$  (decomp.); *nitrate*, yellow needles; and *sulphate*, m. p.  $138$ – $140^\circ$  (decomp.). Similarly, 10-chloro-5-acetyl-5:10-dihydrophenarsazine,  $\text{AcN}(\text{C}_6\text{H}_4)_2\text{AsCl}$ , m. p.  $229$ – $230^\circ$ , from 10-chloro-5:10-dihydrophenarsazine and acetyl chloride in dry benzene, is oxidised to *N*-acetylphenarsazinic acid ( $+2\text{H}_2\text{O}$ ),

m. p. 244—245° (decomp.); 10-chloro-5-propionyl-5:10-dihydrophenarsazine, from 10-chloro-5:10-dihydrophenarsazine and propionic anhydride in pyridine and xylene, yields *N*-propionylphenarsazinic acid, m. p. 232°; and 10-chloro-5-benzoyl-5:10-dihydrophenarsazine, m. p. 180—181°, from 10-chloro-5:10-dihydrophenarsazine and benzoyl chloride in dry xylene, yields *N*-benzoylphenarsazinic acid, m. p. 250° (decomp.). R. B.

### Preparation of Organic Arsenic-Antimony Compounds.

CHEMISCHE FABRIK VON HEYDEN A.-G. (D.R.-P. 396697; from *Chem. Zentr.*, 1924, ii, 760).—Primary aromatic arsines are allowed to interact in acid aqueous or aqueous-alcoholic solution with primary aromatic stibinoxides containing substituents such as  $\text{NH}_2$  which have a favourable therapeutic influence, the resultant products being precipitated by suitable means. Thus, 3:3'-diamino-4-hydroxyarsenostibinobenzene (I) is formed from *m*-amino-*p*-hydroxyphenylarsine and *m*-aminophenylstibinoxide as a brown powder insoluble in water, soluble in aqueous sodium hydroxide to a brownish-red solution in which oxidising agents cause scission of the molecule; with hydrogen chloride, it forms a chloride. *m*-Amino-*p*-hydroxyphenylarsine and *p*-chloro-*m*-aminophenylstibine oxide unite to form 4'-chloro-3:3'-diamino-4-hydroxyarsenostibinobenzene (III) as a reddish-brown mass; hydrochloride, orange-yellow powder, which is fairly stable in air.

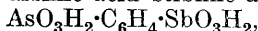


*m*-Amino-*p*-hydroxyphenylarsine condenses with *p*-acetamidophenylstibine oxide to give 3-amino-4'-acetamido-4-hydroxyarsenostibinobenzene (II), as a brown powder soluble in dilute alkali or acid. The products are of value as therapeutic agents for trypanosome and spirochæte infections. F. A. M.

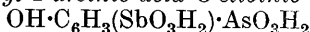
### Preparation of Organic Arsenic-Antimony Compounds.

CHEMISCHE FABRIK VON HEYDEN A.-G. (D.R.-P. 397275, addition to D.R.-P. 396697, *v.s.*; from *Chem. Zentr.*, 1924, ii, 760).—Tervalent inorganic antimony compounds are allowed to react with primary aromatic arsines in alkaline solution. Thus, 3-amino-4-hydroxyphenylarsine reacts with potassium antimonyltartrate in alkaline aqueous solution to give a dark brown arsenic-antimony compound, soluble in acids or alkalis; on shaking with salicylaldehyde, the *N*-hydroxybenzylidene derivative is precipitated. An alkaline antimony solution prepared from antimony trichloride with the addition of glycerol reacts with a solution of *p*-hydroxyphenylarsine in aqueous sodium hydroxide to give a dark brown arseno-stibino compound soluble in dilute alkalis, insoluble in dilute acids (see preceding abstract). F. A. M.

**Preparation of Arsenic-Antimony Compounds.** CHEMISCHE FABRIK VON HEYDEN A.-G. (D.R.-P. 397151; from *Chem. Zentr.*, 1924, ii, 761).—Phenylarsinic acid-stibinic acids,



and their substitution products are reduced in one or two stages. Thus 4-hydroxyphenyl-1-arsinic acid-3-stibinic acid,



obtained by treating diazotised 4-hydroxy-3-aminophenyl-1-arsinic acid with alkaline potassium antimonyltartrate), yields an orange-yellow reduction *product* (hydroxyphenylstibinearsine?) on reduction with stannous chloride and concentrated hydrochloric acid in presence of a trace of iodine. Phenyl-1-arsinic acid-4-stibinic acid is reduced by sulphur dioxide and a trace of iodine in methyl-alcoholic hydrogen chloride solution to *phenyl-1-arsenoxide-4-stibinoxide*, as a colourless powder; reduction in the absence of iodine affords an intermediate product. Reduction of the oxide itself with phosphorous acid in acetic-hydrochloric acid solution in presence of a trace of iodine affords a pale yellow reduction *product*. Phenyl-arsinic acid-stibinic acid is reduced by sodium hyposulphite to a dark brown reduction *product*. The reduced products have therapeutic values (cf. Schmidt, A., 1921, i, 1203).

F. A. M.

**Preparation of Monoarylantimony Compounds.** CHEMISCHE FABRIK VON HEYDEN A.-G., and H. SCHMIDT (D.R.-P. 397458; from *Chem. Zentr.*, 1924, ii, 758).—Monoarylantimony compounds are prepared by treating diarylstibine oxides or their derivatives with acid media such as acetic, formic, or alcoholic hydrochloric acids, either hot or cold (cf. Schmidt, A., 1922, i, 1203).

F. A. M.

**Preparation of Secondary and Tertiary Aromatic Antimony Compounds.** CHEMISCHE FABRIK VON HEYDEN A.-G. (D.R.-P. 389151; from *Chem. Zentr.*, 1924, ii, 759).—Diarylstibine oxides are prepared by heating monoarylstibine oxides, and are themselves transformed on heating to the triarylstibines. Thus, phenylstibine oxide is heated at 100° for several hours in a current of carbon dioxide. The resultant mixture of antimony trioxide and diphenylstibine oxide is extracted with hot alcohol, the diphenylstibine oxide crystallising on cooling; on heating at 180–200° in a current of carbon dioxide and extracting with ether, triphenylstibine crystallises (cf. Schmidt, A., 1922, i, 1203).

F. A. M.

**Preparation of Diarylantimony Compounds.** CHEMISCHE FABRIK VON HEYDEN A.-G. and H. SCHMIDT (D.R.-P. 394795; from *Chem. Zentr.*, 1924, ii, 759).—Triarylstibines are converted into diarylstibinic acids on treatment with peroxides in presence of at least sufficient alkali to dissolve the acid, heating if necessary. In the absence of alkali the triarylstibine is converted into the dihydroxide, whilst in presence of alkali the following reaction occurs:  $\text{R}_3\text{Sb} + \text{H}_2\text{O} + \text{O} = \text{R}_2\text{SbO}(\text{OH}) + \text{RH}$ . Thus *p*-triacetamidotriphenylstibine (prepared by the method of D.R.-P. 389151,

see preceding abstract) in dilute methyl-alcoholic sodium hydroxide, is stirred with 3% hydrogen peroxide or sodium peroxide until dissolved; on passing a current of carbon dioxide *p*-diacetamidodiphenylstibinic acid (decomp. 250°) is precipitated, identical with the product formed on oxidising diacetamidodiphenylstibine. In a similar manner, triphenylstibine is oxidised in dilute alkaline aqueous acetone solution by 3% hydrogen peroxide to diphenylstibinic acid, which is purified by crystallisation from dilute hydrochloric acid as *diphenylstibinyl chloride*, m. p. 175°, which can then be reconverted into the acid.

F. A. M.

**Preparation of Complex Compounds of Aromatic Stibinic Acids.** CHEMISCHE FABRIK VON HEYDEN A.-G., and H. SCHMIDT (D.R.-P. 396864; from *Chem. Zentr.*, 1924, ii, 759).—Aromatic stibinic acids or their salts are treated with metallic salts, oxides, or hydroxides, avoiding the joint presence of salts of ammonium and copper. The *silver complex* compound of *p*-acetamidophenylstibinic acid is formed by the action of silver nitrate on the sodium salt of *p*-acetamidophenylstibinic acid or by the action of moist silver oxide on the free acid; it is soluble in dilute sodium hydroxide, from which sodium chloride does not precipitate silver chloride. The following preparations are also noted: the *mercury*, *antimony*, and *copper complex* compounds of *p*-acetamidophenylstibinic acid, soluble in dilute alkalis; the *ferrous complex* compound of phenylstibinic acid, from the sodium salt of the acid and ferrous sulphate, which forms a powder soluble in dilute sodium hydroxide and devoid of ferrous ion reactions until treated with ammonium sulphide; the *silver complex* compound of benzene-*p*-sulphonamidophenylstibinic acid, from the sodium salt of the acid and silver nitrate. The products have therapeutic values.

F. A. M.

**Preparation of Diarylantimony Compounds.** CHEMISCHE FABRIK VON HEYDEN A.-G., and H. SCHMIDT (D.R.-P. 397079; from *Chem. Zentr.*, 1924, ii, 760—761).—Triarylstibines are treated with hydrogen halides in suitable solvents, with or without the application of heat. Thus, triacetamidotriphenylstibine suspended in methyl alcohol is dissolved in alcoholic hydrogen chloride, with cooling. When kept for 1 hour, *diacetamidodiphenylstibine chloride* crystallises out, which is converted by alkalis into *diacetamidodiphenylstibine oxide*, m. p. 130°, according to the equation:  $(\text{NHAc}\cdot\text{C}_6\text{H}_4)_3\text{Sb} + \text{HCl} = (\text{NHAc}\cdot\text{C}_6\text{H}_4)_2\text{SbCl} + \text{AcNHPh}$ . In a similar manner, *p*-triacetamidotriphenylstibine with glacial acetic and hydrobromic acids affords *p*-diacetamidodiphenylstibine bromide hydrobromide, converted by alkalis into the diacetamidodiphenylstibine oxide. Triphenylstibine on refluxing in saturated alcoholic hydrochloric acid for 1 hour in a current of carbon dioxide and then pouring into dilute sodium hydroxide gives a milky precipitate of diphenylstibine oxide.

F. A. M.

**Organic Derivatives of Silicon. XXX. Complex Silico-hydrocarbons  $[\text{SiPh}_2]_n$ .** F. S. KIPPING (*J. Chem. Soc.*, 1924, 125, 2291—2297).—Further examination of the products obtained

by the action of sodium on diphenylsilicon dichloride (Kipping and Sands, T., 1921, **119**, 830) shows that the relation between substances (C) and (D) is very similar to that between (B) and (A) (cf. Kipping, T., 1923, **123**, 2590). The compound (C), which is separated from (D) by extraction with boiling benzene or toluene and from (A) by treating a suspension in benzene with excess of iodine, is a well-defined crystalline silicohydrocarbon,  $[\text{SiPh}_2]_n$ , the mol. weight of which could not be determined owing to its insolubility and lack of reactivity. From its resemblance to (B), as shown by its stability towards iodine, boiling tetrachloroethane, and nitrobenzene, as well as towards bromine, nitric acid, alkalis, and piperidine, (C) is provisionally regarded as either a dodecaphenylcyclosilicohexane,  $[\text{SiPh}_2]_6$ , formed from  $\text{SiPh}_2\text{Cl} \cdot \text{SiPh}_2\text{Cl}$  (1 mol.) and  $\text{SiPh}_2\text{Cl}[\text{SiPh}_2]_2\text{SiPh}_2\text{Cl}$  (1 mol.), or as a hexadecaphenylcyclosilico-octane, formed from 2 mols. of the latter, the relative insolubility of (C) as compared with (B) favouring the more complex formula. The compound (D), which has not been crystallised, has the formula  $[\text{SiPh}_2]_n$ . It is practically unattacked by boiling tetrachloroethane or by iodine, thereby differing from (A), but, like the latter, it is readily decomposed by alkalis and piperidine, affording hydrogen, diphenylsilicanediol, and a mixture of its condensation products. It is much more readily oxidised by nitric acid in acetic acid than is (A), (B), or (C), yielding a mixture of condensation products of diphenylsilicanediol, oxidation with potassium permanganate in acetic acid solution yielding similar products. The compound is also slowly attacked by boiling nitrobenzene. It is suggested that the molecule of (D), like that of (A) (cf. Kipping, T., 1923, **123**, 2599), contains two tervalent silicon atoms and is represented by the structure



or  $\cdots\text{SiPh}_2[\text{SiPh}_2]_6\text{SiPh}_2\cdots$ .

R. B.

**Formation of Porphyrin from Blood Pigment. II.** O. SCHUMM (*Z. physiol. Chem.*, 1924, **139**, 219—271).—The porphyrin previously described (A., 1924, i, 441), which differed from other porphyrins by its solubility in chloroform, has been obtained in a purer condition; it is now provisionally termed  $\alpha$ -hæmatoporphroidin. By esterification and subsequent hydrolysis, a porphyrin (termed  $\alpha$ -hæmatoporphyrin) has been obtained from it which differs from the majority of porphyrins hitherto described, but resembles the natural porphyrins of Papendieck (A., 1923, i, 732), Fischer and Schneller (A., 1923, i, 1244), and Fischer and Kögl (A., 1924, i, 230), and also certain porphyrins prepared by List (A., 1924, i, 784). Attention is directed to the possibility, in experiments designed to detect the presence of natural porphyrins, of the formation of porphyrins of the above type by the action of the reagents employed on small amounts of hæmoglobin. The above results are largely based on spectroscopic examination of the pigments; the original must be consulted for details. E. S.

**Esterification of Hæmin.** J. ZALESKI and K. LINDENFELD (*Roczniki Chemji*, 1924, **4**, 31—62).—Pure hæmin in the form of

characteristic "Teichmann crystals" can be obtained by adding ammonium chloride to an alcoholic extract of coagulated blood containing oxalic acid; the corresponding bromo and iodo compounds are obtained, although in poorer yield, by substituting ammonium bromide or iodide for the chloride, the method of preparation being described in great detail. Analyses of the chloro compound agree well with Zaleski's formula,  $C_{34}H_{32}O_4N_4FeCl$ . If the alcoholic solution of the colouring matter is boiled for some time, the crystals obtained are spindle-shaped, owing to partial esterification, which proceeds more readily when the oxalic acid is replaced by a mineral acid. These crystals, "Mörner's hæmin," have a varying composition; it is suggested that there exists a definite additive compound of the monoethyl ester with the parent substance, but compounds having a composition approximating to that of the diethyl ester can be obtained; it is inferred that the two carboxyl groups in hæmin are practically equivalent; the esterification process is bimolecular.

The action of alcoholic halogen acids on hæmin esters leads to octahedral crystals, which, in the case of the iodo compound, are shown to have a different composition from that of the original ester, and it is thought that those obtained from the chloro and bromo compounds are similar. The authors do not agree that hæmin exists in two isomeric forms, as suggested by Küster (A., 1914, i, 95).  
G. A. R. K.

**Oxygen Content of Methæmoglobin.** G. QUAGLIARIELLO (*Arch. di Scienze biol.*, 1923, 5, 193—208; *Ber. ges. Physiologie*, 24, 429, from *Chem. Zentr.*, 1924, ii, 664).—In the transformation of oxyhæmoglobin into methæmoglobin by dilute hydrochloric acid, the alteration in concentration of the oxyhæmoglobin was determined spectrophotometrically, and the oxygen evolved was measured in Barcroft's apparatus. The results showed that under these conditions the oxyhæmoglobin loses only half of its oxygen, so that methæmoglobin must contain the remaining half.

F. A. M.

**Gelatin. III. Separation of the Products of Hydrolysis of Gelatin by the Carbamate Method.** H. L. KINGSTON and S. B. SCHRYVER (*Biochem. J.*, 1924, 18, 1070—1078).—Barium aspartate is precipitated from the hydrolysed gelatin with barium hydroxide. By treating the filtrate with alcohol, the barium salts of the aminodicarboxylic acids are precipitated. The resulting filtrate is then treated alternately with carbon dioxide and barium hydroxide, which precipitates the barium carbamates of the amino-acids. On extracting these compounds with ice-cold water, barium glycinecarbamate remains. The filtrate on boiling is decomposed into the amino-acids, which are fractionated with phosphotungstic acid into diamino- and monoamino-acids. The mono-amino fraction is separated into leucine, alanine, phenylalanine, hydroxyproline, serine, and proline by crystallisation and treatment with alcohol.  
S. S. Z.

**Gelatin. IV. Purification of Gelatin by Flocculation in an Electric Field.** J. KNAGGS and S. B. SCHRYVER (*Biochem. J.*, 1924, **18**, 1079—1084).—Gelatin obtained from ossein was first freed from chondroitinsulphuric acid by treating it with 0.2% sodium hydroxide for 60 days. It was then flocculated in an electric field in a 2% solution in order to remove the products of thermal degradation. The electrolytic apparatus is described. S. S. Z.

**Gelatin. V. Properties of a Gelatin Purified by Flocculation in an Electric Field.** A. B. MANNING (*Biochem. J.*, 1924, **18**, 1085—1094).—The amount of nitrogen remaining in solution after electrodialysis (see preceding abstract) of a gelatin forms a good criterion of its degree of separation from the impurities of degradation products. The previous determination of the solubility of 0.056 part of gelatin in 100 c.c. of water is too high. If a purified gelatin has any true solubility in water, it does not exceed 1 part in 10,000 parts. It is soluble in very dilute solutions of acids and alkalis. Very much more concentrated solutions of neutral salts such as potassium chloride are necessary to produce corresponding effects. It possesses a higher state of hydration than globulins, which is responsible for its great capacity of forming gels. Globulins can form a gel when dispersed in a relatively small amount of dispersion medium. Gelatin solutions show an irreversible diminution in viscosity when kept even at 35°. S. S. Z.

**Gelatin. VI. Influence of the Treatment of the Precursor on the Character of the Gelatin.** J. KNAGGS and S. B. SCHRYVER (*Biochem. J.*, 1924, **18**, 1095—1101).—Gelatins differ in their Hausmann numbers and this depends on the previous treatment of the precursors before extracting the gelatin. Gelatin extracted from a precursor which has had acid treatment before extraction has a lower value for the diamino nitrogen than gelatin extracted from the precursor which has had alkali treatment. The rate of extraction of gelatin from an acid-treated precursor is much greater than from the same precursor if submitted to alkali treatment or electrodialysis. Even the purest gelatin does not behave as a chemical entity. In the process of flocculation of a 2% solution of gelatin in the electric field, it separates in three fractions, one near the anode with a low diamino nitrogen value, one which diffuses through the membrane to the cathode, which is reduced there into simple products, and the flocculated portion, which forms the greater part of the gelatin. S. S. Z.

**Gelatin. VII. Non-amino Nitrogen of Gelatin.** J. KNAGGS and S. B. SCHRYVER (*Biochem. J.*, 1924, **18**, 1102—1106).—When a gelatin purified by flocculation (see preceding abstracts) is heated with water and then hydrolysed, a marked increase in the nitrogen of the hydrolysis products which do not react with nitrous acid to give gaseous nitrogen is observed. A similar result is produced by repeated flocculation in an electric field and also when gelatin is treated with cold dilute acids and alkalis. It is suggested that probably a molecular rearrangement takes place with the formation of stable ring compounds. S. S. Z.

**Gelatin. VIII. Osmotic Pressure of Gelatin in Solutions of Sodium Salicylate.** E. V. HORNE (*Biochem. J.*, 1924, **18**, 1107—1113).—In a 3% gelatin solution in *M*-sodium salicylate, the apparent aggregate (molecular) weight as determined by the osmotic pressure is about 16,000. This rises to about 40,000 in 0.9% solutions. The osmotic pressure is not apparently influenced by small amounts of inorganic material in the gelatin. S. S. Z.

**Combination of Acids with Insoluble Albumin.** F. TRENDTEL (*Pflüger's Archiv*, 203, 480—491; from *Chem. Zentr.*, 1924, ii, 667).—Electrometric experiments show that hydrogen ion is combined during the action of acids on completely insoluble albumin (boiled fibrin) as also on soluble albumin. The amount absorbed increases rapidly initially and then more slowly to a maximum. With low concentrations (0.01*N*) 73.66% of the acid present combines with the albumin, but relatively less at higher concentrations. The combination is a maximum for hydrochloric acid, much less for sulphuric acid, and considerably less for acetic acid. During the gradual neutralisation with sodium hydroxide of an acid in presence of insoluble albumin which has combined with a part of the hydrogen ion, the albumin gives up a part of the hydrogen ion corresponding with the diminution of the hydrogen ion in the liquid. F. A. M.

**Action of Paraldehyde on Proteins and Lipins.** E. A. COOPER (*Biochem. J.*, 1924, **18**, 948—950).—Paraldehyde precipitates proteins from anhydrous solvents, but has no action on their aqueous solution or on that of nucleic acid. It also precipitates lecithin from water and from ether and cerebrosides from their pyridine and hot alcohol solutions. It dissolves cholesterol, wax, fats, and the higher fatty acids. S. S. Z.

**Combination of Chloral Hydrate with Protein.** F. LIEBEN (*Biochem. Z.*, 1924, **147**, 174—184).—On treating aqueous solutions of casein with chloral hydrate, an unstable compound is formed which is decomposed on warming or on treatment with 0.1*N*-alkali for 2½ hours or longer. The compound shows the colour and precipitation reactions of the original protein. By plotting bound against total chloral hydrate, curves resembling adsorption curves are obtained, but with continued addition of chloral hydrate to a fixed amount of casein, the relative amount in combination diminishes. This is interpreted as "negative adsorption," or as being due to a change produced in the casein by the highly concentrated chloral hydrate. The amount of chloral hydrate bound by increasing amounts of protein increases absolutely, but diminishes relatively. On precipitation with acid or alcohol, the whole of the chloral hydrate (accompanied by a little protein) is found in the filtrate. When used *in vivo*, the ratio of chloral hydrate to serum proteins is so small that complete combination is assumed.

J. P.

**Halogenated Proteins. III. Bromogluten.** A. J. J. VANDEVELDE (*Rec. trav. chim.*, 1924, **43**, 702—706).—By the action



of a solution of bromine in carbon tetrachloride on dry gluten ( $N=13.8\%$ ), bromogluten-A ( $N=10.02\%$ ,  $Br=30.02\%$ ) is obtained. A quantitative study of this compound is made with regard to the removal of its bromine by the action of water,  $0.5N$ -potassium hydroxide, and heat. By the action of water alone at the ordinary temperature, a large proportion of the bromine goes into solution and becomes ionised.

W. E. E.

**Hydrolysis of Skin and Hair.** H. B. MERRILL (*Ind. Eng. Chem.*, 1924, **16**, 1144—1146).—The comparative hydrolysis of skin and hair was studied as a function of  $p_H$  value, time, and temperature. In alkaline solution, hair was more readily hydrolysed than skin, the reverse applying in acid solution. There was little hydrolysis for  $p_H -0.2$  to  $+13.5$ . Beyond these limits, there was an abrupt increase in the hydrolysis, which was complete. Hair was completely hydrolysed at a lower  $p_H$  than skin in alkaline solution, whereas in acid solution skin was completely hydrolysed at a higher  $p_H$  value than hair. The effect of increasing time of digestion was to lower the  $p_H$  value at which complete hydrolysis occurred in alkaline solution and to increase it in acid solution. Raising the temperature had the same effect, which was more marked with skin than with hair.

D. W.

**Synthetic Lecithins.** P. A. LEVENE and I. P. ROLF (*J. Biol. Chem.*, 1924, **60**, 677—683).—The following synthetic lecithins have been prepared by condensing lysolecithin (A., 1924, i, 438), which consists of a mixture of "stearic" and "palmitic" lysolecithins, with the appropriate acid anhydride in the presence of sodium acetate or (in the case of the acetyl compound) of pyridine: *acetyl-lysolecithin*, *benzoyl-lysolecithin*, *oleyl-lysolecithin*, *elaidyl-lysolecithin*. In each case, purification was effected through the double salts with cadmium chloride. With the exception of elaidyl-lysolecithin, which was a dry powder melting sharply at  $220^\circ$ , the final products were waxy masses; the typical physical properties of natural lecithins are apparently due to the highly unsaturated acidic radicals which they contain. Synthetic lecithins, when completely freed from lysolecithin, have no hæmolytic action.

E. S.

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### Biochemistry.

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**Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen. VII—VIII.** K. FURUSAWA, A. V. HILL, C. N. H. LONG, and H. LUPTON (*Proc. Roy. Soc.*, 1924, **B**, **97**, 155—176; cf. *A.*, 1924, **i**, 1128, 1363).—VII. *Muscular exercise and oxygen intake.*—The oxygen intake increases with increase in the severity of the exercise up to a maximum, conditioned by the limitations of the circulatory-respiratory system. The use of gas mixtures containing a high pressure of oxygen enables a much

higher oxygen intake to be attained. This increase cannot be due simply to more complete saturation of the blood in its passage through the lungs, and it is suggested that a "governor" mechanism exists in the heart-muscle or elsewhere, which tends to co-ordinate the output of the heart with the degree of saturation of the blood leaving it. It is calculated that the output of the heart in man may reach 30 or 40 litres per minute and that in severe exercise the heart-muscle must be supplied with twice its own volume of blood per minute.

**VIII. Muscular exercise and oxygen requirement.**—The oxygen requirement per minute in walking and running rises continually as the speed increases, at high speeds becoming as much as ten times the oxygen intake. The oxygen requirement is a valuable quantitative criterion of the effort made.

The respiratory quotient of the total excess metabolism caused by short-lived muscular effort appears to be unity. Apparently after a short element of muscular exertion the recovery process involves the oxidation simply of lactic acid and carbohydrate, whilst in the intact animal when exercise and recovery are prolonged, a lower respiratory quotient is produced and the oxidation of other substances occurs.

O. O.

**Mechanism of Oxidation of Succinic Acid and *p*-Phenylenediamine. Theory of Cell Respiration.** A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1924, **150**, 195—210).—The inhibition of the oxidation of succinic acid in muscle-tissue produced by potassium cyanide is removed by methylene-blue. It is inferred that the oxidation of this acid involves a combination of Wieland's activated-hydrogen and Warburg's activated-oxygen mechanisms. Molecular oxygen is not a hydrogen acceptor. The oxidation of *p*-phenylenediamine, which is also inhibited by cyanide, is not reactivated by methylene-blue; in this case, it is inferred that activated hydrogen plays no part, but, since the diamine contains labile hydrogen atoms, activated oxygen alone is sufficient.

J. P.

**Carbon Dioxide Equilibrium in Alveolar Air and Arterial Blood.** A. V. BOCK and H. FIELD, jun. (*J. Biol. Chem.*, 1924, **62**, 269—274).—The closest approximation between the tension of carbon dioxide in the alveolar air and that in the arterial blood is obtained if the sample of alveolar air is taken at the end of a normal expiration; under these conditions, the tension in the blood is, on the average, 0.48 mm. higher than that in the alveolar air.

C. R. H.

**Ionic Nature of Hæmoglobin.** H. TAYLOR (*Proc. Roy. Soc.*, 1924, **B**, **96**, 383—397).—By a method similar to that employed by Loeb (A., 1921, i, 627), it is shown that the hæmoglobin in sheep's blood acts as an anion over the whole  $p_H$  range of physiological importance and thus support is given to the Zuntz theory relating to the reaction between carbon dioxide and blood. The interior of the corpuscle has a  $p_H$  about 33% higher than that of

the accompanying plasma, and the chlorine-ion concentration, although variable, lies between the limits 0.034*N* and 0.091*N*. The normality of the indiffusible protein ion in laked corpuscles is variable, but has a mean value of 0.037*N* over a range of carbon dioxide pressure of 0.4–60 mm.

A. J. H.

**Effect of Valency of Cations and Anions on Negatively and Positively Charged Red Blood Cells.** J. OLIVER and L. BARNARD (*J. Gen. Physiol.*, 1924, 7, 225–233).—The valency of the cation determines the degree of the effect on the potential difference at the surface of negatively charged red blood cells in isotonic sucrose solution, that of the anion, the effect on positively charged red cells. Anomalous results obtained with some salts were due in part to change in  $p_H$ , caused by hydrolysis of the salt.

H. J. C.

**Distribution of Ions in the Blood. III.** P. RONA, H. PETOW, and E. WITKOWER (*Biochem. Z.*, 1924, 150, 468–475).—In a study of the influence of hæmoglobin on the diffusibility of the cations of the blood at varying  $p_H$ , it is shown that the distribution of sodium and calcium is in conformity with the Donnan equilibrium, whilst potassium gives similar results only in strongly acid solutions. In the presence of serum, the final distribution of calcium depends on the combined influences of hæmoglobin and serum-proteins, more calcium being associated with the latter than with the former.

J. P.

**Nature, Properties, and Preparation of the Eosinophile Granule Substance of the Blood. II. Chemical and Physical.** A. NEUMANN (*Biochem. Z.*, 1924, 150, 256–264).—The eosinophile granule substance is not a protein, but may be associated with protein as indicated by its nitrogen content, micro Millon's reaction, and oxydase or peroxydase reaction. The substance is characterised by its readiness to become associated with other foreign substances—iron, fat, glycogen, etc.

J. P.

**Blood Clotting. X.** B. STUBER. **Detection of so-called Thrombin in Oxalate Plasma.** S. LEE (*Biochem. Z.*, 1924, 150, 542–547).—Active thrombin can be demonstrated in oxalate plasma after removal of the oxalate. Schmidt's thrombin is therefore inferred to be an artifact of no biological significance.

J. P.

**Influence of Sodium Chloride on Uric Acid of Blood.** V. J. HARDING, K. D. ALLIN, and H. B. VAN WYCK (*J. Biol. Chem.*, 1924, 62, 61–73).—The addition of 15 g. of sodium chloride to the day's diet causes a retention in the blood of water and sodium chloride and a decrease in the serum-proteins and uric acid. It is suggested that the decrease in uric acid is due to increased excretion of the latter caused by the hydræmia.

C. R. H.

**Blood-sugar Reduction Tables for Bang's "New Method" calculated for 50 to 130 mg. of Blood.** H. DREYFUSS (*Biochem. Z.*, 1924, 150, 211–223).—Tables are given for the direct

reading of blood-sugar values from the weight of sample used and the volume of thiosulphate required in Bang's new method ("Mikromethoden," Bergmann, 1922). J. P.

**Sugar Content of Blood-corpuscles.** M. RICHTER-QUITTNER (*Biochem. Z.*, 1924, **150**, 492—493).—If care is taken to ensure complete hæmolytic, the concentration of sugar in blood-corpuscles is found to be the same as that in the plasma (cf. Falta and Richter-Quittner, *ibid.*, 1919, **100**, 148; Hoegler and Ueberrack, *ibid.*, 1924, **148**, 150). J. P.

**Endocrine Glands and Blood Calcium.** S. LEITES (*Biochem. Z.*, 1924, **150**, 183—194).—The blood calcium of the rabbit falls after removal of the thymus or parathyroid glands, slowly in the former case, rapidly in the latter, whilst a temporary rise followed by a fall in blood calcium is produced by thyroidectomy or by removal of testes or ovary. Administration of glandular preparations to the operated animal corrects these abnormalities. J. P.

**Determination of Lipoid Phosphorus in Blood and Plasma.** J. C. WHITEHORN (*J. Biol. Chem.*, 1924, **62**, 133—138).—The method of Bell and Doisy (*A.*, 1920, ii, 769) has been modified by using larger quantities of sulphuric acid during the incineration in order to avoid errors due to local overheating. The large amount of acid used necessitates certain other modifications in the procedure which are described. C. R. H.

**Clinical Method for Determining the Bicarbonate Content of Blood Plasma.** J. HOLLÓ and S. WEISS (*Biochem. Z.*, 1924, **150**, 501—508).—Two methods, one clinical and the other quantitative, for determining the volume percentage of carbon dioxide in the blood are described, both based on the method of Van Slyke, Stillman, and Cullen (*A.*, 1917, ii, 422). J. P.

**Influence of the Method of Obtaining Serum on its Protein Concentration.** A. GROMELSKI (*Biochem. Z.*, 1924, **149**, 261—268).—Leendertz's observations (*Arch. klin. Med.*, 1922, **140**) concerning the lower protein content of serum from whole blood, as compared with that obtained from plasma, are confirmed. J. P.

**Distribution of Ions in Blood-serum. II.** P. RONA, F. HAUROWITZ, and H. PETOW (*Biochem. Z.*, 1924, **149**, 393—398).—Using a rapid method of compensated dialysis (Rona and Petow, *A.*, 1923, i, 728), it is shown that at  $p_H$  7.8 the chlorine, sodium, and potassium of serum, in contrast to the calcium, are wholly diffusible. These ions show a minimum change of concentration during dialysis when the outer liquid contains a rather lower concentration of the ion concerned than does the serum. This is ascribed to the appreciable volume occupied by the hydrated protein particles. J. P.

**Serum Proteins.** G. LEENDERTZ (*Biochem. Z.*, 1924, **150**, 494—495).—A reply to von Frey (*A.*, 1924, i, 1123). J. P.

**Calcium Content of Serum Protein Fractions.** J. CSAPÓ and J. FAUBL (*Biochem. Z.*, 1924, **150**, 509—514).—The calcium contents of fibrin, citrate fibrinogen, serum-globulin, and serum-albumin increase in the order cited, *i.e.*, the finer the dispersion of the protein the greater its calcium content. J. P.

**Occurrence of Porphyrin in Blood-serum.** A. PAPENDIECK (*Z. physiol. Chem.*, 1924, **140**, 111—112).—Polemical (cf. Fischer, *A.*, 1924, i, 1131). E. S.

**Electro-dialysis.** H. FREUNDLICH and L. F. LOEB (*Biochem. Z.*, 1924, **150**, 522—534).—The method of electro-dialysis (Pauli, *Kolloid-Z.*, 1922, **31**, 252), whilst convenient in general, is not suited for the dialysis of serum if two parchment membranes are used. In practice, a chromate-gelatin membrane at the anode and a parchment-paper membrane at the cathode as recommended by Ruppel (*Ber. deuts. pharm. Ges.*, 1920, **30**, 314) is at present the most suitable arrangement. J. P.

**Simple Clinical Method for Determining Small Amounts of Potassium in Blood-serum and other Fluids.** F. LEBERMANN (*Biochem. Z.*, 1924, **150**, 548—559).—The potassium is precipitated as the cobaltinitrite, washed, dried, and dissolved in 27% hydrochloric acid, and the resulting bluish-green solution compared with known standards in a colorimeter. Potassium can be determined with reasonable accuracy in 0.1 c.c. of serum by this method. J. P.

**Behaviour of Precipitin and Agglutinin Adsorbed on Charcoal or Kaolin to their Antigen.** M. EISLER (*Biochem. Z.*, 1924, **150**, 350—360).—Bone charcoal adsorbs precipitin from typhus and cholera extracts and from the corresponding immune sera if the adsorbent has been previously treated with sodium chloride solution. Charcoal and kaolin previously treated with immune sera adsorb typhus and cholera bacilli, untreated adsorbents only the latter. Horse-serum precipitin adsorbed on charcoal no longer reacts with its antigen. Charcoal or kaolin kept in contact with a sheep-serum agglutinin develops a specific power of adsorbing sheep corpuscles. J. P.

**Determination of Bismuth.** L. KÜRTHY and H. MÜLLER.—(See ii, 73.)

**Determination of Lactic Acid in Animal Organs.** H. HIRSCH-KAUFFMANN (*Z. physiol. Chem.*, 1924, **140**, 25—46).—A modification of the von Furth-Charnass method has been elaborated which obviates the necessity of extracting the lactic acid with ether or similar solvents and is similar to that of Anrep and Cannan (*J. Physiol.*, 1923, **58**, 244). The essential feature of the modification is the removal of all carbohydrates from the protein-

free solution. These are precipitated by addition of copper sulphate and milk of lime on the lines of the method of Van Slyke (A., 1918, ii, 86). The filtrate is then employed for the determination of lactic acid. E. S.

**Extractives of the Lungs.** S. KAPLANSKY (*Z. physiol. Chem.*, 1924, **140**, 69—73).—Creatinine has been isolated from ox lungs in the form of its double salt with zinc chloride; the presence of neither carnosine, methylguanidine, nor carnitine could be detected. The author has failed to confirm the presence of pulmo-tartaric acid (Poulet, *Archives de Physiol.*, 1888, [iv], **1**, 178) in the dialysate from pig's lungs. E. S.

**Colour Test for Guanidine Bases, with Physiological Applications.** O. W. TIEGS (*Austral. J. Expt. Biol.*, 1924, **1**, 93—97).—A solution of sodium nitroprusside which has been exposed to air and sunlight for a day gives a red colour with guanidine in neutral solution; the same colour is given in alkaline solution with methyl- and dimethyl-guanidine and with creatine, the colour obtained with creatine fading on keeping. By the use of this test, it has been shown that methylguanidine is not present in skeletal muscle or in putrid meat extract; traces of guanidine bases can be detected in normal human urine. Contrary to the statement of Mellanby (A., 1908, ii, 308), creatine occurs in the chick embryo as early as the fourth day. C. R. H.

**Colorimetric Method for Determination of Guanidine and Methylguanidine.** H. R. MARSTON (*Austral. J. Expt. Biol.*, 1924, **1**, 99—103).—A reagent consisting of a mixture of sodium nitroprusside and potassium ferrocyanide in sodium hydroxide solution, treated just before use with hydrogen peroxide, gives a red colour with guanidine and methylguanidine, but not with creatine. The reagent has been applied to the colorimetric determination of guanidine bases, using as standard a known solution of guanidine carbonate. C. R. H.

**"Lecitiburin," a Lecithin from the Eggs of the Shark.** H. P. PONCE (*Anal. Asoc. Quím. Argentina*, 1924, **12**, 103—113; cf. A., 1924, i, 1371).—Further chemical data are given for "lecitiburin." It is shown to be similar to the lecithin obtained from hens' eggs. The possibility of its use in pharmacology is discussed. G. W. R.

**Fractional Analysis of Incomplete Protein Hydrolysates.** H. WASTENFYS and H. BORSOOK (*J. Biol. Chem.*, 1924, **62**, 1—14).—Protein is precipitated by trichloroacetic acid, metaprotein (in an aliquot portion) by adjusting the reaction to  $p_H$  6.0, proteoses by sodium sulphate at 33°, peptones by tannic acid, and the remaining peptides and amino-acids by alcohol; the amount of each fraction is ascertained by nitrogen determinations before and after precipitation. C. R. H.

**Tryptophan and Cystine Content of Various Proteins.**

D. B. JONES, C. E. F. GERSDORFF, and O. MOELLER (*J. Biol. Chem.*, 1924, **62**, 183—195).—Tryptophan was determined by the method of May and Rose (A., 1923, i, 160) and cystine by that of Folin and Looney (A., 1922, ii, 539). Figures are given for the percentages of these amino-acids in numerous proteins derived from common foodstuffs.

C. R. H.

**Organic Phosphorus of the Urine.**

G. E. YOUNGBURG and G. W. PUCHER (*J. Biol. Chem.*, 1924, **62**, 31—44).—The inorganic phosphates of the urine were removed by precipitation with magnesia mixture and the organic phosphorus in the filtrate determined by the method of Bell and Doisy (A., 1920, ii, 769). In normal individuals, variations of 100% were found in the excretion of organic phosphorus in successive 2-hour periods. The total daily excretion varies from 0.089 mg. to 0.187 mg. per kg. body-weight.

C. R. H.

**Stalagmometric Investigations on Urine, in particular that of the Large Herbivora. I. Methods. II. Nature of the Capillary-active Substance of Urine. III. Adsorption of the Capillary-active Substance of Urine.** K. KIESEL (*Biochem. Z.*, 1924, **149**, 399—414, 415—429, 430—446).—I. In various urines, the dynamic weight per drop when the latter is formed in constant time is a direct measure of the static surface tension: This principle is adopted in stalagmometric investigations on urine.

II. To be effective in lowering the surface tension of urine, colloidal proteins must have at least the molecular dimensions of albumoses.

III. An investigation of the adsorption of the capillary-active substance of urine using as adsorbents charcoal, cellulose, and the froth produced by shaking the urine.

J. P.

**An Unknown or Little-known Volatile Urinary Substance.**

E. PITTARELLI (*Arch. Farm. sperim. Sci. aff.*, 1924, **38**, 8—12).—Normal urine contains a volatile ketonic compound which gives a greenish-yellow precipitate with Nessler's reagent and a white precipitate with a sulphuric acid solution of mercuric sulphate, and differs from acetone. It is to this compound that the odour of urine is due, either wholly or partly.

T. H. P.

**Detection of Bilirubin and Urobilin in the Fæces with Trichloroacetic Acid.** D. ADLERSBERG and O. PORGES (*Biochem. Z.*, 1924, **150**, 348—349).—A simple and quick test depending on the fact that on treating fæces with trichloroacetic acid the particles containing bilirubin display a green colour, whilst those containing urobilin become red.

J. P.

**The Porphyrin of Human Fæces. III.** A. PAPENDIECK (*Z. physiol. Chem.*, 1924, **140**, 16—24).—Experiments are reported which indicate that the porphyrin excreted in the fæces is formed in the intestine by the action of bacteria on bilirubin.

E. S.



**Intestinal Chemistry. I. Determination of Intestinal Reductions. II. Intestinal Reductions as a Measure of Putrefaction. Influence of Diet.** O. BERGEIM (*J. Biol. Chem.*, 1924, 62, 45—48, 49—60).—I. A known amount of ferric oxide was added to the diet of experimental animals, the faeces were collected, and the percentage of the total iron present in the ferrous condition was determined, this percentage being taken as an index of intestinal reduction.

II. In the intestine of the rat, reduction takes place almost entirely in the caecum and large intestine; the amount of reduction is large when the protein of the diet contains much cystine, indicating that the production of hydrogen sulphide is concerned in the process; the carbohydrates and fat of the diet have little effect except in the cases of dextrin and lactose, which diminish the amount of reduction; intestinal antiseptics are without effect, whilst reduction is much increased in intestinal stasis. C. R. H.

**Reducing Power of Normal and Cancer Tissue.** C. VOEGTLIN, J. M. JOHNSON, and H. A. DYER (*J. Pharm. Exp. Ther.*, 1924, 24, 305—334).—The rates of reduction of equimolecular proportions of certain dyes under standard anaërobic conditions by different normal and cancer tissues were compared. The most sensitive indicator for the process was found to be *m*-bromophenol-indophenol. Blood plasma, serum, and the necrotic part of carcinoma tissue were found to possess no reducing power; all other tissues tested were able to reduce the dyes, the greatest activity being observed with liver, kidney, and testis; the reducing power of actively growing carcinoma tissue is similar to that of normal tissue. The toxic effects following injection of dyes such as methylene-blue can be, in part at least, abolished by simultaneous injection of glutathione, but not by cysteine or thioglycollic acid, from which it is inferred that the function of glutathione may be the regulation of the equilibrium between oxidising and reducing substances in the living cell. The rates of reduction of the dyes employed increase with an increase in their electrode potential.

C. R. H.

**Determination of Hydrogen-ion Concentration in Tissues and in Cells.** M. SCHMIDTMANN (*Biochem. Z.*, 1924, 150, 253—255).—A method is described for the direct introduction of indicators into living cells and tissues whereby the local hydrogen-ion concentration may be determined.

J. P.

**Transformation of Glucal into Deoxyglucose in the Rabbit.** M. KONDO (*Biochem. Z.*, 1924, 150, 337—340).—Glucal administered subcutaneously or orally to the rabbit is found in the urine to the extent of 2 to 3% as 2-deoxyglucose, whilst if the latter is administered orally 7% is recovered unchanged in the urine.

J. P.

**Occurrence of Salicyluric Acid in the Urine after Administration of Salicylic Acid.** H. DRZIMAL (*Rec. trav. chim.*, 1924, 43, 600—605; cf. A., 1918, i, 142).—The urine is made neutral

to litmus, treated with neutral lead acetate solution, and the precipitate filtered off, and washed free from salicylic acid. The precipitate from two successive treatments of the filtrate with basic lead acetate and ammonia, which contains all the organic acids of the urine except uric acid, is suspended in water and decomposed by means of hydrogen sulphide. The filtrate is extracted with a mixture of equal volumes of ethyl acetate and ether, the residue from this extract is redissolved in a mixture of dry ethyl acetate and ether, and the solution is filtered. The residue finally obtained is heated at 100° in order to sublime away the salicylic acid. The non-volatile residue crystallises from water in needles, m. p. 170—172°, and is identified as salicyluric acid. W. E. E.

**Comparative Metabolism of Aromatic Acids. VII. Fate of *p*-Chloro-, *p*-Bromo-, and *p*-Amino-acids.** L. R. CERECEDO and C. P. SHERWIN (*J. Biol. Chem.*, 1924, **62**, 217—230).—After feeding *p*-chloro- and *p*-bromo-phenylacetic acids to dogs and men, the corresponding phenaceturic acids were found in the urine, whilst in the case of the rabbit the acids were excreted unchanged. Administration of *p*-aminophenylacetic acid to man or to the rabbit resulted in the excretion of *p*-acetamidophenylacetic acid; in the case of the dog, there was found instead *p*-aminophenylaceturic acid. C. R. H.

**Amino-acid Synthesis in the Animal Organism. Availability of Caproic [*n*-Hexoic] Acid Derivatives for Synthesis of Lysine.** D. A. MCGINTY, H. B. LEWIS, and C. S. MARVEL (*J. Biol. Chem.*, 1924, **62**, 75—92).—Neither  $\alpha$ -hydroxy-*n*-hexoic,  $\epsilon$ -hydroxy-*n*-hexoic,  $\epsilon$ -amino-*n*-hexoic, nor  $\alpha$ -hydroxy- $\epsilon$ -amino-*n*-hexoic acid was able to induce proper growth in rats whose diet was deficient in lysine; none of these acids can therefore be considered as a possible natural precursor of lysine. C. R. H.

**Chemical and Physiological Investigations on Bismuth. III. Determination of Bismuth in Urine.** L. KÜRTHY and H. MÜLLER (*Biochem. Z.*, 1924, **149**, 235—238).—The urine is evaporated with nitric acid and potassium nitrate and the bismuth determined, either colorimetrically by conversion into brown colloidal bismuth sulphide using gum arabic as a protective colloid, or by electrolytic deposition on a platinum cathode. J. P.

**Chemical and Physiological Investigations on Bismuth. IV. Excretion of Orally Administered Bismuth.** H. MÜLLER and L. KÜRTHY (*Biochem. Z.*, 1924, **149**, 239—244).—Bismuth oxide administered *per os* to a dog is eliminated slowly, thirty times as much appearing in the faeces as in the urine, whilst during continued administration of large amounts of bismuth the faeces may contain up to 1000 times that present in the urine. Considerable quantities of bismuth may be retained for prolonged periods. J. P.

**Chemical and Physiological Investigations on Bismuth. V. Excretion of Subcutaneously and Intramuscularly Administered Bismuth.** L. KÜRTHY (*Biochem. Z.*, 1924, **150**, 173—176).—The elimination of bismuth ("Oleobi") injected intramuscularly into the dog is slow, some 20% of the total quantity administered being excreted in 4 weeks, 58.8% in the urine and 41.2% in the faeces. Of another bismuth preparation ("Bismokutan") administered by external rubbing, 30% was excreted in 20 days, 94.3% in the faeces and 5.7% in the urine. J. P.

**Action of Undissociated Drugs.** E. KEESER (*Biochem. Z.*, 1924, **150**, 515—521).—Phenol is more toxic to *Staphylococcus* in acid solution in which it is undissociated than in the dissociated condition in alkaline solution. Similar findings by other observers are discussed in relation to the increase of surface action associated with larger molecules or lessened solubility. J. P.

**Power of Adsorption and Detoxication of Various Charcoals.** KAP-SOO-LEE (*Biochem. Z.*, 1924, **150**, 341—347).—Various charcoals tested *in vivo* show the same detoxicating properties with regard to sodium arsenite, sodium salicylate, and strychnine, but their activities in this respect are not indicated by the extent to which they adsorb iodine *in vitro*. The latter is therefore not a trustworthy pharmacological test of the detoxicating power of charcoal. J. P.

**Hepatic Function. VI. Pharmacological Behaviour of Phthalein Dyes. Value of Phthalein Compounds in Estimation of Hepatic Function.** S. M. ROSENTHAL and E. C. WHITE (*J. Pharm. Expt. Ther.*, 1924, **24**, 265—288).—The disulphonic acid derivatives of phenoltetrahalogenophthaleins are excreted in the bile, after intravenous injection, to the extent of 60—90%, traces only appearing in the urine. Of this group of substances, the sodium disulphonate of phenoltetrabromophthalein is the most rapidly excreted in the bile in the normal individual, and therefore shows the most marked retention in the blood-stream when hepatic function is impaired. Mercurochrome, which has a strong bactericidal action, is excreted in the bile to the extent of 30—55%, and its use is suggested as a biliary antiseptic.

C. R. H.

**Passage of Boric Acid through the Skin by Osmosis.** L. KAHLBERG (*J. Biol. Chem.*, 1924, **62**, 149—156).—After immersion of the feet in a warm solution of boric acid, the latter could be detected in the urine; this was not so if sodium or lithium borate were substituted for boric acid, nor could passage through the skin of numerous other diffusible substances, under the same conditions, be demonstrated.

C. R. H.

**Possibility of Identifying Chemical Processes in Living Matter.** W. J. CROZIER (*Proc. Nat. Acad. Sci.*, 1924, **10**, 461—464).—On the assumption that the critical increments of reactions influenced by a common catalyst are the same, the values of the

critical thermal increments of vital processes permit of the classification of protoplasmic activities on a dynamic basis and of the identification of reactions in living matter on the basis of the catalysts involved. J. S. C.

**Biological Oxidations as Function of Temperature.** W. J. CROZIER (*J. Gen. Physiol.*, 1924, 7, 189—216).—The critical thermal increments for the respiratory processes of various plants and animals have been calculated, and may be of two, possibly three, types:  $\mu=11,500$ , 16,100, or 16,700. For the reduction of methylene-blue by bacteria by removal of hydrogen from succinic acid,  $\mu=16,700$ , a result similar to that obtained for biological respirations in which a dehydrogenation mechanism appears to be of general occurrence, and in which iron has probably a catalytic function. The critical thermal increment for the oxidation of  $\text{Fe}''$  is 16,140, which may be compared to respiration in sea-urchins' eggs, for which iron is a catalyst. H. J. C.

**Autolysis. XIII. Kinetics of Autolytic Mechanism.** A. B. HERTZMANN and H. C. BRADLEY (*J. Biol. Chem.*, 1924, 62, 231—243).—In the autolysis of liver at optimum  $p_{\text{H}}$  the primary cleavage of the proteins, measured by the proportion of the total nitrogen which cannot be precipitated by trichloroacetic acid, is complete in 15 days, but only about one-third of the total nitrogen is found in the form of free amino acid nitrogen. This indicates that the secondary hydrolysis of proteoses and peptones to amino-acids reaches an equilibrium; the equilibrium constant for this secondary reaction has a value of about 0.56. The inhibition of autolysis brought about by the presence of a foreign protein previously noted (A., 1924, i, 1149) is due to a combination of the latter with the primary protease, which is thus removed from the sphere of action. C. R. H.

**Taka-rennin.** J. HATANO (*Biochem. Z.*, 1924, 149, 228—231).—Taka-diaestases contain, in variable amounts, a rennin-like enzyme which acts on fresh milk and on calcium-casein solutions. J. P.

**Enzymic Synthesis of Protein. I. Synthesising Action of Pepsin.** H. WASTENEYS and H. BORSOOK (*J. Biol. Chem.*, 1924, 62, 15—29).—By the action of pepsin at  $p_{\text{H}}$  4.0 on a concentrated solution of the products of peptic hydrolysis of egg-albumin, a precipitate corresponding with the plastein of Sawjalov (A., 1908, i, 234) was obtained. This substance may contain as much as 39% of the nitrogen of the original solution, and is of the order of molecular complexity of egg-albumin. Plastein is rapidly hydrolysed by pepsin at  $p_{\text{H}}$  1.7, whereas the proteoses left in solution after plastein has been synthesised are not attacked by the enzyme; it is therefore assumed that the synthesis of plastein involves the re-synthesis by pepsin of some particular linking, which, under other conditions of dilution and acidity, is hydrolysed. Plastein is almost insoluble in water, fairly easily soluble in dilute acid, and still more easily soluble in dilute alkali; in alkaline solution, it is heat-coagulable and is partly precipitated by half-saturation with

sodium chloride. If a solution of albumin be added to a concentrated solution of the products of its peptic hydrolysis, the albumin is quantitatively precipitated and the precipitate resembles plastein in its physical properties; it is thought that this phenomenon may account for the differences between plastein and natural egg-albumin. No synthetic action of pepsin on the products of peptic hydrolysis of gelatin could be demonstrated. C. R. H.

**Nephelometric Investigations on Enzymic Protein Hydrolysis. II. Influence of Ions on Peptic Digestion.** P. RONA and H. KLEINMANN (*Biochem. Z.*, 1924, **150**, 444—467).—Using the methods already described (A., 1923, ii, 890; i, 1145; 1924, i, 790), the optimum  $p_H$  for peptic digestion is found to be 2.1 to 2.2. The influence of sodium, potassium, calcium, aluminium, chloride, nitrate, and sulphate ions on peptic digestion is qualitatively similar, all having an inhibiting action at the optimum and on the acid side of it, whilst on the alkaline side, when present in low concentration, they increase the activity of the enzyme, but display an inhibitory effect in higher concentrations. J. P.

**Tryptic Digestion with Dilute Enzyme Solutions.** R. EHRENBERG (*Biochem. Z.*, 1924, **149**, 269—293).—From a lengthy series of observations on the proteolytic action of trypsin in very dilute solutions on casein, egg-albumin, and gelatin, support is gained for the view that the enzyme undergoes a change in the course of its action, whereby its activity is lowered, by an association formed with inhibitory substances liberated or built up during the hydrolysis (cf. also A., 1922, i, 597). J. P.

**Milk and Gastric Lipase.** F. DEMUTH (*Biochem. Z.*, 1924, **150**, 392—406).—The stalagmometric determination of lipase, using tributyrin, is influenced by the presence of fat and protein. The inhibition of gastric lipase by casein is removed on coagulation of the casein by rennin. J. P.

**Fat-hydrolysing Enzyme of Taka-diastrase.** I. OGAWA (*Biochem. Z.*, 1924, **149**, 216—227).—Taka-diastrase contains a lipase which shows an optimum activity at  $p_H$  8.5 to 9.3, and, unlike other lipases with the exception of bacterial lipase (Michaelis and Nakahara, *Z. Immun. Forsch.*, 1923, **36**, 449), is inhibited by borates. It is stable in the presence of quinine and potassium cyanide, and is but slightly affected by atoxyl and sodium fluoride. J. P.

**Hydrolysis of Leucine Ester by Pancreatic Enzymes.** P. RONA and P. E. SPEIDEL (*Biochem. Z.*, 1924, **149**, 385—392).—The ethyl and propyl esters of isohexoic acid are hydrolysed by the lipase of the pancreas, and not by the trypsin. Similar conclusions are reached regarding the hydrolysis of the ethyl and propyl esters of *dl*-leucine by pancreatic enzymes (cf. Warburg, A., 1905, i, 176). J. P.

**Influence of Dextrose and Lævulose on Rate of Hydrolysis of Sucrose by Invertase from Honey.** J. M. NELSON and C. T. SOTTERY (*J. Biol. Chem.*, 1924, **62**, 139—147; cf. A., 1924, i, 1143).—The addition of dextrose up to 2% accelerates the inversion of sucrose by honey invertase; above 2%, the reverse effect is obtained; similar, but less marked, effects are obtained with lævulose.  $\alpha$ -Glucose has less influence on the reaction than  $\beta$ -glucose or ordinary dextrose, whilst the effects of ordinary lævulose and of  $\beta$ -fructose are identical. C. R. H.

**Approximative Colorimetric Method for the Determination of Urea, with an Application to the Detection and Determination of Arginase.** A. HUNTER and J. A. DAUPHINEE (*Proc. Roy. Soc.*, 1924, **B**, **97**, 209—226).—Kay's method (A., 1923, i, 722) with certain refinements has been used for the determination of urea in urine and in the blood of elasmobranch fishes. The method has also been extended to the determination of urea formed in the hydrolysis of arginine by arginase. In this way, the activities of arginase in different extracts are compared. O. O.

**Distribution of Arginase in Fishes and other Animals.** A. HUNTER and J. A. DAUPHINEE (*Proc. Roy. Soc.*, 1924, **B**, **97**, 227—242).—Using the colorimetric method (cf. preceding abstract), the distribution of arginase has been determined in various organs of fishes and other animals. It is present in the livers of all fishes examined, and in this organ appears to be constant and characteristic for any one genus. The livers of mammals are much more active than those of fishes. In fishes, next to the liver, the heart is the most active organ, but in mammals, birds, and Chelonia it is inactive. Apart from the liver, kidney, and heart, the distribution of the enzyme in other organs of fishes is variable, whilst in mammals it is confined to the liver and kidneys. It is rarely, if ever, found in the tissues of invertebrates. O. O.

**Auxoureases.** T. HOSOKAWA (*Biochem. Z.*, 1924, **149**, 363—373).—By precipitation of urease preparations with cholesterol, a fractional separation of urease from its naturally occurring auxo-substances is achieved. The inactive enzyme so obtained is reactivated by the addition of auxo-substances. Fibrin may act as one of the latter, since practically inactive urease shows a marked increase in activity when adsorbed on this protein. Calcium and strontium chlorides also increase the activity of urease, but not so markedly as does potassium cyanide, whilst barium chloride is practically devoid of such action. Sodium citrate, oxalate, and fluoride similarly act as auxo-ureases, whilst potassium and sodium chlorides have little action. The action of magnesium chloride is antagonistic to that of strontium chloride, and under proper conditions sodium chloride shows a similar antagonism to strontium. The activity of the enzyme is enhanced if the activating salts are kept in contact with urea for 10 minutes before the urease is added. J. P.

**Fermentation Co-enzyme (Co-zymase) of Yeast. VI. Further Isolation Experiments.** H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **139**, 281—306).—After purification by fractional precipitation with lead acetate (A., 1924, i, 1141), the co-enzyme can be further concentrated by precipitating with silicotungstic acid, grinding the precipitate with water, removing the silicotungstic acid by cautiously adding barium hydroxide until no further precipitate is produced, and filtering. Precipitation may also be effected with phosphotungstic acid or tannin, but recovery is more difficult in the case of the former reagent whilst it cannot be effected with the latter, although the tannin precipitate is itself highly active. The most active solution of the co-enzyme gave the ninhydrin, the diazo, and Molisch's reactions. The biuret, xanthoproteic, and Millon's reactions diminished in intensity as the purification progressed and finally failed with the most active preparation. Neither hydrogenation in the presence of platinum-black nor treatment with iodine appears to destroy the co-enzyme. The authors' work on the co-enzyme is summarised.

E. S.

**Action of Living Yeast on Lactic Acid.** K. MYRBÄCK and B. EVERITT (*Z. physiol. Chem.*, 1924, **139**, 272—280).—The experiments of von Fürth and Lieben (A., 1922, i, 502, 1219) on the destruction of lactic acid by yeast have been confirmed.

E. S.

**Behaviour of Oxygenated Yeast to  $\beta$ -Hydroxybutyric Acid.** J. MARIAN (*Biochem. Z.*, 1924, **150**, 281—289).—Under conditions which lead to the oxidation, assimilation, or decarboxylation of lactic, pyruvic, and acetoacetic acids by yeast,  $\beta$ -hydroxybutyric acid is unaffected.

J. P.

**Assimilation of Glycerol by Oxygenated Yeast.** J. MARIAN (*Biochem. Z.*, 1924, **150**, 290—303).—In the presence of oxygen, yeast assimilates glycerol with no corresponding formation of carbon dioxide. The assimilation is independent of the glycerol concentration and proceeds according to the equation:  $2nC_3H_8O_3 + nO_2 = (C_6H_{10}O_5)_n + 3nH_2O$ , an easily hydrolysable polysaccharide being formed. It is supposed that a triose may play an intermediate part in the synthesis.

J. P.

**Behaviour of the Reserve Carbohydrate of Yeast in Assimilation and Dissimilation.** J. WARKANY (*Biochem. Z.*, 1924, **150**, 271—280).—Glycogen and gums form a source of reserve carbohydrate in yeast, the former increasing by 84 to 288% and the latter by 28 to 56% in a nutrient medium, and both diminishing during self-fermentation. A third reserve carbohydrate is also formed in yeast. This yields on hydrolysis with 2.7% hydrochloric acid a compound which reduces Fehling's solution in the cold. It is formed in much smaller amounts than the other two sugars and disappears completely during self-fermentation.

J. P.

**Synthesis of Coproporphyrin by Yeast and the Factors which Influence it.** I. H. FISCHER and H. FINK (*Z. physiol. Chem.*, 1924, **140**, 57—68).—Kammerer's porphyrin has been

detected in summer yeast, but its presence is probably due to impurities of animal origin. With winter yeast and yeast cultures grown on synthetic media, only coproporphyrin could be detected. The suggested dualism of the pigment in yeast (A., 1924, i, 894) cannot therefore be maintained. E. S.

**Regularity of Lactic Fermentation in the Presence of Mercuric Chloride.** A. LUMIÈRE (*Ann. Inst. Pasteur*, 1924, 38, 1045—1051).—The irregularities in lactic fermentation experiments observed by Richet (cf. B., 1924, 112) are shown to be due to the precipitation of proteins by mercuric chloride, forming clots in which the bacteria are segregated. [Cf. B., 1924, 193, 227, 532.] G. S. W.

**Formation of Plant Growth-promoting Substances by Micro-organisms.** (Miss) F. A. MOCKERIDGE (*Ann. Bot.*, 1924, 38, 723—734).—Nucleic acid derivatives had a favourable effect on the growth of *Lemna minor*. Similar results were obtained with a sterilised culture of *Azotobacter* and with autolysed and autoclaved yeast; of the last two, the latter was the more effective. All these substances contain residues which are found in nucleic acid. *Azotobacter* and *B. radiculicola*, both nitrogen-fixing organisms, show a positive Folin-Macallum vitamin reaction. O. O.

**Staling of Fungal Cultures. II. Alkaline Metabolic Products and their Effect on the Growth of Fungal Spores.** (Miss) C. A. PRATT (*Ann. Bot.*, 1924, 38, 599—615).—"Staling" is suggested as being due to the formation of hydrogen carbonate, particularly of potassium and to a less degree of ammonium. At  $p_H$  8.2 produced by potassium bicarbonate, the growth of *Botrytis cinerea* is inhibited. O. O.

**Ammonification of Amino-nitrogen by the *Microsiphonæ* of the Soil.** G. GUITTONNEAU (*Compt. rend.*, 1924, 179, 512—514; cf. A., 1924, i, 807).—The action of cultures of seven different species of *Microsiphonæ* in synthetic media containing mineral salts and either glycine, alanine, leucine, or tyrosine shows that these amino-acids are not attacked with equal facility by all the organisms. H. J. E.

**Insulin. I. Preparation and Standardisation of Insulin. II. Effect of  $p_H$  on Activity of Insulin subjected to High Temperatures.** F. M. CHEADLE (*Austral. J. Expt. Biol.*, 1924, 1, 121—128, 129—130).—I.—A method of preparation (involving no new features) of insulin is described by which the yield obtained is about 250 rabbit units per kg. of fresh pancreas. Mice were used for the standardisation of the insulin; defining a "mouse-unit" as the amount of insulin necessary to cause convulsions in 60% of the animals used, when injected subcutaneously under constant conditions, it was found that 167 such units were equivalent to one 2-kg. rabbit unit.

II.—If solutions of insulin are autoclaved at 125° for 20 minutes at  $p_H$  2, the loss of activity is about 20%; in some cases, however, a precipitate was formed which carried down much of the active



substance, causing a greater loss of activity. At  $p_H$  4, the loss is much greater, even if the solution remains clear. C. R. H.

**Effect of Insulin on the Lactic Fermentation.** A. A. NOYES and H. W. ESTILL (*Proc. Nat. Acad. Sci.*, 1924, 10, 415—418).—The possibility of assaying insulin by simpler methods than the use of tests on animals has been studied. The insulin was precipitated from a technical aqueous solution in two fractions: the first by adding much alcohol, the second from the mother-liquors of the first by adding ether. By tests on rabbits, the second fraction was found to be twice as strong as the first. Solutions of the two fractions were made up of the same strength, calculated on this basis; suitable amounts of these solutions were added to cultures of *Lactobacillus bulgaricus* and *L. acidophilus* in diluted skim-milk containing glucose. After coagulation had occurred (in about 20 hours), the liquor was filtered off and titrated with 0.05*N*-sodium hydroxide solution. The mixture containing insulin coagulated more quickly than the "controls," and from 20 to 25% more lactic acid was produced when insulin was present. Similar results were obtained with both fractions, *i.e.*, the impurity in the first fraction had no effect. This finding was confirmed by a further "control" in which boiled ("inactivated") insulin solution was used. The effect on *L. bulgaricus* was greater than that on *L. acidophilus*. W. A. S.

**May Insulin Affect the Assimilatory or Dissimilatory Functions of Oxygenated Yeast?** O. FÜRTH (*Biochem. Z.*, 1924, 150, 265—270).—Insulin has no influence on the carbon dioxide produced, the sugar consumed, or the glycogen and gums formed by yeast shaken in contact with air. J. P.

**Fat-soluble Vitamins. XX. Modified Technique for Determination of Vitamin-A.** H. STEENBOCK, M. T. NELSON, and A. BLACK (*J. Biol. Chem.*, 1924, 62, 275—286).—The material to be tested was added to a basal diet lacking both vitamin-A and the anti-rachitic factor; the deficiency of the latter was made good by irradiation of the animals with ultra-violet light; the amount of vitamin-A was determined by the rate of growth induced. It was found that hog millet and ordinary millet, which are deficient in the anti-rachitic factor, contain vitamin-A, as does also lucerne which has been cured in the dark. C. R. H.

**Colour Reactions of the Fat-soluble Vitamins.** BEZSSONOFF (*Compt. rend.*, 1924, 179, 572—574; cf. A., 1921, ii, 608).—By using pure crystalline phosphomolybdotungstic acid as reagent, the anti-rachitic principle may be detected by the orange and vitamin-A by the blue colorations produced. The former colour is due to the presence of a derivative of the anti-rachitic substance which is formed from it by prolonged heating and also by atmospheric oxidation. H. J. E.

**Fat-soluble Vitamins. XIX. Induction of Calcifying Properties in a Rickets-producing Ration by Radiant Energy.** H. STEENBOCK and M. T. NELSON (*J. Biol. Chem.*, 1924, 62, 209—

216).—The previous work by Steenbock and Black (A., 1924, i, 1272) is confirmed by histological observations. C. R. H.

**Calcium Assimilation. V. Effect of Light on Calcium and Phosphorus Equilibrium in Mature Lactating Animals.** E. B. HART, H. STEENBOCK, and C. A. ELVEHJEM (*J. Biol. Chem.*, 1924, 62, 117—131).—Goats fed on a diet deficient in the anti-rachitic factor were found to fall into a negative calcium balance, this condition coming on more rapidly if the animal was lactating; on exposure of the animals to ultra-violet light for a daily period of 20 minutes, without change of diet, the calcium balance became positive and the inorganic phosphorus of the blood increased.

C. R. H.

**Jendrassik Reaction for Vitamin-B.** V. E. LEVINE (*J. Biol. Chem.*, 1924, 62, 157—161).—The reaction described by Jendrassik (A., 1923, ii, 892) is given by almost all compounds containing a phenolic group; such compounds, in common with vitamin-B, fail to give the reaction after boiling with sodium hydroxide; the test is therefore not specific for vitamin-B.

C. R. H.

**Vitamin Studies. Water-soluble Growth-promoting Factor. I. Determination of the Factor Promoting Growth in Bacteria.** H. DAVIDSOHN (*Biochem. Z.*, 1924, 150, 304—336).—It is proposed to classify in one group the growth-promoting vitamins which act on yeast, bacteria, etc. In particular methods of determining the vitamins promoting bacterial growth have been investigated. Optical methods of measuring the opacity produced by the growth of the bacteria are preferred, the amount required to cause the opacity of a culture to increase twofold in 4 hours at 37° when compared with a standard suspension of *Bacillus coli* being determined. The relationship of this group of vitamins to others is discussed.

J. P.

**Relation of Treatment of Natural Foodstuffs to their Effect on Growth and Reproduction.** H. G. MILLER and W. W. YATES (*J. Biol. Chem.*, 1924, 62, 259—268).—Extraction with cold water removes from maize the dietary factor necessary for reproduction in rats; this factor could be supplied by adding fresh maize, kale, wheat embryo, or an alcoholic extract of the latter (cf. Mattill, Carman, and Clayton, A., 1924, i, 1389).

C. R. H.

**Chemistry of Alkatan.** J. S. HEPBURN and R. H. STROH (*Amer. J. Pharm.*, 1924, 96, 804—809).—The dried leaves of alkatan (*Piper acuminatissimum*) contain no alkaloid. An oleoresin and a saponin were found.

E. M. C.

**Sterol of Scopolia Root.** A. WINDAUS and J. BRUNKEN (*Z. physiol. Chem.*, 1924, 140, 109—110).—This sterol has been identified as sitosterol.

E. S.

## Organic Chemistry.

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**Pyrogenic Dissociation of Hexadecane.** H. GAULT and F. A. HESSEL (*Ann. Chim.*, 1924, [x], 2, 319—377).—A more extended account of work, in part previously abstracted (*A.*, 1924, i, 701, 1025). Dissociation of hexadecane only begins to be apparent above 390°. The volume of gaseous products varies directly with the temperature and the length of the dissociation tube, but inversely with the rate of flow of the hexadecane. Hydrogen is only detected at 549° and its percentage increases sharply from 540° to 615°, and varies directly with the temperature and length of the tube, inversely with the velocity of the hexadecane. The percentage of unsaturated hydrocarbons in the gas varies inversely with the temperature and the length of the tube, and directly with the velocity of the hexadecane; the reverse relations hold with the percentage of saturated hydrocarbons. The amount of liquid products obtained at temperatures of 470—815° varies inversely with the length of the dissociation tube and the temperature, directly with the velocity; the iodine numbers of the liquid products and the percentage distilling before hexadecane vary in the same way, the refractive indices and densities showing the reverse relations. Above 750°, however, with the longer tubes the iodine value of the liquid products tends to decrease with rising temperature. The solubility of the liquid products in methyl sulphate varies directly with the temperature and the length of the tube, inversely with the rate of flow, but is only appreciable at 685° and above. Distillation of the liquid products obtained in experiments at 470° and 540° gave fractions in which the refractive indices varied directly and the iodine values inversely with the temperature of distillation. The above results lead to the conclusion that terminal dissociation of the hydrocarbon predominates. At 470°, the preponderating reaction is decomposition into ethylene and saturated hydrocarbons, accompanied by decomposition to a smaller extent into olefines and methane,  $\text{Me} \cdot [\text{CH}_2]_{14} \cdot \text{Me} \rightarrow \text{Me} \cdot [\text{CH}_2]_{12} \cdot \text{CH} : \text{CH}_2 + \text{CH}_4$ , thereby accounting for the presence of saturated hydrocarbons in the gas produced at this temperature. The olefinic hydrocarbons under the influence of heat yield naphthenes. At 540°, the same reactions take place, but a further decomposition,  $\text{R} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{R}^2 \rightarrow \text{R} \cdot \text{CH} : \text{CH}_2 + \text{CH}_2 : \text{CH} \cdot \text{R}^2 + \text{H}_2$ , is assumed, to account for the appearance of hydrogen. At temperatures of 685° upwards, aromatic cyclisation takes place, and the formation of hydrogen is attributed to dehydrogenation of naphthenes.

R. B.

**Spontaneous Combustion of Ethylene during the Preparation of Ethylene Dichloride.** R. K. SHARMA (*J. Chem. Soc.*, 1924, 125, 2676).—A periodic flash has been observed during the

passage of purified ethylene into chlorine water, even at temperatures below 15°, a small quantity of carbon being deposited in the liquid.

L. F. H.

**Pyrogenic Decomposition of Hexadecene.** H. GAULT and Y. ALTCHIDJIAN (*Ann. Chim.*, 1924, [x], 2, 209—268).—Re-publication in greater detail of work previously described (cf. A., 1924, i, 701, 1025). The results obtained lead to the following general conclusions. At low temperatures, the proportion of saturated hydrocarbons formed is greatest; decomposition appears to commence between two singly-linked carbon atoms at the extremity of the molecule. This is in accord with the thermochemical view and leads to the inference that the hexadecene molecule loses carbon atoms, saturated and unsaturated, from both extremities in different proportions according to the respective amounts of energy linking these atoms to the rest of the molecule. Between the low temperatures which condition the formation of mono- and di-ethylenic chain hydrocarbons and the high temperatures at which aromatic hydrocarbons and tar are formed, there is an intermediate zone within which the decomposition products include a series of more or less saturated hydrocarbons; these, by loss of hydrogen, may be converted into the substances formed at high temperatures.

H. J. E.

**Bromotrinitromethane. III.** E. SCHMIDT and W. BARTHOLOMÉ.—(See i, 136.)

**Synthesis of Methyl Alcohol by Reduction of Carbon Monoxide.** G. PATART (*Compt. rend.*, 1924, 179, 1330—1332).—Gas containing 1 volume of carbon monoxide to 1.5—2 volumes of hydrogen is circulated over zinc oxide at 400—420°/150—250 atm.; the liquid obtained on cooling part of the circuit to 20° consists almost entirely of water and methyl alcohol. [Cf. B., 1925, 83.]

F. M. H.

**Behaviour of Sodium Ethoxide Solutions towards Nitric Oxide.** W. TRAUBE (*Ber.*, 1924, 57, [B], 2063—2065; cf. Stechow, A., 1924, i, 1157).—Nitric oxide does not react with sodium ethoxide solutions so long as they remain undecomposed; reaction occurs as a consequence of the production of ketones derived by auto-decomposition of the ethoxide. The compound  $\text{CH}_2[\text{N}(\text{NO})\cdot\text{ONa}]_2$  is produced almost immediately in alcoholic solutions of sodium ethoxide containing 8—9% of acetone, whereas in the absence of the latter the reaction is not complete until after about a fortnight.

H. W.

**Magnesium Alkoxides and their Application to the Synthesis of Alcohols.** A. TERENTIEV (*Bull. Soc. chim.*, 1924, [iv], 35, 1145—1152).—Magnesium alkoxides may be obtained by passing the vapours of methyl, ethyl, *n*-propyl, isobutyl, or isoamyl alcohol over magnesium at 270—280°; the presence of moisture inhibits the reaction even at 450°, and at high temperatures catalytic decomposition of the alcohol takes place. The

hydrogen escaping contains traces of aldehydes (probably, *e.g.*,  $\text{EtOH} \rightarrow \text{C}_2\text{H}_4\text{O} + \text{H}_2$ ). With ethyl alcohol, the formation of magnesium ethoxide is complete in 1 hour and the temperature is then raised to 400—410° for 2½ to 3 hours, when by the further action of the alcohol vapour on the ethoxide butyl alcohol is produced in yields of 12—18% (cf. Guerbet, A., 1899, i, 472; 1901, i, 625). Similarly, propyl alcohol yields, besides some propylene and propaldehyde, dipropyl alcohol [ $\beta$ -methylpentanol] in 30% yield, identical with the product obtained by Guerbet (A., 1902, i, 130). Magnesium methoxide does not behave in this way; at 440—475°, the alcohol vapour undergoes catalytic decomposition into carbon monoxide and hydrogen, and no trace of ethyl alcohol was detected (cf. Guerbet, A., 1902, i, 583). The magnesium alkoxides are decomposed by water, with regeneration of the original alcohol. Phenol reacts with magnesium at about 300°, forming a phenoxide. More complex products, which have not yet been studied, are formed in all these condensations. R. B.

**Action of Organo-magnesium Compounds on  $\Delta^7$ -Hepten- $\beta$ -one and on its Olefinic Alcohol.** V. GRIGNARD and M. DUBIEN (*Ann. Chim.*, 1924, [x], 2, 282—318).—Organo-magnesium compounds react with  $\Delta^7$ -hepten- $\beta$ -one, yielding olefinic tertiary alcohols (cf. Gry, A., 1908, i, 307); the  $\alpha\delta$ -addition, yielding a saturated ketone, reported by Kohler (A., 1905, i, 207; 1907, i, 1050) was not observed.

*n*-Butaldehyde, on mechanical agitation with acetone, ether, and 12—15% sodium hydroxide, gives 80% of the theoretical yield of  $\delta$ -hydroxyheptan- $\beta$ -one, b. p. 92—94°/12 mm.,  $d_4^{15}$  0.9466,  $n_D^{15}$  1.4368, from which on distillation at atmospheric pressure in the presence of a trace of iodine, 70—75% of the theoretical yield of  $\Delta^7$ -hepten- $\beta$ -one (butylideneacetone), b. p. 61—62°/19 mm.,  $d_4^{10}$  0.8667,  $n_D^{10}$  1.4448, is obtained (on the *n*-butaldehyde). At the same time,  $\gamma$ -hydroxy- $\beta$ -ethylhexaldehyde, b. p. 85—87°/6 mm.,  $d_4^{15}$  0.9466,  $n_D^{15}$  1.4368 (semicarbazone, m. p. 147°), which gradually changes to a solid dimeric form, is probably formed.

Attempts to vary the experimental conditions to obtain  $\delta$ -methylheptan- $\beta$ -one by  $\alpha\delta$ -addition were unsuccessful; the action of magnesium methyl iodide on  $\Delta^7$ -hepten- $\beta$ -one gives in 75% yield,  $\beta$ -methyl- $\Delta^7$ -hepten- $\beta$ -ol, b. p. 62—63°/14 mm.,  $d_4^{10.5}$  0.8398,  $n_D^{10.5}$  1.4416. Similarly, magnesium ethyl bromide gives (yield 65%)  $\gamma$ -methyl- $\Delta^8$ -octen- $\gamma$ -ol, b. p. 74—75°/15 mm.,  $d_4^{12}$  0.8614,  $n_D^{12}$  1.4390; magnesium propyl bromide gives (55% yield)  $\delta$ -methyl- $\Delta^9$ -nonen- $\delta$ -ol, b. p. 87—88°/15 mm.,  $d_4^{10.5}$  0.8422,  $n_D^{10.5}$  1.4424.  $\epsilon$ -Methyl- $\Delta^5$ -decen- $\epsilon$ -ol, b. p. 94—95°/14 mm.,  $d_4^{12.5}$  0.8395,  $n_D^{12.5}$  1.4481 (yield 45%),  $\beta\delta$ -dimethyl- $\Delta^9$ -nonen- $\delta$ -ol, b. p. 91—92°/15 mm.,  $d_4^{10}$  0.8364,  $n_D^{10}$  1.4412, and  $\beta\epsilon$ -dimethyl- $\Delta^5$ -decen- $\epsilon$ -ol, b. p. 82—83°/5 mm. (yield 30%, owing to formation of diisoamyl), are similarly prepared. Magnesium phenyl bromide gives diphenyl, condensation products, and a 20% yield of  $\beta$ -phenyl- $\Delta$ -hepten- $\beta$ -ol, b. p. 115—116°/6 mm.,  $d_4^{10}$  0.9614,  $n_D^{10}$  1.5345, which on distillation even under 12—15 mm., but best at 50 mm., undergoes ketonic decomposition

(cf. Grignard and Escourrou, A., 1923, i, 739) yielding acetophenone and  $\Delta^{\alpha}$ -pentene; under atmospheric pressure, simple dehydration takes place, yielding  $\beta$ -phenyl- $\Delta^{\alpha\gamma}$ -heptadiene, b. p. 246—248°,  $d_4^{15}$  0.9384,  $n_D^{15}$  1.5422, which is also obtained by dehydration with metaphosphoric acid.

$\beta$ -Methyl- $\Delta\gamma$ -hepten- $\beta$ -ol on warming with acetic anhydride or sulphuric acid yields  $\beta$ -methyl- $\Delta^{\alpha\gamma}$ -heptadiene, b. p. 129—131°/745 mm.,  $d_4^{13}$  0.7673,  $n_D^{13}$  1.4605.  $\gamma$ -Methyl- $\Delta^{\delta}$ -octen- $\gamma$ -ol on distillation with a trace of sulphuric acid similarly yields a mixture of  $\gamma$ -methylene- $\Delta^{\delta}$ -octene (20—25%) and  $\gamma$ -methyl- $\Delta^{\beta\delta}$ -octadiene (75—80%), the proportions of which are approximately determined by ozonising the dehydration product and determining the proportions of formaldehyde, acetaldehyde, and butaldehyde produced.  $\delta$ -Methyl- $\Delta^{\gamma\epsilon}$ -nonadiene has b. p. 170—172°/745 mm.,  $d_4^{13}$  0.7873,  $n_D^{13}$  1.4595.  $\epsilon$ -Methyl- $\Delta^{\zeta}$ -decen- $\epsilon$ -ol on warming with metaphosphoric acid yields  $\epsilon$ -methyl- $\Delta^{\delta\zeta}$ -decadiene, b. p. 187—189°/742 mm.,  $d_4^{14}$  0.7858,  $n_D^{14}$  1.4603, probably with some of the isomeride.  $\beta\delta$ -Dimethyl- $\Delta^{\gamma\epsilon}$ -nonadiene, b. p. 181—183°/752 mm.,  $d_4^{14}$  0.7931,  $n_D^{14}$  1.4573, is similarly obtained.

Magnesium ethoxy iodide and *n*-butaldehyde in ether yield chiefly the aldol condensation product,  $\text{Me}[\text{CH}]_2\cdot\text{CH}(\text{OH})\cdot\text{CHEt}\cdot\text{CHO}$ , together with some ethyl and butyl butyrates. With acetone, isohexan- $\delta$ -ol- $\beta$ -one was the only product isolated. Similarly, the magnesium iodo-alkoxide of  $\beta$ -methyl- $\Delta\gamma$ -hepten- $\beta$ -ol reacts with  $\Delta\gamma$ -hepten- $\beta$ -one, giving a compound,

(?)  $\text{Me}[\text{CH}_2]_2\cdot\text{CH}:\text{CH}:\text{CMe}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{CH}:[\text{CH}_2]_2\cdot\text{Me}$ ,  
b. p. 145—147°/15 mm.,  $d_4^0$  0.8833,  $n_D^{10}$  1.4761, identical with that obtained in the preparation of the olefinic alcohols.

Magnesium methyl iodide and  $\delta$ -hydroxyheptan- $\beta$ -one give in 90% yield  $\beta$ -methylheptan- $\beta\delta$ -diol, b. p. 98—99°/5 mm.,  $d_4^{11}$  0.9127,  $n_D^{11}$  1.4405, which on distillation at atmospheric pressure gives a mixture of methylheptadienes and  $\beta$ -methyl- $\Delta^{\beta}$ -hepten- $\delta$ -ol, b. p. 162—163°/750 mm., 61—62°/17 mm.,  $d_4^{16}$  0.8462,  $n_D^{16}$  1.4425, which on oxidation with potassium permanganate yields acetone. The *allophanate* has m. p. 171°.  $\gamma$ -Methyloctane- $\gamma\epsilon$ -diol, b. p. 111—112°/5 mm.,  $d_4^{11}$  0.9174,  $n_D^{11}$  1.4473, similarly prepared, gives  $\gamma$ -methyl- $\Delta\gamma$ -octen- $\epsilon$ -ol (?), b. p. 181—182°/750 mm.,  $d_4^{13}$  0.8530,  $n_D^{13}$  1.4515, together with a mixture of diolefines and their polymerisation products.  $\beta$ -Phenylheptane- $\beta\delta$ -diol, b. p. 151—152°/5 mm.,  $d_4^{11}$  1.021,  $n_D^{11}$  1.5170, is obtained, together with benzene and diphenyl, by the action of magnesium phenyl bromide on  $\delta$ -hydroxyheptan- $\beta$ -one.

R. B.

**Aliphatic Nitro-alcohols. III.** M. TRÉNEL and R. WILKENDORF (*Ber.*, 1924, 57, [B], 2126—2130; cf. A., 1923, i, 288; 1924, i, 362).—Nitrotrihydroxyisobutane is converted by the successive action of potassium hypobromite and bromine into bromopicin, *potassium bromodinitromethane*, and  $\beta$ -bromo- $\beta$ -nitropropane- $\alpha\gamma$ -diol. The latter compound is transformed under similar conditions into the *potassium* salt of  $\beta$ -bromo- $\beta$ -nitroethyl alcohol,  $\text{C}_2\text{H}_2\text{O}_3\text{NBrK}_2\cdot\text{H}_2\text{O}$ , bromopicin, and  $\beta\beta$ -dibromo- $\beta$ -nitroethyl

alcohol, b. p.  $118^{\circ}/16$  mm.  $\beta$ -Chloro- $\beta$ -nitropropane- $\alpha\gamma$ -diol is converted by potassium hypobromite into  $\beta$ -chloro- $\beta$ -bromo- $\beta$ -nitroethyl alcohol, b. p.  $116^{\circ}/15$  mm., and by potassium hypochlorite into a mixture of mono- and di-chloronitroethyl alcohols.  $\beta$ -Bromo- $\beta$ -nitropropane- $\alpha\gamma$ -diol is conveniently prepared by the action of a solution of sodium in ethyl alcohol (94%) on nitromethane and paraformaldehyde and subsequent treatment of the product with bromine followed by the removal of bromopierin with steam.  $\beta$ -Chloro- $\beta$ -nitropropane- $\alpha\gamma$ -diol is prepared similarly. It is transformed by a solution of sodium in ethyl alcohol into the *monohydrated sodium* derivative of chloronitroethyl alcohol, which separates from absolute alcohol with 2 mols. of solvent. H. W.

**General Method for the Preparation of Ethers.** J. B. SENDERENS (*Compt. rend.*, 1924, **179**, 1015—1019; cf. A., 1923, i, 432, 742).—A number of the aliphatic ethers has been prepared by heating the corresponding alcohols with proportions of sulphuric acid carefully adjusted so as to produce that temperature on heating the mixture which is most favourable to the formation of the ether concerned. The volumes of acid given are those required for 100 volumes of the respective alcohols. *n*-Propyl ether, b. p.  $86$ — $88^{\circ}$ , 40 vols. of concentrated sulphuric acid or, better, 60 vols. of  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  at  $125$ — $130^{\circ}$ . *n*-Butyl ether, b. p.  $140$ — $141^{\circ}$ , 20—25 vols. of concentrated sulphuric acid with reflux condenser, or 100 vols. of  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  with ordinary condenser; yield 30%. *iso*Butyl ether, b. p.  $102$ — $106^{\circ}/750$  mm., 20 vols. at  $120$ — $122^{\circ}$ ; above this temperature much butylene is evolved; yield 30%. *iso*Amyl ether, b. p.  $171$ — $172^{\circ}$  (corr.), 60% yield with 10 vols. of acid at  $130$ — $135^{\circ}$ ; 16 vols. of  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  or 20 vols.  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  gives 40% yield. The secondary alcohols require much less sulphuric acid. *iso*Propyl alcohol etherifies badly with concentrated sulphuric acid, but with  $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  or, better,  $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  (volume equal to the alcohol) gives *isopropyl* ether, b. p.  $67$ — $68^{\circ}/750$  mm.,  $d^{17}_4$  0.7282, in 40% yield. *sec*-Butyl ether, b. p.  $120$ — $122^{\circ}/748$  mm.,  $d^{17}_4$  0.761, was obtained in 30% yield. *sec*-*Octyl* ether, b. p.  $263$ — $264^{\circ}/753$  mm.,  $d^{15}_4$  0.807, required only 1—1.5 vols. of concentrated acid; 2 vols. convert it completely into water and octylene; yield 35%. Methods for the separation and purification of the ethers are given. A. C.

**Organic Polysulphides. III. Action of the Disulphides of the Alkali Metals and of Sodium Tetrasulphide on some Organic Halogen Compounds.** J. S. THOMAS and R. W. RIDING (*J. Chem. Soc.*, 1924, **125**, 2460—2468; cf. this vol., i, 4).—The interaction of the disulphides of the alkali metals with organic halides in ether gives rise to organic disulphides. In aqueous media, however, a sodium polysulphide solution containing sufficient sulphur to form the disulphide reacts with allyl iodide, forming diallyl pentasulphide tetraiodide. Sodium tetrasulphide and organic halides interact, forming a mixture of organic di- and penta-sulphides, the latter preponderating. Diethyl

disulphide, allyl iodide, and mercuric oxide give the compound  $\text{Et}_2\text{S}_2\cdot\text{C}_3\text{H}_5\cdot\text{I}\cdot\text{HgI}_2$ , m. p.  $94\cdot6^\circ$  (decomp.). A substance,  $\text{C}_6\text{H}_{12}\text{O}_2\text{Cl}_2\text{S}_2\text{Hg}_2$ , was prepared from diallyl disulphide and mercuric chloride.

Evidence is produced for the X·S·S·X structure of the disulphides of the alkali metals (cf. Thomas and Rule, T., 1917, **111**, 1063).

L. F. H.

**Preparation of Ethyl Acetate and Ethyl Acetoacetate.** K. G. ROBERTS (*J. Soc. Chem. Ind.*, 1924, **43**, 295—297r).—Ethyl acetate of high purity is best obtained by heating equimolecular proportions of absolute alcohol and glacial acetic acid under a reflux condenser with 0·1 part of sulphuric acid for 10 minutes and then distilling from an oil-bath at  $130^\circ$ . Purified from alcohol by shaking with water and fractionation, and dehydrated over potassium carbonate, the ester is finally heated with phosphoric oxide and fractionated. The best yields of ethyl acetoacetate resulted from the pure ethyl acetate condensed by means of perfectly clean sodium and 5% of absolute alcohol. Factors to be guarded against are traces of water or of sodium hydroxide in the reaction mixture. B. W. A.

**Glycerides of Cacao Fats.** K. AMBERGER and J. BAUCH (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 371—390).—The fatty acids of unhardened cacao fat consist of 43—45% of oleic acid, 23—25% of palmitic acid, and 31—33% of stearic acid; in the hardened condition, 22·7% of palmitic acid and 77% of stearic acid are present. The glycerides of the unhardened fat comprise about 55% of glyceryl  $\alpha$ -palmitate  $\beta\gamma$ -dioleate, 20% of glyceryl  $\beta$ -palmitate  $\alpha\gamma$ -distearate, 25% of glyceryl  $\alpha\beta$ -distearate- $\gamma$ -oleate, and small quantities of tristearin and glyceryl  $\beta$ -palmitate  $\alpha\gamma$ -distearate. The hardened fat contained 25% of tristearin, 20% of glyceryl  $\beta$ -palmitate  $\alpha\gamma$ -distearate, and 55% of glyceryl  $\alpha$ -palmitate  $\beta\gamma$ -distearate.

G. S. W.

**Higher Fatty Acids. Eicosanoic and Stearic Acids.** G. T. MORGAN and A. R. BOWEN (*J. Soc. Chem. Ind.*, 1924, **43**, 346—348).—Hydrolysis of cacao butter cannot be used as a method for obtaining eicosanoic acid, no acid higher than stearic acid being isolated. The graph showing the relationship between m. p. and composition of mixtures of stearic and eicosanoic acids indicates the formation of a compound,  $\text{C}_{18}\text{H}_{36}\text{O}_2\cdot\text{C}_{20}\text{H}_{40}\text{O}_2$ . Mixtures of 50% of each acid are inseparable by fractional crystallisation. I. E. B.

**Catalysis of Linseed Oil Oxidation.** I. P. SLANSKY (*Chem. Umschau*, 1924, **31**, 277—280).—Various substances such as calcium carbonate, calcium sulphate, and barium sulphate, insoluble in cold linseed oil, considerably accelerate the "drying" of the oil when incorporated with it to form a paste, and a more marked acceleration is produced under these conditions by compounds of lead, manganese, and cobalt, insoluble in cold linseed oil. The catalytic activity of these substances is greater the finer their state of division. Substances such as graphite, carbon-black, and various organic dyes which inhibit the drying of linseed oil similarly show



a greater effect when more finely divided. These effects are due to surface adsorption, and no sharp distinction can be drawn between these heterogeneous catalysts and the homogeneous (micro-heterogeneous) catalysts such as the colloiddally soluble driers. Doubt is thrown on the theories of the production of intermediate chemical compounds between the catalyst and the reacting substances.

P. M.

**Catalysis of Linseed Oil Oxidation. II. Theory of the Mechanism of Catalysis.** P. SLANSKY (*Chem. Umschau*, 1924, **31**, 281—282).—Oxides and carbonates of metals such as lead and calcium have a far stronger accelerating effect on the drying of linseed oil than have the sulphates of these metals. These basic substances have some affinity for the unsaturated carboxyl group and this is held to accelerate the oxidation of the oil according to a development of the views of Harkins and Langmuir on the polar distribution of the molecules at a liquid surface. According to these views, the more reactive unsaturated carbon chains of the oil molecule would be directed towards the interior of the liquid, while the less reactive glyceride group would be directed towards the surface. The basic catalysts adsorb the molecules of the oil by virtue of their affinity for the carboxyl groups of the glyceride end of the molecule, which therefore becomes directed inwards, leaving the unsaturated carbon chains outwards so that they now more readily undergo oxidation. Conversely, "carbophilic" substances such as graphite and lampblack adsorb the oil by attraction of the unsaturated carbon chains, so that these become directed inwards with consequent inhibition of their rate of oxidation.

P. M.

**Hydrolysis of Esters of Ketonic Acids.** A. SKRABAL, F. PFAFF, and H. AIROLDI.—(See ii, 139.)

**$\alpha$ -Alkyl-lævulic Acids.** H. GAULT and T. SALOMON (*Ann. Chim.*, 1924, [x], **2**, 133—209).—A republication in greater detail of work previously abstracted (A., 1922, i, 427, 873). The general conclusion is reached that complete hydrolysis of alkylacetonyl-malonic esters increases in difficulty with rise in the weight of the substituting alkyl group by reason of the steric effects thus produced.

H. J. E.

**Rate of Hydrolysis of Ethyl Orthocarbonate.** A. SKRABAL and M. BALTADSCHEWA.—(See ii, 139.)

**Optical Superposition. VI. Methyl-*n*-hexylcarbinyl Dimethoxysuccinates.** T. S. PATTERSON and C. BUCHANAN (*J. Chem. Soc.*, 1924, **125**, 2579—2590; cf. T., 1907, **91**, 705; 1915, **107**, 142; A., 1924, i, 1041).—In the case of the *l*-octyl dimethoxysuccinates, the rotatory power of the *i*-form is not identical with the mean of the rotatory powers of the esters of the *d*- and *l*-acids, in contradiction to the principle of optical superposition. The divergence from the principle of the substances described in this paper is, however, small. The assumption by Hudson (A., 1917, i, 445) of the integrity of the principle is criticised.

l-sec.-Octyl d-dimethoxysuccinate, b. p.  $196^{\circ}/4$  mm.,  $d_4^{20}$  0.9794,  $[\alpha]_{5461}^{20} + 48.27^{\circ}$ , l-sec.-octyl l-dimethoxysuccinate, b. p.  $190^{\circ}/4$  mm. ca.,  $d_4^{20}$  0.9764,  $[\alpha]_{5461}^{20} - 77.50^{\circ}$ , and l-sec.-octyl i-dimethoxysuccinate, b. p.  $199-201^{\circ}/4$  mm.,  $d_4^{20}$  0.9775,  $[\alpha]_{5461}^{20} - 14.17^{\circ}$ , are described, together with the rotatory powers under different conditions of temperature and solution. d-sec.-Octyl d-dimethoxysuccinate, b. p.  $202^{\circ}/5$  mm.,  $[\alpha]_{5461}^{15} + 77.11^{\circ}$  (in alcohol), d-sec.-octyl l-dimethoxysuccinate, b. p.  $194^{\circ}/4$  mm., and d-sec.-octyl i-dimethoxysuccinate, b. p.  $202^{\circ}/5$  mm., are also described. L. F. H.

**Derivatives of Tetra-acetylmucic Acid.** L. J. SIMON and A. J. A. GUILLAUMIN (*Compt. rend.*, 1924, 179, 1324—1326; cf. Maquenne, A., 1888, 676; Skraup, A., 1894, i, 15).—Tetra-acetylmucic acid, m. p.  $258^{\circ}$  or  $276^{\circ}$ , is converted by water into acetic acid and mucolactone, but may be rapidly recrystallised. Its potassium (+8H<sub>2</sub>O), barium, ammonium, and hydroxylamine salts were isolated; it is completely hydrolysed on warming with alkali hydroxide. The action of hydrochloric acid on its methyl-alcoholic solution gives methyl mucate, which with acetic anhydride and zinc chloride yields methyl tetra-acetylmucate, m. p.  $197^{\circ}$ , b. p.  $250^{\circ}/1$  mm., whence the amide and anilide may be prepared. A trace of sulphuric acid causes reaction of thionyl chloride with solution of tetra-acetylmucic acid in acetyl chloride and the acid chloride so obtained shows remarkable stability towards boiling water but with alcohols forms the corresponding esters. F. M. H.

**Vapour Pressure and Chemical Constant of Formaldehyde.** S. MALI and J. GHOSH (*J. Indian Chem. Soc.*, 1924, 1, 37—43).—Liquid formaldehyde can be preserved unchanged at temperatures below  $-30^{\circ}$  if dried by means of phosphoric oxide. The results of determinations of vapour pressure are given by  $\log p = -6500/4.6T + 1.75 \log T - 0.035T/4.6 + 3.3$ , where  $\lambda_0 = 6500$  cal. and the chemical constant is 3.3. The liquid has b. p.  $-21^{\circ}$  and  $\lambda$  is calculated as 5160 cal., whence  $\lambda/T$  is 20.5 units. G. M. B.

**Condensation of Formaldehyde. I. Condensation with Magnesium Oxide.** H. SCHMALFUSS and K. KALLE (*Ber.*, 1924, 57, [B], 2101—2104).—Formaldehyde undergoes condensation with remarkable ease when heated under 2 atm. pressure in aqueous solution in the presence of magnesium oxide. The primary change, consisting in the formation of methyl alcohol and formic acid, is complete as soon as the magnesium oxide is dissolved and the solution is neutral. Somewhat later, the formation of sugars commences and is complete within a few minutes. Finally, the sugars become converted into an acid and a coloured compound. The latter substances are produced independently of one another. If formaldehyde is in excess, the acid is formed, but not the coloured compound, the production of which is a certain indication that the formaldehyde has been utilised completely. The sugars contain dihydroxyacetone and a pentose; aldoses do not appear to be formed. H. W.

**Autoxidation and Anti-oxygenic Action. XII. Active Autoxidisable Form of Acraldehyde.** C. MOUREU, C. DUFRAISSE, and M. BADOCHÉ (*Compt. rend.*, 1924, 179, 1229—1235; cf. A., 1924, i, 635; ii, 602).—The results are given of experiments made to test the authors' theory, according to which anti-oxygens hinder the autoxidation of an autoxidisable substance, by converting the active form into the ordinary form.

Besides the ability to unite directly with free oxygen, the active form of acraldehyde exhibits also the capacity to undergo condensation to an insoluble resin, disacryl, this change commencing only when the oxidation of the aldehyde is complete. It has been shown previously that quinol retards the autoxidation of acraldehyde, and it is now found that the same compound retards also the condensation of the aldehyde to disacryl, even when such condensation is effected apart from autoxidation. It is, therefore, possible that quinol exerts a de-activating action on acraldehyde, but this action cannot be of sufficient intensity to explain the anti-oxygenic action.

The light of the visible spectrum appears to exert either no effect or but a very slight one on acraldehyde molecules, the activation of the aldehyde being due either to internal causes or to radiations outside the visible spectrum.

T. H. P.

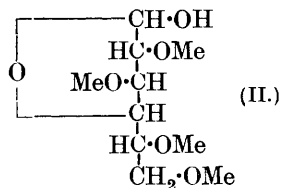
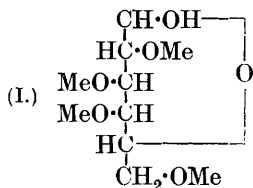
**Aluminium Amalgam as a Reducing Agent in the Sugar Series.** D. R. NANJÍ and F. J. PATON (*J. Chem. Soc.*, 1924, 125, 2474—2476).—In neutral solution aluminium amalgam is almost without action on sugars, but in the presence of a trace of ammonia dextrose, mannose, and galactose are reduced to the extent of 80—95% and the corresponding alcohols may be isolated in a yield of 55% of the sugar employed. The catalytic effect of the ammonia is attributed to the formation of compounds of the aldehyde-ammonia type. The reduction of the disaccharides, lactose and maltose, proceeds less satisfactorily, presumably owing to hydrolysis.

L. F. H.

**Amylene- and Butylene-oxidic Forms of Tetramethylgalactose.** W. N. HAWORTH, D. A. RUELL, and G. C. WESTGARTH (*J. Chem. Soc.*, 1924, 125, 2468—2474).—Pryde (T., 1923, 123, 1808) has provided evidence to show that the usual form of tetramethylgalactose has the amylene-oxide structure (I). In the course of his work, however, a tetramethylgalactose was employed which must have contained structural isomerides. The work has been repeated using a specimen of the sugar stated to be free from isomerides. The same conclusion as that of Pryde has been reached, there being too small an amount of impurity in his specimens to invalidate the results.

A new form of *methylgalactoside* has been isolated and converted into the corresponding *tetramethylmethylgalactoside*, b. p. 112°/0.015 mm.,  $n_D$  1.4405,  $[\alpha]_D$  -45.2° in water, from which a *tetramethylgalactose*, b. p. 136°/0.05 mm.,  $n_D$  1.4540,  $[\alpha]_D$  -21.2° in water, was obtained. This sugar is probably 2 : 3 : 5 : 6-tetramethylgalactose (II) since, on oxidation, it yields the 2 : 3 : 5 : 6-tetramethylgalac-  
f\*

tonolactone described by Pryde (*loc. cit.*). It therefore probably has the butylene-oxide structure ( $\gamma$ -form), a conclusion which is confirmed by its instability towards permanganate. On the basis of these results it is suggested that former claims to have isolated tetramethyl- $\gamma$ -galactose (Cunningham, T., 1918, **113**, 596) should be revised. The formation of octamethyldigalactose from tetramethyl- $\gamma$ -galactose (Cunningham, *loc. cit.*) is also called in question.



L. F. H.

**Cellulose.** K. HESS (*Z. angew. Chem.*, 1924, **37**, 993—1003).—From the optical activity and mass-action relationships it has been shown (A., 1924, i, 142) that in cuprammonium solution the cellulose molecule reacts in its simplest chemical-structural form,  $\text{C}_6\text{H}_{10}\text{O}_5$ . Celluloses of all origins, whatever their degree of solubility or dispersity, are substantially identical in cuprammonium solution with normal cotton cellulose. Further, the Röntgen diagram shows that the cellulose regenerated from cuprammonium solution is identical with the original cotton; no chemical change is detected. Hydrocellulose has been resolved into a mixture of structurally intact cellulose with cupric-reducing cellulodextrins. Hydrocellulose prepared by the method of Knoevenagel and Busch (A., 1922, i, 636), also the cellulose regenerated by hydrolysis of certain types of cellulose acetate, are completely soluble in 8% sodium hydroxide solution. These solutions can be fractionated by precipitation with ammonia and the resulting celluloses are structurally intact when examined in cuprammonium solution, identical with cotton cellulose but retaining each its own specific solubility or degree of dispersion. Cellulose of this type has been described as "cellulose A" (*loc. cit.*); it can be prepared directly by Knoevenagel and Busch's method by working at sufficiently low temperatures. A series of different cellulose acetates of various degrees of solubility has been examined; these all yield intact cellulose after hydrolysis, differing somewhat in solubility in 8% sodium hydroxide. Cellulose triacetate has been prepared as large, well-defined crystals from solutions in tetrachloroethane or tetrachloroethylene, the colloid presumably crystallising in combination with the solvent. By the optical method, in cuprammonium solution it has been shown that lichenin is not identical with cellulose. [Cf. Karrer, A., 1924, i, 373, 501.]

J. F. B.

**Reserve Cellulose and Cellulose.** P. KARRER (*Z. angew. Chem.*, 1924, **37**, 1003—1007).—Lichenase (cf. A., 1923, i, 1182) is a mixture of enzymes, the true lichenase being always accompanied by cellobiase and gentiobiase. The various components are affected

differently on storage or by diffusion, the cellobiase disappearing first. The rapidity of saccharification depends essentially on the preparation of the substrate in a highly dispersed condition. The unit of lichenase is defined as the quantity of enzyme in 0.1 g. of dry material which at 37° in a medium having an acidity of  $p_H$  5.28 will saccharify 1 g. of lichenin to the extent of 20% in 2 hours. Within the limits of 10–40% conversion the quantity of lichenin saccharified is proportional to the square root of the enzyme concentration. Two kg. of green malt contain lichenase equivalent to the product obtained from 35–40 snails (about 95 units); germinated oats and maize contain only  $\frac{1}{3}$ – $\frac{1}{4}$  of this amount. Cotton cellulose precipitated from cuprammonium solution is saccharifiable by lichenase to the extent of 50%; by repeating the process of solution, precipitation, and digestion with the enzyme the whole of the cellulose may ultimately be converted into dextrose. Thus it appears that to a certain extent the resistance of the permanent celluloses as compared with the reserve celluloses depends on the compactness of the micellar structure which is resolved on dispersion.

J. F. B.

**Absorption of Sodium Hydroxide by Cellulose from Solutions.** W. VIEWEG (*Z. angew. Chem.*, 1924, **37**, 1008–1010).

—The absorption curve of sodium hydroxide from aqueous solutions by cellulose shows the formation of a compound,  $(C_6H_{10}O_5)_2NaOH$ , in solutions containing from 16 to 35 g. of sodium hydroxide per 100 c.c.: there are indications of another compound,  $C_6H_{10}O_5NaOH$ , at concentrations above 40 g. per 100 c.c. The experimental evidence has been repeated in consequence of contrary statements by Rassow and Wadewitz (*A.*, 1924, i, 374), whose conclusions are shown to be based on analytical errors.

J. F. B.

**Alkali-cellulose.** E. HEUSER (*Z. angew. Chem.*, 1924, **37**, 1010–1013).—The conclusions of Vieweg (preceding abstract) are confirmed and the evidence of the formation of a compound,  $(C_6H_{10}O_5)_2NaOH$ , in solutions of sodium hydroxide between 16 and 24% concentration by weight is definite. At higher concentrations, the alkali-cellulose seems to attract sodium hydroxide by adsorption, and the quantity is influenced by working at higher temperatures. Additional confirmation of the chemical combination between cellulose and sodium hydroxide is afforded by the establishment of similar relations with other alkali hydroxides. Lithium, sodium, and potassium hydroxides all show absorption curves with a characteristic flattening corresponding with the molecular ratios  $(C_6H_{10}O_5)_2 : M'OH$ . This region is obtained with solutions of lithium hydroxide at 9–11%, sodium hydroxide at 16–24%, and potassium hydroxide at 25–35%. Cæsium hydroxide differs from the other alkalis in that the curves indicate a combination in the ratio  $(C_6H_{10}O_5)_3 : CsOH$  in liquors containing 45–60% of cæsium hydroxide.

J. F. B.

**Relations between Age of Cellulose and the Properties of Nitrocellulose prepared from it.** L. MEUNIER and A. BREGUET (*Rev. gén. Colloid.*, 1924, **2**, 289–294).—Preparations were made

by dissection of the stem of the common poplar representing four different periods of growth of the same tree; these were separately converted into cellulose by digestion with sodium hydroxide. The region of the heart gave the lowest yield of cellulose and the peripheral region consisting of wood of not more than 8 years' growth came next. The highest yield was obtained from the wood of 8 to 24 years. The copper value of the purified cellulose decreased regularly from the heart to the periphery, and the content of  $\alpha$ -cellulose increased in the same order. In general it was observed that the older portions of the wood yielded a weaker cellulose and one more easily swollen by water than the younger portions, the cellulose of which could be regarded as more resistant and more highly polymerised. These four celluloses were nitrated under similar conditions, giving nitrates containing from 10.5 to 10.9% of nitrogen, and the relative viscosities of the acetone solutions of the products were ranged in a series of increasing values from the centre outwards as follows: 128; 201; 248; 697. J. F. B.

**Nitrates of Oxycelluloses, Hydrocelluloses, and Cellulose Hydrates.** K. ATSUKI (*J. Fac. Engin. Imp. Univ. Tokyo*, 1924, 15, 55—108).—The degree of chemical modification of the cellulose portion of a cellulose nitrate may be determined by the copper value of the regenerated cellulose. Hydrolysis without secondary changes is effected by digesting for 6—10 hours at 25—30° with 100 parts of a 16% solution of ammonium hydrosulphide. The copper value of the purified regenerated cellulose is always higher than that of the original, the difference being due to the unavoidable hydrolysis taking place during nitration. This difference is greater the higher the percentage of water in the nitrating acid and the greater the divergence of the proportions of the two acids from the ratio 1 : 1 by weight. The nitration of oxycelluloses of increasing degrees of oxidation yields a series of products in which the yield and percentage of nitrogen decrease, the solubility in 10% camphor-alcohol increases, and the viscosity in acetone decreases in proportion as the copper value of the original oxycellulose rises. When, however, this value reaches about 10 a sudden deterioration in all the characters of the nitrate is observed and it is inferred that this point represents a definite rupture of the cellulose nucleus, beyond which the copper value ceases to be a true measure of the degree of chemical modification. Nitrates of oxycellulose, as distinguished from those of normal cellulose, are susceptible to decomposition by boiling with 2% sodium sulphite solution and a certain degree of fractional separation may be carried out by this reagent. Mercerised cotton differs from normal cotton by the more profound hydrolysis induced by the nitrating acid, the lower viscosity of its nitrates, and the higher copper value of the regenerated cellulose. J. F. B.

**Primary  $\beta$ -Amino-alcohols having the General Formula  $R\cdot CH(NH_2)\cdot CR'R''\cdot CH_2\cdot OH$ .** P. BILLON (*Compt. rend.*, 1924, 179, 1054—1056).— $\gamma$ -Amino- $\beta\beta$ -diethylbutan- $\alpha$ -ol, b. p. 132°/22 mm. (hydrochloride, m. p. 115°), has been prepared by reducing the oxime (cf. Betti, A., 1898, i, 649) of ethyl  $\alpha\alpha$ -diethylacetoacetate

with sodium in absolute alcohol. The *benzoyl* derivative of the hydrochloride has m. p. 180°. A. C.

**Synthesis of certain Dipeptides of Complex Natural Amino-acids.** L. HAVESTADT and R. FRICKE.—(See i, 162.)

**Preparation of Ethyl Cyanoacetate.** O. C. STEPHENS (*J. Soc. Chem. Ind.*, 1924, **43**, 313—314t; 327—328t).—The usual method of preparing ethyl cyanoacetate from chloroacetic acid, although giving an 85% yield, involves the laborious separation of cyanoacetic acid. It was found that: (a) by preparing ethyl chloroacetate from trichloroethylene (cf. Imbert, A., 1909, i, 453, 694, 873), and thence forming ethyl cyanoacetate, yields of 48% were obtained; the process is simple and economical; (b) by esterifying chloroacetic acid, and then transforming the ethyl chloroacetate into ethyl cyanoacetate, the yield is 35%; (c) preparing cyanoacetic acid from chloroacetic acid and esterifying without isolation of the acid, yields, under favourable conditions, 60% of ethyl cyanoacetate and some ethyl malonate. B. W. A.

**Synthesis of Carbamide from Carbon Dioxide and Ammonia under Atmospheric Pressure.** I. K. C. BAILEY (*Sci. Proc. Roy. Dublin Soc.*, 1924, **18**, [1—4], 23—28).—A mixture of carbon dioxide and ammonia was passed, at atmospheric pressure, through the annular space between a water-cooled glass tube and an outer quartz tube, heated at 500° and above in an electric furnace. Carbamide and ammonium cyanate were deposited on the cold tube. The best results were obtained by using the gases in the ratio of 1 vol. of ammonia to 4 vols. of carbon dioxide. The yield of carbamide increases with the temperature up to about 700°, and is improved by the use of catalysts such as aluminium oxide or thorium oxide. In one instance, a yield of 25% (on ammonia) of carbamide was obtained. By again passing the exhaust gases, together with the vapour of the ammonium salts which had been deposited on the portions of the tube outside the furnace, through the apparatus, a yield of about 50% was obtained. C. J. S.

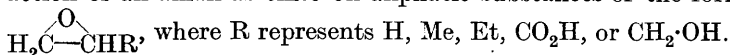
**Interaction of Sulphur Monochloride with Organic Acid Amides.** II. K. G. NAIK and C. S. PATEL (*J. Indian Chem. Soc.*, 1924, **1**, 27—35; cf. T., 1921, **119**, 1166).—The type of product obtained from sulphur monochloride and an acid amide depends on the strength of the acid residue of the latter. *s*-*Di*hexoylhydrazine ( $C_5H_{11}CO)_2N_2H_2$ , m. p. 111—112°, from sulphur monochloride and hexoamide, is reconverted into the latter by reduction. *s*-*Di*valerylhydrazine,  $(C_4H_9CO)_2N_2H_2$ , m. p. 123°, and *s*-*di*isobutyrylhydrazine, m. p. 120—121°, are described. Chloroacetamide gives the compound  $(CH_2ClCO\cdot NH)_2S$ , m. p. 165° (decomp.). The following substances are described: *s*-hexachlorodiacylhydrazine,  $(CCl_3CO)_2N_2H_2$ , m. p. 148—149°, from trichloroacetamide; cyanoacetamide C-disulphide,  $[CN\cdot CH(CO\cdot NH_2)]_2S_2$ , m. p. 103° (decomp.), from cyanoacetamide; *s*-*di*(isobutyramidophenyl) disulphide,  $(CHMe_2CO\cdot NH\cdot C_6H_4)_2S_2$ , m. p. 100—102° (decomp.), from isobutyranilide; *s*-*di*(phenylacetamidophenyl) disulphide,

$(\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4)_2\text{S}_2$ , m. p. 162—163°, from phenylacetanilide, which yielded, on nitration, a *tetranitro* derivative, m. p. 148—150°; *s-di(acetoxymethylanilidophenyl) trisulphide*,  
 $[\text{NHPh}\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OAc})]_2\text{S}_3$ ,  
 m. p. 78° (decomp.), from acetylsalicylanilide. G. M. B.

**Hydroferrocyanides and Hydroferricyanides of Organic Bases.** IV. W. M. CUMMING (*J. Chem. Soc.*, 1924, **125**, 2541—2542; cf. T., 1922, **121**, 1287; 1923, **123**, 2457; A., 1924, i, 778).—A description is given of the *hydroferrocyanides* of mono- and di-methylaniline, *p*-bromodimethylaniline, *p*-nitrosodimethylaniline, and *o*-dianisidine, and of the *hydroferricyanides* of aniline, *o*-, *m*-, and *p*-toluidine, *o*- and *m*-phenylenediamine, mono- and di-methylaniline, *p*-bromodimethylaniline, *p*-nitrosodimethylaniline, pyridine, quinoline, *isoquinoline*,  $\beta$ -naphthylamine, piperazine, piperidine, benzylamine, hexamethylenetetramine, *o*-anisidine, *p*-xylydine, and dimethylaminoazobenzene. The *hydroferricyanides* of hydrazobenzene and *o*-hydrazotoluene have been prepared.

Certain isomerides (*o*- and *p*-toluidine, quinoline and *isoquinoline*) may be separated by means of the different solubilities of their hydroferricyanides. L. F. H.

**Preparation of Hydroxylated Aliphatic Arsinic Acids.** LES ETABLISSEMENTS POULENC FRÈRES and C. OECHSLIN (Brit. Pat. 206152; cf. A., 1923, i, 906).—The former patent is extended to the action of an alkali arsenite on aliphatic substances of the formula



W. T. K. B.

### Irreversible Catalysis of Unsaturated Cyclic Hydrocarbons.

II. N. D. ZELINSKI (*Ber.*, 1924, **57**, [B], 2055—2057; cf. A., 1923, i, 767).—*cyclo*Hexene is quantitatively and rapidly decomposed by palladised asbestos at temperatures below 164·5° into benzene (1 mol.) and *cyclo*hexane (2 mols.); the catalysis is irreversible since *cyclo*hexene cannot be produced from benzene and *cyclo*hexane under similar conditions. The three methyl*cyclo*hexenes and methylenecyclohexane are decomposed similarly into toluene and hexahydrotoluene at 116—118°. H. W.

**Octahydroindene and its Behaviour towards Catalytic Dehydrogenation.** N. D. ZELINSKI and P. BORISSOV (*Ber.*, 1924, **57**, [B], 2060—2061).—Octahydroindene, b. p. 163·5—164·5°/765 mm.,  $d_4^{15\cdot5}$  0·8790,  $n_D^{15\cdot5}$  1·4711 (cf. Eykman, A., 1904, i, 25), is quantitatively prepared by the catalytic hydrogenation of indene in the presence of palladised asbestos (30%). As expected from a substance containing the hexamethylene and pentamethylene rings, it is dehydrogenated by the same catalyst at 300—305° into *tetrahydroindene*,  $\begin{array}{c} \text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2 \\ \text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_2 \end{array} > \text{CH}_2$ , b. p. 171—172°/757 mm.,  $d_4^{16\cdot5}$  0·9274,  $n_D^{16\cdot5}$  1·5153. A similar dehydrogenation is effected under like conditions by nickelised aluminium oxide, which, at a



slightly higher temperature (320—325°), also causes rupture of the pentamethylene ring and formation of benzene, toluene, and (?) xylene.  
H. W.

**Isomerisation of Decahydronaphthalene.** N. D. ZELINSKI [with M. GAVEDOVSKAJA] (*Ber.*, 1924, **57**, [B], 2062—2063).—Chlorination of decahydronaphthalene under conditions which will be fully described subsequently yields *chlorodecahydronaphthalene* (chloronaphthane), b. p. 114—116°/20 mm.,  $d_4^{21.5}$  1.0588,  $n_D^{21.5}$  1.5121, which is only partly converted by alcoholic potassium hydroxide solution into *octahydronaphthalene*, b. p. 195—196°,  $d_4^{23}$  0.9134,  $n_D^{23}$  1.4965. The chlorodecahydronaphthalene, which is unattacked by alkali hydroxide, is transformed by fuming hydriodic acid at 250° into a *decahydronaphthalene*, b. p. 185—187°/743 mm.,  $d_4^{22}$  0.8681,  $n_D^{23}$  1.4687, which is not identical with the *cis*- or *trans*-decahydronaphthalene described by Eisenlohr and Polenske (*A.*, 1924, i, 1291).  
H. W.

**Mechanism of Substitution Reactions in the Aromatic Nucleus.** E. DE B. BARNETT and J. W. COOK (*Rec. trav. chim.*, 1924, **43**, 897—898).—According to the Dewar formula of benzene (T., 1922, **121**, 1133, 1143; 1923, **123**, 2081; cf. T., 1905, **87**, 1347), the contention of Prins (this vol., i, 18) that substitution in the aromatic nucleus cannot be preceded by the formation of an additive compound is without foundation. On that basis, the additive compound would more probably revert to the aromatic state than undergo further addition. In some cases, however, substitution may take an entirely different course: the substituent may first enter a side-chain and then migrate to the nucleus. W. E. E.

**New Process of Nitration with the Aid of Nitrogen Oxides from the Air or Ammonia.** I. A. SCHAARSCHMIDT (*Ber.*, 1924, **57**, [B], 2065—2072).—Aromatic compounds react readily with nitrogen peroxide in the presence of aluminium chloride, forming *complexes* of the type  $2AlCl_3 \cdot 3PhCl \cdot 3N_2O_4$ , which are very sensitive to water, but otherwise comparatively stable. The nitrogen peroxide may be used in the liquid form or as the mixture obtained from air or by the combustion of ammonia, provided that, in the latter case, the water formed simultaneously is carefully removed. The most suitable molecular proportions of aluminium chloride, benzenoid compound, and nitrogen peroxide are 0.66 : 3 : 1. The complex appears to be saturated, since it does not react with bromine or chlorine or add a second  $N_2O_4$  group. The action of aluminium chloride is influenced by temperature and the nature of the benzenoid compound. With chlorobenzene, the process, when started, proceeds in a uniform manner at the atmospheric temperature. Below 10°, benzene, aluminium chloride, and nitrogen peroxide yield an additive compound which requires to be gently warmed before the desired reaction takes place, whereas this occurs with chlorobenzene at -35°. Ferric chloride acts more slowly, but more nearly quantitatively. With toluene, complications occur because of the oxidising action of nitrogen peroxide on the methyl

group. The complex compounds are decomposed by withdrawal of the metallic chloride by means of water. The resulting additive compound of nitrogen peroxide and benzene is, as a derivative of dihydrobenzene, unstable and its decomposition into nitrobenzene and nitrous acid cannot be prevented by cooling. The nitrated product remains dissolved in the excess of benzenoid compound; it consists almost exclusively of the mononitro derivative, the proportion of saponifiable by-products being negligibly small. The aqueous solution contains aluminium chloride and nitrous acid, which decomposes into nitric acid and pure nitric oxide; the latter, after treatment with oxygen or air, is used for further charges. Subsequent treatment of the aqueous solution with ammonia yields pure aluminium or ferric hydroxide, ammonium nitrate, and ammonium chloride.

Chlorobenzene gives a mixture of *p*- and *o*-chloronitrobenzenes in the ratio 77 : 23, the high proportion of the former allowing 86% of it to be isolated by expression. The ratio is very little affected by variation in temperature.

H. W.

**Arylamine Salts of some Sulphonic Acids of the Benzene Series. I. Benzenemonosulphonic Acid.** C. M. KEYWORTH

(*J. Soc. Chem. Ind.*, 1924, **43**, 341—342T).—The arylamine salts of benzene- and toluene-sulphonic acids are useful for the identification of these sulphonic acids and of small quantities of amines. They have definite melting points and crystallise well. The *N*-substituted arylamines do not readily form salts with the above acids, and the basic salts of diamines were not obtained pure. *m*-Nitro-*p*-toluidine and  $\beta$ -aminoanthraquinone failed to form salts. The following salts of benzenesulphonic acid are described: *aniline*, m. p. 240°; *o*-toluidine, m. p. 176°; *m*-toluidine, m. p. 173°; *p*-toluidine, m. p. 205°;  $\alpha$ -naphthylamine, m. p. 234°;  $\beta$ -naphthylamine, m. p. 248°; *p*-nitro-*o*-toluidine, m. p. 222°; *m*-nitroaniline, m. p. 236°; *m*-xylidine, m. p. 233°; *benzidine*, m. p. above 300°; *o*-toluidine, m. p. 310°; *dianisidine*, m. p. 277°; *m*-phenylenediamine, m. p. above 320°; *p*-phenylenediamine, m. p. above 320°; *p*-chloroaniline, m. p. 235°; *o*-chloroaniline, m. p. 204°;  $\psi$ -cumidine, m. p. 217°; *p*-anisidine, m. p. 182°; *p*-phenetidine, m. p. 171°. The approximate solubility of each salt is given.

I. E. B.

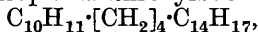
**Extraction of the Isomeric Xylenes from Crude "Xylol."**

T. S. PATTERSON, A. McMILLAN, and R. SOMERVILLE (*J. Chem. Soc.*, 1924, **125**, 2488—2490; cf. A., 1923, i, 451).—Coke-oven xylene (b. p. 137—141°) was shaken with sulphuric acid (*d* 1.84), and *m*-xylene-4-sulphonic acid together with a little *o*-xylene-4-sulphonic acid was formed in the acid layer. Dilution with water precipitated the acids, which when decomposed with superheated steam yielded *m*-xylene, m. p. —45.5°. The mixed *o*- and *m*-xylene-4-sulphonic acids were separated by fractional crystallisation of their calcium salts from water; the solubility of calcium *o*-xylene-4-sulphonate in water increases but that of calcium *m*-xylene-4-sulphonate decreases with rise of temperature. *m*-Xylene-4-sulphonic acid, purified by crystallisation from chloroform, has

m. p. 61—62°, and when decomposed by steam gives chemically pure *m*-xylene, m. p. —53° (corr.). *o*-Xylene-4-sulphonic acid, hygroscopic, has m. p. 63—64°. P. C.

**Chemistry of Syntheses and Degradations by Means of Aluminium Chloride.** G. SCHROETER [with E. VAN HULLE, A. GLUSCHKE, G. STIER, and H. MÜLLER] (*Ber.*, 1924, **57**, [B], 1990—2003).—Technical tetrahydronaphthalene, after purification with sodium hydrogen sulphite, is treated with a small proportion of aluminium chloride during 6—10 hours at 50—70°. The product is fractionally distilled, whereby, in addition to benzene and tetrahydronaphthalene, the following substances are obtained: (i) a hydrocarbon, probably a *perhydroanthracene*,  $C_{14}H_{24}$ , b. p. 128°/11 mm., m. p. 93°, which is indifferent towards bromine, nitric acid, sulphuric acid, or permanganate; (ii) *s*-octahydroanthracene, m. p. 73—74°, b. p. 293—295°/760 mm., 167°/12 mm., which is transformed into anthracene when heated with sulphur, zinc dust, or reduced copper (for proof of constitution, see this vol., i, 128); (iii) *s*-octahydrophenanthrene, m. p. 16·7°, b. p. 295°/760 mm., 167·5°/13 mm.,  $d^{20}_D$  1·026, which yields phenanthrene when heated with sulphur; (iv) a substance,  $C_{14}H_{16}$ , m. p. 54—55°, which has not been identified; (v) a mixture of 2:6'-ditetrahydronaphthyl,  $\begin{matrix} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \end{matrix} > C_6H_3 \cdot CH < \begin{matrix} CH_2 \cdot C_6H_4 \\ | \\ CH_2 \cdot CH_2 \end{matrix}$ , m. p. 53—54°, and (mainly)  $\alpha$ -phenyl- $\delta$ -2-tetrahydronaphthylbutane, which are dehydrogenated by sulphur to 2:2'-dinaphthyl and  $\alpha$ -phenyl- $\delta$ -naphthyl-*n*-butane, m. p. 80·5—82°, respectively. Oxidation of the phenyltetrahydronaphthylbutane fraction with potassium permanganate yields benzoic, benzene-1:2:4-tricarboxylic, and glutaric acids, thus establishing the presence of the normal butyl chain in the hydrocarbon. Oxidation of the fraction with chromic acid in glacial acetic acid solution gives a ketone,  $C_{20}H_{22}O$ , b. p. 214—216°/0·01 mm., which yields a *semicarbazone*,  $C_{21}H_{25}ON_3$ , m. p. 199—200°, an *oxime*,  $C_{20}H_{23}ON$ , m. p. 126—128°, and an *oxime acetate*,  $C_{22}H_{25}O_3N$ , m. p. 91—92·5°; the ketone will be fully described subsequently. Aluminium chloride transforms the fraction into tetrahydronaphthalene.

*s*-Octahydroanthracene is partly converted by a small proportion of aluminium chloride at 70—80° into *s*-octahydrophenanthrene; simultaneously, small amounts of dodecahydrotriphenylene,  $C_{18}H_{24}$ , m. p. 232—234° (cf. Mannich, A., 1907, i, 205), an intensely yellow substance, m. p. 320° (*picrate*, m. p. 198—201°), phenylenebisoctahydroanthracenylbutane,  $C_6H_4(CH_2 \cdot [CH_2]_3 \cdot C_{14}H_{17})_2$ , and tetrahydronaphthyl octahydrophenanthrenylbutane,



are produced. Analogously, *s*-octahydrophenanthrene is partly isomerised to *s*-octahydroanthracene and a similar series of by-products.

The production of the various compounds from tetrahydronaphthalene is explained as a special case of the author's theory of the action of aluminium chloride in which it is assumed that the primary

product,  $\text{Ar} \cdot \text{AlCl}_2 \cdot \text{HCl}$ , has a very marked tendency to replace the acid hydrogen atom by an alkyl group. The latter may be provided by an alkyl halide, thus giving a purely synthetic action, or by an alkylaromatic compound, thus leading to both synthesis and degradation. The first type of change usually requires at least a molecular proportion of aluminium chloride and takes place most satisfactorily at a low temperature in the presence of an inert solvent, whereas the second mode of action needs much less aluminium chloride and usually occurs with the undiluted reactant at a somewhat elevated temperature.

H. W.

**Naphthalenesulphonic Acids. VI. Sulphonation of Naphthalene in the Vapour Phase.** J. A. AMBLER, D. F. J. LYNCH, and H. L. HALLER (*Ind. Eng. Chem.*, 1924, **16**, 1264—1266).—A continuous process is described, in which naphthalene vapours are passed up an electrically heated cast iron tower containing quartz stones, through which sulphuric acid descends and in which 500 g. of naphthalene can be sulphonated in  $1\frac{1}{2}$ —2 hours. The reaction products are withdrawn at the base of the tower, and the excess of naphthalene and gaseous products are led away at the top of the tower, the former being condensed and recovered and the latter absorbed by sodium hydroxide. Working with the reaction tower at 220—245° and with sulphuric acid of 85—95% strength, and using 3—3½ parts of acid to 1 part of naphthalene, a yield of disulphonic acids of 77—80% of the theoretical can be obtained, of which 78—85% is the 2 : 7-disulphonic acid, together with traces of the  $\beta$ -monosulphonic acid and a small quantity of tar.

W. T. K. B.

**Arylamine Salts of the Naphthalenesulphonic Acids. II. Salts of  $\alpha$ - and  $\beta$ -Naphthalenesulphonic Acids.** R. B. FORSTER and C. M. KEYWORTH (*J. Soc. Chem. Ind.*, 1924, **43**, 299—303T).—The aniline, *p*-toluidine, and *m*-xylydine salts are extremely useful for the separation of mixtures of naphthalene- $\alpha$ - and - $\beta$ -sulphonic acids. Generally, the salts of the  $\alpha$ -acid are about three times as soluble as those of the  $\beta$ -acid at the ordinary temperature. The salts of the  $\alpha$ -acid with substituted amines have their melting points  $o > m > p$ , and of the  $\beta$ -acid,  $p > o > m$ . The solubilities of the toluidine salts for both acids are  $p > o > m$ . The titration and solubilities of all the salts described are given. Salts of *N*-substituted anilines are difficult to prepare. The following salts of  $\alpha$ - and  $\beta$ -naphthalenesulphonic acids, respectively, are described: *aniline*, m. p. 183°, m. p. 269°; *o-toluidine*, m. p. 237°, m. p. 213°; *m-toluidine*, m. p. 195—196°, m. p. 205°; *p-toluidine*, m. p. 181°, m. p. 211—212°; *m-xylydine*, m. p. 167°, m. p. 211°;  $\alpha$ -*naphthylamine*, m. p. 230° (decomp. 275°), m. p. 240°;  $\beta$ -*naphthylamine*, m. p. 200—201°, m. p. 275—276°; *benzidine*,  $\alpha$ -, m. p. above 330°; *tolidine*,  $\alpha$ -, m. p. 294° (decomp.); *dianisidine*, m. p. 272° (decomp.), m. p. 290° (decomp.); *o-chloroaniline*, m. p. 237°, m. p. 214°; *m-chloroaniline*, m. p. 176°; m. p. 344°; *p-chloroaniline*, m. p. 231°, m. p. 252—253°; *m-bromoaniline*, m. p. 168°, m. p. 237°; *p-bromoaniline*, m. p. 224°, m. p. 244°; *phenylhydrazine*, m. p. 178°.

m. p.  $217^{\circ}$ ; 2 : 4-dichloroaniline, m. p.  $234^{\circ}$ , m. p.  $178^{\circ}$ ; o-anisidine, m. p.  $208^{\circ}$ , m. p.  $207^{\circ}$ ; p-anisidine, m. p.  $182^{\circ}$ , m. p.  $218^{\circ}$ ; o-phenetidine, m. p.  $185^{\circ}$ , m. p.  $197^{\circ}$ ; p-phenetidine, m. p.  $201-202^{\circ}$ , m. p.  $207^{\circ}$ ;  $\psi$ -cumidine, m. p.  $198^{\circ}$ , m. p.  $236^{\circ}$ ; m-aminophenol, m. p.  $200^{\circ}$ , m. p.  $247^{\circ}$ ; p-phenylenediamine,  $\alpha$ -, m. p. above  $330^{\circ}$ . Examples are given of the use of the salts for separating mixtures of the two acids.

I. E. B.

**Benzyl- $\psi$ -thiocarbamide Salts of Naphthalenesulphonic Acids.** R. F. CHAMBERS and P. C. SCHERER (*Ind. Eng. Chem.*, 1924, **16**, 1272—1273).—The crystalline salts obtained by warming together certain naphthalenesulphonic acids and benzyl- $\psi$ -thiocarbamide in 0.2*N*-hydrochloric acid solution may be used for identifying these acids or for preparing them in a state of purity, the salts being readily hydrolysed. Details are given for preparing salts of the following: naphthalene- $\alpha$ -sulphonic acid, m. p.  $136-137^{\circ}$ ; naphthalene- $\beta$ -sulphonic acid, m. p.  $188-189^{\circ}$ ; naphthalene-1 : 5-disulphonic acid, m. p.  $244-245^{\circ}$  (partial decomp.); naphthalene-1 : 6-disulphonic acid, m. p.  $234-235^{\circ}$  (decomp.); naphthalene-2 : 7-disulphonic acid, m. p.  $199-200^{\circ}$  (decomp.); naphthalene-2 : 6-disulphonic acid, decomp.  $200^{\circ}$  without melting.

W. T. K. B.

**Direct Hydrogenation and Dehydrogenation of Acenaphthene.** M. N. GOSWAMI (*Compt. rend.*, 1924, **179**, 1269—1270).—When acenaphthene vapour is carried by excess of hydrogen over reduced nickel heated at  $150^{\circ}$ , a mixture of tetra- and decahydroacenaphthenes results (cf. Sabatier and Senderens, A., 1901, i, 459; Godehot, *Bull. Soc. chim.*, 1908, [iv], **3**, 529; Ipatiev, A., 1909, i, 466). In the absence of hydrogen, reduced nickel exerts a dehydrogenating action on acenaphthene, converting it into acenaphthylene.

T. H. P.

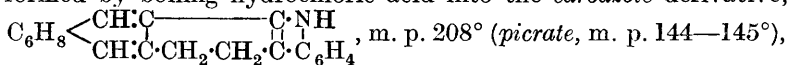
**Hydrogenation of Anthracene.** G. SCHROETER [with A. GLUSCHKE, E. VAN HULLE, and S. GÖTZKY] (*Ber.*, 1924, **57**, [B], 2003—2024).—Anthracene is hydrogenated under 10—20 atmospheres at  $120-150^{\circ}$ , in the presence of tetrahydronaphthalene and a catalyst prepared by the precipitation of reduced nickel on fuller's earth, primarily to 9 : 10-dihydroanthracene and thence to 1 : 2 : 3 : 4-tetrahydroanthracene (tetracene) and *s*-octahydroanthracene (octracene). The wandering of the hydrogen atoms from the positions 9 and 10 is surprising, but its probability is supported by a number of analogous changes.

Under the conditions mentioned above, anthracene is converted in a few seconds into a mixture of 9 : 10-dihydroanthracene, m. p.  $107-109^{\circ}$ , and 1 : 2 : 3 : 4-tetrahydroanthracene, which are conveniently separated from one another by combining the latter with picric acid, with which the dihydro compound does not unite. The constitution of 9 : 10-dihydroanthracene is established in the following manner. 2-Anthramine, which does not behave as a normal amino compound, and to which the constitution

$\text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{C}_6\text{H}_3 \cdot \text{NH}$  is therefore assigned, is reduced to 2-amino-

9:10-dihydroanthracene; diazotisation followed by reduction with stannous chloride and concentrated hydrochloric acid converts the latter substance into 2-hydrazino-9:10-dihydroanthracene hydrochloride, which is transformed by copper sulphate and sodium hydroxide solution into 9:10-dihydroanthracene, identical with the product described above. 1:2:3:4-Tetrahydroanthracene, m. p. 103—105°, yields a *picrate*, m. p. 116—117°, and a dibromo compound, m. p. 166—168°; with permanganate, it yields phthalic acid. Its constitution is established by its oxidation with chromic oxide in glacial acetic acid solution to 1:2:3:4-tetrahydroanthraquinone, m. p. 155·5°, which is reduced by zinc dust and sodium hydroxide to the corresponding quinol, from which the quinone is regenerated by atmospheric oxidation. 1:2:3:4-Tetrahydroanthracene is probably identical with the tetrahydroanthracene of Ipatiev (A., 1908, i, 330) and the  $\gamma$ -tetrahydroanthracene of Godchot (A., 1904, i, 987); the  $\beta$ -tetrahydroanthracene described by Godchot (*loc. cit.*) is probably a mixture of the 9:10-dihydro compound with more fully hydrogenated anthracene derivatives. Further hydrogenation of anthracene yields *s*-octahydroanthracene, m. p. 73—74° (identical with the product obtained from 1:2:3:4-tetrahydronaphthalene and aluminium chloride, this vol., i, 125), and subsequently a *decahydroanthracene*, b. p. 147—152°/10 mm., m. p. 30—35°, which is probably not uniform. The symmetrical structure of octahydroanthracene is established by the following synthesis (cf. A., 1922, i, 1136). 1:2:3:4-Tetrahydronaphthalene is converted by chloroacetyl chloride in the presence of a little phosphoric oxide into a mixture of 2-chloroacetyl-1:2:3:4-tetrahydronaphthalene, b. p. 202—203°/17 mm., m. p. 63—64° (*semicarbazone*, m. p. 173°), the constitution of which is established by its oxidation to 1:2:3:4-tetrahydronaphthalene-2-carboxylic acid, and 1-chloroacetyl-1:2:3:4-tetrahydronaphthalene, b. p. 140—142°/0·2 mm. (*semicarbazone*, m. p. 142—143°). 2-Chloroacetyltetrahydronaphthalene and ethyl sodiomalonate yield *ethyl 2-tetrahydronaphthoylethylmethylmalonate*, from which 2-tetrahydronaphthoylethylmethylmalonic acid,  $C_{10}H_{11} \cdot CO \cdot CH_2 \cdot CH(CO_2H)_2 \cdot H_2O$ , is prepared (the *potassium trihydrogen* and *potassium monohydrogen* salts are described). The acid is converted by loss of carbon dioxide into  $\beta$ -2-tetrahydronaphthoylethylpropionic acid, m. p. 121—122° (the *potassium hydrogen* and the normal *silver* salts are described), which is transformed by acetic anhydride into  $\gamma$ -tetrahydronaphthylcrotonolactone,  $C_{10}H_{11} \cdot C \begin{smallmatrix} \nearrow CH \cdot CH_2 \\ \searrow O \cdot CO \end{smallmatrix}$ , m. p. 97—98°, and reduced by zinc and hydrochloric acid to  $\gamma$ -2-tetrahydronaphthylbutyric acid, b. p. 218—220°/15 mm., m. p. 50—52°. The latter acid is converted by phosphorus pentachloride, followed by distillation of the product, into a mixture of 4-keto-*s*-octahydroanthracene, b. p. 205—207°/13 mm., m. p. 48°, and 4-keto-*s*-octahydrophenanthrene, which are separated from one another by means of their semicarbazones, m. p. 250—251° (decomp.) and 229—231°, respectively. 4-Keto-*s*-octahydroanthracene is reduced

by Clemmensen's method to *s*-octahydroanthracene, m. p. 73—74°, identical with that obtained by the catalytic reduction of anthracene. The mixture of ketones (see above) cannot be separated into its components by crystallisation of the oximes or by phenylhydrazine; the latter reagent readily yields the *phenylhydrazone* of 4-keto-*s*-octahydroanthracene, m. p. 115—118°, which, however, is transformed by boiling hydrochloric acid into the *carbazole* derivative,



whereas the phenylhydrazone of 4-keto-*s*-tetrahydrophenanthrene is similarly converted into the *substance*,  $\begin{array}{c} \text{CH} \cdot \text{CH} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 - \text{C} - \text{C} - \text{NH} \end{array}$ ,

m. p. 142° (*picrate*, m. p. 135—137°). *s*-Octahydroanthracene is oxidised by chromic acid in glacial acetic acid solution to 1-keto-*s*-octahydroanthracene and 1:2:3:4-tetrahydroanthraquinone.

The recognition of the identity of 1-keto-*s*-octahydroanthracene with Godchot's "hexahydroanthrone,"  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH}_2 \\ \text{CO} \end{array} > \text{C}_6\text{H}_{10}$ , has necessitated a lengthy revision of the work of that chemist (cf. A., 1904, i, 987; 1905, i, 201; 1906, i, 76, 494; 1907, i, 308, 836, 840, 841; 1908, i, 16). The action of magnesium benzyl chloride on 1-keto-*s*-octahydroanthracene, followed by distillation of the product, yields (?) 1-benzyl- $\Delta^1$ -hexahydroanthracene, b. p. 240—245°/16 mm., which, contrary to Godchot's statement, does not yield a *picrate*. The hydrocarbon is converted by addition of bromine and loss of hydrogen bromide into 1-benzyl-5:6:7:8-tetrahydroanthracene, which does not add bromine and by catalytic hydrogenation gives 1-benzyl-*s*-octahydroanthracene, b. p. 244—246°/14 mm. (*monobromo* derivative, m. p. 106°). 1-Keto-*s*-octahydroanthracene condenses with benzaldehyde in aqueous-alcoholic solution in the presence of potassium hydroxide to 1-keto-2-benzylideneoctahydroanthracene, m. p. 140°, which is reduced by sodium and alcohol to 1-hydroxy-2-benzyl-octahydroanthracene, m. p. 168—170°, identical with Godchot's "benzyloctahydroanthranol." The alcohol is dehydrated by potassium hydrogen sulphate to 2-benzyl- $\Delta^1$ -hexahydroanthracene, b. p. 255—258°/13 mm. The boiling point of this substance is about 13° higher than that of the isomeric 1-benzyl- $\Delta^1$ -hexahydroanthracene, whereas, according to Godchot, the compounds are identical. Further, 2-benzyl- $\Delta^1$ -hexahydroanthracene yields a very unstable *picrate* and is converted by bromine in glacial acetic acid solution into 1:2-di-bromo-2-benzyl-*s*-octahydroanthracene, m. p. 119—120°, which does not readily lose hydrogen bromide when boiled in glacial acetic acid solution, being thus further differentiated from its isomeride. 2-Benzyl-*s*-octahydroanthracene has b. p. 248—251°/12 mm., m. p. 65—66°.

1-Keto-*s*-octahydroanthracene is reduced by sodium and alcohol to 1-hydroxy-*s*-octahydroanthracene, m. p. 94—95°. Godchot records m. p. 81—82° for his octahydroanthranol, but apart from impurities the substances appear to be identical, since each yields

the phenylurethane, m. p. 153° (Godchot, m. p. 151—152°). 1-*s*-Octahydroanthracenylcarbamide, m. p. 255°, is formed by the action of carbamide on 1-keto-*s*-octahydroanthracene in boiling alcoholic solution in the presence of a little sulphuric acid; since such a ready replacement of a secondary alcoholic group by the carbamido residue is unusual, it is probable that desmotropic change occurs in accordance with the scheme

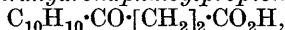


*s*-Octahydroanthracene is readily converted by concentrated sulphuric acid at 70° into *s*-octahydroanthracene-9-sulphonic acid; the sodium salt (+4H<sub>2</sub>O, +5H<sub>4</sub>O, and +CH<sub>3</sub>·CO<sub>2</sub>H), the potassium, ammonium, calcium, lead, and barium salts are described. *s*-Octahydroanthracene-9-sulphonyl chloride, m. p. 87°, is converted into the corresponding amide, m. p. 227—228°, the sodium salt of which is described. The sulphonic acid is hydrolysed by boiling concentrated hydrochloric acid to *s*-octahydroanthracene and sulphuric acid. The sulphonic group appears to be eliminated as sulphuric acid when the sulphonic acid is treated with molten potassium hydroxide or bromine. *s*-Octahydroanthracene-9-sulphonyl chloride is transformed by sodium hydrogen sulphite into sodium *s*-octahydroanthracene-9-sulphinate, which is reduced to 9-thiol-*s*-octahydroanthracene.

*s*-Octahydroanthracene is oxidised by potassium permanganate to benzene-1:2:4:5-tetracarboxylic acid (yield above 90%); the production of phthalic acid (cf. Godehot, *loc. cit.*) could not be established. The di-imide of benzene-1:2:4:5-tetracarboxylic acid is converted by sodium hydroxide into sodium dicarboxylamidobenzenedicarboxylate and by sodium hydroxide and hypochlorite into 2:5-diaminoterephthalic acid, which is readily prepared in this manner.

H. W.

**Hydrogenation of Phenanthrene.** G. SCHROETER [with E. VAN HULLE and H. MÜLLER] (*Ber.*, 1924, 57, [B], 2025—2032; cf. A., 1922, i, 1137).—Hydrogenation of purified phenanthrene proceeds readily as far as the production of *s*-octahydrophenanthrene, m. p. 16.7°, identical with that obtained by the action of aluminium chloride on 1:2:3:4-tetrahydronaphthalene or *s*-octahydroanthracene (this vol., i, 125). The symmetrical nature of the product is established by the synthesis of 4-keto-*s*-octahydrophenanthrene, b. p. 194—196°/12 mm. (oxime, m. p. 164—165°), from  $\gamma$ -2-tetrahydronaphthylbutyric acid (this vol., i, 128) and by the following series of changes. 1-Chloroacetyl-1:2:3:4-tetrahydronaphthalene is converted by condensation with ethyl sodiomalonate and subsequent hydrolysis of the product with concentrated potassium hydroxide solution into potassium trihydrogen 1-tetrahydronaphthoilmethylmalonate, which passes at 130—140° into  $\beta$ -1-tetrahydronaphthoilylpropionic acid,



m. p. 93—94°. Reduction of the keto-acid by amalgamated zinc



and hydrochloric acid gives  $\gamma$ -1-tetrahydronaphthyl-n-butyric acid, m. p. 94–95°, b. p. 219–222°/12 mm., which is converted by phosphorus pentachloride and subsequent distillation of the product into 1-keto-3-octahydrophenanthrene, b. p. 206–208°/12 mm., m. p. 81–82° (semicarbazone, m. p. 254–256°; oxime, m. p. 185–186°). Oxidation of *s*-octahydrophenanthrene with chromic acid in glacial acetic acid solution gives 1-keto-*s*-octahydrophenanthrene with a very small proportion of 4-keto-*s*-octahydrophenanthrene. 1-Keto-*s*-octahydrophenanthrene is reduced by sodium and alcohol to 1-hydroxy-*s*-octahydrophenanthrene, m. p. 94°, which gives 1-octahydrophenanthrenylphenylurethane, m. p. 194°, and 1-octahydrophenanthrenylcarbamide, m. p. 234°.

*s*-Octahydrophenanthrene is readily transformed by concentrated sulphuric acid at 70° into *s*-octahydrophenanthrene-9-sulphonic acid, from which the sodium, potassium, ammonium, magnesium, calcium, barium, and lead salts have been prepared. The corresponding sulphonyl chloride, m. p. 130–131°, anilide, m. p. 188–189°, and amide, m. p. 158–160°, are described. The sulphonic acid is hydrolysed by concentrated hydrochloric acid with rather greater difficulty than is the case with octahydroanthracene-9-sulphonic acid.

*s*-Octahydrophenanthrene and chloroacetyl chloride in the presence of a little phosphoric oxide at 175° yield 9-chloroacetyl-*s*-octahydrophenanthrene,  $C_{14}H_{17} \cdot CO \cdot CH_2Cl$ , m. p. 81°, b. p. 186°/0.33 mm., which is oxidised by boiling alkaline hypochlorite solution to *s*-octahydrophenanthrene-9-carboxylic acid, m. p. 239–240° (the silver salt is described). The acid is also prepared by the action of aluminium chloride on a solution of *s*-octahydrophenanthrene and oxalyl chloride in carbon disulphide.

*s*-Octahydrophenanthrene is oxidised by aqueous potassium permanganate to benzene-1 : 2 : 3 : 4-tetracarboxylic acid, m. p. 238–242° (decomp.), or 264–267° (decomp.) in an open or closed capillary. The anhydride obtained from it by means of acetic anhydride has m. p. 227–229° or 190–195°, according as the operation is rapidly or slowly performed.

The dehydrogenation of *s*-octahydrophenanthrene by sulphur (cf. this vol., i, 125) can be so conducted that 1 : 2 : 3 : 4-tetrahydrophenanthrene, m. p. 33–34° (picrate, m. p. 107–108°), is isolated; this hydrocarbon is also obtained by the partial hydrogenation of phenanthrene.

H. W.

**Poly-arylated Vinylcarbinols and their Derivatives. IV. Course of the Dimerisation of Triphenylallene.** K. ZIEGLER, H. GRABBE, and F. ULRICH (*Ber.*, 1924, 57, [B], 1983–1990; cf. A., 1924, i, 308).—The “triphenylallene” obtained by Meyer and Schuster (A., 1922, i, 540) by the action of acids on diphenylstyrylcarbinol has double the molecular weight required for the simple hydrocarbon (cf. Ziegler and Ochs, A., 1922, i, 1047). It is smoothly reduced by hydriodic acid to 1 : 3-diphenylhydrindene in place of  $\alpha\gamma$ -triphenylpropane expected from a substance of the simpler structure and hence is to be regarded as tetraphenyltruxane

(I or II). Since, however, preformed 1:3-diphenylhydrindene cannot be converted into the truxane derivative, it appears probable



that triphenylallene is polymerised initially to a *cyclobutane* derivative, in which the indene rings are subsequently formed.

Magnesium diphenylvinyl bromide is readily converted by benzaldehyde into *ααγ-triphenylallyl alcohol*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CPh}_2\cdot\text{OH}$ , m. p. 77—78°, which in the presence of the requisite alcohol and a trace of mineral acid is transformed with unusual ease into the corresponding *methyl ether*, m. p. 97—98°, whereas in the absence of an alcohol *di-ααγ-triphenylallyl ether*, m. p. 156°, is produced. Each of these compounds is converted by boiling glacial acetic acid in the presence of a trace of sulphuric or hydrochloric acid into tetraphenyltruxane, m. p. 210°, which is most readily prepared in this manner. Hydrogen chloride converts *ααγ-triphenylallyl alcohol* or its ethers suspended in cold, anhydrous ether into *ααγ-triphenylallyl chloride*, m. p. 90° (decomp.). 3-Phenylhydrind-1-one is transformed by magnesium phenyl bromide and subsequent distillation of the product under reduced pressure into 1:3-diphenylindene, m. p. 71—72° (cf. Czerny, *Diss.*, Halle, 1912) which, together with some tetraphenyltruxane, is also obtained by the action of phosphoric oxide on *ααγ-triphenylallyl alcohol* or its methyl ether. It is reduced by sodium and alcohol to 1:3-*di-phenylhydrindene*, m. p. 156—157°, identical with the product of the action of hydriodic acid and red phosphorus on “dimeric triphenylallene.”

Ethyl β-phenylpropionate and magnesium phenyl bromide give *ααγ-triphenylpropyl alcohol*, m. p. 88°, which is dehydrated by acetic anhydride to *ααγ-triphenyl-Δ<sup>α</sup>-propene*, m. p. 31—32°; sodium and alcohol reduce the latter substance to *ααγ-triphenylpropane*, m. p. 46—47°. H. W.

**Preparation of Aromatic Amines by Reduction of the Corresponding Nitro Compounds.** FARBENFABRIKEN VORM. F. BAYER & Co., and A. ENGELHARDT (D.R.-P. 388185; from *Chem. Zentr.*, 1924, ii, 545—546).—Aromatic nitro compounds are treated with gases containing hydrogen sulphide (*e.g.*, crude coal-gas), preferably admixed with a basic substance such as ammonia, by passing simultaneously through a layer of porous animal or vegetable charcoal (cf. D.R.-P. 290656). The nitro compound is reduced to the amine with evolution of heat, the sulphur formed being deposited within the pores of the carbon. The carbon loses its activity when it has absorbed about its own weight of sulphur, but can be reactivated by removing the sulphur either by melting, heating, or extraction with a solvent. The rate of reduction is greatly increased by the presence of a small percentage of basic substance. Thus, nitrobenzene vapour is reduced to aniline by a gas containing 10 g. of hydrogen sulphide and 0.5 g. of ammonia per cub. m. Examples are also quoted of the reduction of sodium

1-chloro-2-nitrobenzene-4-sulphonate and of sodium 1-nitronaphthalene-6-sulphonate in aqueous solution in presence of wood charcoal.

F. A. M.

**Preparation of Diarylthiocarbamides.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION, R. MAY, and B. SZELINSKI (D.R.-P. 387762; from *Chem. Zentr.*, 1924, ii, 404).—Diarylthiocarbamides are prepared by heating arylamines with carbon disulphide in presence of water and in absence of organic solvents or oxidising agents. Thus, diphenylthiocarbamide is prepared from aniline, carbon disulphide, sulphur, and water at 60°. The *thiocarbamide* from benzidine melts above 270°. *Dihydrothio-2-perimidone* is obtained from 1 : 8-naphthylenediamine.

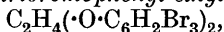
F. A. M.

**Acenaphthene Series. I. 2-Aminoacenaphthene.** G. T. MORGAN and H. M. STANLEY (*J. Soc. Chem. Ind.*, 1924, 43, 343—346r).—Nitration of 3-formamidoacenaphthene, m. p. 172°, gives 2-nitro-3-formamidoacenaphthene, m. p. 227°, which on hydrolysis gives the nitroamine, of which the *benzoyl* derivative, m. p. 233°, is not hydrolysed by hydrochloric acid under pressure. Subjected to the Sandmeyer reaction, the nitroamine gives 3-iodo-2-nitroacenaphthene, m. p. 148°, and reduction of this compound by tin and hydrochloric acid gives 2-aminoacenaphthene, m. p. 87°. The reduction was unsuccessful employing sodium hyposulphite or hydrogen and palladium in alcoholic solution. The new base gives a colourless diazo solution, forming red pigments with  $\beta$ -naphthol and resorcinol, but gives no colour reaction with ferric chloride. The *picrate*, decomp. 190—200°, *acetyl*, m. p. 176°, and *benzoyl*, m. p. 196°, derivatives are described. Nitration of 3-iodoacenaphthene gives 3-iodo-4-nitroacenaphthene, m. p. 179—180°, and 3-iodo-?nitroacenaphthene, m. p. 151—153°, the former on reduction giving 3-aminoacenaphthene (*picrate*, decomp. 190—200°), thereby orienting the nitro group, whereas the latter has not been obtained pure in sufficient quantity for further examination. The nitro group probably occupies the 1- or 6-position, the 5-, 7-, and 8-positions being less likely.

I. E. B.

**Bromo Derivatives of Phenol and the Mobility of their Bromine Atoms.** M. KOHN and A. FINK (*Monatsh.*, 1924, 44, 183—195; cf. Kohn and Müller, A., 1909, i, 567; Kohn and Bum, A., 1912, i, 760).—Tetra- and penta-bromophenols when subjected to the Friedel and Crafts reaction in the presence of benzene have their ortho and para bromine atoms replaced by hydrogen, only those in the meta position remaining. 2 : 3 : 4 : 6-Tetrabromophenol, prepared by the methods of Benedikt (A., 1880, 246) and of Auwers and Büttner (A., 1899, i, 36) reacts with benzene in the presence of anhydrous aluminium chloride at 100° to form bromobenzene and *m*-bromophenol. *m*-Bromophenyl benzoate, tri-clinic crystals, has m. p. 87—89°. Pentabromophenol, prepared by adding phenol to a solution of aluminium bromide in bromine, forms 3 : 5-dibromophenol, b. p. 274—276°/755 (uncorr.), m. p. 81°. The crystals are monoclinic,  $a : b : c = 3.5576 : 1.53019$ ,  $\beta = 90^\circ$

143'. This method of preparation is more convenient than those previously described (cf. Blanksma, *Rec. trav. chim.*, 1907, **27**, 25—41). 3:5-Dibromophenyl benzoate has m. p. 80°. Tribromophenol bromide under the same conditions as tetrabromophenol yields phenol and bromobenzene (cf. Kohn and Müller, *loc. cit.*), together with higher-boiling bromophenols, especially if the reaction period is short. 2:4:6-Tribromophenol has b. p. 282—290°/746 mm. (very slight decomp.). Tribromoanisole, prepared by methylation of the phenol with methyl sulphate, has b. p. 297—299°, higher (unusual) than the corresponding phenol. It forms monoclinic crystals,  $a:b:c=2.0461:1:3.1888$ ,  $\beta=92^{\circ}20'10''$ . 2:3:4:6-Tetrabromoanisole has m. p. 105—106°; pentabromoanisole, m. p. 173—174°. Di-2:4:6-tribromophenyl ethylene ether,



m. p. 222—223°, is prepared from tribromophenol, ethylene bromide, and sodium ethoxide, and the corresponding trimethylene ether, m. p. 165°, from trimethylene bromide. Similarly, from tetrabromophenol, di-2:3:4:6-tetrabromophenyl ethylene ether, m. p. 177°, and the corresponding trimethylene ether, m. p. 149°, were prepared. That the ethylene have higher m. p. than the corresponding trimethylene derivatives is in agreement with similar dihydroxybenzene ethers (cf. Kohn and Wilhelm, A., 1923, i, 558; Kohn and Safrin, A., 1923, i, 559). A. C.

**Behaviour of Nitrophenols with *p*-Toluenesulphonyl Chloride.** S. M. SANÉ and S. S. JOSHI (*J. Chem. Soc.*, 1924, **125**, 2481—2484).—It has previously been shown that nitrophenols react with *p*-toluenesulphonyl chloride in two ways: mononitrophenols form *p*-toluenesulphonyl esters in presence of sodium carbonate or diethylaniline: polynitrophenols, with sodium carbonate as condensing agent, also yield such esters, but in presence of diethylaniline are converted into chloropolynitrobenzenes (A., 1908, i, 525; 1909, i, 23; 1912, i, 104). This rule was followed by all compounds examined with the exception of 6-chloro-2:4-dinitro-*m*-cresol, which in presence of diethylaniline gave 6-chloro-2:4-dinitro-*m*-tolyl *p*-toluenesulphonate, m. p. 125°.

The following *p*-toluenesulphonyl esters were prepared: 4:6-dibromo-2-nitrophenyl *p*-toluenesulphonate, m. p. 140°; 2:6-dibromo-4-nitrophenyl *p*-toluenesulphonate, m. p. 128—129°; 2-bromo-4:6-dinitrophenyl *p*-toluenesulphonate, m. p. 157°; 2:4:6-tribromophenyl *p*-toluenesulphonate, m. p. 113°.

1-Chloro-2-bromo-4:6-dinitrobenzene, m. p. 63°, obtained by the action of *p*-toluenesulphonyl chloride on 2-bromo-4:6-dinitrophenol in presence of diethylaniline, contains a very labile chlorine atom. By action of dry ammonia in boiling alcoholic solution, it yields 2-bromo-4:6-dinitroaniline, m. p. 153°. When heated with aniline and sodium acetate in alcohol, it forms 2-bromo-4:6-dinitrodiphenylamine, orange-yellow crystals, m. p. 150°. 2:4-Dinitrophenoxazine, reddish-violet, silky needles, m. p. 215°, was obtained in a similar way from *o*-aminophenol, and dibromotetranitrodiphenyl-*p*-phenylenediamine, purple-red crystals, m. p. above 340°, was

produced by condensation with *p*-phenylenediamine. Condensation with dimethylaniline in alcohol gave 2-bromo-4 : 6-dinitrodimethylaniline, orange-red crystals, m. p. 96°.

Nitration of *m*-chlorophenol with a mixture of fuming nitric acid and acetic acid gave a 3-chlorodinitrophenol, m. p. 92°, apparently identical with 3-chloro-4 : 6-dinitrophenol (A., 1912, i, 659). With *p*-toluenesulphonyl chloride and diethylaniline, this yielded crystals, m. p. 102°, probably 1 : 3-dichloro-4 : 6-dinitrobenzene. P. C.

**Bromo Derivatives of *o*-Cresol and the Mobility of their Bromine Atoms.** M. KOHN and M. JAWETZ (*Monatsh.*, 1924, 44, 197—207).—3 : 5-Dibromo-*o*-hydroxybenzyl bromide, prepared by the method of Auwers and Schröter (A., 1906, i, 259), reacts with the dihydroxybenzenes to form diphenylmethane derivatives instead of (as might be expected) hydroxybenzyl ethers. When heated with 4 mols. of pyrocatechol and 1 mol. of potassium hydroxide, it gives 3 : 5-dibromo-2 : 3' : 4'(or 2 : 2' : 3')-trihydroxydiphenylmethane (from analogy the 2 : 3' : 4'-structure is more probable) m. p. 157—159°. The benzoyl derivative, C<sub>31</sub>H<sub>22</sub>O<sub>6</sub>Br<sub>2</sub>, has m. p. 75°. 3 : 5-Dibromo-2 : 3' : 6'-trihydroxydiphenylmethane, which colours at 160° and carbonises at higher temperatures, is formed on heating with quinol; benzoyl derivative, m. p. about 145°. With resorcinol, 3 : 5-dibromo-2 : 2' : 4'(or 2 : 2' : 6' or 2 : 3' : 5')-trihydroxydiphenylmethane, becoming yellow at 190°, m. p. about 202°, is formed; benzoyl derivative, m. p. 132° (not sharp). Reasons are given in favour of the 2 : 2' : 4'-formula. Tetrabromo-*o*-cresol heated with benzene and aluminium chloride (this vol., i, 133) gives bromobenzene and a dibromocresol differing from those known, probably 4 : 6-dibromo-*o*-cresol, m. p. 98—101°, triclinic crystals; benzoyl derivative, m. p. 91—93°. 3 : 5-Dibromo-*o*-hydroxybenzyl bromide, when heated with benzene and aluminium chloride, does not form a diphenylmethane derivative, but phenol and bromobenzene (cf. this vol., i, 133). A. C.

**Substituted Carbonates derived from *p*-Cresol.** R. H. GRIFFITH (*J. Chem. Soc.*, 1924, 125, 2625—2628).—Bromination of 3 : 3'-dinitroditolyl carbonate yields a tetrabromocarbonate which hydrolyses to a dibromocresol, pale yellow needles, m. p. 135°, presumably 2 : 5-dibromo-*p*-cresol. Sulphonation of the dinitroditolyl carbonate with fuming sulphuric acid (18% SO<sub>3</sub>) gives, after hydrolysis, a nitro-*p*-cresolsulphonic acid, monopotassium salt, pale brown, dipotassium salt, scarlet, presumably 2-nitro-*p*-cresol-6-sulphonic acid.

3 : 3'-Dibromoditolyl carbonate, m. p. 134°, is best prepared by the action of carbonyl chloride on 2-bromo-*p*-cresol. Direct bromination of ditolyl carbonate yields a mixture of 3 : 3'- and 2 : 2'-dibromoditolyl carbonates. 2 : 2'-Dibromoditolyl carbonate has m. p. 119°.

The nitration product of 3 : 3'-dibromoditolyl carbonate yields on hydrolysis mainly 6-bromo-3-nitro-*p*-cresol (configuration not certain), yellow crystals, m. p. 62°, volatile in steam. A little non-

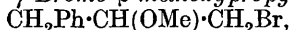
volatile material, possibly 3-bromo-5-nitro-*p*-cresol, is produced at the same time. P. C.

**Boric Acid Compounds of Pyrocatechol.** H. WEIL and M. ADLER (*Ber.*, 1924, **57**, [B], 2091).—The pyrocatechol-boric acid derivatives described by Rosenheim and Vermehren (*A.*, 1924, i, 1194) have been obtained previously by the authors (cf. Adler, *Diss.*, Giessen, 1923). H. W.

**Preparation of 4-Chloro-6-nitro-*m*-anisidine.** J. R. H. WHISTON (*J. Soc. Chem. Ind.*, 1924, **43**, 370r).—2:5-Dichloroacetanilide in sulphuric acid solution is nitrated to 2:5-dichloro-4-nitroacetanilide by treatment at 5° with a mixture of nitric and sulphuric acids. After hydrolysis by heating with aqueous sodium hydroxide solution, the free amine is converted into 4-chloro-6-nitro-*m*-anisidine (m. p. 156°) by heating under a reflux condenser at 100° with methyl alcohol in the presence of sodium hydroxide.

**Preparation of *r*-o-Dihydroxyphenylethanolmethylamine Hydrochloride.** SOC. CHIMIQUE DES USINES DU RHÔNE, ANCIENNEMENT GILLIARD, P. MONNET ET CARTIER (D.R.-P. 388534; from *Chem. Zentr.*, 1924, ii, 545).—*r*-o-Dihydroxyphenylethanolmethylamine (*β*-o-dihydroxyphenyl-*β*-methylaminoethyl alcohol) hydrochloride, m. p. about 140°, prepared from the free base, is stable in the solid state and non-hygroscopic. F. A. M.

**Bromotrinitromethane. III.** E. SCHMIDT and W. BARTHOLOMÉ [and, in part, R. ASMAS] (*Ber.*, 1924, **57**, [B], 2039—2040; cf. *A.*, 1923, i, 645).—*γ*-Bromo-*β*-methoxypropylbenzene,



b. p. 80—81°/0.05 mm.,  $d_4^{20}$  1.3134,  $n_D^{20}$  1.5349, is obtained by the action of bromotrinitromethane on a solution of allylbenzene in methyl alcohol. *γ*-Bromo-*β*-ethoxypropylbenzene has b. p. 85—86°/0.04 mm. Safrole in the presence of methyl alcohol yields 3:4-methylenedioxy-*γ*-bromo-*β*-methoxypropylbenzene, b. p. 138—139°/0.08 mm.,  $d_4^{20}$  1.4672,  $n_D^{20}$  1.5595. 2-Methoxy-*γ*-bromo-*β*-methoxypropylbenzene, b. p. 101—103°/0.1 mm.,  $d_4^{20}$  1.3570,  $n_D^{20}$  1.5428, and 4-methoxy-*γ*-bromo-*β*-methoxypropylbenzene, b. p. 126—127°/0.6 mm.,  $d_4^{20}$  1.3355,  $n_D^{20}$  1.5370, are also described. H. W.

**Diphenylphenylacetylenylcarbinol [Triphenylpropargyl Alcohol]. Ethers. II.** C. MOUREU, C. DUFRAISSE, and H. BLATT (*Bull. Soc. chim.*, 1924, [iv], **35**, 1412—1424; cf. *A.*, 1923, i, 921).—Triphenylpropargyl alcohol, like triphenylcarbinol, is converted into ethers on treatment with an alcohol and sulphuric acid, but under the influence of the acid simultaneously isomerises to phenyl *β*-phenylstyryl ketone,  $\text{CPh}:\text{C}\cdot\text{CPh}_2\cdot\text{OH} \rightarrow \text{COPh}\cdot\text{CH}:\text{CPh}_2$ , and special precautions are necessary for the isolation of the ethers. The constitution of the methyl ether is established as  $\text{CPh}:\text{C}\cdot\text{CPh}_2\cdot\text{OMe}$  by its synthesis by methylation of the alcohol with methyl iodide in the presence of potassium, and by the action of sodium methoxide on the chloride,  $\text{CPh}:\text{C}\cdot\text{CPh}_2\text{Cl}$ , by the absence of reaction for

hydroxyl with magnesium ethyl bromide, and by thermochemical data (see following abstract). The methyl ether is much the most insoluble of the ethers and the solubility increases in the order methyl, ethyl, propyl, the solubility of the propyl ether in light petroleum being exceptionally great. These ethers are very stable towards alkalis but are readily hydrolysed by acids, regenerating the carbinol, which at once undergoes isomerisation. The velocity with which the phenyl  $\beta$ -phenylstyryl ketone is formed differs in the three cases, being most rapid with the more soluble ethyl and propyl ethers. That hydrolysis precedes isomerisation is shown by the precipitation of the methyl ether when either the propyl or ethyl ether is treated with methyl alcohol and sulphuric acid. The mechanism of the isomeric change is discussed; in view of Meyer and Schuster's results (A., 1922, i, 556), it probably involves the addition of water or hydrogen chloride, or, essentially, migration of hydroxyl and enol-keto isomeric change:  $\text{CPh:C:CPh}_2\cdot\text{OH} \rightarrow \text{CPh(OH):C:CPh}_2 \rightarrow \text{COPh:CH:CPh}_2$ .

*Triphenylpropargyl methyl ether*, m. p.  $124^\circ$ , is obtained almost quantitatively by the action of excess of methyl alcohol on the alcohol in the presence of sulphuric acid in the cold. The *ethyl ether*, m. p.  $51\text{--}52^\circ$ , is similarly obtained, the reaction product being treated with water and ether after 5 minutes. The *propyl ether*, similarly obtained, has m. p.  $42\text{--}43^\circ$ . On treatment with hydrogen bromide, the methyl ether is converted quantitatively into phenyl  $\beta$ -phenylstyryl ketone.

R. B.

**Thermochemical Study of Triphenylpropargyl Alcohol and its Derivatives.** P. LANDRIEU and H. BLATT (*Bull. Soc. chim.*, 1924, [iv], 35, 1424—1436).—Determinations of the heats of combustion of triphenylpropargyl alcohol,  $\text{CPh}_2(\text{OH})\cdot\text{C:CPh}$ , and its ethers and of phenyl  $\beta$ -phenylstyryl ketone and phenyl  $\beta$ -hydroxy- $\beta\beta$ -diphenylethyl ketone confirm the conclusions previously reached regarding the constitution of these substances. The difference between the heats of combustion of triphenylpropargyl alcohol and its methyl ether is normal. Similarly, the differences between the heats of combustion of the methyl, ethyl, and propyl ethers are normal for members of a homologous series. The transformation of triphenylpropargyl alcohol into phenyl  $\beta$ -phenylstyryl ketone is attended by evolution of heat, and the difference between the heats of combustion of the latter and phenyl  $\beta$ -hydroxy- $\beta\beta$ -diphenylethyl ketone agrees with that normally required for the addition of water to an ethylenic linking, thereby confirming the formula assigned to the ethylenic ketone.

R. B.

**$\alpha$ - and  $\beta$ -Naphthalenesulphonylalanines.** W. M. COLLES and C. S. GIBSON (*J. Chem. Soc.*, 1924, 125, 2505—2510).—*dl*- $\alpha$ -Naphthalenesulphonylalanine, m. p.  $133\cdot5^\circ$ , prepared from *dl*-alanine and  $\alpha$ -naphthalenesulphonyl chloride, was resolved by using first brucine and then strychnine (cf. A., 1915, i, 801). The *brucine* salt of *d*- $\alpha$ -naphthalenesulphonylalanine ( $2\frac{1}{2}\text{H}_2\text{O}$ ) has

m. p.  $145^{\circ}$ ,  $[\alpha]_{5461}^{20} - 12.3^{\circ}$  in ethyl alcohol. The *strychnine* salt of *l*- $\alpha$ -naphthalenesulphonylalanine has m. p.  $132^{\circ}$ ,  $[\alpha]_{5461}^{20} - 19.63^{\circ}$  in ethyl alcohol. The rotatory power of the optically active  $\alpha$ -naphthalenesulphonylalanines in alcohol or acetone is opposite in sign to that of solutions of their sodium salts in water. *d*- $\alpha$ -Naphthalenesulphonylalanine, m. p.  $141.5-142.5^{\circ}$ ,  $[\alpha]_{5461}^{20} - 23^{\circ}$  in alcohol or acetone; sodium salt  $[\alpha]_{5461}^{20} + 35^{\circ}$  in water. *l*- $\alpha$ -Naphthalenesulphonylalanine, m. p.  $141.5-142.5^{\circ}$ ,  $[\alpha]_{5461}^{20} + 23^{\circ}$  in alcohol; sodium salt  $[\alpha]_{5461}^{20} - 34.5^{\circ}$  in water.

The physical constants now determined for the  $\beta$ -naphthalenesulphonyl derivatives are more accurate than those published by previous workers (A., 1903, i, 24; 1907, ii, 489). A solution of *dl*- $\beta$ -naphthalenesulphonylalanine, m. p.  $150-150.5^{\circ}$ , readily precipitates the sparingly soluble *strychnine* salt of the *d*-acid, and the crude *l*- $\beta$ -acid remaining in the mother-liquor was purified by first separating the very sparingly soluble *brucine* salt of the racemic  $\beta$ -acid. The almost pure *l*- $\beta$ -acid left in solution was completely purified by one recrystallisation of the ammonium salt from alcohol. The *strychnine* salt of *d*- $\beta$ -naphthalenesulphonylalanine,  $1\frac{1}{2}\text{H}_2\text{O}$ , m. p.  $197^{\circ}$ , has  $[\alpha]_{5461}^{20} - 9.94^{\circ}$  in ethyl alcohol. The *brucine* salt of *dl*- $\beta$ -naphthalenesulphonylalanine,  $\text{H}_2\text{O}$ , m. p.  $188.5^{\circ}$ , has  $[\alpha]_{5461}^{20} - 19.9^{\circ}$  in ethyl alcohol. The  $\beta$ -naphthalenesulphonylalanines in solution in alcohol show an optical rotation having the same sign as the solutions of their respective sodium salts in water. Their constants are, *d*- $\beta$ -naphthalenesulphonylalanine, m. p.  $127-128^{\circ}$ ,  $[\alpha]_{5461}^{20} + 51.74^{\circ}$  as sodium salt in water; *l*- $\beta$ -naphthalenesulphonylalanine, m. p.  $127-128^{\circ}$ ,  $[\alpha]_{5461}^{20} - 22.0^{\circ}$  in ethyl alcohol. P. C.

**Action of Organo-magnesium Compounds on Nitriles. Benzonitrile.** E. ECTORS (*Bull. Soc. chim. Belg.*, 1924, 33, 521-524; cf. A., 1924, i, 853).—The magnesium compound from the action of magnesium benzyl chloride on benzonitrile is decomposed by water at a low temperature. With hydrogen chloride, the ethereal solution of the products gives a precipitate, m. p.  $213^{\circ}$  (indef.), from which, by treatment with ammonia, phenyl benzyl ketone and 3:4:5-triphenylpyrazoline are isolated. The substance, m. p.  $213^{\circ}$ , is therefore probably a mixture of the hydrochlorides of 3:4:5-triphenylpyrazoline and phenylbenzylketimine or diphenylbenzylbenzylideneketoisoketimine (cf. Moureu and Mignonac, A., 1921, i, 108). The action of acetic anhydride on the same magnesium compound gives *N*-acetylphenylbenzylketimine, m. p.  $197-198^{\circ}$  (40% yield). In alcoholic solution dry hydrogen chloride converts this product into phenylbenzylketimine hydrochloride, m. p.  $137^{\circ}$ , from which the free base, m. p.  $92-93^{\circ}$ , is liberated by the action of ammonia in ether solution. Attempts to condense the ketimine with itself or with benzonitrile in the presence of sodium carbonate or anhydrous zinc chloride failed. When the magnesium compound is added slowly to a large excess of water, only phenyl benzyl ketone is formed. Hence the tetraphenylhexahydrodiazine and the triphenylpyrazoline, formed as by-products when water is gradually added to the magnesium



compound, must arise from slow decomposition of the latter by water, possibly through local rise of temperature or through the action of magnesium chloride.

W. E. E.

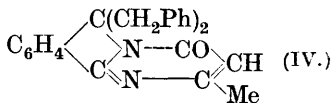
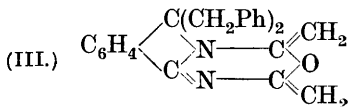
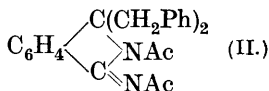
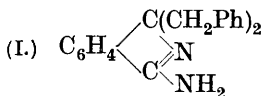
**Dioximes. XXI.** G. PONZIO (*Gazzetta*, 1924, **54**, 887—890).—The author regards Gastaldi's statements (A., 1923, i, 1236; 1924, i, 733, 1208) on the  $\alpha$ -modification of the oxime of benzoylformhydroxamic acid as erroneous, since phenylhydroxyglyoxime,  $\text{NOH:CPh}\cdot\text{C(OH):NOH}$ , exists in only one form and the supposed  $\alpha$ -modification of the above oxime is the supposed  $\beta$ -modification in an impure state, as may readily be shown by crystallising the product from ether. Similar considerations hold also for the supposed  $\alpha$ - and  $\beta$ -forms of the oxime of *p*-toluoylformhydroxamic acid. Further criticisms on Gastaldi's work are advanced.

T. H. P.

**Preparation of Acetylsalicyloyl Peroxide.** L. VANINO and F. HERZER (*Arch. Pharm.*, 1924, **262**, 441—442).—A solution of acetylsalicyloyl chloride in a little acetone is added to an excess of an ice-cold, moderately concentrated hydrogen peroxide solution, which is rapidly stirred (cf. Vanino and Uhlfelder, A., 1904, i, 1014). The product (yield, 39% of theory) is filtered off, dried, dissolved in chloroform, and precipitated by adding light petroleum; m. p. 109—110° (decomp.).

W. A. S.

**Action of Organo-magnesium Compounds on Phthalonitrile. I.** R. WEISS and E. FREUND (*Monatsh.*, 1924, **45**, 105—114).—3-Amino-1:1-dibenzyl- $\psi$ -isoindole (I), m. p. 180.5° (hydrochloride, hygroscopic, m. p. 85—94°), was obtained by the action of ethereal magnesium benzyl chloride on phthalonitrile in benzene. When heated with acetic anhydride, this yielded diacetyl-dibenzyliminophthalimidine (II), m. p. 122—123°, which afforded the anhydro derivative (III) or (IV), m. p. 167—168°, together with a substance, m. p. 135°, when boiled with alcoholic potassium hydroxide. The anhydro derivative was unaffected by heating at 180°. Dibenzylphthalimidine, m. p. 196—197°, was obtained,



together with a substance, m. p. 160°, by heating the above diacetyl derivative with hydrochloric acid at 180°. N-Methyldibenzylphthalimidine, m. p. 150—152°, was obtained by the exhaustive methylation of the above 3-amino-1:1-dibenzyl- $\psi$ -isoindole.

F. G. W.

**Nuclear Hydrogenation of Aromatic and Heterocyclic Compounds with Colloidal Platinum as Catalyst.** A. SKITA (*Ber.*, 1924, 57, [B], 1977—1982).—Colloidal platinum is more active than the spongy metal in causing hydrogenation in the nucleus of cyclic compounds, but the intensity of its action depends frequently on the concentration as well as on the fineness of division of the metal. Further, in the majority of cases there is a limit of temperature and gaseous pressure below which hydrogenation proceeds slowly if at all.

[With K. WARNAT.]—Phenylene-1-acetic-2-propionic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ , is more readily hydrogenated at  $50^\circ$  under 3 atm. pressure in the presence of colloidal platinum than in that of spongy platinum, giving hexahydrophenylene-1-acetic-2-propionic acid, m. p.  $107^\circ$ , in almost quantitative yield (contrast Helfer, A., 1923, i, 1228).

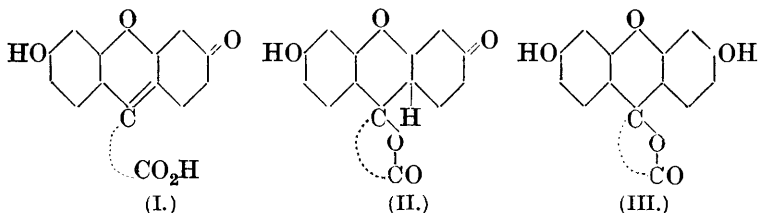
[With H. REITMEYER.]—Technical benzylamine, which cannot be hydrogenated by nickel at  $170$ — $180^\circ$ , is transformed by hydrogen at 3 atm. pressure and  $50$ — $60^\circ$  in the presence of colloidal platinum rapidly and quantitatively into *cyclohexylmethylamine*, b. p.  $162^\circ$ ; under closely similar conditions,  $\beta$ -phenylethylamine gives  $\beta$ -*cyclohexylethylamine*, b. p.  $188^\circ$ . *iso*Quinoline is reduced only to 1 : 2 : 3 : 4-tetrahydro*iso*quinoline when hydrogenated in the presence of colloidal platinum under conditions which lead to the decahydrogenation of quinoline (cf. Helfer, *loc. cit.*; Skita and Schön, *Chem.-Ztg.*, 1914, 38, 605); if, however, the concentration of the catalyst is increased, a further absorption of hydrogen occurs steadily, although not very rapidly, and decahydro*iso*quinoline, b. p.  $207^\circ$  (*phenylcarbimide* derivative,  $\text{C}_{16}\text{H}_{22}\text{ON}_2$ , m. p.  $123^\circ$ ), is quantitatively produced.

1 : 2 : 3 : 4-Tetrahydro*iso*quinoline is converted by ethylene chlorohydrin into 2- $\beta$ -hydroxyethyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, b. p.  $166$ — $167^\circ/12$  mm. (*methiodide*, m. p.  $148^\circ$ ; *acetate* of methiodide, m. p.  $127^\circ$ ).  
H. W.

**Preparation of Naphthalic Acid by Oxidation of Acenaphthaquinone.** J. R. H. WHISTON (*J. Soc. Chem. Ind.*, 1924, 43, 370r).—A suspension of acenaphthenequinone in aqueous sodium hydroxide solution is oxidised by excess of hydrogen peroxide to naphthalic acid, which passes into solution as its sodium salt. The naphthalic acid is obtained from the filtrate, in yields of 95% of theory, by precipitation with hydrochloric acid.

**Ring-chain Tautomerism. XI. The Fluoresceins and Rhodamines.** S. DUTT and J. F. THORPE (*J. Chem. Soc.*, 1924, 125, 2524—2538).—In the fluoresceins and rhodamines, the change from colourless base to coloured salt is generally accepted as being due to a change in structure from the lactone to the quinone form, but the precise mechanism of this change has not hitherto been determined. The authors advance the hypothesis that this change is a typical example of ring-chain tautomerism; for example, between the individuals I and III, with transient formation of the

intermediate compound II. Experimental evidence in favour of this hypothesis is obtained by examination of the absorption bands

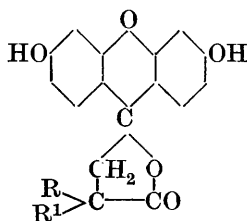


(in the ultra-violet) of the fluoresceins and rhodamines derived from succinic and glutaric acids.

In earlier papers (T., 1922, **121**, 650, 1430, 1765; 1923, **123**, 113, 1206) it has been shown that the conditions of ring-chain tautomerism between two substances of types IV and V are



primarily determined by the distance apart of the elements  $\text{E}_3$  and  $\text{E}_2$ , the dotted line representing a chain of elements. This distance is affected by the number of elements in the chain or by the influence exerted by groups, attached to the elements in the chain, on the carbon tetrahedral angle. It has been proved that the attachment



of groups to the carbon atoms of succinic or glutaric acid depresses the tetrahedral angle so as to affect the stability of ring complexes formed from these acids. Consequently, in the fluoresceins and rhodamines of the type of the annexed formula (succinylfluoresceins) the stability of the lactone ring will be affected in a series where R R<sup>1</sup> are made H H, Me Me, Me Et, Et Et, and the *cyclohexane* ring. This

would be evident in the neutral solution of the base or phenol by the fact that the absorption spectra would diminish in intensity in the order given.

The following compounds have been prepared, and their absorption spectra agree with the hypothesis; there is an equilibrium in neutral solution between the lactone and quinone forms and this equilibrium changes with the alteration of the tetrahedral angle.

*Succinylfluorescein*, pinkish-brown needles, m. p. 234°; as-*dimethyl*-, brown needles, m. p. 262—264°; as-*methylethyl*-, brown needles, m. p. 252°; as-*diethyl*-, yellow needles, m. p. 262°; as-*cyclohexane-succinylfluorescein*, brown needles, m. p. 278°. *Glutarylfluorescein*, pinkish-brown needles, m. p. 235°;  $\beta\beta$ -*dimethyl*-, brownish-yellow needles, m. p. 240—245°;  $\beta\beta$ -*methylethyl*-, brown needles, m. p. 278—280°;  $\beta\beta$ -*diethyl*-, yellowish-brown needles, m. p. 162—165°;  $\beta$ -*cyclohexaneglutarylfluorescein*, yellowish-brown needles, m. p. 238—242°.

*Succinylrhodamine hydrochloride*, brown, m. p. 225—230°; *as-dimethyl-*, brown, m. p. 282—284°; *as-methylethyl-*, brown, m. p. 260—265°; *as-diethyl-*, brown, m. p. 250—252°; *as-cyclohexane* derivative, dark red, m. p. 110—112° (free base). *Glutaryl-rhodamine*, reddish-violet, m. p. 190—195°;  $\beta\beta$ -*dimethyl-*, violet-red, m. p. 165—170°;  $\beta\beta$ -*methylethyl-*, violet-red, m. p. 112—115°;  $\beta\beta$ -*diethyl-*, m. p. 120—125°;  $\beta$ -*cyclohexane* derivative, dark violet-red, m. p. 150—153°. The rhodamines in each case are derived from *m*-dimethylaminophenol.

$\alpha\alpha$ -*Diethylsuccinic acid*, m. p. 108°, was prepared by allowing ethyl  $\alpha$ -cyano- $\beta\beta$ -diethylacrylate and potassium cyanide to react in alcohol for 2 weeks at the ordinary temperature, followed by hydrolysis with hydrochloric acid. The condensation of *as*-disubstituted succinic anhydrides with resorcinol (or *m*-dimethylaminophenol) occurs at the carbon atom next to the CH<sub>2</sub> group. This was proved by fusing *as*-dimethylsuccinylfluorescein with potassium hydroxide at 250°, when resorcinol and *isovaleric acid* were formed.

P. C.

**Some [in Part Corrective] Data from Dissertations and Other Literature.** E. BAMBERGER (*Ber.*, 1924, 57, [B], 2082—2091).— $\gamma$ -Phenylacryl-*N*-phenylnitron [cinnamalldoxime *N*-phenyl ether] (cf. A., 1923, i, 60; Hindermann, *Diss.*, Zürich, 1897; Weitnauer, *Diss.*, Zürich, 1904) is converted by sodium amalgam and alcohol into a mixture of benzidine and diphenylene (which are probably due to fission of the nitron into its components by the alcoholic alkali), *N*- $\gamma$ -phenylpropylaniline, b. p. 190—190.5°/8 mm.,  $d^{17}_4$  1.034,  $n^{19}_D$  1.59191 (*hydrochloride*, m. p. 169—170° after softening at 160°; nitrate, m. p. 171°; nitroso derivative), and a secondary amine, C<sub>15</sub>H<sub>17</sub>ON, m. p. 90—91°, which is certainly not identical with  $\gamma$ -phenylpropionanilide (contrast Bigiavi and Marri, A., 1924, i, 518). Phenyl-*N*-phenylnitron is reduced similarly to benzylaniline, whilst *o*-hydroxyphenyl-*N*-phenylnitron, m. p. 116°, *o*-hydroxyphenyl-*N*-*p*-tolylnitron, m. p. 117°, and *o*-hydroxyphenyl-*N*-*p*-bromophenylnitron, m. p. 186—187°, yield, respectively, *o*-hydroxybenzylaniline, m. p. 113°, *o*-hydroxybenzyl-*p*-toluidine, m. p. 122°, and *o*-hydroxybenzyl-*p*-bromoaniline, m. p. 126°.

The nitrons are adapted to the identification of arylhydroxylamines and aldehydes. The following individual substances are described: *N*-phenyl ethers of *p*-nitrobenzalldoxime, m. p. 184—185° (Blaskopf, *Diss.*, Basel, 1895); *p*-hydroxybenzalldoxime, m. p. 214° (cf. Hindermann, *Diss.*, Zürich, 1897); *furfuralldoxime*, m. p. 92°; *piperonalldoxime*, m. p. 133—134°; *vanillinldoxime*, m. p. 217—218° (cf. Weitnauer, *Diss.*, Zürich, 1904). *N*-*p*-Tolyl ethers of benzalldoxime, m. p. 123°; *p*-nitrobenzalldoxime, m. p. 147—148°; *m*-nitrobenzalldoxime, m. p. 133°; *anisalldoxime*, m. p. 129°; *cinnamalldoxime*, m. p. 168° (cf. L'Orsa, *Diss.*, Zürich, 1896). *N*-Xylal ethers of benzalldoxime, m. p. 130°; *p*-nitrobenzalldoxime, m. p. 121—122°; *m*-nitrobenzalldoxime, m. p. 113.5°; *anisalldoxime*, m. p. 94°; *cinnamalldoxime*, m. p. 153° (cf. Baum, *Diss.*, Zürich, 1899).

*p*-Chlorophenyl ethers of benzaldoxime, m. p. 177·5—178°; *p*-nitrobenzaldoxime, m. p. 192°; *m*-nitrobenzaldoxime, m. p. 179—180°; cinnamaldoxime, m. p. 176—176·5°; salicylaldoxime, m. p. 179·5—180·5°; anisaldoxime, m. p. 174—175° (cf. Devas, *Diss.*, Zürich, 1896). *N*-*p*-Bromophenyl ethers of benzaldoxime, m. p. 179·5°; *p*-nitrobenzaldoxime, m. p. 209°; *m*-nitrobenzaldoxime, m. p. 187·5°; cinnamaldoxime, m. p. 183—184° (cf. Stiegelmann, *Diss.*, Zürich, 1896).

The product obtained by Ter-Sarkissanz (*Diss.*, Zürich, 1899) by the action of hydrobromic acid on *m*-tolylhydroxylamine is shown to be the 6-bromo compound, and not the 2-derivative. The following derivatives are described: acetyl compound, m. p. 103—104°; phenylbromotolylthiocarbamide, m. p. 137°; phenylbromotolylcarbamide, m. p. 207°; *N*-salicylidenebromotoluidine, m. p. 83°.

H. W.

**Benzene Substitution. I. Indirect Substitution.** S. SKRAUP and K. POLLER (*Ber.*, 1924, 57, [B], 2033—2038).—The action of zinc chloride on *m*-tolyl acetate at 140—160° yields unchanged material, a little *m*-cresol, and *o*-acetyl-*m*-cresol. *p*-Acetyl-*m*-cresol is not formed when *m*-tolyl acetate remains in contact with zinc chloride during several weeks at the atmospheric temperature, and hence cannot be an intermediate product in the formation of the ortho isomeride. The probability that the production of the latter substance from *m*-tolyl acetate is due to resubstitution and not to intramolecular change is strengthened by the observation that the acetate undergoes fission, probably into chlorozinc tolyloxide,  $C_6H_4Me \cdot O \cdot ZnCl$ , and acetyl chloride, which then undergo a type of Friedel-Crafts reaction. This view is confirmed by the production of 3'-chloro-2-hydroxy-4-methylbenzophenone, m. p. 147°, when the reaction is carried out in the presence of *m*-chlorobenzoyl chloride, which displaces the more volatile acetyl chloride. If, however, the mixture of *m*-tolyl acetate and zinc chloride (*v. s.*) is saturated with hydrogen chloride and preserved at the atmospheric temperature during several weeks, *p*-acetyl-*m*-cresol is obtained in 30% yield (cf. Eykman, A., 1904, i, 664). The ortho isomeride is produced as an intermediate phase, since its yield diminishes as that of the para compound increases, and, further, the conversion of pre-formed ortho into para compound occurs under almost identical conditions. The change in the reverse direction is effected by zinc chloride at 140°. The sharp contrast in the modes of formation of *o*- and *p*-acetyl-*m*-cresol is attributed to the directive influence of the methyl group. With phenyl acetate, on the other hand, the action of zinc chloride and hydrogen chloride yields exclusively *p*-hydroxyacetophenone, whereas both isomerides are formed with zinc chloride alone, which is certainly not the case with *m*-tolyl acetate. It appears that changes involving a unimolecular transformation as an intermediate phase are restricted to substances which can exist in more or less completely ionised forms.

H. W.

**Preparation of isoBenzylidenedeoxybenzoin.** J. PASCUAL (*Anal. Fis. Quím.*, 1924, 22, 509—512; cf. García Banús and Pascual, A., 1922, i, 734).—By the action of bromine on benzyldeoxybenzoin in carbon tetrachloride solution  $\beta$ -bromobenzyldeoxybenzoin, m. p. 86—87°, is obtained. On treating it with silver acetate in cold acetic acid solution, isobenzylidenedeoxybenzoin is obtained.

G. W. R.

**Isomeric Benzoyl Derivatives from Vinyl-diacetonamine.** F. S. KIPPING and T. GREASLEY (*J. Chem. Soc.*, 1924, 125, 2611—2616).—Vinyl-diacetonamine cannot be benzoylated by the Schotten-Baumann method. By heating benzoyl chloride with vinyl-diacetonamine on the water-bath, two products can be formed according to the proportions taken, the products being structural isomerides.

With 1 mol. of benzoyl chloride and 2 mols. of the vinyl base, *N*-benzoylvinyldiacetonamine,  $C_{15}H_{19}O_2N$ , m. p. 155—156°, is formed, giving an *oxime*, m. p. 183—184°, and a *semicarbazide*, m. p. 186—187°. The compound does not combine with bromine nor does it reduce potassium permanganate in the cold, and when distilled it yields by decomposition benzonitrile and benzamide. The compound is doubtless, therefore, the normal *N*-benzoylvinyldiacetonamine.

Vinyldiacetonamine with slightly more than 1 mol. of benzoyl chloride yields an oil from which ill-defined crystals, m. p. 110—111°, can be separated. This compound is isomeric with the *N*-benzoyl derivative, gives benzonitrile and benzamide on distillation, but is unsaturated. Its *semicarbazide* has m. p. about 200°. The constitution is doubtful, but it may be a *N*-benzoylaminomethylheptenone,  $COPh \cdot NH \cdot CMe_2 \cdot CH_2 \cdot CO \cdot CH : CHMe$ , or



*N*-Benzoylvinyldiacetonamine gives the isomeride of m. p. 110—111° on warming with excess of benzoyl chloride, or with less benzoyl chloride in benzene solution only after saturation with hydrochloric acid.

P. C.

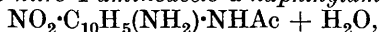
**Attempts to Synthesise 2-Nitro-1:4-naphthaquinone.** G. PANIZZON-FAVRE (*Gazzetta*, 1924, 54, 826—844).—Various unsuccessful attempts to prepare 2-nitro-1:4-naphthaquinone are described. When treated with nitric acid, diacetyl-1:4-dihydroxynaphthalene is oxidised to  $\alpha$ -naphthaquinone, whilst the dibenzoyl compound yields *o*-phthalic and benzoic acids. Nitration of 4-bromoaceto- $\alpha$ -naphthylamide could not be effected, and 4-bromo- $\alpha$ -naphthylamine underwent oxidation with destruction of the naphthalene nucleus. Reduction of 2:4-dinitro- $\alpha$ -naphthol by means of ammonium sulphide proved useless, and the product similarly obtained from dinitrophenol (cf. Ebell, A., 1875, 272, 900) is a mixture. Treatment of 4-acetamido- $\alpha$ -naphthol (naphthacetol) with nitric acid in acetic acid solution gives 2:2'-di-1:4-naphthaquinone (cf. Witt and Dedichen, A., 1897, i, 193; 1898, i, 144). 2-Nitro- $\alpha$ -naphthol resists the action of chromic acid or ammonium persulphate.

Hydrolysis of 3-nitro-1:4-diacetamidonaphthalene by means

of 95% sulphuric acid yields 3-nitro-4-aminoaceto- $\alpha$ -naphthylamide, the remaining acetyl group resisting attempts to remove it. Decomposition of the corresponding diazo compound with concentrated copper sulphate solution proceeds more profoundly than that of diazophenol, which yields nitroquinol under these conditions; the diazo group causes replacement of the nitro group by hydroxyl prior to the decomposition, the final product being 2-hydroxy- $\alpha$ -naphthaquinone.

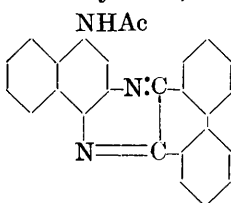
Treatment of 3-nitro-4-aminoaceto- $\alpha$ -naphthylamide with sodium hydroxide results in the elimination of ammonia and the formation of 2-nitro-4-acetamido- $\alpha$ -naphthol, which is not hydrolysed when heated with 30% sulphuric acid solution under a pressure of 5 atmospheres.

1 : 4-Naphthylene dibenzoate,  $C_{10}H_6(OBz)_2$ , has m. p.  $169^\circ$ ; 3-nitro-1 : 4-diacetamidonaphthalene forms yellow, acicular crystals, m. p.  $295^\circ$ , and 3-nitro-4-aminoaceto- $\alpha$ -naphthylamide,



orange-yellow, acicular crystals, m. p.  $273^\circ$ , which assume a deeper colour and lose their water of crystallisation at  $120^\circ$ . 4-Bromo-3-nitroaceto- $\alpha$ -naphthylamide, prepared by diazotising the preceding compound and treating with potassium bromide and copper sulphate, forms canary-yellow crystals, m. p.  $223^\circ$ , and 4-bromo-3-nitro- $\alpha$ -naphthylamine, silky, red crystals, m. p.  $132^\circ$ . 4-Chloro-3-nitroaceto- $\alpha$ -naphthylamide forms pale yellow crystals, m. p.  $223^\circ$ , and 4-chloro-3-nitro- $\alpha$ -naphthylamine, bright red, silky crystals, m. p.  $156^\circ$ .

4-Acetamido-1 : 2-naphthylenediamine, prepared by reducing 3-nitro-4-aminoaceto- $\alpha$ -naphthylamide by means of iron and acetic acid, m. p.  $238^\circ$ , readily undergoes oxidation, becoming dark green. On acetylation, it forms 1 : 3 : 4-triacetamidonaphthalene,



$C_{10}H_5(NHAc)_3$ , m. p.  $301^\circ$ , and on condensation with phenanthraquinone it yields the acetamidonaphthaphenanthrazine (annexed formula), a pale yellow compound not melting at  $325^\circ$ . 2-Nitro-4-acetamido- $\alpha$ -naphthol, silky, yellow needles, m. p.  $238^\circ$  (decomp.), has phenolic properties.  
T. H. P.

**New Dyes of the Anthraquinone Series.** BRITISH DYE-STUFFS CORP., LTD., J. BADDILEY, and W. W. TATUM (Brit. Pat. 224363).—A suitable aminoanthraquinone is condensed with a carboxylic acid of an alkylene oxide, in glacial acetic acid solution, with or without the addition of a catalyst (e.g., copper). The products dye wool in bright shades having good general fastness properties, and are also applicable to the dyeing of cellulose acetate. The dyes obtained from  $\beta$ -methylglycidic acid or the potassium salt of phenylglycidic acid and 1 : 4-diaminoanthraquinone give blue shades, whilst the latter acid gives a red dye with  $\alpha$ -aminoanthraquinone and a purple with 1-amino-4-hydroxyanthraquinone.

W. T. K. B.

**Irreversible Catalysis of Unsaturated Cyclic Hydrocarbons.**

**III. Contact Transformation of Limonene.** N. D. ZELINSKI (*Ber.*, 1924, 57, [B], 2058—2059).—*d*-Limonene resembles cyclohexene and the methylcyclohexenes and methylenecyclohexane (this vol., i, 122) in that it is smoothly and irreversibly transformed, by palladised asbestos at 180—185° or at 130°/120 mm., into *p*-cymene (2 mols.) and menthane (1 mol.). H. W.

**Catalytic Reduction of Thymol to Menthol.** M. DOMINKIEWICZ (*Roczniki Farmacji*, 1924, 2, 28—32; from *Chem. Zentr.*, 1924, ii, 327).—When 30 g. of thymol were reduced catalytically with nickel and hydrogen at 300—350° by Sabatier's process, 10 g. of menthol and 10 g. of hexahydrocymene were obtained.

F. A. M.

**Presence of  $\Delta^1$ -Menthen-3-one in the Essential Oil of Sicilian *Mentha pulegium*.** V. MORANI (*Annali Chim. Appl.*, 1924, 14, 292—303).—The essential oil of Sicilian *Mentha pulegium* var. *hirsuta*, Guss (cf. Pellini, *ibid.*, 1923, 13, 97), is free from pulegone, the principal ketone present being  $\Delta^1$ -menthen-3-one or piperitone (cf. Wallach, A., 1908, i, 811) in both the levorotatory and racemic modifications. The oil thus differs chemically from that obtained on the mainland of Italy and in Central Europe, and differences in odour and physical characteristics are also observed.

T. H. P.

**Essential Oil of *Ptychotis verticillata*, Duby.** V. MORANI (*Annali Chim. Appl.*, 1924, 14, 275—281).—The essential oil of *Ptychotis verticillata*, Duby, which is widespread in Italy and other parts of Southern Europe, contains about 42% of thymol and is free from carvacrol. [Cf. *B.*, 1925, 53.]

T. H. P.

**Olive Resin.** F. REINITZER (*Monatsh.*, 1924, 45, 87—94).—"Olive resin," the dried aqueous sap exuding from roots of *Olea europaea*, L., forms yellow to brown, brittle, odourless lumps, m. p. 54—90°, *d* 1.326, with a bitter taste and a sweet after-taste. It consists generally of masses of crystals contained in a vitreous medium. It is soluble in glacial acetic acid, aqueous chloral hydrate solution, acetone, or ethyl acetate, partly soluble in glycerin, slightly soluble in chloroform, carbon tetrachloride, benzene, light petroleum, or carbon disulphide. When heated, it turns brown, froths, and gives off water and an oil with an odour of carnation oil and acid to litmus. It softens in contact with water, and the proportion of crystalline material increases, whilst tufts of *Styptothrix* grow on the resin and on the containing vessel. In contact with methyl and ethyl alcohols, crystalline products are deposited before they and the resin dissolve. The solution of the resin in concentrated hydrochloric acid deposits a dirty rust-red, flocculent precipitate. With sulphuric acid (*d* 1.839), the resin gives a blood-red colour, which deepens to reddish-violet. It dissolves in sodium hydroxide (5%) to a clear reddish-brown solution which reduces Fehling's solution and ammoniacal silver solutions on boiling. It is soluble in ammonia and partly soluble in sodium carbonate solution. The



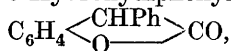
solution in alcohol gives a deep red colour with nitric acid, whilst ferric chloride gives, with aqueous-alcoholic solutions, a dirty violet coloration, which changes to rust-brown as more of the reagent is added, a paler precipitate eventually separating. Early research on the resin is surveyed, and its constitution discussed.

F. G. W.

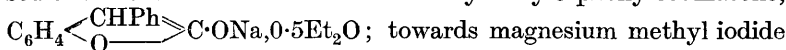
**Presence of a Glucoside Hydrolysed by Emulsin in *Baillonia spicata*, H. Bn., and its Products of Hydrolysis.** H. HÉRISSEY (*Compt. rend.*, 1924, 179, 1419).—Extraction of the leafy branches of the plant by boiling alcohol gives a mixture from which, after removal of alcohol, addition of water, and extraction with ethyl acetate, a solution of a glucoside is obtained. Hydrolysis of the ethyl acetate extract by means of emulsin yields dextrose, and a neutral lactonic compound, *baillonigenole*, prismatic needles, m. p. 185—186°,  $[\alpha]_D$  in 90% alcohol —36·37°. The glucoside could not be isolated.

A. E. C.

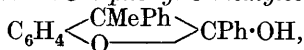
**Enolates of *o*-Hydroxydiphenylacetolactone.** A. LÖWENBEIN and H. SIMONIS [with H. LANG and W. JACOBUS] (*Ber.*, 1924, 57, [B], 2040—2048).—*o*-Hydroxydiphenylacetolactone,



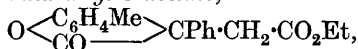
dissolved in anhydrous ether, is readily converted by metallic sodium into the *sodium* derivative of 2-hydroxy-3-phenylcoumarone,



towards magnesium methyl iodide it behaves in the enolic form. The *potassium* derivative is transformed by methyl iodide into 3-phenyl-3-methylcoumaran-2-one, b. p. 181°/10 mm., the constitution of which is established by its formation from phenol and atrolactic acid in the presence of sulphuric acid (73%) at 125°. Magnesium phenyl bromide transforms the ketone into 2 : 3-diphenyl-3-methylcoumaran-2-ol,

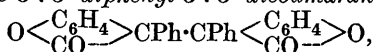


m. p. 108°. 3-Phenyl-5-methylcoumaran-2-one is transformed by methyl iodide and an alcoholic solution of potassium ethoxide into 3-phenyl-3 : 5-dimethylcoumaran-2-one, b. p. 188°/12 mm., which is also obtained from atrolactic acid and *p*-cresol. 3-Phenyl-3-benzylcoumaran-2-one, m. p. 128°, and 3-phenyl-3-benzyl-5-methylcoumaran-2-one, m. p. 131°, are described; the latter substance is converted by potassium hydroxide into *potassium phenylbenzyl-p-hydroxytolylacetate*,  $\text{C}_{22}\text{H}_{19}\text{O}_3\text{K}$ . Phenyl- $\beta$ -hydroxy- $\alpha$ -naphthylacetolactone is converted by benzyl bromide into 3-phenyl-3-benzyl-4 : 5-benzocoumaran-2-one, m. p. 209°, and by  $\omega$ -bromoacetophenone into 3-phenyl-3-phenacyl-4 : 5-benzocoumaran-2-one, m. p. 190°; 3-phenyl-3-phenacyl-5-methylcoumaran-2-one has m. p. 181°. Ethyl 2-keto-3-phenyl-5-methylcoumaranyl-3-acetate,



m. p. 133°, prepared from the corresponding ketone and ethyl

bromoacetate, is hydrolysed to the corresponding acid, m. p. 169°. 3-Phenyl-3-benzoylcoumaran-2-one has m. p. 186°. The action of iodine on the sodium derivative of 2-hydroxy-3-phenylcoumarone yields 2 : 2'-diketo-3 : 3'-diphenyl-3 : 3'-dicoumaranyl,



m. p. about 175°, which is colourless and yields colourless solutions in cold solvents but becomes blue when melted and gives coloured solutions in hot solvents, probably owing to dissociation into radicals; 2 : 2'-diketo-3 : 3'-diphenyl-5 : 5'-dimethyl-3 : 3'-dicoumaranyl, m. p. 190—195°, behaves similarly. The following substances are also described : 3-phenyl-3-ethylcoumaran-2-one, m. p. 72°; 3-phenyl-5-methyl-3-ethylcoumaran-2-one, m. p. 52°; 3-phenyl-3-allylcoumaran-2-one, m. p. 68°; 3-phenyl-5-methyl-3-allylcoumaran-2-one, m. p. 64°; 3-phenyl-3-methyl-4 : 5-benzocoumaran-2-one, m. p. 119° (prepared also by the condensation of β-naphthol with atrolactic acid in the presence of 73% sulphuric acid at 100—130°); 3-phenyl-3-ethyl-4 : 5-benzocoumaran-2-one, m. p. 143°; 3-phenyl-3-allyl-4 : 5-benzocoumaran-2-one, m. p. 96°. H. W.

**Preparation of 4-Acetamidocoumaranone.** B. DIRKS (D.R.-P. 394850; from *Chem. Zentr.*, 1924, ii, 761).—4-Acetamidocoumaranone, obtained by treating 5-acetamido-2-hydroxyacetophenone with permanganate in cold glacial acetic acid, forms yellow crystals, m. p. 240—246° (decomp.). It is tasteless and has anti-pyretic properties. F. A. M.

**An Accessible Derivative of Chromonol.** J. ALLAN and R. ROBINSON (*J. Chem. Soc.*, 1924, 125, 2192—2195).—Various chromone derivatives have been prepared by a modification of Tahara's method (A., 1892, 846; Nagai, *ibid.*, 845; Kostanecki and Rozycki (A., 1901, i, 222). 7-Acetoxy-3-methoxy-2-methylchromone, m. p. 113°, was obtained on heating ω-methoxyresacetophenone with fused sodium acetate and acetic anhydride at 170°. Boiling it with hydriodic acid causes hydrolysis and demethylation and gives 3 : 7-dihydroxy-2-methylchromone, m. p. 249° (decomp.), which is a homologue of the product formed by the aerial oxidation of brazilin (cf. Schall and Drall, A., 1889, 56). Hydrolysis of the acetoxymethoxymethylchromone with 5% sodium hydroxide gave 7-hydroxy-3-methoxy-2-methylchromone, m. p. 214°, which with excess of methyl sulphate yielded 3 : 7-dimethoxy-2-methylchromone, m. p. 120°. The colourless sulphuric acid solutions of all the above substances show bright violet fluorescence. 3 : 7-Dimethoxy-2-methylchromone reacts with magnesium phenyl bromide, followed by hydroferriehloric acid, to form 3 : 7-dimethoxy-4-phenyl-2-methylbenzopyrylium ferrichloride,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \begin{array}{c} \text{O} \text{---} \text{CMe} \\ \text{CPh} \cdot \text{C} \cdot \text{OMe} \end{array} \text{FeCl}_4$ , yellow tablets, m. p. 120°, the sulphuric acid solution of which shows vivid green fluorescence. Under similar conditions, magnesium anisyl bromide yields 3 : 7-dimethoxy-4-p-methoxyphenyl-2-methylbenzopyrylium ferrichloride, m. p. 114° (decomp.). This synthesis

can be extended to the preparation of flavone derivatives. 7-Hydroxy-3-methoxyflavone, m. p. 227°, weak green fluorescence in sulphuric acid, was obtained on heating *o*-methoxyresacetophenone with sodium benzoate and benzoic anhydride at 180–185°. Resacetophenone in a similar manner gives small yields of 7-hydroxyflavone, m. p. 240°, whilst 7-hydroxy-3-benzoylflavone, m. p. 260°, is formed as an intermediate product. The method is more generally applicable to the preparation of flavonols than of flavones.

A. C.

**Preparation of Dixanthylen from Xanthion.** A. SCHÖNBERG [with H. KRÜLL] (*Ber.*, 1924, 57, [B], 2133; cf. Arndt, this vol., i, 57).—Xanthion is converted into dixanthylen when heated with copper powder at 200° in an atmosphere of carbon dioxide.

H. W.

**Reactivity of the Methylene Group in Coumarin-4-acetic Acids and their Esters. Condensation with Salicylaldehyde to 4 : 3'-Dicoumaryls.** B. B. DEY and K. K. ROW (*J. Indian Chem. Soc.*, 1924, 1, 107–122).—Esters of coumarin-4-acetic acids readily give yellow sodium derivatives like those from ethyl phenyl- or cyano-acetate. These esters also condense with salicylaldehyde in presence of piperidine to yield dicoumaryl derivatives, whereas with phenylacetic acid the conditions of the original Perkin reaction are necessary to cause condensation. 3'-Coumaryl-4- $\alpha$ -naphthapyrone,

$\text{CO}-\text{CH}=\text{C} \cdot \text{C} \begin{array}{l} \nearrow \text{CH} \cdot \text{C}_6\text{H}_4 \\ \searrow \text{CO}-\text{O} \end{array}$ , m. p. 255°, from  $\alpha$ -naphthapyrone-4-acetic acid or ester and salicylaldehyde. Acidification of an alkaline solution at 0° yields an unstable coumarinic acid. The following substituted compounds were obtained from the corresponding substituted salicylaldehydes: 6'-bromo-3'-coumaryl-4- $\alpha$ -naphthapyrone, m. p. 292°; 6'-chloro-3'-coumaryl-4- $\alpha$ -naphthapyrone, m. p. 276–277°; 6' : 8'-dichloro-3'-coumaryl-4- $\alpha$ -naphthapyrone, m. p. 301°; 6'-nitro-3'-coumaryl-4- $\alpha$ -naphthapyrone, m. p. 310°; 7'-acetoxy-3'-coumaryl-4- $\alpha$ -naphthapyrone, m. p. 282–284°, after darkening at 270° (from resorcyaldehyde by the Perkin method). 2-Hydroxy-1-naphthaldehyde and ethyl  $\alpha$ -naphthapyrone-4-acetate gave 3'- $\beta$ -naphthacoumaryl-4- $\alpha$ -naphthapyrone, pale yellow crystals not melting at 310°. Condensation of ethyl  $\beta$ -naphthapyrone-4-acetate with salicylaldehyde or the respective substituted aldehyde gave the following: 3'-coumaryl-4- $\beta$ -naphthapyrone, m. p. 282°; 6'-chloro-3'-coumaryl-4- $\beta$ -naphthapyrone, m. p. 276–278° (after darkening at 270°), and 6'-bromo-3'-coumaryl-4- $\beta$ -naphthapyrone, m. p. 260°. From 7-methylcoumarin-4-acetic acid or its ester with salicylaldehyde and substituted derivatives the following were obtained: 7-methyl-4 : 3'-dicoumaryl, m. p. 247° (from which the corresponding coumaric acid was formed by the action of alkali and isolated as silver salt): 6'-bromo-7-methyl-4 : 3'-dicoumaryl, m. p. 292°; 6'-chloro-7-methyl-4 : 3'-dicoumaryl, m. p. 288°, and 6' : 8'-dichloro-7-methyl-4 : 3'-dicoumaryl, m. p. 286°. Bromination of the parent dicoumaryl in glacial acetic acid gave 3 : ( ? )-dibromo-

g\*

7-methyl-4 : 3'-dicoumaryl, m. p. 280—282°, which was converted by alcoholic sodium hydroxide into (?)-bromo-6'-methyl-3(3'-coumaryl)-benzofuran-2-carboxylic acid, m. p. 260°.

Ethyl-7-hydroxycoumarin acetate and salicylaldehyde yielded 7-hydroxy-4 : 3'-dicoumaryl, m. p. 311° (after darkening at 300°) (acetyl derivative, m. p. 253°; benzoyl derivative, m. p. 234°). 7-Methoxy-4 : 3'-dicoumaryl, from methoxybenzaldehyde, has m. p. 241° and 6'-bromo-7-hydroxy-4 : 3'-dicoumaryl, m. p. 308—310° (decomp.), from 5-bromosalicylaldehyde (acetyl derivative, m. p. 247—248°).

Phenylacetic acid, condensed with various substituted salicylaldehydes by Perkin's method, gave the following: 6-chloro-3-phenylcoumarin, m. p. 200°; 6-bromo-3-phenylcoumarin, m. p. 193°; 6 : 8-dichloro-3-phenylcoumarin, m. p. 195·5°, and 7-acetoxy-3-phenylcoumarin, m. p. 186°, hydrolysed to 7-hydroxy-3-phenylcoumarin, m. p. 209—210°, fluorescent in solution. G. M. B.

**Spectrochemistry of Thiophen Derivatives.** K. VON AUWERS and W. KOHLHAAS (*J. pr. Chem.*, 1924, [ii], **108**, 321—331).—Pure specimens of thiophen and the following derivatives were examined spectrochemically: 2-methyl-, 2-ethyl-, 2-propyl-, 2-isoamyl-, 2-*o*-methylbenzyl-, 2-chloro-, 2-bromo-, 3-methyl-, 2 : 5-dimethyl-, 2 : 5-dibromo-, 3 : 4-dimethyl-, and 2-nitro-thiophen, 2-aceto-, 2-propiono-, 2-butyro-, 2-isovalero-, 2-methyl-5-aceto-, 2-ethyl-5-aceto-, 2-propyl-5-aceto-, and 2-benzo-thienone; ethyl 2-thienylglyoxylate, and ethyl 2-thiophencarboxylate. Tables show b. p.,  $d_4^{20}$ ,  $n_D^{20}$ ,  $n_D^{25}$ ,  $n_D^{30}$ ,  $n_D^{35}$ ; from the experimental and calculated values of  $M_a$ ,  $M_D$  ( $M_\beta - M_a$ ), and ( $M_\gamma - M_a$ ) are deduced  $EM_a$ ,  $EM_D$ ,  $E(M_\beta - M_a)$ , and  $E(M_\gamma - M_a)$ ;  $E\Sigma_a$ ,  $E\Sigma_D$ ,  $E(\Sigma_\beta - \Sigma_a)$ , and  $E(\Sigma_\gamma - \Sigma_a)$  are tabulated. Thiophen itself exhibits optical depression, which is diminished by a 2-methyl group and more so by higher alkyl groups; the influence of chlorine is equal to that of methyl, but that of bromine is more powerful. A second substituent further diminishes the depression and groups have the same effect whether in the 2- or 3-position. The ketones illustrate exaltation caused by introduction of an "active" conjugation, whilst high exaltation due to accumulation of double bonds is shown by ethyl thienylglyoxylate and benzothienone. The fact that thiophen behaves as though it were more unsaturated than benzene, although the contrary would be expected from the  $E\Sigma$  values, may be due to its more labile character. The optical properties of thiophen are best explained by the V. Meyer formula.

An optical investigation of Weissgerber's methylthionaphthen, m. p. 52°, obtained from coal tar oil (*Brennstoffchem.*, 1921, **2**, 1), shows the constants to approximate to those for  $\alpha$ -alkyl-, and not for  $\beta$ -alkyl-coumarone, whence it is regarded as  $\alpha$ -methylthionaphthen. The structure of ethyl thionaphthen-2-carboxylate must resemble that of ethyl  $\alpha$ -coumarilate, since their optical properties are similar (cf. Weissgerber and Kruber, A., 1920, i, 754).

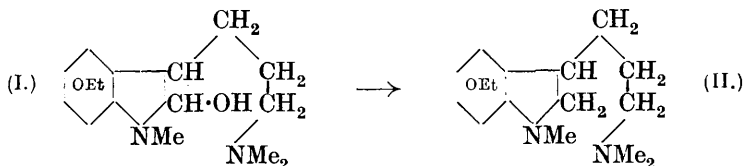
F. M. H.

**Isomerism between Pilocarpine and *iso*Pilocarpine.** W. LANGENBECK (*Ber.*, 1924, **57**, [B], 2072—2076).—It has been assumed by Pinner (A., 1905, i, 463) that the isomerism between pilocarpine and *isopilocarpine* is due to the attachment of the side-chain to the glyoxaline nucleus in positions 4 and 5, respectively. This hypothesis cannot, however, be maintained, since the methiodides formed from the alkaloids are not identical, as, according to Pyman (T., 1910, **97**, 1814), is the case with the methiodides of 4- and 5-substituted glyoxalines. The direct comparison of *isopilocarpine* methiodide, m. p. 114°, with *pilocarpine* methiodide is impossible, since the latter could not be caused to crystallise. The compounds are therefore converted through the *methochlorides* into the *methochloroplatinates*, m. p. 224—225° and 223—224°, respectively (mixed m. p. about 210°). The cause of the isomerism lies in the structure of the side-chain. Ozonisation of pilocarpine dissolved in chloroform followed by decomposition of the ozonide with water gives in good yield the *methylamide* of homopilopie acid,  $\begin{array}{c} \text{CO} \cdot \text{CHEt} \\ | \\ \text{O} - \text{CH}_2 \end{array} > \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHMe}$ , m. p. 104°,  $[\alpha]_{\text{D}}^{15} + 103.7^\circ$ ,  $[\alpha]_{\text{D}}^{15} + 127.7^\circ$ ,  $[\alpha]_{\text{D}}^{15} + 147.0^\circ$ ,  $[\alpha]_{\text{D}}^{15} + 252.9^\circ$  in *s*-tetrachloroethane, whereas *isopilocarpine* under similar conditions yields the *methylamide* of the isomeric homoisopilopie acid,  $\text{C}_9\text{H}_{15}\text{O}_3\text{N}$ , m. p. 53°,  $[\alpha]_{\text{D}}^{15} + 74.5^\circ$ ,  $[\alpha]_{\text{D}}^{15} + 93.9^\circ$ ,  $[\alpha]_{\text{D}}^{15} + 104.9^\circ$ ,  $[\alpha]_{\text{D}}^{15} + 173.5^\circ$  in *s*-tetrachloroethane. The methylamides are hydrolysed by hydrochloric acid to methylamine hydrochloride and homopilopie and homoisopilopie acids, respectively, which could not be caused to crystallise. If the accepted formula for homopilopie acid be correct, the isomerism must be stereochemical.

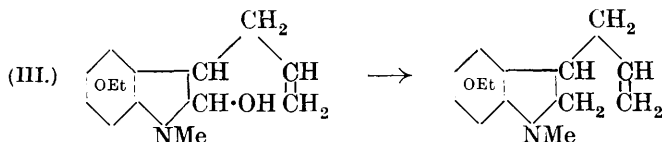
H. W.

**Alkaloids of the Calabar Bean. XIII. Tautomeric Forms of Eserine : Nitroso and Benzoyl Derivatives.** MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1924, [iv], **35**, 1492—1522).—Part of this work has already been published (cf. A., 1924, i, 980, 1093, 1094). Further results have confirmed the formula proposed for eserine (A., 1924, i, 1094) and support the view that on reduction in acid solution the pyridine ring is opened and not an ethylene linking reduced. Reduction of eserine, eseroline, and eserethole does not take place in neutral solution. Reduction of eseretholemethine in acid solution, or with platinum black in alkaline solution, yields a dihydroeseretholemethine giving a methiodide, m. p. 140°, which has also been obtained (1) by reduction of eserine, displacement of the  $\cdot\text{OR}$  group by  $\cdot\text{OEt}$ , and methylation of the dihydroeserethole; (2) by displacement, in eserine, of  $\cdot\text{OR}$  by  $\cdot\text{OEt}$ , giving eserethole, action on this of methylalcoholic methyl iodide, affording eseretholemethine methiodide, and reduction; (3) by action of methylalcoholic methyl iodide on eserine, reduction of the quaternary base so obtained to dihydroeserimethine, displacement of  $\cdot\text{OR}$  by  $\cdot\text{OEt}$ , and methylation of the dihydroeseretholemethine (II). Accordingly, the reduction of

eseretholemethine (I) is represented as involving reduction of  $\cdot\text{CH}(\text{OH})\cdot$  to  $\cdot\text{CH}_2\cdot$ .

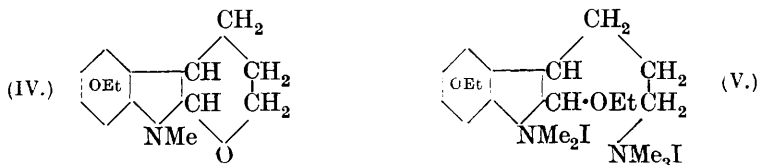


This view is confirmed by the degradation of the dihydroeseretholemethine with concentrated alkali hydroxide into trimethylamine, dihydroeseretholemethine, and dihydroetherserolene,  $\text{C}_{14}\text{H}_{19}\text{ON} + \text{NMe}_3 \cdot \text{HI} \rightarrow (\text{C}_{14}\text{H}_{20}\text{ON})\text{NMe}_3\text{I} \rightarrow (\text{C}_{14}\text{H}_{20}\text{ON})\text{NMe}_2 + \text{MeI}$ , the dihydroetherserolene being identical with that obtained by the reduction of etherserolene using colloidal platinum or platinum black, a reaction which indicates that in reduction of etherserolene (III) it is the hydroxyl group which is reduced.

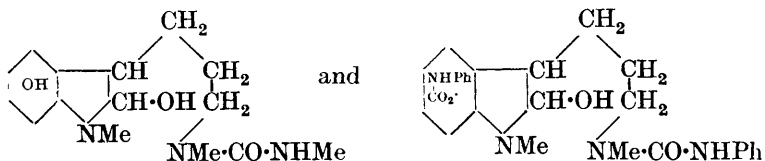


Since, however, etherserolene forms no alkoxide or sodium salt or cyano derivative the existence of the hydroxyl group is somewhat doubtful and its structure is possibly (IV).

In view of the results recently obtained (A., 1924, i, 980), eseretholemethine dimethiodide (A., 1923, i, 939) is regarded as having the structure (V), and the dimethiodides of the reduction



products of eserine will possess analogous structures. The ease with which the heterocyclic ring in eserine is opened on reduction supports the tautomeric structures previously suggested, and the structure suggested for the hydrate (eseranol) allows of the formulation of *iso*eserine and the dicarbanilide (dipheneserine) (A., 1916, i, 221, 284) as



Dihydroeserine has  $[\alpha]_D +10^\circ$ , the hydrochloride,  $[\alpha]_D +13.5^\circ$ . Eserethole has  $[\alpha]_D -81^\circ$  (alcohol),  $-133^\circ$  (light petroleum), or  $-131^\circ$  (dilute acid); its zinc chloride *additive* compound has m. p.  $200^\circ$  (decomp.). Eseretholemethine gives a zinc chloride *additive* compound, m. p.  $199^\circ$ . The zinc chloride *additive* compound of dihydroeseretholemethine has m. p.  $248-249^\circ$  (not  $242^\circ$ , as previously stated). Eseretholemethine methiodide has m. p.  $130^\circ$ , and gives a zinc chloride *additive* compound, m. p.  $207^\circ$ . Dihydroeserimethine methiodide,  $C_{16}H_{25}O_2N_3, MeI$ , has m. p.  $202-203^\circ$ . Dihydroeserethole has  $[\alpha]_D +3^\circ$  (zinc chloride *additive* compound, m. p.  $250^\circ$ ). Trimethylamine gives a zinc chloride *additive* compound, m. p.  $241-242^\circ$ . R. B.

**Extraction of Opium Alkaloids.** S. I. KANEWSKAJA (*J. pr. Chem.*, 1924, [ii], 108, 247—256).—The gums and colouring matter of the opium plant are soluble in aqueous alcohol. By extracting the plant with warm water and adding an equal volume of alcohol and excess of ammonia, morphine and narcotine are precipitated in good yield. They may be separated by dissolving the narcotine in benzene or chloroform, in which morphine is insoluble. The mother-liquors are treated with dilute acetic acid, whereby the strong bases, codeine and thebaine, form salts, and the weak base, papaverine, may then be extracted with benzene. On addition of alkali to the mother-liquors, thebaine is precipitated, codeine remaining in solution. The yields are usually between 80 and 95% of the theoretical. A. E. C.

**Nuclear Hydrogenation of Aromatic and Heterocyclic Compounds with Colloidal Platinum as Catalyst.** A. SKITA. —(See i, 140.)

**Arylated Pyridines. VI. N-Alkylquinopyridans.** W. DILTHEY [with A. SCHAEFER] (*J. pr. Chem.*, 1924, [ii], 108, 332—340; cf. A., 1924, i, 553).—2 : 6-Diphenyl-4-*p*-methoxyphenylpyrylium perchlorate is precipitated from the product of reaction of phenyl *p*-methoxystyryl ketone, acetophenone, acetic anhydride, and a little sulphuric acid; by boiling it with hydrogen bromide in aqueous acetic acid, or by heating its pseudo-base (liberated with sodium hydrogen carbonate) with hydrogen chloride under pressure, 2 : 6-diphenyl-4-*p*-hydroxyphenylpyrylium bromide (or chloride) is formed. The bromide on heating with *m*-nitroaniline at  $150^\circ$  yields 2 : 6-diphenyl-1-*m*-nitrophenyl-4-*p*-hydroxyphenylpyridinium bromide, m. p. above  $360^\circ$ . The chloride (a) on boiling with alcoholic *m*-phenylenediamine gives 2 : 6-diphenyl-1-*m*-aminophenyl-4-quinopyridan (anhydrous and  $+1H_2O$ ), m. p.  $305^\circ$ ; picrate, m. p.  $233^\circ$ ; monoacetyl derivative, m. p.  $322-324^\circ$ ; (b) with *p*-phenylenediamine gives a nearly quantitative yield of 2 : 6-diphenyl-1-*p*-aminophenyl-4-quinopyridan ( $+4H_2O$  [?],  $+1H_2O$ , and anhydrous), m. p.  $265-267^\circ$  or  $308-309^\circ$  (decomp.); hydrochloride, m. p.  $275^\circ$  ( $+1H_2O$  and anhydrous); hydrobromide, m. p.  $299^\circ$ ; picrate, m. p.  $214^\circ$ ; monoacetyl derivative ( $+4H_2O$ ,  $+3H_2O$ , and anhydrous), m. p.  $352^\circ$ . The red quinopyridans, which are

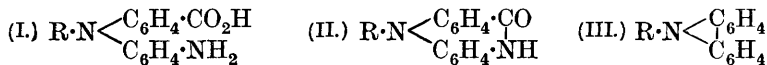
regarded as quinonoid (as are their additive products with water), are converted by 1 mol. of acid into the yellow (benzenoid) salts. From the colour of the acetyl derivatives, the acetyl group is considered to be attached to the nitrogen.

With the reaction product of 2:4:6-tri-*p*-hydroxyphenylpyrylium bromide and aniline, hydrogen bromide forms 1-phenyl-2:4:6-tri-*p*-hydroxyphenylpyridinium bromide, m. p. 252°. From 4:6-diphenyl-2-*p*-hydroxyphenylpyrylium chloride and *p*-phenylenediamine is produced 4:6-diphenyl-1-*p*-aminophenyl-2-*p*-hydroxyphenylpyridinium chloride hydrochloride, m. p. 245°. F. M. H.

**Sulphonation of 4-Amino- and 4-Hydroxy-pyridine.** E. KOENIGS and O. JUNGFER (*Ber.*, 1924, 57, [B], 2080—2082).—4-Aminopyridine is converted by a mixture of concentrated and fuming sulphuric acid at 275° into 4-aminopyridine-3-sulphonic acid, m. p. 336°; the barium salt (+4H<sub>2</sub>O) is described. The acid can be diazotised by cautious addition of it to a solution of sulphur dioxide in fuming nitric acid, and the diazonium compound couples with an alkaline solution of resorcinol to give resorcinol-4-azopyridine-3-sulphonic acid and is converted by alcohol into pyridine-3-sulphonic acid, m. p. 339°. Cautious treatment with water transforms the diazonium compound into 4-hydroxypyridine-3-sulphonic acid, m. p. 265°, which is also obtained by direct sulphonation of 4-hydroxypyridine at 220°; the tetrahydrated barium salt is described.

H. W.

**Preparation of 9-Alkylcarbazoles.** H. BURTON and C. S. GIBSON (*J. Chem. Soc.*, 1924, 125, 2501—2504).—The method is an extension of Ullmann's carbazole synthesis to *N*-alkyl-2'-nitrodiphenylamine-6-carboxylic acids, which are readily obtained by condensation of methyl- and ethyl-anthranilic acids with *o*-bromonitrobenzene in boiling amyl alcohol (methylaniline fails to react).

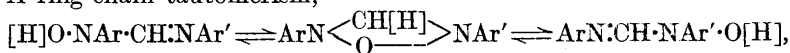


2'-Nitro-*N*-methyldiphenylamine-6-carboxylic acid, deep red crystals, m. p. 136—137° (decomp.), is reduced by ferrous sulphate and ammonia to the 2'-amino-acid (I), m. p. 130° (decomp.) (silver salt described). This is converted into an *anhydro* compound (II), m. p. 213—214°, by heating above its m. p., by dissolving in boiling xylene, by evaporation of the aqueous ammonium salt, or by heating with glycerol. The acetyl derivative of the amino-acid melts at 194° (decomp.). 1-Nitro-*N*-methylacridone has m. p. 176—177°. 9-Methylcarbazole (III), m. p. 88° (picrate, m. p. 147°), is obtained in 82% yield by heating the diazotised amino-acid with alkali at 40° for 12 hours.

2'-Nitro-*N*-ethyldiphenylamine-6-carboxylic acid, yellow crystals, m. p. 135—136°, gives by reduction the 2'-amino-acid (I), m. p. 98° (acetyl derivative, m. p. 145—146°; silver salts of both described). The *anhydro* compound (II) melts at 234—235°. The yield of 9-ethylcarbazole (III), m. p. 67—68° (picrate, m. p. 104—105°), is only 41% (cf. Delétra and Ullmann, A., 1904, i, 270). C. H.

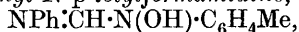


**Tautomerism Depending on the Mobility of a Hydroxyl Group. I. Open-chain Triad Systems.** M. D. FARROW and C. K. INGOLD (*J. Chem. Soc.*, 1924, **125**, 2543—2553).—The possibility of mobile hydroxyl groups in triad systems  $[\text{OH}]\cdot\text{X}\cdot\text{Y}\cdot\text{Z} \rightleftharpoons \text{X}\cdot\text{Y}\cdot\text{Z}\cdot[\text{OH}]$  is investigated in the case of diaryl-*N*-hydroxyformamidines,  $\text{Ar}\cdot\text{N}(\text{OH})\cdot\text{CH}\cdot\text{NAr}'$ . The isomerides (Ar and Ar' interchanged) are not interconvertible and each gives rise to its own fission products. The double bond hence appears to be static. A ring-chain tautomerism,



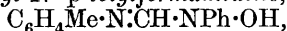
is not, however, excluded if it be supposed that the cycloid isomerises to one or other of the amidines at the moment of formation.

*N*-Hydroxy-*N'*-phenyl-*N*-*p*-tolylformamidine,



prepared by condensing methoxymethyleneaniline with *p*-tolylhydroxylamine in alcohol at 60°, is partly hydrated and melts at 151—152° (decomp.); anhydrous, it has m. p. 158° (blackens). On adding boiling water to its alcoholic solution, it forms a *monohydrate*, possibly  $\text{NHPh}\cdot\text{CH}(\text{OH})\cdot\text{N}(\text{OH})\cdot\text{C}_6\text{H}_4\text{Me}$ , m. p. 142°. The *copper* compound, m. p. 249°, and the *hydrochloride*, m. p. 196° (decomp.), are described. Boiled with aqueous-alcoholic 8% sodium hydroxide, the amidine is decomposed into *p*-azoxytoluene, formic acid, aniline (no *p*-toluidine), and probably 4-*amino-m-cresol*. It could not be converted into the isomeric *N*-phenyl-*N'*-tolyl compound.

*N*-Hydroxy-*N*-phenyl-*N'*-*p*-tolylformamidine,



is prepared similarly from methoxymethylene-*p*-toluidine and phenylhydroxylamine in an impure hydrated form, m. p. 130—140°. A mixture of the pure anhydrous compound, m. p. 151° (decomp.), with the above isomeride melts below 140°. The *monohydrate*, m. p. 138°, *copper* compound, m. p. 253°, and *hydrochloride*, m. p. 200°, are described. On boiling with aqueous-alcoholic alkali it gives azoxybenzene, formic acid, *p*-toluidine, and probably *p*-aminophenol (no azoxytoluene and no aniline).

*N*-Hydroxy-*N*-*p*-chlorophenyl-*N'*-*p*-bromophenylformamidine, m. p. 171° (decomp.), prepared similarly, is identical with the additive product of *p*-chloronitrosobenzene with methylene-*p*-bromoaniline or of *p*-bromonitrosobenzene with methylene-*p*-chloroaniline, but differs markedly from the isomeride described below. The *copper* compound melts at 275° (decomp.), and the *hydrochloride* at 260° (decomp.). It forms no hydrate. The alkaline decomposition products are *pp'*-dichloroazoxybenzene, formic acid, and *p*-bromoaniline. *Methoxymethylene-p*-bromoaniline boils at 245—246°.

*N*-Hydroxy-*N'*-*p*-chlorophenyl-*N*-*p*-bromophenylformamidine, m. p. 168° (decomp.), is prepared from *methoxymethylene-p*-chloroaniline, b. p. 230—231°, and *p*-bromophenylhydroxylamine. It gives a very stable *hydrate*, m. p. 144—145°, a *copper* compound, m. p. 255°, and a *hydrochloride*, m. p. 295° (decomp.). The hydrate

gives on alkaline decomposition *pp'*-dibromoazoxybenzene, formic acid, and *p*-chloroaniline.

C. H.

**Nitration of Stereoisomeric Aromatic Diamines.** G. T. MORGAN and W. J. HICKINBOTTOM (*J. Soc. Chem. Ind.*, 1924, **43**, 307—310r).—Of the four stereoisomeric forms of  $\beta\gamma$ -di-*p*-tolylaminobutane, the *dl* and the *meso* form behave in a precisely similar manner when nitrated. Two methods were adopted, nitration in acetic acid or anhydride and nitration of the sulphate of the base with concentrated nitric and sulphuric acids. The first method gave respectively *dl*- and *meso*- $\beta\gamma$ -3 : 3'-*dinitro*di-*p*-tolylaminobutane (*dl* compound, brownish-red needles, m. p. 200°; *meso* compound, small, scarlet plates, m. p. 195°). With stronger acid, *dl*- and *meso*-3 : 5 : 3' : 5'-*tetranitro*di-*p*-tolylaminobutane were obtained (*dl* compound, orange-yellow needles, m. p. 230°; *meso* compound, small, orange plates, m. p. 212°). Under these conditions, the alkylenediamino group is the orienting agent, the nitration probably taking place through intermediate nitroamine formation. In the second method, this is precluded, the methyl group becoming the orienting factor. The bases then yielded respectively *dl*- and *meso*- $\beta\gamma$ -2 : 2'-*dinitro*di-*p*-tolylaminobutane (*dl* compound, orange needles, m. p. 132°; *meso* compound, yellow needles, m. p. 186°). When heated with sulphuric acid, these compounds give nitro-*p*-toluidine.  $\beta\gamma$ -3 : 5 : 3' : 5'-*Tetranitro*di-*p*-tolylaminobutane, with sodium hydroxide and benzoyl chloride, gives dibenzamidobutane, NHBz·CHMe·CHMe·NHBz, which when heated in a current of hydrogen chloride forms 2-*phenyl*-4 : 5-*dimethylglyoxaline*, m. p. 101—103°; *picrate*, m. p. 190°.  $\beta\gamma$ -Diaminobutane was obtained by fractionation of the product of the interaction of  $\beta\gamma$ -dibromobutane and ammonia in an autoclave at 110—125°.

B. W. A.

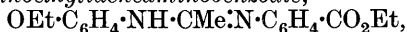
**Preparation of isoDiphenetidine.** J. R. H. WHISTON (*J. Soc. Chem. Ind.*, 1924, **43**, 369—370r).—*m*-Nitrophenetole is obtained by treating *m*-nitrophenol with ethyl *p*-toluenesulphonate, and then reduced to *mm'*-diethoxyhydrazobenzene by zinc dust in alkaline solution. On treatment with hydrochloric acid, this is transformed into *isodiphenetidine*. Like other *ortho*-substituted benzidines, it does not form azo dyes substantive to cotton.

**Electrolytic Reduction of *mm'*-Dinitrodiphenylsulphone to *mm'*-Diaminodiphenylsulphone.** J. LACROIX (*Bull. Soc. chim.*, 1924, [iv], **35**, 1436—1450).—*mm'*-Diaminodiphenylsulphone is readily obtained in 94—95% of the theoretical yield (66·5% on the current consumed) by the electrolytic reduction of *mm'*-dinitrodiphenylsulphone in alcoholic solution, using a lead anode in dilute sulphuric acid (cf. Chilesotti, A., 1901, i, 587). The best results are obtained using a cathode of nickel gauze covered with spongy tin and acidifying the cathodic liquid with hydrochloric acid. Zinc gives very inferior results, and with sulphuric acid the diaminodiphenylsulphone sulphate tends to deposit and stop the electrolysis. The yield is practically unaffected by the concentra-

tion of the acid, but decreases with increase of current density. Agitation of the cathodic liquid and a fine state of division of the dinitrosulphone increase the yield, which also increases with the temperature of the cathodic liquid up to 65–70°. Above 70°, the yield decreases, with formation of resinous by-products. The yield tends to decrease on prolonged electrolysis, and better results are obtained when the dinitrodiphenylsulphone is added in several portions and the electrolysis is stopped before reduction is complete. Owing to the secondary reactions, the volume of hydrogen liberated is not proportional to the amount of diaminodiphenylsulphone produced. The course of the electrolysis is followed by titrating the amine with sodium nitrite, using a solution of diphenylamine in sulphuric acid as indicator, in place of starch-iodide paper.

R. B.

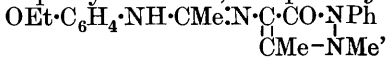
**Local Anæsthetics.** S. WEIL (*Roczniki Farmacji*, 1924, 2, 1–28; from *Chem. Zentr.*, 1924, ii, 208–209).—The author has prepared the following compounds: *phenylethyl chloroacetate*, b. p. 265°/760 mm., 206°/125 mm., 196°/93 mm.; *phenylethyl piperidinoacetate*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NC}_5\text{H}_{10}$ , b. p. 234°/75 mm., 215°/36 mm.; its *hydrochloride*, crystals, m. p. 120°; *phenylethyl diethylaminoacetate*, b. p. 222–223°/135 mm.; *ethyl 4- $\alpha$ -anilinoethylidenaminebenzoate*,  $\text{NHPh}\cdot\text{CMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ , m. p. 132°; *ethyl 4- $\alpha$ -p-ethoxyanilinoethylidenaminebenzoate*,



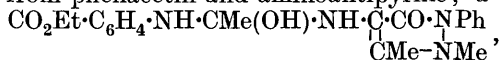
m. p. 138.5°; a *compound*,



m. p. 192°, obtained from the condensation of lactophenine with anæsthesin in the presence of phosphoryl chloride; *4- $\alpha$ -p-ethoxyanilinoethylidenamineantipyrine*,



m. p. 196°, from phenacetin and aminoantipyrine; a *compound*,



m. p. 186–187°, from aminoantipyrine and acetylanæsthesin; a *compound*, m. p. 194–195°, from *p*-aminoacetophenone and para-formaldehyde.

G. W. R.

**Synthetic Experiments in the Glyoxaline Group.** A. SONN, E. HOTES, and H. SIEG (*Ber.*, 1924, 57, [B], 2134).—On the basis of Sarasin's observations (A., 1923, i, 771), it has been assumed that the chlorine atom occupies the position 4 in the chloro-1-methylglyoxaline used by the authors (A., 1924, i, 877). It has since been shown (Sarasin and Wegmann, A., 1924, i, 1115; Balaban and Pyma, J., 1924, 125, 1564) that the substance is 5-chloro-1-methylglyoxaline. The correction should be extended to all the chloro compounds described in the memoir.

H. W.

**Substitution in the Benzene Nucleus on Nitration of 2-Phenylglyoxaline and its Carboxylic Acids.** F. L. PYMAN and E. STANLEY (*J. Chem. Soc.*, 1924, 125, 2484–2488).—Nitration of 2-phenylglyoxaline leads to an easily separable mixture of the

*o*-, *m*-, and *p*-nitro compounds, the yields being 1.5%, 0.2%, and 50%, respectively. The introduction of carboxyl groups progressively diminishes the ratio of para to meta nitration, and this effect is associated with the fact that 2-phenylglyoxaline and its 4(or 5)-carboxylic acid form salts with mineral acids, whilst the 4:5-dicarboxylic acid does not. 2-Phenylglyoxaline-4(or 5)-carboxylic acid gives a mixture of *m*- and *p*-nitro derivatives, from which by decarboxylation the corresponding nitrophenylglyoxalines result in 18% and 52% yield, respectively. Fargher's 2-nitrophenylglyoxaline-4:5-dicarboxylic acid (T., 1921, **119**, 163) is a mixture of *m*- and *p*-isomerides, since it yields on decarboxylation 19% of *m*- and 52% of *p*-nitrophenylglyoxalines. The following compounds are new (all temperatures are corrected).

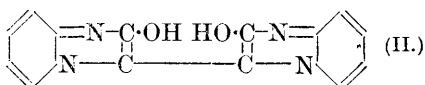
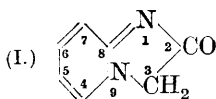
2-*p*-Nitrophenylglyoxaline, m. p. 310—315° (decomp.); nitrate, m. p. 172° (decomp.); picrate, m. p. 262°. 2-*m*-Nitrophenylglyoxaline, m. p. 193—194°; nitrate, m. p. 182° (decomp.); picrate, m. p. 245—246°. 2-*o*-Nitrophenylglyoxaline, m. p. 188—189°; nitrate, m. p. 153—154°; picrate, m. p. 212°. All three nitro compounds are soluble in aqueous sodium hydroxide, but not in ammonia or sodium carbonate solutions.

2-Phenylglyoxaline-4-carboxylic acid forms a nitrate, m. p. 188°. 2-*p*-Nitrophenylglyoxaline-4-carboxylic acid melts and effervesces at 288°, and solidifies and remelts at 308°. The sulphate, m. p. 286° (decomp.), contains about 2H<sub>2</sub>O. 2-*m*-Nitrophenylglyoxaline-4-carboxylic acid melts at 248° (decomp.) (sulphate, m. p. 230°).

C. H.

**Tautomerism of 2-Aminopyridine. III. Dicyclic Derivatives of the Tautomeric Form of 2-Aminopyridine with a Glyoxaline Nucleus.** A. E. TSCHITSCHIBABIN (*Ber.*, 1924, **57**, [B], 2092—2101).—The preparation of pyridylglycine and its conversion into a dicyclic compound regarded as pyridoxyl has been described by Reindel (A., 1924, i, 1235). The latter substance has been prepared in a variety of ways which show that ring closure occurs at the pyridine nitrogen atom and not at the 3-carbon atom, thus yielding a glyoxaline compound; this view is confirmed by the production of similar derivatives from pyridine compounds in which the positions 3 or 5 are already substituted.

2-Aminopyridine is converted by ethyl bromoacetate in warm alcoholic solution into 2-keto-2:3-dihydropyriminazole hydrobromide (cf. I); the corresponding hydriodide (+2EtOH) is described.



2-Pyridoneimine-1-acetic acid (+H<sub>2</sub>O), m. p. 249—250° (decomp.), is obtained from chloroacetic acid and 2-aminopyridine at 75—85° (cf. Reindel, *loc. cit.*); its constitution is established by its conversion when heated into 1-methyl-2-pyridoneimine. It gives a chloroplatinate (+5H<sub>2</sub>O) which does not melt below 310°. The acid

passes slowly in alkaline, rapidly in hydrochloric acid solution into 2-ketodihydropyriminazole hydrochloride (Reindel's pyrimidoxyl hydrochloride); the corresponding *potassium* salt and the *chloroplatinate*, decomp. 240—250°, are described. 3-Oximino-2-ketodihydropyriminazole, m. p. 229° (decomp.), yields a *hydrochloride* and a *chloroplatinate*.

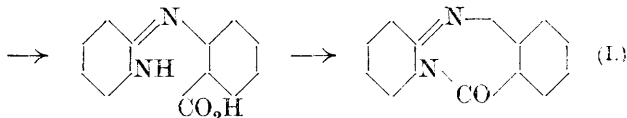
The action of chloroacetyl chloride on 2-aminopyridine in ethereal solution in the presence of pyridine gives 2-chloroacetamidopyridine, m. p. about 110°, and, after re-solidification, m. p. 200—220° (decomp.). 2-Bromoacetamidopyridine has m. p. 91°; after re-solidification, it decomposes at 240° after darkening at 225°. The compounds pass slowly when preserved, rapidly when heated, into the corresponding salts of 2-ketodihydropyriminazole.

2-Amino-3-methylpyridine is converted by ethyl bromoacetate into 2-keto-7-methyldihydropyriminazole hydrobromide; the corresponding *chloroplatinate* darkens at 240—250°. Similarly, ethyl bromoacetate and 3:5-dibromo-2-aminopyridine yield 5:7-dibromo-2-keto-2:3-dihydropyriminazole hydrobromide; the corresponding *chloroplatinate* is described.

Oxidation of the dicyclic compounds to the corresponding dyes is effected with a single equivalent of potassium ferricyanide. Reindel's conception of the compounds as pyrimidogins (*loc. cit.*) is therefore rendered untenable. The constitution (II) is suggested. The *dyes*,  $C_{16}H_{14}O_2N_2$  and  $C_{14}H_6O_2N_2Br_4$ , from 2-amino-3-methylpyridine and 3:5-dibromo-2-aminopyridine are amorphous.

H. W.

**Constitution of "α-Quinoquinolone."** O. SEIDE (*Annalen*, 1924, 440, 311—321).—*o*-Chlorobenzoic acid condenses with 2-aminopyridine in presence of potassium carbonate and copper-bronze at 190—195° with formation of 2:3-dihydrobenzquinazolone-4 (I), pale yellow, m. p. 211°; *hydrochloride*, pale yellow, m. p. 293°; *picrate*, yellow, m. p. 238° (decomp.); *chloroplatinate* (+2H<sub>2</sub>O), orange, anhydrous at 130—140°, m. p. 248°, identical with Reissert's α-quinoquinolone (A., 1895, i, 244). The reaction is formulated  $NH_2 \cdot Py + ClC_6H_4 \cdot CO_2H \rightarrow NHPy \cdot C_6H_4 \cdot CO_2H$



(cf. Tschitschibabin, A., 1921, i, 450, 451; 1924, i, 987), the reactions of the product being more in accord with formula (I) than with Reissert's acridone-analogue structure. On oxidation with acid permanganate, (I) yields carbon dioxide and 2:4-dihydroxyquinazoline, m. p. 356° (cf. Bischler, A., 1895, i, 250; Busch, A., 1895, i, 306; Niementowski, A., 1896, i, 578). The action of phosphorus pentachloride at 180—190° yields a *trichloro* derivative, grey, m. p. 328°, and a yellow *product* containing chlorine, whilst bromine in acetic acid affords a *bromo* derivative, yellow, m. p. 162°, which, on oxidation, yields a *bromo-4-hydroxyquinazoline*,

m. p.  $227^{\circ}$  (decomp.). The *methiodide*, orange needles, obtained by heating (I) with methyl iodide in methyl alcohol, or with methyl sulphate, with subsequent treatment with aqueous potassium iodide, loses methyl iodide at  $270\text{--}290^{\circ}$  in a vacuum, and, on oxidation, yields 1-methyl-2:4-diketotetrahydroquinazoline. Alcoholic sodium ethoxide converts (I) into *sodium  $\alpha$ -pyridyl-anthranilate*, needles ( $+\text{H}_2\text{O}$ ), which is transformed by acids into the sodium salt of the quinazolone. Boiling barium hydroxide solution yields the corresponding barium salt, which, when heated, yields  $\alpha$ -anilinopyridine (cf. Tschitschibabin, A., 1923, i, 597; Fischer, A., 1899, i, 633; 1903, i, 52). The 1:1-*phenyliodide*, brown, m. p.  $365^{\circ}$ , was obtained by boiling the above sodium salt with iodobenzene and copper-bronze, and also by boiling *o*-iodobenzoic acid with  $\alpha$ -anilinopyridine in presence of potassium carbonate and copper-bronze; it yielded 1-phenyl-2:4-diketotetrahydroquinazoline on oxidation.

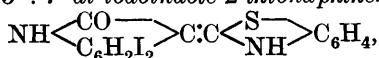
F. G. W.

**Indigotin Group. V. 5:7:5':7'-Tetraiodoindigotin and Related Substances.** L. KALB and E. BERRER (*Ber.*, 1924, 57, [B], 2105—2117).—Dehydroindigotin sodium hydrogen sulphite (cf. A., 1909, i, 967) dissolved in water is converted by iodine chloride at  $5^{\circ}$  into 5:7:5':7'-*tetraiododehydroindigotin sodium hydrogen sulphite* (the corresponding *potassium* salt is described). The compound is about three times as sensitive towards light as the tetrabromo derivative, which is four and a half times as sensitive as the tetrachloro derivative. Dehydroindigotin sodium hydrogen sulphite is twice as sensitive as the tetrachloro compound. The tetraiodo compound is transformed by boiling hydrochloric acid into 5:7:5':7'-*tetraiodoindigotin*, which in tinctorial properties resembles closely the other tetrahalogeno derivatives (*loc. cit.*). Oxidation of 5:7:5':7'-*tetraiododehydroindigotin* sodium hydrogen sulphite with potassium dichromate and sulphuric acid leads to the production of 5:7-*di-iodoisatin*, which exists as a stable red form, decomp.  $240^{\circ}$ , and a less stable yellow modification which passes into the red variety at  $200\text{--}205^{\circ}$ . The yellow product is isolated by crystallisation of the crude product from pyridine and removal of the latter by the use of an indifferent solvent such as benzene. Crystallisation from alcohol, glacial acetic acid, or nitrobenzene gives the red variety exclusively; toluene yields a mixture of the forms, whereas mixed crystals separate from acetone. The two varieties are not polymorphs or polymerides and possibly represent lactam and lactim isomerides.

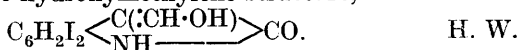
5:7-Di-iodoisatin yields a *phenylhydrazone*, decomp. above  $200^{\circ}$ , an *additive* compound with sodium hydrogen sulphite, and a *cyanohydrin*. Its constitution is established by its conversion into sodium 5:7-di-iodoisatoate and oxidation of the latter to 3:5-di-iodo-2-aminobenzoic acid. It is reduced by hypophosphorous acid to 5:7-*di-iododioxindole*, decomp. above  $200^{\circ}$  after darkening at  $175^{\circ}$ .

5:7-Di-iodoisatin is converted by 3-hydroxythionaphthen-2-

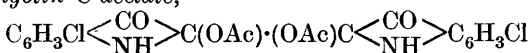
carboxylic acid in the presence of alcohol and sodium carbonate solution into "3-5':7'-*di-iodoindole-2-thionaphthenindigo*,"



which is transformed by sodium ethoxide in alcoholic solution into 5:7-*di-iodo-oxindole-3-aldehyde*, decomp. 230—265° after darkening at 180—200°. The compound gives an *oxime*, a *phenyl-hydrazone*, m. p. 226° (decomp.), and an *anil*, decomp. above 275°; it does not yield a cyanohydrin and cannot be oxidised to the corresponding carboxylic acid. It has strongly acidic properties and gives a blue coloration with ferric chloride. It appears most probably to have the hydroxymethylene structure,



**Indigotin Group. VI. 4:4'-Dichloro-5:7:5':7'-di-iodo-indigotin, 5:6:7:5':6':7'-Hexaiodoindigotin, and Related Substances.** L. KALB and L. VOGEL (*Ber.*, 1924, 57, [B], 2117—2125).—Iodination of the sodium hydrogen sulphite compounds of dehydroindigotin (cf. preceding abstract) can be effected also in cases in which the 4:4' or 6:6' positions are occupied by halogen atoms. Thus, 4:4'-dichloroindigotin, suspended in glacial acetic acid, is oxidised by potassium permanganate to 4:4'-*dichlorodehydroindigotin C-acetate*,



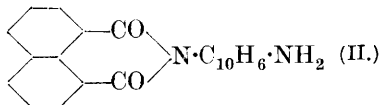
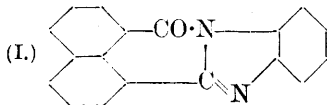
(4:4'-*dichlorodehydroindigotin* is described), which is transformed into 4:4'-*dichlorodehydroindigotin sodium hydrogen sulphite*,  $\text{C}_{16}\text{H}_6\text{O}_2\text{N}_2\text{Cl}_2\cdot 2\text{NaHSO}_3\cdot 2\text{H}_2\text{O}$  (the corresponding *potassium* salt is described); the action of iodine chloride on the sodium salt gives 4:4'-*dichloro-5:7:5':7'-tetraiododehydroindigotin sodium hydrogen sulphite*,  $\text{C}_{16}\text{H}_2\text{O}_2\text{N}_2\text{Cl}_2\text{I}_4\cdot 2\text{NaHSO}_3\cdot 7\text{H}_2\text{O}$ , which is converted by boiling hydrochloric acid into 4:4'-*dichloro-5:7:5':7'-tetraiodoindigotin*. 4-*Chloro-5:7-di-iodoisatin* has m. p. 222—225°; the *sodium* derivative is described.

2-Nitro-*p*-toluidine is converted into 4-iodo-2-nitrotoluene, which is dissolved in a mixture of glacial acetic acid and acetic anhydride and oxidised by sulphuric acid and chromium trioxide at 5—15° to 4-iodo-2-nitrobenzoic acid, which is reduced by ferrous sulphate and ammonia to 4-iodo-2-aminobenzoic acid. The latter substance is converted by chloroacetic acid into 4-*iodophenylglycine-o-carboxylic acid*, m. p. 253—255°, which is transformed into 6:6'-*di-iodoindigotin* (cf. Grandmougin and Seyder, A., 1914, i, 1142). 6:6'-*Di-iododehydroindigotin C-acetate*, prepared from the latter compound in the usual manner (6:6'-*di-iododehydroindigotin* is described), is transformed into its *additive* compound with sodium hydrogen sulphite (the corresponding *potassium* salt is described), and thence into 5:6:7:5':6':7'-*hexaiodoindigotin* 5:6:7-*Tri-iodoisatin* and *sodium* 5:6:7-*tri-iodoisatoate* are described.

The introduction of four iodine atoms into the molecule of

4:4'-dichloroindigotin causes a slight weakening of the green shades of the latter. Among indigoid dyes, the hexaiodo compound approaches most nearly to pure green in colour. H. W.

**Colour of Complex Diazoles. I.** G. C. CHAKRAVARTI (*J. Indian Chem. Soc.*, 1924, **1**, 19—26).—The substitution of the naphthalene for the benzene nucleus in substituted glyoxaline derivatives causes an intensification of the colour. *Toluylene-amidine-2-phenyl-o-carboxylic acid* [4-methylbenzimidazole-2-benzoic acid],  $C_6H_3Me \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} > C \cdot C_6H_4 \cdot CO_2H$ , m. p. 260—262°, from *o*-toluylenediamine and phthalic anhydride, is converted on heating into 1:2-*o*-benzoylene benzimidazole,  $C_6H_3Me \begin{smallmatrix} \text{N:C} \\ \diagup \quad \diagdown \\ \text{N:CO} \end{smallmatrix} > C_6H_4$ , yellow crystals, m. p. 166°. 1':2'-*Naphthiminazole-2-benzoic acid*, m. p. above 300° (cf. Lieb, A., 1919, i, 175), from 1:2-naphthylenediamine and phthalic anhydride, is converted into the corresponding diazole on heating. Naphthalic anhydride and *o*-phenylenediamine yield *o*-aminonaphthalanil, m. p. 245° (decomp.) (acetyl derivative, m. p. 224°; benzoyl derivative m. p., 209°; *N*-ethyl derivative, m. p. 235—237°), and benzimidazole-2-naphthyl-8'-carboxylic acid, m. p. 265—269°. Either of these on heating yields 1:2(1':8')-naphthoylenebenzimidazole (I), yellow needles, m. p. 198°.

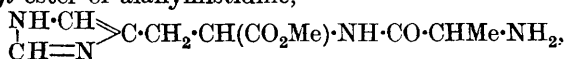


With *o*-toluylenediamine, the corresponding products are *o*-aminotolynaphthalimide, m. p. 196°, 4-iminazole-2(1')-naphthyl-8'-carboxylic acid, m. p. 273—275°, and 1:2(1':8')-naphthoylene-4-methylbenzimidazole, deep yellow needles, m. p. 187°. Naphthalic anhydride and 1:2-naphthylenediamine yield 2'-amino-N-(1')-naphthyl naphthalimide (II), m. p. 300°, which is converted on heating into 1:2(1':8')-naphthoylene-1:3-naphthiminazole,

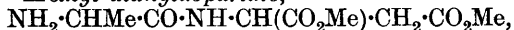
$C_{10}H_6 \begin{smallmatrix} \text{CO:N} \\ \diagup \quad \diagdown \\ \text{C:N} \end{smallmatrix} > C_{10}H_6$ , orange-red crystals, m. p. 256°.

G. M. B.

**Syntheses of certain Dipeptides of Complex Natural Amino-acids.** L. HAVESTADT and R. FRICKE (*Ber.*, 1924, **57**, [B], 2048—2054).—Methyl  $\alpha$ -amino- $\beta$ -glyoxaline-4(or 5)-propionate is converted by alanyl chloride in the presence of chloroform into the methyl ester of alanylhistidine,



from which *alanylhistidine*, a hygroscopic powder, is obtained by hydrolysis. *Methyl alanylaspartate*,



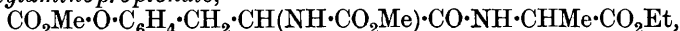
m. p. 187—188°, is derived from methyl aspartate and alanyl chloride hydrochloride; it is hydrolysed to *alanylaspartic acid*,



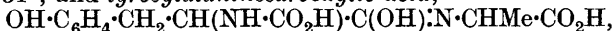
decomp. 155—160°. Tyrosine is converted by methyl chloroformate and sodium hydroxide into *dicarbomethoxytyrosine*,



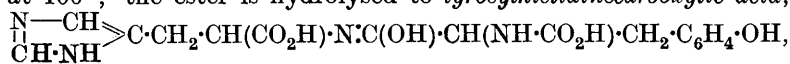
m. p. 97°, which is transformed into the corresponding *chloride* and thence by ethyl  $\alpha$ -aminopropionate into *ethyl  $\alpha$ -dicarbomethoxytyrosylaminopropionate*,



m. p. 131°, and *tyrosylalaninecarboxylic acid*,



decomp. 230° after softening at 140°. *Methyl dicarbomethoxytyrosylaminosuccinate*, m. p. 127°, and *tyrosylaspartic acid*, decomp. 260° after softening at 120°, are described. *dl-Dicarbomethoxytyrosine*, m. p. 96—97°, is converted by phosphorus pentachloride into the corresponding *chloride*, which, with methyl  $\alpha$ -amino- $\beta$ -glyoxaline-4(or 5)-propionate yields *methyl  $\alpha$ -dicarbomethoxytyrosylamino- $\beta$ -glyoxaline-4(or 5)-propionate*, decomp. 140° after softening at 100°; the ester is hydrolysed to *tyrosylhistidinecarboxylic acid*,



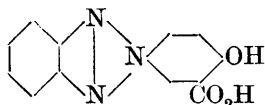
decomp. 275° after softening at about 125°. The optical activity of the dipeptides has not been examined, since, in part, they have been derived from optically inactive compounds and, in addition, racemisation takes place during some of the reactions.

H. W.

**Phenyltriazoles.** K. ELBS (*J. pr. Chem.*, 1924, [ii], **108**, 209—233).—The preparation of several phenyltriazoles by the reduction of *o*-nitroazo compounds is described.

*o*-Nitrobenzeneazophenol on reduction with zinc dust in sodium hydroxide solution gives *2-p-hydroxyphenylbenztriazole*, grey needles, m. p. 219—220°. From this by chlorination, either with nascent or gaseous chlorine, the *mm'-dichloro-s-p-hydroxyphenyl* derivative is obtained as white needles, m. p. 230°. The corresponding *dibromo* derivative melts at 223°, and the *methoxy* derivative has m. p. 136°, and on nitration gives *nitroanisylphenyltriazole*, yellow needles, m. p. 198°. Hydroxyphenylbenztriazole does not couple readily with all diazotised aromatic amines, but diazotised *m*- and *p*-nitroaniline afford *azo* compounds which form respectively a dark yellow powder, m. p. 225°, and a brownish-yellow powder sintering at 275°. The latter gives an *acetyl* derivative, m. p. 253°. Hydroxyphenylbenztriazole on oxidation with potassium permanganate gives phenyltriazole, the *silver* salt being isolated as a white precipitate.

*o*-Nitrobenzeneazosalicylic acid on reduction yields *benztriazole-2 : 5'-salicylic acid* (annexed formula), white needles, m. p. 305°.



The *sodium*, *potassium*, *calcium*, *barium*, and *magnesium* salts, and the *acetyl* derivative ("aspirin benztriazole"), white plates, m. p. 315° (decomp.), are

described.

*o*-Nitrobenzeneazo-*p*-acetamidophenol, small, red crystals, m. p.

153—155°, on hydrolysis and subsequent reduction, yields 2-m-*amino-o-hydroxyphenylbenztriazole*, pale yellow needles, m. p. 282°. The *acetyl* derivative of this (needles, m. p. 266°) and of the *ethyl ether* ("phenacetin benztriazole," yellowish-white needles, m. p. 184°) are described. The pharmacological properties of aspirin benztriazole and phenacetin benztriazole are similar to those of aspirin and phenacetin. The aminohydroxybenztriazole could not be oxidised to the corresponding *p*-quinone.

*o*-Nitrobenzeneazoresorcinol is a red precipitate, m. p. 180° (decomp.), and on reduction gives 2-op-*dihydroxyphenylbenztriazole*, white needles, m. p. 188°, which yields a *dinitro* derivative, yellow needles, decomp. 248°. This gives well-defined *barium* and *copper* salts and an *additive* compound,  $C_{12}H_7O_6N_5 \cdot C_{10}H_8$ , with naphthalene (yellow needles, m. p. 242—243°). *Dibromodihydroxyphenylbenztriazole*, white needles, has m. p. 206°.

*o*-Nitrobenzeneazoresorcinol, a yellow, crystalline powder, on reduction, gives 4 : 6-di-2-benztriazolyldresorcinol, pale yellow needles, m. p. 196—198° (decomp.), in poor yield.

*o*-Nitrobenzeneazoaniline, obtained by coupling diazotised *o*-nitroaniline and phenylaminomethanesulphonic acid, with subsequent hydrolysis, forms red needles, m. p. 192—194°, and on reduction with zinc dust and ammonia yields 2-p-*aminophenylbenztriazole*, white needles, m. p. 155°, which when diazotised is converted into the corresponding *p*-hydroxy derivative. 2-p-*Aminophenylbenztriazole-1-oxide* is produced by the action of ammonium sulphide on nitrobenzeneazoaniline, as pale yellow needles, m. p. 241—243°.

*o*-Nitrobenzeneazodimethylaniline, red plates, m. p. 127°, forms a *hydrochloride* (red crystals), and on reduction with zinc dust and sodium hydroxide yields 2-p-*dimethylaminophenylbenztriazole*, greenish-yellow prisms or yellow needles, m. p. 182—183°; the *hydrochloride*, m. p. 208°, and *methiodide*, white crystals, m. p. 209°, are described, the latter being very unstable in hydroxylic solvents. The corresponding *oxide*, yellow needles, m. p. 167°, is produced by the action of ammonium sulphide on nitrobenzeneazodimethylaniline; the *hydrochloride* melts at 187—188°. If the reduction be carried out with alcoholic sodium sulphide, the products are *o*-aminobenzeneazodimethylaniline, yellowish-red needles, m. p. 133—134°, and *azoxybenzenebisazodimethylaniline*,

$(NMe_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4)_2 N_2 O$ ,  
red needles, m. p. 93—94°.

By coupling diphenylamine with diazotised *o*-nitroaniline, *o*-nitrobenzeneazodiphenylamine results as red needles, m. p. 121°; the *hydrochloride*, m. p. 135° (decomp.), *picrate*, and the *nitrosoamine* (reddish-yellow needles, m. p. 115°) are described. The latter on reduction with ammonium sulphide yields 2-p-*phenylaminophenylbenztriazole-1-oxide* (yellowish-red needles, m. p. 185°), the *hydrochloride* [m. p. 180—190° (decomp.)], and the *nitrosoamine* (yellow prisms, m. p. 154—155°) of which are described. On reduction of *o*-nitrobenzeneazodiphenylamine with zinc dust and alkali (or ammonia), the product is 2-p-*phenylaminophenyl*-

*benztriazole*, yellowish-green plates, m. p.  $137^{\circ}$ , which may also be obtained by the reduction of the above oxide. The *hydrochloride* [m. p.  $158-165^{\circ}$  (decomp.)], *acetyl* derivative (colourless needles, m. p.  $166^{\circ}$ ), *nitrosoamine* (colourless needles, m. p.  $178^{\circ}$ ), and *p'-nitroso* derivative (brownish-green needles, m. p.  $149^{\circ}$ ) are described; the latter on reduction yields 2-pp'-aminophenylaminophenylbenztriazole, yellow plates, m. p.  $132^{\circ}$ , which is easily diazotised. Nitration of diphenylaminophenyltriazole gave a mixture: *op*-Dinitrophenylaminophenylbenztriazole [needles, m. p.  $211^{\circ}$  (decomp.)], and the corresponding *oop*-derivative [stout, brownish-yellow needles, m. p.  $223^{\circ}$  (decomp.)], were obtained by the condensation of aminophenylbenztriazole with chlorodinitrobenzene and picryl chloride, respectively. On nitration, these gave a mixture of derivatives,

$\text{C}_6\text{H}_4\text{N}_3\cdot\text{C}_6\text{H}(\text{NO}_2)_2(\text{op})\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3(\text{oop})$ ,  
m. p.  $244^{\circ}$  (yellow needles), and

$\text{C}_6\text{H}_4\text{N}_3\cdot\text{C}_6\text{H}(\text{NO}_2)_2(\text{mm})\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3(\text{oop})$   
(deep yellow needles). *Diphenylethylamine hydrochloride* (colourless needles) will not couple with diazotised *o*-nitroaniline, but with diazotised sulphanilic acid, an *acid*,  $\text{NPhEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$  (dark blue plates) is obtained.

4-*o*-Nitrobenzeneazo-1-naphthol, reddish-bronze needles, m. p.  $244-245^{\circ}$  (decomp.), on reduction with zinc dust and ammonia, yields 2- $\alpha$ -hydroxynaphthylbenztriazole, pale red needles, m. p.  $204^{\circ}$ ; the  $\beta$ -nitroso derivative, ochre crystals, has m. p.  $154-156^{\circ}$  (decomp.).

By the reduction of *o*-nitrobenzeneazo- $\alpha$ -naphthylamine, dark brown needles, m. p.  $170^{\circ}$ , with zinc dust and ammonia, 2- $\alpha$ -aminonaphthylbenztriazole, is formed as pale yellow needles, m. p.  $150^{\circ}$ , and on diazotisation couples readily with phenols and aromatic primary amines.

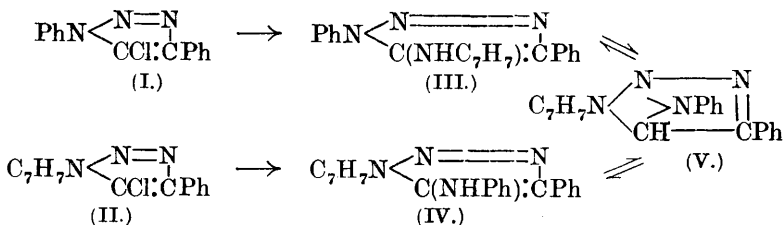
A. E. C.

**Spontaneous Oxidation of 1-Methyluric Acid and 1 : 3-Dimethyluric Acid in Alkaline Solution.** L. PIAUX (*Compt. rend.*, 1924, **179**, 1326—1329; cf. A., 1924, i, 430, 431; *Compt. rend.*, 1924, **179**, 901).—The velocities of oxidation at  $19^{\circ}$  of solutions of uric acid, and its 1-methyl and 1 : 3-dimethyl derivatives, made alkaline with potassium hydroxide, are in the ratio 100 : 91 : 82.5, whilst in presence of manganese hydroxide at  $13^{\circ}$  these ratios become 314 : 323 : 87. By oxidation without a catalyst, 1-methyluric acid yields potassium 3-methyloxonate and, with the catalyst, 3-methylallantoin, thus resembling uric acid, but 1 : 3-dimethyluric acid (with or without a catalyst) gives potassium oxalurate, potassium oxalate, and methylamine.

F. M. H.

**2 : 5-Iminodihydro-1 : 2 : 3-triazole.** II. H. W. CARNELLEY and P. K. DUTT (*J. Chem. Soc.*, 1924, **125**, 2476—2481; cf. T., 1923, **123**, 265).—The product either from 5-chloro-1 : 4-diphenyl-1 : 2 : 3-triazole (I) and *p*-toluidine or from 5-chloro-4-phenyl-1-*p*-tolyl-1 : 2 : 3-triazole (II) and aniline is a mixture of two isomerides, A and B,  $\text{C}_{21}\text{H}_{18}\text{N}_4$ , which are probably the

expected products (III) and (IV) (cf. Dimroth, A., 1909, i, 267; 1910, i, 518):



Dimroth's suggestion that an aliphatic diazo compound,  $\text{NHAr}\cdot\text{C}(\text{NAr}')\cdot\text{CPh}\cdot\text{N}_2$ , is an intermediate in the interconversion of (III) and (IV) is rejected, since no nitrogen is evolved on boiling either isomeride with alcoholic sodium ethoxide. An alternative intermediate (V) is now put forward. The isomeric products A and B behave differently towards nitrous acid in acetic acid, A giving an additive compound, whilst from B a mononitro derivative results.

By a slight modification of Dimroth's method 5-hydroxy-1:4-diphenyl-1:2:3-triazole is obtained in slender needles from alcohol, m. p. 166° (decomp.; Dimroth gives 150—151°).

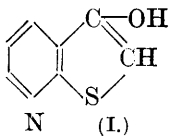
5-Hydroxy-4-phenyl-1-p-tolyl-1:2:3-triazole, m. p. 173—174° (decomp.), similarly prepared, is converted by phosphorus pentachloride in boiling benzene into the 5-chloro compound (II), m. p. 124—125°. The condensation of (I) with *p*-toluidine and of (II) with aniline takes place in absolute alcohol in sealed tubes at 110—145°. The products A and B are the same in both cases and are separated by crystallisation from absolute alcohol, B being the more soluble. Compound A (III or IV), m. p. 227—228°, treated in acetic acid solution with sodium nitrite, yields a yellow substance,  $\text{C}_{21}\text{H}_{18}\text{N}_4\text{HNO}_2$ , m. p. 135—140° (decomp.), which does not give the Liebermann reaction, but when boiled with alcohol is converted into a compound, m. p. 196—198°, not obtained pure. The yellow substance gives a dinitro derivative, m. p. 193—194°, which is stable to boiling alcohol. Compound B (IV or III), m. p. 171—172°, treated in acetic acid solution with sodium nitrite, yields a yellow mononitro derivative, m. p. 197—198°. Both A and B are acetylated by a boiling mixture of acetic anhydride and acetyl chloride. The acetyl derivatives melt at 114—115° and 126—127°, respectively. Nitrosoamines are obtained from A and B by the action of sodium nitrite and alcoholic hydrochloric acid. That from A decomposes at about 140° and on hydrolysis yields an equilibrium mixture of A and B, m. p. 210—217°.

C. H.

**3-Hydroxy-4:5-pyridothiophen.** E. KOENIGS and H. GEISLER (*Ber.*, 1924, 57, [B], 2076—2079).—2-Pyridylthiolacetic acid,  $\text{C}_5\text{H}_4\text{N}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is converted by warm, concentrated sulphuric acid into 2-thiolmethylpyridine, m. p. 54° (hydrochloride, m. p. 152°; chloroplatinate, m. p. 159°; silver salt, m. p. 79—80°); the methyl

group appears to be attached to one of the carbon atoms of the pyridine ring.

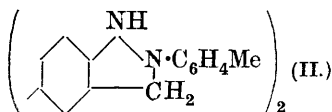
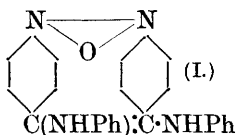
2-Pyridylthiolacetic acid is converted smoothly by boiling acetic anhydride into 3-hydroxy-4:5-pyridothiophen (I) or the tautomeric 3-keto-4:5-pyrido-2:3-dihydrothiophen, m. p. 182°. The corresponding phenylhydrazone, m. p. 146°, and 2:2-dibromo-3-keto-4:5-pyrido-2:3-dihydrothiophen hydrobromide, m. p. 185° (corresponding chloroplatinate, m. p. 171°), are described. H. W.



**Thiodiazines. I. Condensation of Thiosemicarbazide with  $\omega$ -Bromoacetophenone.** P. K. BOSE (*J. Indian Chem. Soc.*, 1924, **1**, 51—62).—Thiosemicarbazide and  $\omega$ -bromoacetophenone yield as the main product of interaction 2-amino-5-phenyl-1:3:4-thiodiazine,  $\text{CPh} \begin{smallmatrix} \text{CH-S} \\ \text{NH-N} \end{smallmatrix} > \text{C} \cdot \text{NH}_2$ , m. p. 125—126° [hydrochloride, m. p. 205°; hydrobromide, m. p. 197°; picrate, m. p. 215° (decomp.); chloroaurate, m. p. 166—167° (decomp.); acetyl derivative, m. p. 172—173°; benzoyl derivative, m. p. 170°; methiodide, m. p. 223° (decomp.); ethiodide, m. p. 234° (decomp.); compound with phenylthiocarbimide, m. p. 179—180°; benzene-sulphonyl derivative, isolated as potassium salt; dithiocarbamic acid derivative, m. p. 181—182°, and its methyl compound, m. p. 159°]. A secondary product of the condensation was isolated as 2-keto-4-phenyl-2:3-dihydro-1:3-thiazoleisopropylidenehydrazone,  $\text{CPh} \begin{smallmatrix} \text{NH} \\ \text{CH-S} \end{smallmatrix} > \text{C} \cdot \text{N} \cdot \text{N} \cdot \text{CMe}_2$ , m. p. 123° [hydrobromide, m. p. 235° (decomp.)], also obtained by the condensation of acetone-thiosemicarbazone with  $\omega$ -bromoacetophenone. This second mode of reaction is the sole one when acetylthiosemicarbazide is used, the product obtained being 2-keto-4-phenyl-2:3-dihydro-1:3-thiazoleacetylhydrazone,  $\text{Ph} \cdot \text{C}_3\text{H}_2\text{NS} \cdot \text{N} \cdot \text{NHAc}$ , m. p. 196—197° [hydrobromide, m. p. 234—235° (decomp.)], hydrolysed to 2-keto-4-phenyl-2:3-dihydro-1:3-thiazolehydrazone, m. p. 167—168°, which reacts with acetone to yield the above isopropylidene derivative, from which it is also obtainable by hydrolysis. [*Anisylidene* derivative, m. p. 225° (decomp.)]. G. M. B.

**Electrochemical Reduction of Nitrobenzylanilines in Weakly Alkaline Solution.** K. ELBS and M. GAUMER (*J. pr. Chem.*, 1924, [ii], **108**, 234—239).—*p*-Nitrobenzylaniline by electrochemical reduction in alcoholic solution, in the presence of sodium acetate, yields dianilino-*p*-azoxystilbene, yellowish-red plates, m. p. 223°, (I). *o*-Nitrobenzylaniline similarly yields a mixture of *o*-azoxybenzylaniline,  $(\text{NHPh} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4)_2\text{N}_2\text{O}$  (colourless needles, m. p. 81°), and *o*-azobenzylaniline (yellowish-red needles, m. p. 142°). The hydrazo compound is very unstable; its oxidation may be prevented by conversion into the corresponding benzidine compound by means of concentrated hydrochloric acid and sodium hydrogen sulphite. The benzidine compound forms brown plates,

m. p. 75°, and may be diazotised and coupled with R-salt to give a deep red *bisazo dye*, absorbed by wool or cotton.



*o*-Nitrobenzyl-*o*-toluidine on electrolytic reduction yields a mixture of *o*-azoxybenzyl-*o*-toluidine,  $(\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4)_2\text{N}_2\text{O}$  (deep yellow plates, m. p. 128°), and *o*-azobenzyl-*o*-toluidine, red needles, m. p. 160°; on further reduction, *o*-hydrazobenzyl-*o*-toluidine (white crystals, m. p. 184°) is produced, with some *o*-aminobenzyl-*o*-toluidine. The hydrazo compound is converted into the unstable benzidine compound by concentrated hydrochloric acid. *o*-Nitrobenzyl-*p*-toluidine on reduction yields *o*-azoxybenzyl-*p*-toluidine, yellow needles, m. p. 99°, and *o*-azobenzyl-*p*-toluidine, yellowish-red needles, m. p. 127°. The hydrazo compound is unstable (m. p. 104°) and conversion into the benzidine base is not effected by dilute sulphuric acid, the product being the *sulphate* of a base,  $\text{C}_{28}\text{H}_{24}\text{N}_4$ , m. p. 180°; the free base (white needles, m. p. 100°) could be neither diazotised nor acetylated and may have the formula (II).

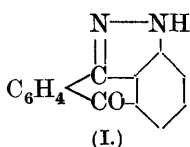
A. E. C.

**Dianilino-*p*-azoxystilbene.** K. ELBS, H. NACKEN, and H. HOFMANN (*J. pr. Chem.*, 1924, [ii], **108**, 240—246; cf. preceding abstract).—By the reduction of *p*-nitrobenzylaniline with zinc dust and sodium hydroxide, dianilino-*p*-azoxystilbene is produced. The *hydrochloride* (yellow crystals, m. p. 193°), *diacetyl* derivative (yellow crystals, m. p. 173°, accompanied by the unstable *diacetyl* derivative of an unstable isomeride), and *dinitrosoamine* (yellow crystals, m. p. 61°) are described; the latter on reduction with zinc dust and hydrochloric acid yields *dianilinodiaminostilbene*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NHPh})\text{:C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)\text{NHPh}$ . Dianilino-*p*-azoxystilbene is reduced with difficulty, but zinc dust and alcoholic hydrochloric acid yield the above diamino derivative, the *oxalate* of which is described. The free base may be diazotised, and on coupling this with resorcinol and R-salt, a deep red dye results. Dianilino-*p*-azoxystilbene with methyl sulphate yields the *dimethyl* derivative as the *hydrogen methyl sulphate* (yellow needles); the free base forms yellow needles. The *hydrogen ethyl sulphate* of the *diethyl* derivative is also described. A *dinitro* derivative and a *disulphonic acid* have also been prepared. By the action of chromic acid in acetic anhydride on the *diacetyl* derivative, *p*-azoxybenzoic acid is produced.

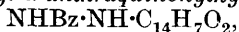
*Dianilinoazoxystilbene dibromide* forms yellowish-white needles, m. p. 123°, and exhibits the peculiar property of being volatile in steam only in the presence of alcohol and acetic acid (cf. Elbs and Diery, *ibid.*, 1893, **47**, 44). It is reduced in alkaline media by zinc dust to dianilinoazoxystilbene and by zinc dust and acid to dianilinodiaminostilbene. The *dinitroso* (yellow crystals, m. p.

189°), *diacetyl* (yellow crystals, m. p. 186°), and *dibenzoyl* (yellow crystals, m. p. 176°) derivatives are described. The dibromide exhibits no basic properties; methyl sulphate yields the free *dimethyl* derivative (yellow crystals, m. p. 192°) and not the salt, and benzyl chloride the free *dibenzyl* derivative (golden-yellow plates, m. p. 196°).  
A. E. C.

**Acylhydrazidoanthraquinones.** M. BATTEGAY and A. M. AMUAT (*Bull. Soc. chim.*, 1924, [iv], **35**, 1450—1462).—In view of the greater auxochromic effect of the hydrazide group,  $-\text{NH}\cdot\text{NH}_2$ , as compared with the amino group, a number of acylhydrazidoanthraquinones have been prepared by the action of acid chlorides or anhydrides on the anthraquinonylhydrazines in nitrobenzene solution.  $\alpha$ -Anthraquinonylhydrazine tends to lose water, yielding

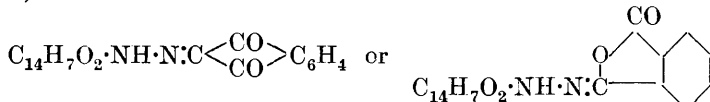


pyrazoleanthrone (I), especially at high temperatures and in the presence of strong acid. The symmetrical structure of the compounds obtained is shown by the facts that they do not react with aldehydes and ketones, that they react with magnesium ethyl bromide yielding 2 mols. of ethane, and that the acyl- $\alpha$ -hydrazinoanthraquinones do not yield pyrazole derivatives by intramolecular condensation. The acylhydrazinoanthraquinones are brilliantly coloured and dissolve in cold concentrated sulphuric acid, yielding an intense red colour. On warming this solution, the acyl- $\alpha$ -hydrazides are converted into pyrazoleanthrones. Sodium and potassium hydroxides give intensely coloured salts, varying from green to violet in colour; these have not been obtained pure and are decomposed even by atmospheric carbon dioxide, regenerating the hydrazine. The potassium salts of the  $\alpha$ -anthraquinonyl derivatives are more strongly coloured than those of the  $\beta$ -derivatives. The acylantraquinonylhydrazines are insoluble in the usual solvents with the exception of pyridine and of nitrobenzene, but they are readily reduced by alkaline hyposulphite, and the solutions, on subsequent exposure to air, dye fast yellow or orange shades on wool, but not on cotton. The shades produced are deeper than those obtained from the corresponding acylamino compounds. Although benzoyl- $\alpha$ -aminoanthraquinone is only slightly coloured, its absorption curve in sulphuric acid resembles that of the highly-coloured benzoyl- $\alpha$ -anthraquinonylhydrazine; the form of the curve for the latter (bands at  $\lambda$  264 and 300) is considerably changed by the addition of boric acid. Benzoyl- $\beta$ -anthraquinonylhydrazine in sulphuric acid shows bands at  $\lambda$  504, 400, 303, and 254. A comparison of the absorption spectra of benzanilide and of benzphenylhydrazide in alcohol also shows the greater auxochromic power of the hydrazine group, the latter compound showing two well-marked bands at  $\lambda$  275 and 232. *Benzoyl- $\alpha$ -anthraquinonylhydrazine*,



yellow, m. p. 269—270°, is obtained from  $\alpha$ -anthraquinonylhydrazine and benzoyl chloride in the presence of sodium acetate; in the absence of the latter reagent and with excess of benzoyl

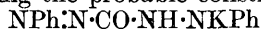
chloride, benzoylpyrazoleanthrone, pale yellow, m. p. 235°, is produced; this compound is also obtained by benzoylating pyrazoleanthrone. *Benzoyl-β-anthraquinonylhydrazine*, yellow, has m. p. 292°. *Formyl-α-anthraquinonylhydrazine*, brownish-yellow, m. p. 282°, is obtained by boiling the anthraquinonylhydrazine with 90% formic acid. *Formyl-β-anthraquinonylhydrazine*, similarly prepared, has m. p. 304°. *Acetyl-α-anthraquinonylhydrazine*, orange, has m. p. 312°; the *acetyl-β-anthraquinonylhydrazine*, yellow, has m. p. 284°. Phthalic anhydride and α-anthraquinonylhydrazine yield *phthaloyl-α-anthraquinonylhydrazine*, orange-yellow, m. p. 300°, the structure of which is either



*Phthaloyl-β-anthraquinonylhydrazine*, pale yellow, has m. p. 320°. *Tetrachlorophthaloyl-α-anthraquinonylhydrazine*, orange-yellow, m. p. 310°, and *tetrachlorophthaloyl-β-anthraquinonylhydrazine*, greenish-yellow, m. p. 320°, were similarly obtained. R. B.

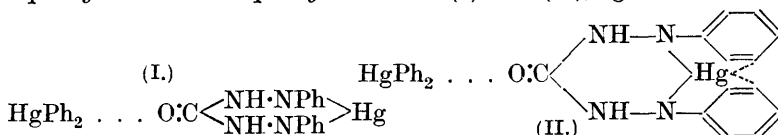
### Relation between Atomic Grouping and Specific Affinity.

I. F. FEIGL (*Monatsh.*, 1924, **45**, 115—132).—*Tetraphenylcarbazide*,  $\text{CO}(\text{NH}\cdot\text{NPh}_2)_2$ , m. p. 236°, obtained by heating *as.*-dimethylcarbamide with *as.*-diphenylhydrazine at 185°, does not form metallic salts, indicating the probable constitution



for the potassium salt of diphenylcarbazone. Oxadiphenylhydrazide,  $(\text{CO}\cdot\text{NH}\cdot\text{NPh})_2$ , has also no salt-forming power, indicating that salt formation takes place by saturation of the residual valency of the ketonic oxygen, as well as by replacement of the labile hydrogen atom.

[With F. L. LEDERER.]—Diphenylcarbazide is a specific reagent for metals of the beryllium—mercury group (cf. Feigl and Neuber, A., 1923, ii, 508). Diphenylcarbazide reacts with mercury diphenyl in alcohol-toluene solution with formation of *mercuri-diphenyl mercuri diphenylcarbazide* (I) or (II), green needles,



violet by transmitted light, decomposing at 200°. *Mercuri-dibenzyl mercuri diphenylcarbazide*, decomp. 150°, was also prepared. *Cadmium dipyrindine diphenylcarbazide*,  $\text{Cd}(\text{C}_5\text{H}_5\text{N})_2[\text{CO}(\text{NH}\cdot\text{NPh})_2]_2$ , dark bluish-green, ruby-red by transmitted light, decomp. below 100°, was obtained by warming diphenylcarbazide, cadmium nitrate, and pyridine in alcohol. *Cadmium diaquodiphenylcarbazide*, similar, is described. *Cadmium diphenylcarbazide*, bluish-green, dichroic, m. p. 200° (decomp.), was obtained by warming diphenylcarbazide with cadmium nitrate in alcohol in presence of pyridine.



If cadmium chloride is used instead of the nitrate, the products contain chlorine (cf. Neuber, *Diss.*, Wien, 1922). *Zincdiphenylcarbazide*,  $\text{Zn}[\text{CO}(\text{NH}\cdot\text{NPh}\cdot)_2]_2$ , dark green, m. p.  $180^\circ$  (decomposition starts below  $100^\circ$ ), obtained by the action of zinc diethyl on diphenylcarbazide in benzene, and *zinc diaquodiphenylcarbazide*,  $\text{Zn}[\text{CO}(\text{NH}\cdot\text{NPh}\cdot)_2]_2(\text{H}_2\text{O})_2$ , bluish-green, cherry-red by transmitted light, m. p.  $178\cdot5^\circ$ , obtained from diphenylcarbazide, zinc acetate, and pyridine, in alcohol, are described. Yields of magnesium compounds, obtained analogously, were poor. By the action of ethereal magnesium ethyl bromide on diphenylcarbazide in benzene, *di(magnesium bromide) diphenylcarbazide di(magnesium ethyl bromide)*,  $(\text{MgBr}_2)_2\text{CO}(\text{NH}\cdot\text{NPh}\cdot)_2\cdot 2\text{MgEtBr}$ , violet, decomposing on exposure to air, was obtained. F. G. W.

**Reactions of Diazo Compounds with Secondary Aromatic Amines.** G. R. LEVI and M. FALDINO (*Gazzetta*, 1924, 54, 818—826).—The coupling of the diazo derivative of sulphanilic acid with phenyl- $\alpha$ -naphthylamine, phenyl- $\beta$ -naphthylamine, and  $\alpha : \alpha$ -,  $\beta : \beta$ -, and  $\alpha : \beta$ -dinaphthylamines, in both acetic and hydrochloric acid solutions, has been investigated.

In either acid solution, phenyl- $\alpha$ -naphthylamine gives 1-anilino-naphthalene-4-diazobenzenesulphonic acid, which imparts to wool an orange-red colour stable to hot 20% sulphuric acid, and, when reduced with sodium hyposulphite, yields  $\alpha$ -phenylnaphthylene-1 : 4-diamine, m. p.  $148^\circ$  (cf. Wacker, A., 1888, 466). Phenyl- $\beta$ -naphthylamine yields  $\alpha$ -anilinonaphthalene- $\beta$ -diazobenzenesulphonic acid, which gives  $\alpha\beta$ -naphthaphenazine when heated with 20% sulphuric acid, forms  $\beta$ -phenylnaphthylene-1 : 2-diamine (cf. Zincke and Lawson, A., 1887, 730) when reduced by sodium hyposulphite, and imparts to wool in a bath rendered slightly acid with sulphuric acid an orange-red colour destroyed by hot 20% sulphuric acid.

$\alpha\alpha$ -Dinaphthylamine reacts with diazotised sulphanilic acid in either acetic or hydrochloric acid solution, forming 1-naphthylaminonaphthalene-4-diazobenzenesulphonic acid, which is violet-black from hydrochloric, and brown from acetic acid, and, when reduced with sodium hyposulphite, gives  $\alpha$ -naphthyl-naphthylene-1 : 4-diamine (cf. Wacker, *loc. cit.*; Cobenzl, A., 1916, i, 77), this having an indefinite m. p. and forming an *acetyl* derivative, white needles, m. p.  $219^\circ$ .

$\beta\beta$ -Dinaphthylamine does not react in acetic acid solution, but in hydrochloric acid solution it gives 1-naphthylaminonaphthalene-2-diazobenzenesulphonic acid, which yields 1-amino-2 : 2'-dinaphthylamine (cf. Fischer, Fritzen, and Eilles, A., 1909, i, 616) when reduced by sodium hyposulphite, and in acid solution is gradually converted into  $s$ - $\alpha\beta$ -dinaphthazine.

In hydrochloric acid solution,  $\alpha\beta$ -dinaphthylamine reacts with diazotised sulphanilic acid to form 1-naphthylaminonaphthalene-4-diazobenzenesulphonic acid, which resists heating with dilute acid and on reduction yields 1- $\alpha$ -naphthylaminonaphthyl-4-amine,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ ; the *acetyl* derivative of this amine has m. p.  $180^\circ$ . In acetic acid solution, however, the product obtained

is 1-naphthylaminonaphthalene-2-diazobenzenesulphonic acid, this, on reduction, giving 1- $\beta$ -naphthylaminonaphthyl-2-amine, colourless needles, m. p. 195° (reddening), which forms an *acetyl* derivative, m. p. 291°.

T. H. P.

### Orientation of Derivatives of Triphenylphosphine Oxide.

F. CHALLENGER and J. F. WILKINSON (*J. Chem. Soc.*, 1924, **125**, 2675—2676).—By the nitration of triphenylphosphine and its oxide, Michaelis and Soden (A., 1884, 1180) obtained a trinitrophenylphosphine oxide (m. p. 242°) which they considered to be the para compound, whilst another product, m. p. 66—68°, was regarded as the ortho derivative. The formation of the compound, m. p. 242°, is confirmed, but not that of the other derivative. It is reduced to the triamino derivative, which is converted into the corresponding trichlorophenylphosphine oxide by the diazo reaction. This compound is identical with *tri-m-chlorophenylphosphine oxide*, m. p. 135°, obtained by the interaction of magnesium *p*-chlorophenyl bromide and phosphoryl chloride. *Tri-p-chlorophenylphosphine oxide* has m. p. 174°.

L. F. H.

**Preparation of a New Arsenic Compound of the Aromatic Series.** L. CASSELLA & Co., G. M. B. H. (Brit. Pat. 214628).—Carbonyl chloride is passed into a solution of 4-amino-3-hydroxyphenylarsinic acid in aqueous sodium acetate. The purified *product* (white crystals) is relatively non-toxic and has valuable effects in diseases caused by spirochaetes and on trypanosomes.

W. T. K. B.

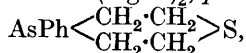
**Organic Derivatives of Silicon. Action of Mercuric Oxide on Diaryldichlorosilicanes.** L. R. VYLE and F. S. KIPPING (*J. Chem. Soc.*, 1924, **125**, 2616—2622).—The attempt to obtain silicones, SiR<sub>2</sub>O, by the action of mercuric oxide on diphenyl- and dibenzyl-dichlorosilicanes, SiR<sub>2</sub>Cl<sub>2</sub>, results in the formation of thick, glue-like substances which probably have the formula (SiR<sub>2</sub>O)<sub>8</sub>. When diphenyldichlorosilicane in toluene is boiled for about 1½ hours with scarlet mercuric oxide, the latter becomes brown and the filtrate on evaporation leaves a thick yellow "glue," from which small quantities of trianhydrotris(diphenyl)silicanediol (Kipping, T., 1912, **101**, 1215) and mercuric phenyl chloride may be extracted by alcohol-acetone. The *M* in benzene after removal of other impurities by steam distillation is 1605. The product is not volatile at 350°/30 mm., and is converted almost completely by alcoholic potassium hydroxide into diphenylsilicanediol. It is soluble in many organic solvents. The mercuric phenyl chloride is probably produced according to the equations: (SiPh<sub>2</sub>O)<sub>n</sub> + nHgO = nHgPh<sub>2</sub> + nSiO<sub>2</sub> and HgPh<sub>2</sub> + HgCl<sub>2</sub> = 2HgPhCl, for trianhydrotris(diphenyl)silicanediol is converted completely by mercuric oxide at 200° into mercury diphenyl and the latter reacts with mercuric chloride in toluene to give mercuric phenyl chloride.

Dibenzyl-dichlorosilicane reacts more slowly with mercuric oxide, six hours' heating in toluene being necessary. The purified product

dissolves readily in ether, acetone, benzene, etc., and has the composition  $\text{Si}(\text{CH}_2\text{Ph})_2\text{O}$ , but like the diphenyl compound it must be regarded as a highly polymerised substance. C. H.

**Existence of Magnesium-arsines and some of their Reactions.** A. JOB, R. REICH, and P. VERGNAUD (*Bull. Soc. chim.*, 1924, [iv], 35, 1404—1412).—Primary and secondary arsines react with magnesium ethyl bromide similarly to primary and secondary amines, yielding magnesium-arsines, with quantitative evolution of ethane (cf. Job and Reich, A., 1923, i, 873). In the same way, phenylarsine (1 mol.) and zinc ethyl iodide (2 mols.) yield *zinc phenylarsine iodide*,  $\text{AsPh}(\text{ZnI})_2$ , and ethane (2 mols.).

Diphenylarsine and magnesium ethyl bromide in ethereal solution yield a crystalline substance,  $\text{AsPh}_2\text{MgBr}$ , which is less soluble and absorbs carbon dioxide less readily than the oily product,  $\text{AsPh}(\text{MgBr})_2$ , previously obtained from phenylarsine. Solutions of the latter substance readily absorb carbon dioxide, giving a precipitate which probably has the composition  $\text{AsPh}(\text{CO}_2\cdot\text{MgBr})_2$ , and on treatment with water or dilute acid is decomposed into magnesium hydrogen carbonate and phenylarsine. Although the acid  $\text{AsPh}(\text{CO}_2\text{H})_2$  is unstable, its ethyl ester is obtained by the action of ethyl chloroformate on the magnesium-arsine in benzene solution in the absence of air. *Ethyl phenylarsinodicarboxylate*,  $\text{AsPh}(\text{CO}_2\text{Et})_2$ , an oil, which does not crystallise at  $-60^\circ$ ,  $d_4^{25}$  1.312,  $n_D^{25}$  1.5442, b. p.  $146^\circ/5$  mm., has a slight ethereal odour and is hydrolysed by alcoholic potassium hydroxide yielding mainly phenylarsine and potassium carbonate, but also a little arsine oxide and ethyl formate. Iodine in aqueous alcohol converts it quantitatively into phenylarsinic acid. The magnesium-arsine,  $\text{AsPh}_2\text{MgBr}$ , similarly gives a *product* distilling at  $160^\circ/3$  mm., yielding carbonate on hydrolysis. Acetyl chloride in benzene solution converts the compound  $\text{AsPh}(\text{MgBr})_2$  into *diacetylphenylarsine*,  $\text{AsPhAc}_2$ , a yellow oil which rapidly oxidises in the air and with methyl iodide yields phenyltrimethylarsonium iodide and acetyl iodide. The compound  $\text{AsPh}_2\text{MgBr}$  behaves similarly. With dihalogen compounds, such as carbonyl chloride and ethylene dibromide, the magnesium arsines are more reactive than ordinary Grignard reagents. Unstable compounds are formed, which decompose, yielding arsenobenzene and carbon monoxide in the first case and arsenobenzene and ethylene in the second. The compound from  $\text{AsPh}_2\text{MgBr}$  and carbonyl chloride yields some phenylacetyl with the carbon monoxide. With  $\beta\beta$ -dichloroethyl sulphide, this doubling of the arsine radical does not take place, and from the compound  $\text{AsPh}(\text{MgBr})_2$ , *phenylthiarsane*,



is obtained. It has m. p.  $38^\circ$ , b. p.  $134^\circ/4$  mm.,  $177^\circ/16$  mm., yields a white *chloromercurate*, m. p.  $181^\circ$  (decomp.), and a yellow *iodomercurate*, m. p.  $153^\circ$  (decomp.), and with methyl iodide a *monomethiodide*, m. p.  $226^\circ$  (*iodomercurate*, m. p.  $147^\circ$ , and *nitrate* described). The resinous substances formed together with phenyl-

thiarsane appear to be polymerides, but their depolymerisation could not be effected.

R. B.

**Pyocyanine, the Blue Pigment of *Bacillus pyocyaneus*. I.**

F. WREDE and E. STRACK (*Z. physiol. Chem.*, 1924, **140**, 1—15).—The most suitable medium for the cultivation of *Bacillus pyocyaneus* is a bouillon prepared from human placenta and containing 1% of peptone and 0.5% of sodium chloride. The optimum reaction of the medium for the formation of pyocyanine (cf. McCombie and Scarborough, T., 1923, **123**, 3279) is at  $p_H$  7.4. This pigment is apparently reduced by the bacillus to a colourless form, from which it can be readily regenerated by shaking the solution with air; the same reduction can be effected with sodium hyposulphite. Pyocyanine,  $C_{26}H_{24}O_2N_4 \cdot H_2O$ , has m. p.  $133^\circ$ ; it is stable at the ordinary temperature, but is decomposed by heat and by oxidising agents. When its solution in alkali is allowed to stand for some hours, the colour changes from blue to wine-red; the same change occurs instantaneously on boiling. Acidification of this solution with acetic acid precipitates the feebly basic, phenolic, yellow substance, *hemipyocyanine*, needles or plates, m. p. about  $146^\circ$ . The latter has not been obtained in a perfectly pure state, but the formula  $C_{13}H_{12}ON_2$  is attributed to it from analyses of its derivatives. Hemipyocyanine may also be prepared by the dry distillation of pyocyanine. *Acetylhemipyocyanine*,  $C_{15}H_{14}O_2N_2 \cdot 2H_2O$ , greenish-yellow needles, m. p.  $120^\circ$ , and *benzoylhemipyocyanine*,  $C_{20}H_{16}O_2N_2$ , green needles, m. p.  $173^\circ$ , are formed by acetylation and benzylation, respectively, of either hemipyocyanine or pyocyanine. The formulæ and constants of the following salts of pyocyanine differ from those given by McCombie and Scarborough: picrate,  $C_{26}H_{24}O_2N_4 \cdot 2C_6H_3O_7N_3 \cdot C_2H_6O$ , decomp. between  $160^\circ$  and  $190^\circ$ , according to rate of heating; picrolonate,

$C_{26}H_{24}O_2N_4 \cdot 2C_{10}H_8O_5N_4 \cdot C_2H_6O$ ,  
decomp. between  $170^\circ$  and  $190^\circ$ ; chloraurate,  $C_{26}H_{24}O_2N_4 \cdot 2HAuCl_4$ ,  
decomp. between  $160^\circ$  and  $185^\circ$ ; chloroplatinate,

$C_{26}H_{24}O_2N_4 \cdot H_2PtCl_6$ ,

does not melt below  $265^\circ$ .

E. S.

**Metallic Salts of Simple Nucleic Acids [Mononucleotides].**

S. IZUMI (*Z. physiol. Chem.*, 1924, **140**, 80—91).—Some amorphous metallic salts of adenylic and guanylic acids have been prepared. The latter acid formed two series according as precipitation was effected in faintly acid or neutral solution; these had the general formulæ  $MA$  and  $M_3A_2$ , respectively, where  $M = Cu, Ca, Ba$ , or  $Pb$  and  $A$  represents the acidic radical. Only the neutral lead salt was prepared. Adenylic acid gave the same copper salt,  $Cu_3(C_{10}H_{12}O_7N_5P)_2$ , from both faintly acid and neutral solutions.

E. S.

**Structure of the Protein Molecule. E. ABDERHALDEN,**

E. KLARMANN, and E. KOMM (*Z. physiol. Chem.*, 1924, **140**, 92—98).—Further evidence pointing to the presence of diketopiperazine rings in proteins is advanced (cf. A., 1924, i, 1345, 1346). Proteins

are known to yield oxamide and oxamic acid on oxidation. When the anhydrides of glycine, alanylglycine, and *dl*-leucylglycine are oxidised with zinc permanganate, oxamide is formed in each case; oxidation of dipeptides (*dl*-alanylglycine, *dl*-leucylglycine) under the same conditions, however, yields a hygroscopic, crystalline substance, which has not been identified, but no trace of oxamide. Silk peptone gives both oxamide and the hygroscopic substance obtained from dipeptides. Glycylglycine differs from the above dipeptides in yielding oxamide. A substance which is probably oxamic acid has also been isolated from *dl*-leucylglycine anhydride. The method of preparation of glycine ester hydrochloride from silk has been slightly improved. E. S.

**Anhydride Structure of Proteins.** E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **140**, 99—108).—The following two additional colour reactions which serve to distinguish between diketopiperazine compounds and polypeptides and depend on the presence of carbonyl groups in the former substances are described: (1) A saturated aqueous solution of 3:5-dinitrobenzoic acid is boiled with 4—5 parts of saturated aqueous sodium carbonate until a light yellowish-red colour appears. Addition of a diketopiperazine compound and further boiling produces an intense red coloration. (2) A small quantity of dilute alcoholic sodium ethoxide is added to a saturated alcoholic solution of 2:4-dinitrostilbene. Addition of a diketopiperazine compound and boiling produces a strong reddish-brown coloration. Both reagents gave positive reactions with all the amino-acid anhydrides tested, with *NN'*-disubstituted diketopiperazines, with most proteins, but not with polypeptides or *OO'*-disubstituted diketopiperazines. Cystine and its derivatives also gave a positive reaction with the first but not with the second reagent. The second reagent is not very suitable for use with proteins owing to their insolubility in alcohol. The contents of the stomach and duodenum of dogs gave positive diketopiperazine reactions for several hours after a protein meal.

*Sarcosine anhydride*, m. p. 145—150°, is prepared by heating sarcosine at 210—220°; *NN'*-dibenzoylglycine anhydride, m. p. 219—221°, from glycine anhydride and benzoic anhydride; *OO'*(?)-diacetylglycine anhydride, m. p. 132—135°, by treating the silver salt of glycine anhydride with acetyl chloride; and *NN'*-diacetylalanylglycine anhydride, m. p. 175—180°, and the corresponding *OO'*-diacetyl compound, m. p. 155—160°, from alanylglycine anhydride and acetic anhydride. E. S.

**Products of the Catalytic Hydrolysis of Goose Feathers (Investigation of the Syrup Soluble in Amyl Alcohol).** W. S. SSADIKOV (*Biochem. Z.*, 1924, **150**, 361—364).—From the amyl-alcoholic extract of hydrolysed goose feathers (A., 1924, i, 1122), a triaminotetracarboxylic acid has been obtained as a bromo derivative,  $C_{33}H_{47}O_9N_3Br_2$ . A copper salt has been isolated of the formula  $C_{18}H_{18}O_8N_3Br_3Cu_2 \cdot 8H_2O$ . The acid is probably present in the extract, not as such, but as an anhydride. J. P.

**Proteins. VIII. Destructive Distillation of Silk Fibroin.**

T. B. JOHNSON and P. G. DASCHAVSKY (*J. Biol. Chem.*, 1924, **62**, 197—207; cf. A., 1919, i, 559).—The destructive distillation of silk fibroin affords carbon dioxide, acetic and propionic acids, aliphatic amines, phenol, *p*-cresol, pyrrole, indole, and quinoline, together with unidentified material, the total fluid and gaseous products amounting to 59% of the silk fibroin; the residual 41% is amorphous carbon (silk coke).  
C. R. H.

**Identity of Gluten Proteins from various Wheat Flours.**

M. J. BLISH and A. J. PINCKNEY (*Cereal Chem.*, 1924, **1**, 309—316).—Determinations of the rates of racemisation in *N*/2-sodium hydroxide of seven samples of glutenin from widely different flours of both high and low baking strengths revealed no significant differences in optical behaviour except in the case of one sample from Polish wheat, an unusual variety with extremely poor baking value. Three samples of pure gliadin were also examined in the same manner; two appeared to be identical, the third, again from Polish wheat, differing slightly. It is concluded that, although there may be cases in which both glutenins and gliadins vary slightly in their respective molecular configurations, it is most unlikely that such differences are the basic cause of variations in flour strength. This is in disagreement with the conclusions of Woodman (*J. Agric. Sci.*, 1922, **12**, 231).  
C. T. G.

**Nitrogen Distribution in Individual Fractions of Catalytically Hydrolysed Collagen.** W. S. SSADIKOV (*Biochem. Z.*, 1924, **150**, 365—367).—An investigation of the nitrogen distribution in various extracts of the product of the catalytic hydrolysis of tendon collagen, from the results of which it is inferred that cyclic compounds of the piprin type, relatively poor in nitrogen, are present, more especially in the ethereal and amyl-alcoholic extracts.

J. P.

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## Biochemistry.

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**I. Determination of the Carbon Dioxide Tension in Alveolar Air. II. Acetylene Narcosis.** H. W. KNIPPING (*Z. physiol. Chem.*, 1924, **141**, 1—10, 11—12).—I. The method previously described (*ibid.*, **137**, 285) for the determination of nitrous oxide in air, which depends on the different thermal conductivities of different gases, is suitable for the determination of carbon dioxide in alveolar air. Clinical applications of the method are discussed, but the apparatus itself is not described in detail.

II. The same apparatus (*loc. cit.*), suitably modified to avoid compression of the gases, may be employed for the administration of acetylene as a narcotic. Since the gases are retained in a closed system, many of the dangers attached to the use of this substance are avoided.

E. S.

**Apparatus for the Graphic Recording of Oxygen Consumption and Carbon Dioxide Output, especially adapted for Clinical Work.** H. C. HAGEDORN (*Biochem. J.*, 1924, **18**, 1301—1307).—A modification of the apparatus designed by Hanriot and Richet based on a system of gas meters in which the inspired and the expired air before and after carbon dioxide absorption are measured. Sources of error arising from the gas meters are reduced to a degree which enables accurate determination of the human respiratory exchange to be made. S. S. Z.

**Influence of the Hydrogen-ion Concentration on the Oxygen Consumption in Sea-water Fishes.** J. R. PEREIRA (*Biochem. J.*, 1924, **18**, 1294—1296).—Over a range of  $p_H$  8.0—4.0, the more acid the water the less is the oxygen consumption of the fishes studied. S. S. Z.

**Dependence of the Excitability of the Respiratory Centre on a definite Ionic Equilibrium in the Blood.** K. GOLLWITZER-MEIER (*Biochem. Z.*, 1924, **151**, 54—83).—In rabbits, the excitability of the respiratory centre depends on the magnitude of the ratio  $[HPO_4^{''} + H_2PO_4']/[K^+]/[Ca^{++}][Mg^{++}]$ , the irritability rising with an increase in the numerator components and *vice versa*. J. P.

**Chemical Regulation of Respiration in Blood of Alkaline Reaction.** K. GOLLWITZER-MEIER (*Biochem. Z.*, 1924, **151**, 424—434).—Slow infusion of sodium carbonate or sodium hydroxide solution scarcely affects the carbon dioxide tension of arterial blood, and respiration likewise remains unaffected despite the alkalinity of the blood. On the other hand, sodium hydrogen carbonate, which also increases blood alkalinity, increases the carbon dioxide tension and the extent of ventilation. Injection of hydrochloric acid following sodium carbonate causes increased respiration similar to that produced by hydrochloric acid alone. J. P.

**New Hæmoglobinometer.** K. BÜRGER (*Pflüger's Archiv*, **203**, 274—284; from *Chem. Zentr.*, 1924, ii, 516).—The apparatus has already been described as a colorimeter (*Z. angew. Chem.*, 1924, **36**, 427). For the exact colorimetry of hæmoglobin, comparison must be made with hæmoglobin itself, and not with substitutes; reduced hæmoglobin keeps well and is suited for colorimetric use. Blood is diluted 100 times with 0.1% sodium carbonate solution and reduced with a trace of sodium hyposulphite, and the determination is made before the atmospheric oxygen can attack the solution. The average error is 1%. F. A. M.

**Replacement of Blood by Solutions containing Gum Arabic.** R. UEKI (*Arch. Exp. Path. Pharm.*, 1924, **104**, 239—249).—In cats, 50% of the total blood can be replaced by Tyrode solution. As a result, the blood pressure begins to fall in a few minutes, and within 1½ hours the injected fluid has disappeared from the blood-vessels. When a solution of gum arabic is used, up to 70% of the blood can be replaced. After this infusion, the blood pressure remains constant and the presence of the solution in the blood-vessels can be demonstrated 24 hours later. O. O.



**Carbon Dioxide Content of Capillary Blood and its Determination.** F. VERZÁR and B. VÁSÁRHELYI (*Biochem. Z.*, 1924, **151**, 246—253).—A modified Barcroft differential manometer is described, together with the method of using it for the determination of the carbon dioxide content of capillary blood. The latter is found to be 50 vols. %, with extremes of 40·8 and 62·3, falling to 35·5 vols. % after exercise. J. P.

**Biochemistry of Irradiation. II. Influence of Ultra-violet and Röntgen Rays on the Water, Salt, and Protein Content of Serum.** C. KROETZ (*Biochem. Z.*, 1924, **151**, 449—463).—In most patients, the water content of the serum increases after irradiation with ultra-violet or X-rays, but is again normal after 24 hours. The alteration of ionic equilibrium in the serum of the irradiated individual is summarised as an increase in the ratio  $K' \times (H_2PO'_4 + HPO''_4) / Ca''$ . Refractometric measurements reveal an alteration in the serum proteins after treatment. J. P.

**Biochemistry of Irradiation. III. Effect of Radiant Heat on the Reaction, the Alkali Reserve, and the Salt Equilibrium of the Blood.** C. KROETZ (*Biochem. Z.*, 1924, **153**, 165—172).—An electric light-bath was used as the source of radiant heat (carbon filament lamps). Human subjects were placed up to the neck in this chamber for periods of 30 to 45 mins. Alveolar air and blood analyses were made before, immediately after, and some 24 hours after the exposure to heat. There was no appreciable rise in body temperature, but a marked fall in the alveolar carbon dioxide unaccompanied by any appreciable change in the alkali reserve or the ionic equilibrium in the blood. H. D. K.

**Action of Sunlight on Complement.** M. JACOBY and M. JACOBY (*Biochem. Z.*, 1924, **151**, 314—317).—Insolation has little or no influence on the activity of complement. J. P.

**Influence of Hydrogen-ion Concentration on the Precipitation of Serum Proteins by Salts. I.** J. CSAPÓ and D. v. KLOBUSITZKY (*Biochem. Z.*, 1924, **151**, 90—97).—The precipitating action of sodium sulphate and chloride solutions on serum proteins is minimal at a  $p_H$  between 7·4 and the isoelectric point and increases at higher or lower  $p_H$ . The protein fractions precipitated at various  $p_H$  show no difference in composition. J. P.

**Mineral Content of Blood Plasma.** M. RICHTER-QUITTNER (*Wien. med. Woch.*, 1924, **74**, 948—951; from *Chem. Zentr.*, 1924, ii, 197).—Calcium salts administered *per os* or intravenously cause an increase in calcium and a decrease in sodium, not only in the plasma, but also in the serous body-fluids. Administration of sodium causes retention of water, whilst in the case of calcium, diuresis with elimination of sodium in the urine is produced. G. W. R.

**Colorimetric Determination of the Inorganic Phosphorus of Serum.** R. ESSINGER and P. GYÖRGY (*Biochem. Z.*, 1924, **149**, 339—343).—The methods of Tisdall (*A.*, 1922, ii, 392), Bell

and Doisy (A., 1920, ii, 769), and Marriott and Haessler (A., 1918, ii, 20) for determining inorganic serum phosphates give concordant results. If hæmoglobin be present, the last-mentioned method gives high results, which are ascribed to the liberation of inorganic phosphoric acid from the red blood-corpuscles during the precipitation in alkaline solution.  
J. P.

**Blood-sugar Curves after Intravenous Injection of  $\alpha$ -,  $\beta$ -, and  $\alpha\beta$ -Glucose in Rabbits.** F. LIPMANN and J. PLANELLES (*Biochem. Z.*, 1924, 151, 98—101).—No significant difference in the magnitude of the hyperglycæmias produced by injection into rabbits of the  $\alpha$ - and  $\beta$ -stereoisomerides of glucose was detected. On the other hand, injection of the equilibrium mixture of  $\alpha$ - and  $\beta$ -forms produced a more marked hyperglycæmia of longer duration than that following injection of either component of the mixture. Equilibrium was attained in this case by addition of ammonia (0.01%).  
J. P.

**Sugar and Fat in (Human) Blood.** W. ARNOLDI and J. A. COLLAZO (*Z. ges. exp. Med.*, 1924, 40, 323—340; from *Chem. Zentr.*, 1924, ii, 198).—After administration of sucrose the blood-sugar increases for 90 minutes, showing a maximum at 15—30 minutes. The ether and ethyl alcohol extract (blood fat) is decreased for 2 hours with a maximum decrease at 50—60 minutes. In obesity, diabetes, and Basedow's disease different curves are obtained. After administration of fat, a small increase in blood-sugar is observed. A slow increase in blood fat occurs. Egg-protein also produces only a small increase in blood-sugar. In diabetes and to some extent in Basedow's disease the blood-sugar is increased during fasting, whilst in obesity it is decreased. It is supposed that after administration of sugar an increased formation of fat from sugar takes place which represses the transference to the blood of fat from the reserve. The depression in blood fat after protein intake may be due to fat being yielded up from the blood to the organs (liver). In diabetes, the formation of fat from sugar is inhibited. Sugar and fat metabolism are closely related.  
G. W. R.

**Micro-determination of Free Sugar in Total Blood.** H. BIERRY and L. MOQUET (*Compt. rend. Soc. Biol.*, 90, 1316—1318; from *Chem. Zentr.*, 1924, ii, 516.)—The authors use the method of Folin and Wu (A., 1920, ii, 337), except that they employ mercuric nitrate instead of tungstic acid for the removal of the protein.  
F. A. M.

**Determination of Sugar in Small Amounts of Blood.** M. GILBERT and J. C. BOCK (*J. Biol. Chem.*, 1924, 62, 361—369).—The method of Folin and Wu (A., 1920, ii, 337) has been adapted for use with about 0.15 g. of blood, the amount of blood being measured by drawing into a weighed capillary tube and weighing on a torsion balance.  
C. R. H.

**Determination of Sugar in Blood.** E. G. B. CALVERT (*Biochem. J.*, 1924, 18, 839—844).—The blood is diluted with

water and treated with 10% sodium tungstate and 0.67*N*-sulphuric acid, filtered, an aliquot portion of the filtrate treated with standard copper solution, boiled, and phosphomolybdic acid is added. The blue colour produced is compared with that of a standard sugar solution or of a standard blue disc. S. S. Z.

**Colorimetric Determination of Sugar in Blood.** F. J. PATON (*Biochem. J.*, 1924, **18**, 965—970).—The blood is boiled with a solution of sodium sulphate, and treated with dialysed iron to remove the protein. The filtered liquid is treated with sodium hydroxide and dinitrosalicylic acid on a boiling water-bath and the colour produced compared with that of a standard sugar solution in a Nessler cylinder. Accurate results can be obtained with 0.5 c.c. of blood. Sodium dinitrosalicylate is not appreciably affected by the presence of other reducing substances in the blood, and no error due to reoxidation need be feared with this method. S. S. Z.

**Iodometric Determination of Sodium in Small Amounts of Serum.** B. KRAMER and I. GITTLEMAN (*J. Biol. Chem.*, 1924, **62**, 353—360).—The sodium is precipitated as the pyroantimonate by the method of Kramer and Tisdall (*A.*, 1921, ii, 463), the precipitate centrifuged, dissolved in excess of concentrated hydrochloric acid, and the liberated antimonious acid determined iodometrically. The maximum error of the method is  $\pm 2\%$ . C. R. H.

**Influence of some Aliphatic Substances on the Level of Lactic Acid and Sugar in the Blood.** F. KNOOP and H. JOST (*Z. physiol. Chem.*, 1924, **141**, 55—61).—The increased excretion of lactic acid by dogs following the administration of propionic and  $\beta$ -hydroxybutyric acids (*A.*, 1923, i, 1261) is not preceded by a rise in the levels of lactic acid and sugar in the blood. Acetaldehyde, on the other hand, increases the blood-sugar and blood lactic acid without causing an increased excretion of the latter substance. These results seem to exclude the possibility that the effect of propionic and  $\beta$ -hydroxybutyric acids is due to the intermediate formation of acetaldehyde, but rather suggest that it is due to the action of the acids on the kidneys. Hence there is no evidence of the direct conversion of the acids into lactic acid, *i.e.*, of the occurrence of a physiological  $\alpha$ -oxidation of fatty acids. E. S.

**Behaviour of a Substance giving the Nitroprusside Reaction in Skin and in Hair.** M. KAYE (*Biochem. J.*, 1924, **18**, 1289—1293).—The substance is connected with active metabolism and varies with the degree of metabolism. It is present in the cellular and absent from the extracellular structures of the skin. It is present in the roots of healthy hair, and the intensity of the glutathione reaction varies with the vitality of the hair. S. S. Z.

**Isolation of Spermine Phosphate from Semen and Testis.** O. ROSENHEIM (*Biochem. J.*, 1924, **18**, 1253—1262).—(1) Modified Vauquelin's method: After keeping for some hours, semen is

mixed with 0.9% sodium chloride solution and centrifuged. The residue is repeatedly washed and eventually boiled with alcohol and washed with ether. On extracting this purified residue with boiling water, spermine phosphate passes into solution and separates on cooling. (2) Modified Schreiner's method: Semen is precipitated with alcohol and the precipitate dried. This is washed in the centrifuge with water until an adhering water-soluble protein is removed. The precipitate is finally washed with alcohol and ether and extracted with boiling water from which spermine phosphate crystallises on cooling. (3) Dialysis method: The alcohol precipitate prepared as above is dialysed under sterile conditions. After concentrating the dialysate, spermine phosphate is deposited. (4) Butyl alcohol method: The alcohol precipitate from semen is precipitated with saturated lead acetate after being taken up in acidified boiling water, freed from lead, and extracted from alkaline solution continuously with butyl alcohol. Spermine is removed from the extract with phosphotungstic acid and liberated in the usual way. (5) Steam distillation method: The alcohol precipitate from semen is dissolved in alkali and steam-distilled. The distillate is evaporated nearly to dryness, taken up in little water, and treated with ammonium phosphate, when spermine phosphate crystallises out. Spermine is also present as the phosphate in testis. Chemical and crystallographical evidence is brought which proves the identity of spermine from semen with the base obtained by similar methods from various animal organs and also from yeast. S. S. Z.

**Bile Acids. XXI. Human Bile. I. H. WIELAND and G. REVEREY** (*Z. physiol. Chem.*, 1924, **140**, 186—202).—The human bile employed in this investigation was obtained from the gall bladders of corpses. It was preserved with toluene or chloroform, but nevertheless had undergone some putrefaction before the constituents were examined. For the isolation of the bile acids, it was boiled with 10% potassium hydroxide for 12 hours, made just acid to Congo-red by the addition of 7*N*-sulphuric acid, and the precipitate allowed to settle. From the supernatant liquid succinic acid was isolated by continuous extraction with ether (0.5 g. per litre of bile). The sediment consisted mainly of bile acids, bile pigments, fatty acids, and cholesterol. Biliverdin (formed from bilirubin by autoxidation during the hydrolysis) was isolated in a pure state (12—14 g. per litre of bile). The bile acids were separated by fractional extraction of their ethereal solution with *N*/2-sodium hydroxide and were found to consist of cholic and deoxycholic acids and a new acid,  $C_{24}H_{40}O_4$ , m. p. 105—110°,  $[\alpha]_D^{25} + 11.1^\circ$  in alcohol. This acid, which occurs in considerable amount in human bile, has been named anthro-po-deoxycholic acid; it is identical with the cheno-deoxycholic acid isolated by Windaus, Böhne, and Schwarzkopf (*ibid.*, 177) from goose bile and yields derivatives identical with those described by these authors. It gives a deep reddish-brown coloration changing to olive-brown with the Liebermann-Burchard reaction, and a *diformyl* derivative which melts and foams at 137°,  
h\*

solidifies with further heating, and again melts at 172°. Dehydro-anthropo(cheno-)deoxycholic acid is reconverted into anthropo-deoxycholic acid by catalytic hydrogenation. The choladiene-carboxylic acid, m. p. 138°, obtained by distillation of anthropo-deoxycholic acid is possibly a mixture of two isomerides. In agreement with Windaus, Bohne, and Schwarzkopf (*loc. cit.*), the authors consider that anthropo-deoxycholic acid is 3 : 13-dihydroxy-cholanic acid.  
E. S.

**Nucleic Acid of Pancreas.** E. JORPES (*Biochem. Z.*, 1924, **151**, 227—245).—From an alkaline extract of ox-pancreas, after removal of protein and nucleic acid, there were obtained, in addition to guanylic acid, uracil pentosephosphoric acid and cytosine pentose phosphoric acid, identified by the solubilities, nitrogen, phosphorus, and pentose contents of their brucine salts. It is suggested that the polynucleotide with which guanylic acid is associated in animal tissues (Feulgen, A., 1919, i, 603) may be yeast-nucleic acid (cf. also Hammarsten and Jorpes, A., 1922, i, 387).  
J. P.

**Occurrence of Plant Nucleotides in Animal Tissues.** W. JONES and M. E. PERKINS (*J. Biol. Chem.*, 1924, **62**, 291—300).—On the addition of potassium acetate to the solution of mixed nucleotides obtained by the hydrolysis with 1.25% sodium hydroxide, at the ordinary temperature, of the  $\beta$ -nucleoprotein from pancreas (cf. Steudel and Brigl, A., 1910, i, 703), the potassium salt of guanine nucleotide separated; from the filtrate were isolated the nucleotides of adenine and cytosine, the latter being separated by fractional crystallisation of their brucine salts. The results indicate that a sharp distinction cannot be drawn between nucleotides of plant and of animal origin.  
C. R. H.

**Determination of Bismuth in Organs, Blood, and Excreta.** W. AUTENRIETH and A. MEYER (*Munch. med. Woch.*, 1924, **71**, 601—603; from *Chem. Zentr.*, 1924, ii, 220—221).—Details are given of a colorimetric method for the determination of minute quantities of bismuth based on the formation of potassium bismuth iodide. The preliminary treatment consists in digestion with hydrochloric acid and potassium chlorate followed by precipitation of the bismuth as sulphide. Bismuth ("Neo-Wismulen") injected intravenously is eliminated principally through the kidneys, to some extent in the fæces, and in traces in the saliva. In one case several mg. of bismuth were found in the kidneys, spleen, and liver 35 days after the last intramuscular injection of "bismugenol."  
G. W. R.

**Determination of Cholesterol and its Esters in Tissues.** II. J. A. GARDNER and F. W. FOX (*Biochem. J.*, 1924, **18**, 1058—1069).—Hydrolysis experiments with cholesteryl oleate, palmitate, stearate, arachidate, and cerotate have shown that by boiling for 4 hours with 60 c.c. of *N*-alcoholic sodium hydroxide complete hydrolysis is attained except with the cerotate, in which case only 45% was hydrolysed. Good results were also obtained when the ethereal

solutions of the esters were kept for 24 hours with cold alcoholic sodium ethoxide. In this case, 84% for cholesteryl cerotate, 98% for cholesteryl stearate, and 100% hydrolysis of the remaining esters was effected. When heated for 4 hours with 10 c.c. of 25% aqueous sodium hydroxide, only cholesteryl oleate was hydrolysed entirely. In all the other esters, the hydrolysis was incomplete. Sodium cholesteryl sulphate is unaffected by boiling with aqueous alkalis and even with sodium ethoxide, but is completely hydrolysed by boiling with acid. The potassium compound is also hydrolysed by acid and is resistant to the action of aqueous alkali. S. S. Z.

**Determination of Small Quantities of Copper in Tissues.** A. N. CURRIE (*Biochem. J.*, 1924, **18**, 1224—1226).—A colorimetric method based on the formation of Scheele's green (copper hydrogen arsenite) by treatment of the copper present with sodium arsenite prepared by the interaction of sodium hydroxide with arsenic chloride. It is sensitive to 1 in 135,000 of copper sulphate. The limits of efficiency of the method are circumscribed, since the upper limit of copper sulphate concentration for which it will give trustworthy results is 0.00508 g. of the salt in 10 c.c. of water. An increase in concentration beyond this point brings about sedimentation of a green substance. S. S. Z.

**Determination of Minute Quantities of Iodine in Biological Material.** F. C. KELLY and A. D. HUSBAND (*Biochem. J.*, 1924, **18**, 951—956).—A modification of Kendall's method. The substance is fused with sodium hydroxide and potassium nitrate, fixing the iodine as sodium iodide. The latter is oxidised to iodic acid with bromine and the iodine is then liberated by treating with potassium iodide and titrated with sodium thiosulphate. S. S. Z.

**Iodine Content of Sea Foods.** D. K. TRESSLER and A. W. WELLS (*U.S. Bureau Fisheries, Document 967*, 1924, 1—12; cf. von Fellenberg, *Mitt. Lebensm. Hyg.*, 1923, **14**, 101; Forbes and Beagle, *J. Med. Res.*, 1916, **34**, 445).—The following are arranged in order of decreasing iodine content: (i) marine algæ, (ii) oysters, clams, and lobsters, (iii) shrimp, (iv) crabs and most ocean fishes, (v) fresh-water fishes, vegetables, beef, milk.

#### CHEMICAL ABSTRACTS.

**Determination of Iron in Small Quantities in Biological Substances.** M. M. MURRAY (*Biochem. J.*, 1924, **18**, 852—854).—The substance is incinerated and the iron reduced in the absence of air by a special "reductor" consisting of a tube packed with zinc treated previously with a 2% cadmium sulphate solution. The reduced iron is then titrated with *N*/80-potassium permanganate. S. S. Z.

**Effect of Ammonium Sulphate and other Salts on the Colorimetric Determination of Phosphorus.** C. RIMINGTON (*Biochem. J.*, 1924, **18**, 1297—1300).—The rate of colour production

in Briggs' method of phosphorus determination is slower in the presence of ammonium sulphate, although the final depth of colour attained after keeping for a lengthy period is practically unaffected. Once the colour has developed ammonium sulphate is without effect. Anticoagulants such as ammonium oxalate, sodium oxalate, sodium sulphate, sodium fluoride, and sodium citrate also interfere with the colour production if their concentrations are sufficiently high. S. S. Z.

**Determination of Uric Acid by Benedict's Method.** H. COHEN (*Biochem. J.*, 1924, **18**, 1327—1329).—The author shows from a mathematical point of view that in order to obtain consistently accurate results over a wide range of concentration with Benedict's method for the determination of uric acid in blood (A., 1922, ii, 405; 1923, i, 196), it is essential to make a correction for the colour given in the controls. The uncorrected results are too high when the amount of uric acid present is less than 0.4 mg. % (*i.e.*, the amount of uric acid in the standard solution) and too low when it is more than this. S. S. Z.

**Less Studied Constituents of Cows' Milk. I.** B. BLEYER and O. KALLMANN (*Biochem. Z.*, 1924, **153**, 459—486).—An investigation of the "rest-N" of protein-free milk filtrates using various methods of protein precipitation. Details are given of the methods of determination of total nitrogen, and that of protein, albumose, peptone (precipitated by phosphotungstic acid in the filtrate from the albumose), purine bases, and uric acid. The last was determined colorimetrically by a new arseno-tungstic acid method. Amino-acid nitrogen was determined by Folin's colorimetric method, creatine and creatinine by a modification of Folin's method, urea by urease, ammonia by aëration. Non-protein nitrogen was also determined by Denis and Minot's method.

The following average quantities, in mg. of nitrogen per 100 c.c. of milk, were found for a sample of the mixed milk of a large dairy. Total N, 510.8; protein N, 449.2; albumose N, 31.4; purine-base N, 2.8; uric acid N, 3.5; preformed creatinine N, 1.2; amino-acid N, 2.8; urea N, 11.3; preformed ammonia N, nil. By rennin precipitation or after souring of milk the ammonia nitrogen and amino-acid nitrogen rise definitely. The content of creatinine and urea in milk agrees fairly well with the content of these substances in ox-blood-serum. H. D. K.

**Colorimetric Determination of Ammonia in Urine.** A. P. ORR (*Biochem. J.*, 1924, **18**, 806—808).—The diluted urine, with phenol and sodium hypochlorite solution, yields a blue colour which is allowed to develop for 5 minutes. The solution is then diluted and the colour compared in a Duboscq colorimeter with that of a standard prepared from ammonium sulphate. Results obtained by this method agree well with those obtained by Folin's macro-method of aëration. S. S. Z.

**Excretion of Carbon in the Urine on a Normal and on a Deficient Dietary.** K. SCHIMIZU (*Biochem. Z.*, 1924, **153**, 424—455).—Total carbon and total nitrogen excretion in the urine have been followed under various dietary conditions. Dogs on a normal, calorifically sufficient diet give an almost constant C/N ratio. The carbon excretion and the C/N ratio are increased if the carbohydrate content of such a diet is increased. Complete starvation in the dog leads first to a slight rise in the C/N ratio, which then slowly sinks, diminishing more rapidly in the pre-mortal period owing to the rapid rise in the absolute amount of nitrogen excreted. On a diet deficient in carbohydrate, the absolute amount of carbon and nitrogen excreted rises, and the quotient (C/N) also rises slightly, until the body-weight is reduced to suit the diminished food supply, when the quotient again becomes normal. On a diet deficient in protein, less carbon and less nitrogen are excreted and the quotient sinks, rising again later owing to increased carbon excretion. A vitamin-deficient diet, if uncomplicated by subsequent intestinal disturbance, leads to a rise both in carbon and nitrogen excretion, the former rising more than the latter and giving an increased C/N ratio.

H. D. K.

**Nitrogen and Chloride Excretion in the Urine following Changes in the Relations between Blood and Tissues.** S. TAKANOSU (*Biochem. Z.*, 1924, **153**, 242—252).—After slight hæmorrhage, the daily total nitrogen excretion in rabbits is lowered for some days, with retention of nitrogen from the diet. Chloride excretion is diminished also, but for a shorter period, returning soon to the normal. The injection of pituitrin leads to a diminution in both total nitrogen and chloride in the urine.

H. D. K.

**Clinical Detection of Dextrose in Urine with Alkaline Copper-Glycerol Solution.** H. RUOSS (*Biochem. Z.*, 1924, **151**, 357—362).—Using an alkaline solution of copper sulphate, potassium thiocyanate, and glycerol, and drop-bottles for measuring the reagents etc., simple qualitative and quantitative tests for sugar in diabetic and normal urines are described. The end-point of the reduction is detected by acidifying with acetic acid and adding potassium ferrocyanide.

J. P.

**Nature of Sugar in Normal Urine. I. Comparison of Dextrose Equivalent of Various Sugars in Different Methods for Determination of Dextrose.** I. GREENWALD, J. SAMET, and J. GROSS (*J. Biol. Chem.*, 1924, **62**, 397—399).—Comparative figures are given of the results obtained when known amounts of dextrose and equivalent amounts of various other sugars are determined by the methods in common use for the determination of dextrose.

C. R. H.

**Nature of Sugar in Normal Urine. II. Sugar Excretion on Various Diets; Influence of Diet on Dextrose Tolerance; Nature of Action of Insulin.** I. GREENWALD, J. GROSS, and J. SAMET (*J. Biol. Chem.*, 1924, **62**, 401—434).—The sugar of normal urine consists in part of carbohydrates of the food which are not



easily assimilated (*e.g.*, lactose) and in part of carbohydrates (possibly pentoses) which are a product of protein metabolism. Increased nuclein metabolism does not affect the amount of sugar excreted. Less dextrose than usual will produce an alimentary glycosuria in a normal individual if the latter has been kept on a carbohydrate-free diet, and this is especially the case if the diet preceding the ingestion of dextrose has been composed chiefly of fat. These results, together with the observation that insulin causes a fall in the phosphates of the blood, are made the basis of a theory of the mode of action of insulin, ascribing to the latter, as its first function, the combination of dextrose with phosphate to form a compound available for further metabolism.

C. R. H.

**Determination of Sugar in Diabetic Urine.** J. B. SUMNER (*J. Biol. Chem.*, 1924, **62**, 287—290).—The author's previous method (A., 1921, ii, 564) for the determination of dextrose by means of a colour reaction with dinitrosalicylic acid has been modified by the addition of Rochelle salt to the reagent which prevents oxidation of dextrose by dissolved oxygen. The modified reagent will detect 0.1 mg. of dextrose.

C. R. H.

**Detection and Determination of Indican in Urine by the Cotton-wool Plug Test.** S. N. GORE (*Indian Med. Gaz.*, 1924, **59**, 393—396).—The urine is boiled in a test-tube plugged with cotton-wool moistened with potassium persulphate and *p*-dimethylbenzaldehyde solution; indican, if present, causes the appearance of a pink colour on the under surface of the plug, and may be approximately determined by comparison of the colour with standards.

CHEMICAL ABSTRACTS.

**Glycuronic Acid as a Probable Constituent of Urochrome.** F. POLLECOFF (*Biochem. J.*, 1924, **18**, 1252).—Urochrome prepared from urine gave a positive furfuraldehyde reaction and van der Haar's test for glycuronic acid, in which the substance is boiled with hydrochloric acid and naphthoresorcinol, cooled to 50°, and shaken with benzene. The benzene layer after drying with anhydrous sodium sulphate gave an absorption band on the *D*-line which is not given by any other carbohydrate or derivative.

S. S. Z.

**Form in which Uric Acid is Excreted.** M. RANGIER (*Bull. Soc. Chim. biol.*, 1924, **6**, 935—970).—It is suggested that uric acid is present in the urine in the form of a compound of 2 mols. of uric acid with 1 mol. of an unknown organic complex. Uric acid in the urine is determined by Ducung's method (1892), in which copper thiosulphite is added to the urine. It is assumed that two-thirds of the copper added is used to precipitate copper urate whilst the remainder yields a soluble copper derivative of the compound with which the uric acid was united. The claim is made that all the uric acid is precipitated in this manner, whereas, on treatment with acids alone, a portion only of the urinary uric acid separates. In urines containing crystalline uric acid deposits, it is supposed that a portion of the soluble uric acid complex has decomposed,

liberating free uric acid. A method of analysis of such urines is based on this supposition. L. F. H.

**Form in which Uric Acid occurs in Urines containing Acid Urates.** L. CHELLE and M. RANGIER (*Bull. Soc. Chim. biol.*, 1924, 6, 971—979; cf. preceding abstract).—Analytical evidence is adduced to show that a portion of the uric acid in urines with deposits of acid urates is excreted uncombined with an organic radical. L. F. H.

**Forms in which Uric Acid is Eliminated in the Urine.** L. CHELLE and M. RANGIER (*Bull. Soc. Chim. biol.*, 1924, 6, 980—993; cf. preceding abstracts).—Urines are classified according to the nature of the uric acid deposits, if any. The deposits may be due to decomposition of an organic complex containing uric acid or, mainly in pathological urines, to the excretion of free acid urates. The suggestion (Maillard, A., 1924, i, 459) that uric acid occurs in urine combined with amino-acids, is supported. L. F. H.

**Determination of Uric Acid in Urine.** AUFRECHT (*Pharm. Ztg.*, 1924, 69, 1324—1325).—Several methods are discussed and it is shown that the uricometer method of Ruhemann is unsatisfactory even for clinical work. Hopkins' method is considered very satisfactory. A similar method due to the author gives results which are in good agreement with it. O. O.

**Determination of Blood in Fæces.** P. N. VAN ECK (*Pharm. Weekblad*, 1924, 61, 1318—1325).—The blue coloration given by blood in presence of hydrogen peroxide and benzidine acetate is not sufficiently stable in any solvent for colorimetric determination. Addition of a large excess of alcohol and sodium hydroxide solution transforms the unstable blue colour into an intense, permanent red. Chlorides, sulphates, and nitrates interfere. Satisfactory results are obtained by extraction of the fæces with glacial acetic acid, addition of water and of sodium hydroxide to the extract until nearly neutral, and extraction of this solution with ether; the ether layer is separated, the ether distilled off, and the residue treated with benzidine acetate and hydrogen peroxide; after keeping, alcohol and sodium hydroxide are added, and the solution is compared colorimetrically with a standard blood solution. S. I. L.

**Fluorescent Oxidation Products of Bilirubin and their Importance as Sources of Error in Tests for Urobilin.** H. K. BARRENSCHEEN and O. WELTMANN (*Biochem. Z.*, 1924, 149, 329—330).—A reply to Adler (A., 1924, ii, 280; cf. also A., 1923, ii, 800). J. P.

**Determination of Urobilin in Human Excreta.** OPITZ and BREHME (*Z. ges. exp. Med.*, 41, 681—698; from *Chem. Zentr.*, 1924, ii, 517—518).—An examination of the methods of Adler and Schubert (*Deuts. Arch. klin. Med.*, 1922, 138, 309; *Biochem. Z.*, 1923, 134, 533) showed that comparable results can only be obtained with a constant source of illumination; the Adler scale cannot, however, be utilised. As a suitable standard of comparison, the authors use H. Fischer's mesobilirubinogen. The excreta must be

extracted quantitatively in a Soxhlet apparatus. The average daily value for normal adults was about 64 to 124 mg. of "urobilin" in the fæces and 1.7 to 3.4 mg. in the urine; these results are, however, only relative. F. A. M.

**New Porphyrin-like Constituent of Normal Human Fæces.** D. KÉMÉRI (*Biochem. Z.*, 1924, **151**, 438—448).—The isolation from normal human fæces of a new porphyrin is described. This, although it has not yet been obtained in a pure state, is differentiated from other known porphyrins spectroscopically and by its solubilities and colour reactions in various solvents. J. P.

**Modifications of the Blood during Anaphylactic Shock.** L. BLUM, M. DELAVILLE, and V. CAULAERT (*Compt. rend.*, 1924, **179**, 1294—1295).—Anaphylactic shock is accompanied by an increase of the proportion of the calcium of the blood-serum which is able to pass through the ultra-filter from 45—60% to 75—100%. This phenomenon appears suddenly, and disappears suddenly when the symptoms subside. Normally, the calcium not removable by ultra-filtration is associated with a colloidal protein complex, so that the phenomenon involves a change in the reaction of the colloid and is intimately related to the alteration in the value of  $p_H$  and the lowering of the alkali reserve. T. H. P.

**Acid-combining Power of the Serum of Healthy and Diseased Children.** A. BOSÁNYI and J. CSAPÓ (*Biochem. Z.*, 1924, **153**, 185—196).—The protein content of the serum was determined refractometrically, the amount of acid (hydrochloric) taken up by the serum proteins determined, under standard conditions, by titration. The quotient, acid taken up/percentage of protein, was found to be highest in the suckling, diminishing with age, and markedly diminished in cases of pulmonary tuberculosis. Certain other diseases were found to give either an increase or a decrease in this quotient. The change in the value may be due to a change either in the alkali reserve of the blood or in the relative amount of globulin to albumin in the serum. H. D. K.

**Calcium and Phosphorus Content of Blood in Normal and Rachitic Children.** II. Phosphorus. G. H. ANDERSON (*Brit. J. Children's Dis.*, 1924, **21**, 107; cf. A., 1923, i, 502).—From 2 months to 11 years of age, the calcium content of the blood varies between 6.4 and 9.5 mg. per 100 c.c., the corpuscles containing an appreciable quantity. Variation of the intake over short periods has no appreciable effect. No correspondence was observed between a rachitic condition and the level of the blood calcium. Between 3 months and 13 years of age, the phosphorus content of the blood varied from 3.7 to 5.8 mg. per 100 c.c. The amount was not varied by greater phosphorus ingestion, but was lower in rachitic conditions. CHEMICAL ABSTRACTS.

**Hydrogen-ion Concentration of the Whole Blood of Normal Males and of Cancer Patients Measured by means of the Quinhydrone Electrode.** J. W. CORRAN and W. C. McC. LEWIS (*Biochem. J.*, 1924, **18**, 1358—1363).—The average values for the

$p_H$  of the blood of normal human subjects and of cancer patients are identical, namely, 7.33. The  $p_H$  is temporarily lowered after an intravenous injection of a lead suspenoid prepared by the Bredig sparking method. A gold foil electrode was found more satisfactory than a platinum one in the case of blood. S. S. Z.

**Storage of Cerebrosides in Splenomegaly (Gaucher's Type).** H. LIEB (*Z. physiol. Chem.*, 1924, **140**, 305—313).—The substance present in the alcoholic extract of the spleen from cases of Gaucher's disease (cf. Epstein, A., 1924, i, 791) has been identified as kersin; the amount isolated represented approximately 10% of the dry weight of the spleen. No kersin could be detected in the normal spleen. E. S.

**Syphilis. IX. Arsenic Content of the Blood after Intravenous Injection of Neosalvarsan. X. Arsenic in Human Milk after Intravenous Injection of Salvarsan. XI. Partition of Arsenic in Serum and Clot after Intravenous Administration of Salvarsan, Neosalvarsan, and Silver Salvarsan. XII. Arsenic Content of the Blood after Intravenous Injection of Tryparsamide. XIII. Arsenic Content of the Cerebrospinal Fluid after Intravenous Injection of Hypertonic Saline Solutions and Neosalvarsan. XIV. Localisation and Fate of Salvarsan, Neosalvarsan, Silver Salvarsan, and Tryparsamide in the Viscera after Intravenous Administration in Rats.** J. A. FORDYCE, L. ROSEN, and C. N. MEYERS (*Amer. J. Syphilis*, 1924, **8**, 34—64, 65—73, 193—263, 264—296, 297—307, 377—557).—IX.—3.71 mg. of elementary arsenic per 100 g. of dried blood is present.

X.—From 0.70 to 1.31 mg. of elementary arsenic per 100 g. of dried milk were found; its presence is more constant than in blood or urine.

XI.—The following average values were obtained for serum and clot, respectively:—salvarsan, 9.37, 30.52%; neosalvarsan, 8.80, 31.52%; silver salvarsan, 9.34, 29.95%. Salvarsan probably first forms in the blood an insoluble precipitate which gradually dissolves. Comparison curves (arsenic content—time) are given for the three arsenicals.

XII.—In blood taken immediately after injection, 53.2% was present; after 15 minutes, 7.65%; after 72 hours, 0.012%.

XIII.—Preliminary injection of saline does not favour the passage of large amounts of arsenic into the cerebrospinal fluid.

XIV.—Large amounts of arsenic were found in the liver, spleen, kidney, and blood. CHEMICAL ABSTRACTS.

**Basic Constituents in the Urine in Advanced Pulmonary Tuberculosis.** H. REINWEIN (*Deut. Arch. klin. Med.*, 1924, **144**, 37—44; from *Chem. Zentr.*, 1924, ii, 71).—From the urine in advanced pulmonary tuberculosis a base *juline*,  $C_{15}H_{33}O_4N_3$ , was isolated as *chloroaurate*,  $C_{15}H_{33}O_4N_3 \cdot 2HAuCl_4$ . G. W. R.

**Aminogenesis in the Grey and White Substances of the Brain during Hunger. II. Rabbit's Brain.** A. PALLADIN and W. BJELJAEWA (*Z. physiol. Chem.*, 1924, **141**, 33—39).—The results are identical with those obtained with dogs (A., 1924, i, 1256). E. S.

**Calcium Metabolism in the Laying Hen. II.** G. D. BUCKNER, J. H. MARTIN, and A. M. PETER (*Kentucky Agr. Exp. Sta. Bull.*, 1924, No. 252, 1—36; cf. A., 1922, i, 488).—Dietary deficiency of calcium does not change the calcium content of the liquid portion of eggs, but reduces the number, and therefore the production of shell, and diminishes the amount of calcium oxide and phosphoric oxide in the leg-bones. CHEMICAL ABSTRACTS.

**Calcium Metabolism in Man. Effect of Different Salts of Calcium.** W. H. JANSEN (*Klin. Woch.*, 1924, **3**, 715—719; from *Chem. Zentr.*, 1924, ii, 73; cf. A., 1918, ii, 174).—The excretion of calcium in urine is to a certain extent affected by the amount of calcium administered. A more marked effect is shown on the calcium content of the faeces. In adults, increase in the calcium content of the urine after administration of soluble calcium salts is accompanied by an increase in calcium in the blood. The increases obtained for different salts are in the order: phosphate < sulphate < chloride < bromate < bicarbonate. No effect is produced by calcium lactate. Other ions, *e.g.*, in natural mineral waters, exert an appreciable effect on the calcium balance. Whilst with normal adults no sustained increase in blood calcium can be maintained, when the calcium of the blood is subnormal increases may be produced. For the administration of large amounts of calcium the  $\alpha$ -isobutyrate has been found most suitable. G. W. R.

**Effect of Amino-acids on the Metabolism of Isolated Organs of Dogs.** L. MÉLON (*Compt. rend. Soc. Biol.*, 1924, **90**, 636—637; from *Chem. Zentr.*, 1924, ii, 208; cf. Fredericq and Mélon, A., 1924, i, 461).—By perfusion of the spleen and paw of dogs with Locke's solution, containing glycine, alanine, valine, leucine, or phenylalanine, marked acidity to phenolphthalein is produced. The thyroid gland is without appreciable effect on the reaction of the perfusing liquid, which is also the case with all three organs when unmodified Locke's solution is used. The content of nitrogen titratable by formaldehyde is never increased by perfusion. In half of the experiments with the spleen and in a few cases with the paw an increase in amino-nitrogen was obtained. G. W. R.

**Oxidation of Cystine and Cysteine in the Animal Organism.** A. R. ROSE, G. J. SHIPLE, and C. P. SHERWIN (*Amer. J. Physiol.*, 1924, **69**, 518—530).—Oxidation of derivatives of cystine or cysteine, when administered to animals, is prevented only when the amino group and the sulphur atom are simultaneously blocked; the carboxyl group is not a vulnerable point. Cystine and cysteine are interconvertible by the rabbit. CHEMICAL ABSTRACTS.

**Acetaldehyde in Intermediary Cell Metabolism.** A. GOTTSCHALK (*Klin. Woch.*, 1924, **3**, 713—715; from *Chem. Zentr.*, 1924, ii, 73).—A review of earlier work, according to which acetaldehyde occurs as an intermediate stage in carbohydrate metabolism. In more recent work, it has been found that the presence of acetaldehyde in surviving cells of guinea-pigs and rabbits is closely connected with the presence of free oxygen. After addition of potassium cyanide in 0.001*M* concentration, acetaldehyde is not found. Acetaldehyde may be formed from pyruvic acid by the liver cells if the hæmoglobin present is reduced and oxygen excluded.

G. W. R.

**Ketosis. I. Relation between Alkalosis and Ketosis.** V. B. WIGGLESWORTH (*Biochem. J.*, 1924, **18**, 1203—1216).—When deprived of carbohydrate in the diet the rat shows a marked ketosis which increases during the first few days, reaches a maximum at about the third day, and subsides thereafter rapidly. Adaptation to the diet is established by the fifth day. The administration of sodium bicarbonate, calcium lactate, sodium acetate, and of an alkali-forming food such as carrots to the rat causes a rise in the output of lactic and  $\beta$ -hydroxybutyric acids but no change in the excretion of total acetone. Acids reverse this effect. The injection of large doses of dextrose during alkalosis causes a fall in the excretion of  $\beta$ -hydroxybutyric acid. The injection of large amounts of sodium bicarbonate produces a distinct rise in the total acetone in the rat. The presence of 6% of sodium bicarbonate in a diet of fat eliminates the usual adaptation.

S. S. Z.

**Ketosis. II. Oxidation of Ketone Bodies by the Isolated Liver of the Rat.** V. B. WIGGLESWORTH (*Biochem. J.*, 1924, **18**, 1217—1221).—The fresh liver of the rat shows an increased uptake of oxygen in the presence of acetoacetic acid and inactive  $\beta$ -hydroxybutyric acid. The former causes the more marked increase. This oxidation does not seem to be affected by fasting the animal for 36 hours nor at any stage in the adaptation to a diet of fat. It is also unaffected by the presence of dextrose or its degradation products, of pancreatic extract, or of insulin. Ketosis is probably not due to a diminished direct oxidation of ketone substances.

S. S. Z.

**Action of Acetoacetic Acid on Nitrogen Metabolism.** H. LABBÉ and LAVAGNA (*Compt. rend.*, 1924, **179**, 1442—1445).—A dog was given, mixed with a constant diet, 2 g. of ethyl acetoacetate for 20 days, and then 3.5 g. for a further period of 8 days. The total nitrogen eliminated was not altered by this treatment, but a marked diminution of the percentage of uric acid was apparent, accompanied by an increase in the percentage of nitrogen excreted as ammonia and amino-acids.

A. E. C.

**Metabolism of Phosphoric Acid in the Submaxillary Gland.** M. CAMIS (*Arch. Intern. Physiol.*, 1924, **22**, 345—362).—During activity of the submaxillary gland, its free phosphoric acid content

is increased more than threefold. Some of the additional phosphoric acid is carried away by the venous blood.

CHEMICAL ABSTRACTS.

**Intermediate Carbohydrate Metabolism of the Liver and its Gaseous Exchange (Normal, Starving, Insulin-treated, and Depancreatized Animals).** VII. T. BRUGSCH, H. HORSTERS, and G. SHINODA (*Biochem. Z.*, 1924, **151**, 318—334).—The normal excised guinea-pig liver has a respiratory quotient approximating to unity. It is lowered by insulin *in vitro*. The lowering of the respiratory quotient—most marked in the hypoglycæmic state—when insulin is administered to starving guinea-pigs is ascribed to the formation of sugar from fats. In normal dogs, the excised liver has a respiratory quotient of 0.51 to 0.68, whilst that of the liver from depancreatized animals is 0.73 to 0.79, the oxygen consumption in the latter case being much below that of the normal liver. J. P.

**Effect of Continued Administration of Sugar on the Formation of Glycogen.** A. GIGON (*Z. ges. exp. Med.*, 1924, **40**, 1—12; from *Chem. Zentr.*, 1924, ii, 204).—Experiments on the effect on different animals of continued administration of large amounts of dextrose or lævulose. In certain cases death and in others loss of weight took place. No glycogen was found in liver or muscles, although in one case actual deposition of fat occurred. Continued hyperglycæmia was observed. The cause of death was not found, but it was possibly associated with acidity of the tissue fluids. G. W. R.

**Inositol. III. Metabolic Behaviour of *D*-Inositol in the Developing Avian Egg.** J. NEEDHAM (*Biochem. J.*, 1924, **18**, 1371—1380).—The total inositol in the egg increases during development. The general shape of the curve of this rise is doubly peaked, the first maximum occurring about the tenth day and the second being coincident with hatching. The injection of dextrose into the fertilised unincubated egg causes a very large rise in the inositol content of the egg during its subsequent development. It is concluded that dextrose is normally a likely precursor of inositol. S. S. Z.

**Behaviour of Fatty-aromatic Compounds in the Animal Body.** H. THIERFELDER and E. KLENK (*Z. physiol. Chem.*, 1924, **141**, 13—28; cf. A., 1923, i, 1264).—When injected subcutaneously into rabbits, phenyl isoamyl ketone, phenyl *n*-hexyl ketone, and phenylethyl *n*-hexyl ketone are oxidised to benzoic acid and excreted as hippuric acid. On the supposition that the first stage of the oxidation would occur at the methylene group adjacent to, and on the benzene side of, the carbonyl group, it was expected that, as a result of subsequent  $\beta$ -oxidation, phenylethyl *n*-hexyl ketone would yield phenylacetic acid. No trace of phenaceturic acid could, however, be detected in the urine. The substances excreted in the urine following the injection of  $\alpha$ -phenylethyl alcohol were identical with those obtained from acetophenone

(*loc. cit.*), but less alcohol (conjugated with glycuronic acid) was excreted than in the latter case. Of the hydrocarbons investigated, *n*-propylbenzene and *n*-amylbenzene were excreted as hippuric acid, and *n*-butylbenzene and *n*-hexylbenzene as phenaceturic acid. The amounts excreted corresponded with 60–70% of the hydrocarbon injected. *n*-Butylbenzene also gave rise to a small amount of an alcohol conjugated with glycuronic acid. The form in which isopropylbenzene is excreted could not be determined. When injected subcutaneously, the resorption of *n*-butylbenzene and the higher hydrocarbons was extremely slow; these substances were therefore administered by intraperitoneal injection.

*Phenylethyl n-hexyl ketone* has b. p. 178–181°/30 mm., 295–298°/720 mm.,  $d^{12}_4$  0.9388. E. S.

**Behaviour of Acetophenone and Benzene in the Animal Body.** H. THIERFELDER and E. KLENK (*Z. physiol. Chem.*, 1924, 141, 29–32).—The amounts of benzoic and mandelic acids and of  $\alpha$ -phenylethyl alcohol excreted in the urine of rabbits following the intraperitoneal injection of acetophenone account for 91.7% of the substance so administered. Hence the benzene ring in acetophenone is unattacked by the organism. The results previously obtained (A., 1923, i, 1264) were evidently due to the fact that the acetophenone is less completely resorbed when administered subcutaneously (cf. preceding abstract). Following the intraperitoneal injection of benzene, muconic acid has been isolated from the urine of rabbits in an amount representing 3.7% of the benzene administered. The smaller amounts obtained by other observers (Jaffé, A., 1909, ii, 914; Fuchs and Soós, A., 1917, i, 716) can be accounted for by the more rapid resorption of benzene by the peritoneum than by subcutaneous tissue. E. S.

**Animal Calorimetry. IV. Specific Dynamic Action of Completely Hydrolysed Protein, with a Note on Method of Evaluation.** J. MELLY and A. VON RÖTTB (*Biochem. Z.*, 1924, 153, 285–297).—The feeding of “erepton”—completely hydrolysed muscle protein—to curarised dogs leads to a definite increase in metabolism, as determined by indirect calorimetry. The method of evaluation of the specific dynamic action of an ingested foodstuff is discussed in some detail. The not particularly large specific dynamic action of erepton is in accordance with what might be expected from the relatively low glycine and alanine content of the muscle protein from which it is prepared. H. D. K.

**Emanation and Calcium.** H. ZWAARDEMAKER, T. P. FEENSTRA, and M. E. J. M. STEYNS (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 425–429).—Frogs' hearts were perfused with solutions containing emanation and calcium ion, buffered with sodium bicarbonate and with sodium chloride added. The largest and smallest amounts respectively of emanation which just permitted regular pulsation were determined for various concentrations of calcium. Taking the horizontal centres of the two lines obtained, the product of the emanation (curies) and the calcium-ion concentrations is a constant,  $2.5 \times 10^{-10}$ . Both factors have a limit, but



calcium ion can be omitted whilst emanation cannot. Thus calcium is not an emanation substitute but an emanation intensifier.

L. J. H.

**Anthelmintic Properties of the Constituents of the Oil of Chenopodium.** W. G. SMILLIE and S. B. PESSÔA (*J. Pharm. Exp. Ther.*, 1924, **24**, 359—370).—The active anthelmintic principle of oil of chenopodium is ascaridole, which can be separated from the oil by fractional distillation under reduced pressure (b. p.  $110^{\circ}/15$  mm.,  $d_{15}^{15}$  1.0120,  $[\alpha]_D^{15}$   $-5^{\circ}$ ). None of the other substances present has an anthelmintic action. The lighter fractions of the oil consist of a mixture of terpenes and methyl salicylate. Ascaridole glycol (b. p.  $230-245^{\circ}/15$  mm.) and the glycol anhydride (b. p.  $135-160^{\circ}/15$  mm.) are also present; owing to improper preparation, inferior oils may contain the two last-named substances in considerable amounts, their anthelmintic action being correspondingly decreased. The toxicity of the oil is due for the most part to the ascaridole.

H. J. C.

**Action of Ephedrine, the Active Principle of the Chinese Drug, Ma Huang.** K. K. CHEN and C. F. SCHMIDT (*J. Pharm. Exp. Ther.*, 1924, **24**, 339—357).—Solutions of ephedrine, the active principle of Ma Huang—*Ephedra vulgaris* var. *Helvetica*—are indefinitely stable to light and air, and are not decomposed by boiling. The physiological action of the drug is similar to, but much more prolonged than, that of adrenaline. Intravenous injection of 0.25 to 20 mg. of the hydrochloride or sulphate into dogs, cats, or rabbits causes a prolonged rise of blood pressure, together with cardiac acceleration and usually vaso-constriction. The drug causes relaxation of the intestine, stimulation of the uterus, and bronchial dilatation, and is a more powerful mydriatic than cocaine. Its effect on the secretion of saliva, sweat, and urine has been studied. The minimum fatal dose for rats is 100—145 mg. per kg. body-weight. The crude drug contains 0.018—0.072% of ephedrine.

H. J. C.

**Metabolism Studies with Chaulmoogra Oil. I. Influence of Chaulmoogra Oil on Calcium Metabolism. II. Influence of Hydnocarpates on Urinary Nitrogen Partition in the Dog.** B. E. READ (*J. Biol. Chem.*, 1924, **62**, 515—540, 541—550).—I.—In rabbits, administration of large doses of chaulmoogra oil causes increased excretion of calcium with lowering of the blood calcium and resultant tetany; large doses given to dogs also cause increased excretion of calcium, but long-continued small doses bring about the reverse effect. During the periods of hyper-excretion of calcium no parallel increase could be observed in the excretion of phosphates or of fats.

II.—The first effect on nitrogenous metabolism of chaulmoogra oil or ethyl hydnocarpate is to produce an increased urinary excretion of total nitrogen, the preformed creatinine and ammonia being especially large in amount; with continued administration, the output of total nitrogen falls below the normal, whilst that of ammonia

remains high, indicating a condition of acidosis accompanied by deficient oxidation.

C. R. H.

**Fatty Degeneration caused by some Essential Oils.** F. VON GRAEVENITZ (*Arch. exp. Path. Pharm.*, 1924, **104**, 289—320).—Safrole, isosafrole, pulegone, and thujone are known to produce fatty degeneration when injected into white mice. Dihydrosafrole, eugenol, isoeugenol, and their methyl derivatives, menthone, limonene, terpinene, terpinolene,  $\alpha$ - and  $\beta$ -phellandrene, and sabinol are found to have a similar effect, whilst thujyl alcohol, menthenone, and isopulegone are without this action. The toxicity is greatly diminished in the case of the saturated compounds, whilst the causation of fatty degeneration of the liver is independent of the position of the double bond, whether in the nucleus or not, and saturation or unsaturation plays no part in this effect. There appears to be no relationship between toxicity and the power of producing fatty degeneration nor between fatty degeneration of the liver and hæmolysis.

I. E. B.

**Fixation of Chloroform by the Central Nervous System and the Peripheral Nerves.** M. NICLOUX and A. YOVANOVITCH (*Compt. rend.*, 1924, **179**, 1429—1431).—The amount of chloroform taken up by the brain and nervous tissues of dogs in various degrees of anæsthesia has been determined. In deep anæsthesia 52.5 mg. per 100 g. of brain and 166 mg. per 100 g. of tissue in the pneumogastric nerve were found.

A. E. C.

**Acidosis of Operative Anæsthesia.** A. E. KOEHLER (*J. Biol. Chem.*, 1924, **62**, 435—451).—The  $p_H$  of the blood falls rapidly at the commencement of anæsthesia and thereafter more slowly; the acidosis is brought about by a combination of increased tension of carbon dioxide (possibly caused by inefficient respiration) and deficit of alkali (cf. Austin and others, A., 1924, i, 1364).

C. R. H.

**Pharmacology of the Oxidation Products of Ether.** J. MITA (*Arch. exp. Path. Pharm.*, 1924, **104**, 276—288).—Ether which has been stored contains a water-soluble toxic principle formed by autoxidation in the presence of light and air. The effects of this principle on the frog as a whole and on the isolated heart are described and discussed. From a very toxic sample of ether it was isolated as an oily liquid, and proved to be dihydroxyethyl peroxide. Its formation in ether is prevented by aluminium amalgam.

O. O.

**Local Anæsthetics.** S. WEIL.—(See i, 157.)

**Comparison of the Action of some Secondary and Tertiary Alcohols with Special Reference to Local Anæsthesia.** J. P. QUIGLEY and A. D. HIRSCHFELDER (*J. Pharm. Exp. Ther.*, 1924, **24**, 405—422).—The secondary aromatic alcohols benzhydrol,  $\beta$ -trichloro- $\alpha$ -phenylethyl alcohol, and cyclohexanol are weaker local anæsthetics than the primary aromatic alcohols. The tertiary aromatic alcohols  $\gamma$ -phenylpentan- $\gamma$ -ol, phenyldibenzyl glycol, and

*p*-di-( $\beta$ -hydroxyisopropyl)benzene have no local anæsthetic action. The slight action possessed by  $\gamma$ -*o*-hydroxyphenyl- $\gamma$ -pentan- $\gamma$ -ol appears to be due to its phenol group and not to the tertiary alcoholic group, for the corresponding alcohol which does not contain a phenolic OH,  $\gamma$ -phenylpentan- $\gamma$ -ol, has no local anæsthetic action. These alcohols, in general, possess a narcotic action only in toxic doses; on intravenous injection, they depress the circulation and respiration. H. J. C.

**Fate of Hydrocyanic Acid in the Animal Organism. New Method of Detecting Thiocyanates in Organic Material.** P. W. DANCKWORTT and E. PFAU (*Arch. Pharm.*, 1924, 262, 442—449).—The distribution of hydrocyanic acid in the corpses of dogs poisoned by potassium cyanide and buried in the ground for varying lengths of time has been investigated. In winter, but not in summer, it could be detected in the organs 48 days after the death of the dog. It is present in all the tissues immediately after death.

Chelle's conclusion (A., 1919, ii, 529, 530) that hydrocyanic acid is converted into thiocyanic acid in the organism was not confirmed.

Hydrocyanic acid is best separated from organic material by steam distillation.

The usual tests for thiocyanic acid cannot be applied in presence of tissues. The solution is first treated with hydrogen peroxide, and the hydrogen cyanide formed can then be removed by steam distillation, and determined. When thiocyanic and hydrocyanic acids are present together the two procedures are successively applied. Using this method, it was found possible to determine, with tolerable accuracy, 0.0118 g. of thiocyanic acid in a mixture of 100 g. of liver and 50 c.c. of water, and only a small proportion was found to have disappeared after 18 days.

The saliva produced while tobacco is being smoked is four times as rich in thiocyanic acid as that normally secreted. W. A. S.

**Spectrometric Determination of the "Poisoning Coefficient" in Carbon Monoxide Poisoning.** V. BALTHAZARD (*Bull. Soc. Chim. biol.*, 1924, 6, 817—828).—The absorption spectrum of oxyhæmoglobin shows maximum intensities at 5770 and 5400 Å.; that of hæmoglobin saturated with carbon monoxide has maxima at 5700 and 5350 Å. The "poisoning coefficient," or fraction of the total hæmoglobin which is combined with carbon monoxide can be ascertained by spectrometric measurement of the position of the first maximum. The method is rapid and involves only very small quantities of blood and is accurate to 5%. A calibration curve is given. E. M. C.

**Pharmacological Investigations on Iron. VI. Colloidal Ferrous Sulphide prepared in Presence of Sugar.** L. SABBATANI (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 223—228; cf. A., 1924, ii, 116).—Colloidal ferrous sulphide prepared in presence of sucrose is considerably less toxic than that prepared in presence

of gelatin and is fixed by the organism more rapidly and almost exclusively in the liver and spleen. These preparations remain inactive as long as their colloidal character persists, and they penetrate and diffuse more or less profoundly from the blood-vessels into the tissues according to their degree of dispersion and stability. They exert sensible pharmacological action only after they undergo further change.

T. H. P.

**Pharmacological Properties of Tin Hydride and Germanium Hydride.** F. PANETH and G. JOACHIMOGLU (*Ber.*, 1924, 57, [B], 1925—1930).—Tin hydride is exceedingly poisonous to mice and guinea-pigs, but not to frogs. The toxicity appears to depend entirely on the action on the central nervous system; the blood remains unaffected. Germanium hydride is considerably less toxic than tin hydride whilst arsine occupies an intermediate position.

H. W.

**Toxic Action of Neutral-red.** G. POLITZER (*Biochem. Z.*, 1924, 151, 43—47).—Neutral red, used as an intravital stain, exerts on the cells a toxic action which may be accentuated in the presence of light.

J. P.

**Mechanism of the Therapeutic Action of Suspensoids.** J. LOISELEUR (*Bull. Soc. Chim. biol.*, 1924, 6, 861—864).—Colloidal silver has a marked catalytic action on the proteolysis of alkaline solutions of coagulated egg-albumin, but the hydrolysis of egg-albumin present in the colloidal state is impeded by colloidal silver. Similar differences are found with serum and with gold and rhodium suspensoids. It is suggested that the therapeutic effects of suspensoids are connected with their dispersing action on the flocculated materials in the blood and the absence of any action on the normal colloids.

E. M. C.

**Silver-ion Concentration in Solutions of Colloidal and Complex Silver Preparations with Special Reference to their Medicinal Use. II.** H. SCHLEE and W. THIESSENHUSEN (*Biochem. Z.*, 1924, 151, 27—42).—A continuation of earlier observations (*A.*, 1924, i, 1262). Dispargen, fulmargin, argobol belong to the group showing diminishing  $[Ag^+]$  on dilution, silver salvarsan bases to the group showing no change, and collargol, iodocollargol, solargyl to the group showing an increased  $[Ag^+]$  on dilution. The observed ionic concentrations at varying percentage concentrations are given for each preparation. Results similar to those already observed (*loc. cit.*) were obtained in the presence of sodium chloride, serum, and blood. The presence of air does not influence the *E.M.F.* developed in the system silver-silver and water-blood-serum in contact with hydrogen, oxygen, nitrogen, or carbon dioxide.

J. P.

**Colloidal Properties of Wassermann Antigens.** W. O. KERMAK and P. MACCALLUM (*Biochem. J.*, 1924, 18, 1381—1387).—An alcoholic extract of heart-muscle when added to water forms an opalescent sol which is not precipitated by even high concentrations of sodium chloride and by acid only when a  $p_H$  as low as

about 1.9 is reached. It is precipitated by an equal volume of 0.15% calcium chloride solution, but not by an equal volume of calcium chloride solution of 2.5% or more. This action of calcium chloride is little influenced by the  $p_H$ . Precipitation of the antigen sol by solutions of gelatin of the requisite concentration occurs at  $p_H$  values below 4.7. S. S. Z.

**Dispersion of Colloidal Electrolytes in Relation to Mineral Exchanges in Cells.** W. MESTREZAT and (MISS) M. JANET (*Bull. Soc. Chim. biol.*, 1924, 6, 829—853).—The unequal distribution of sodium chloride between water and a soap solution, separated by collodion, is maintained for several days and then decreases and disappears in about 12 days. Renewal of the salt solution gives no unequal distribution, but the phenomenon is reproduced by heating the soap solution. The inequality of distribution is rapidly destroyed by the addition of traces of alum. The maximum inequality of distribution of ions corresponds with a maximum viscosity of the soap solution. The reduction of this inequality is accompanied by a slight flocculation, a marked fall in viscosity, and the commencement of a considerable and maintained increase in electrical conductivity of the soap solution. An intimate relationship exists between the phenomena of unequal distribution of electrolytes and the state of dispersion or aggregation of the colloidal electrolyte. E. M. C.

**Lecithin and Cholesterol in Relation to the Physical Nature of Cell Membranes.** J. W. CORRAN and W. C. McC. LEWIS (*Biochem. J.*, 1924, 18, 1364—1370).—Lecithin and cholesterol lower the interfacial tension between oil and water. In the case of a mixture of the two substances the effect is additive. Experiments with olive oil and water have shown the following. Lecithin favours an oil-dispersed-in-water type of emulsion, whilst cholesterol favours the reverse type. When mixtures of these substances were present in the aqueous phase, antagonistic effects on the type of emulsion were observed. The inversion point of the emulsion occurred when the ratio of the concentrations in grams of lecithin to cholesterol was about 8 : 1, both substances being present initially in the aqueous phase. When cholesterol was present in the oil phase to begin with and the lecithin was in the aqueous phase, the inversion ratio was found to be between 1 : 2 and 2 : 1. This result is significant as it most probably approximates to the conditions found in cell membranes. S. S. Z.

**Position of Electrolytes in the Organism.** F. KRAUS, S. G. ZONDEK, W. ARNOLDI, and E. WOLLHEIM (*Klin. Woch.*, 1924, 3, 735—738; from *Chem. Zentr.*, 1924, ii, 74).—Differences were observed in calcium and potassium contents between the ventricle and auricle in the hearts of frogs and guinea-pigs. Stimulation of the vagus leads to an increase in its content of calcium and potassium. Alterations in the concentration of these ions in the serum after alimentary stimulus are conditioned by changes in their concentration in the portal blood. In general, calcium increases

whilst potassium decreases the oxygen consumption of frogs' hearts. Sodium hydrogen carbonate lengthens the period of functional survival, its principal effect being to neutralise acid products in the tissues. Sodium monohydrogen phosphate and dihydrogen phosphate shorten the survival period. G. W. R.

**$p_H$  Value of the Interior of the Cell Nucleus and its Experimental Variations.** P. REISS (*Compt. rend.*, 1924, **179**, 641—643).—Various eggs and tissues of marine animals give for the  $p_H$  value of the protoplasm results similar to those given by eggs of *Paracentrotus lividus* (Vlès, Achard, and Prikelmaier, A., 1923, i, 627). The larger cells permit of the determination of the  $p_H$  of the nucleus, which was found to be practically 7. Whilst the values for the cell appear to be unaffected by moderate changes in the outer medium, those for the nucleus are considerably affected thereby. Treatment with chloroform, chloral, urethane, or cocaine is followed by a rise and subsequent fall in the  $p_H$  value of the nucleus. H. J. E.

**Hydrogen-ion Concentration of Sea-water in its Relation to Photosynthetic Changes.** III. W. R. G. ATKINS (*J. Marine Biol. Assoc.*, 1924, **13**, 437—446).—In continuation of previous work (*ibid.*, 1922, **12**, 717; 1923, **13**, 93), measurements of the  $p_H$  of the water of Plymouth Sound and of the open sea have been made throughout the year. The seasonal changes in the  $p_H$  of the open sea at various stations and depths have been studied, and compared with the results of the previous year; they have also been correlated with daylight and sunshine. H. J. C.

**Electrodialysis.** CH. DHÉRÉ (*Biochem. Z.*, 1924, **153**, 504—505).—Attention is directed to earlier work of the author on this subject (cf. Freundlich and Loeb; this vol., i, 96). H. D. K.

**Interaction of Colloidal Fats and Lipoids.** F. EICHHOLTZ (*Biochem. Z.*, 1924, **151**, 187—202).—The increase in the catalase activity of old serum solutions produced by oleic acid, triolein, lecithin, and the lipoids of lipæmic sera is referred to an increase in the dispersion of the enzyme. Fats and lipoids do not increase the activity of catalase solutions which have been treated with the salts of the heavy metals or with cyanide, but they are partly effective in protecting the enzyme from, or reactivating it after, X-ray bombardment. The catalase activity of washed rabbit erythrocytes is increased by sodium oleate. J. P.

**Formation of Acetaldehyde in Animal Organs (Acetone Liver).** C. NEUBERG and A. GOTTSCHALK (*Biochem. Z.*, 1924, **151**, 169—176).—Dried preparations of rabbit liver (treated with acetone and ether) show an oxygen consumption of 3.1 to 3.9% of that of the fresh tissue. More acetaldehyde is formed by suspensions of such preparations in 0.9% sodium chloride than by fresh tissues. The formation of aldehyde is inhibited by cyanide. Pyruvic acid is converted by the dried preparation into acetaldehyde, indicating the presence of a carboxylase. J. P.

**Enzymic Deamination of Asparagine.** A. CLEMENTI and G. CANTAMESSA (*Gazzetta*, 1924, **54**, 781—818).—The products of the deamination of asparagine, namely, aspartic acid and ammonia, inhibit the activity of asparaginase. Direct proportionality between increase in concentration of substrate and amount acted on holds only for very low concentrations of asparagine, the velocity of the deamination diminishing when a certain limiting concentration is surpassed. Proportionality between increase in the concentration of the catalyst and the amount of substrate attacked is verified only for high dilutions of asparaginase, the reaction velocity decreasing when the concentration exceeds a definite limit. Inverse proportionality between the velocity of reaction and the duration of action of the enzyme is not always observed in the present instance, the amounts of asparagine decomposed during successive equal intervals of time remaining constant in many cases; on the other hand, in some instances the velocity constant calculated according to the exponential formula continues of constant value, the course of the deamination being thus somewhat analogous to the phenomenon of adsorption. T. H. P.

**Preparation of Enzymes. Rennin from Gastric Mucous Membrane.** G. DE TONI (*Clin. pediatr.*, 1923, **5**, 394—422; from *Chem. Zentr.*, 1924, ii, 56).—An active preparation is obtained by the method of Friedburg and Blumenthal. The solutions obtained by this method after being saturated with sodium chloride, brought to an acidity of 0.5%, and kept several days at 25—30° and then at 37°, deposit rennin as a flocculent precipitate which can be kept several years when dried. Rennin obtained by Porcher's method by extraction of the mucous membrane with 0.4% hydrochloric acid is twice as active. The Hammersten method yields much less active preparations, whilst precipitation with cholesterol further depresses the activity of the enzyme. G. W. R.

**Pigment Metabolism in the Living Organism. I. Action of Gastric Juice on Chlorophyll.** M. W. KORTSCHAGIN (*Biochem. Z.*, 1924, **153**, 510—515).—Gastric juice, *in vivo* or *in vitro*, acting either on isolated chlorophyll or on the pigment still present in the leaves, removes magnesium from it, yielding phæophytin.

H. D. K.

**Gastric Urease.** J. M. LUCK and T. N. SETH (*Biochem. J.*, 1924, **18**, 1227—1231).—Gastric urease and soya-bean urease are identical, since they show a common dependence of the optimum  $p_H$  on substrate concentration, a common specificity, and a similar action on butylcarbamide. A partial explanation of the origin of the ammonia of gastric juice is advanced. S. S. Z.

**Auxoureases. Mechanism of the Action of Calcium.** R. KOCHMANN (*Biochem. Z.*, 1924, **151**, 259—267).—Calcium, which acts as an auxourease and protects urease from spontaneous inactivation, is most effective when it has been in contact with urea before the addition of the enzyme. It has no effect if the enzyme has previously been in contact with urea in an aqueous solution,

or if acetate is used in place of a phosphate buffer. The action of calcium in the presence of phosphate is not due to adsorption of the enzyme by precipitated calcium phosphate (cf. Jacoby, A., 1916, i, 517). Magnesium alone acts as an auxorease, but it inhibits the similar action of calcium. J. P.

**Possible Significance of Hexosephosphoric Esters in Ossification. V. The Enzyme in the Early Stages of Bone Development.** M. MARTLAND and R. ROBISON (*Biochem. J.*, 1924, **18**, 1354—1357).—An investigation of cartilages and of bones in early stages of development from human embryos and young infants has shown that the enzyme which hydrolyses monophosphoric esters is not present in any cartilage prior to the appearance of a centre of ossification but is found wherever active ossification is taking place. Therefore the two phenomena are probably connected and the production of the enzyme is a part of those cellular activities which result in the formation of bone.

S. S. Z.

**Hydrolysis of Silk Fibroin Peptone by Taka-diastrase.** J. HATANO (*Biochem. Z.*, 1924, **151**, 335—336).—Taka-diastrase contains an enzyme capable of hydrolysing silk fibroin peptone, tyrosine being isolated from the hydrolysate. J. P.

**Hydrolysis of Amygdalin by Taka-diastrase.** J. HATANO (*Biochem. Z.*, 1924, **151**, 498—500).—Taka-diastrase hydrolyses amygdalin to the extent of 98% in 72 hours, yielding dextrose, benzaldehyde, and hydrocyanic acid. J. P.

**Hydrolysis of Various  $\beta$ -Glucosides by Taka-diastrase.** J. HATANO (*Biochem. Z.*, 1924, **151**, 501—503).— $\beta$ -Methyl,  $\beta$ -saligenyl, and  $\beta$ -æsculetlyl glucosides are hydrolysed by taka-diastrase.

J. P.

**Lipases from the Thyroid Stable to Quinine and Atoxyl.** E. HERZFELD and W. ENGEL (*Biochem. Z.*, 1924, **151**, 310—313).—Sheep and ox thyroids contain lipases stable to quinine and atoxyl, the enzyme from the former animal being more active than that from the latter. J. P.

**Specificity of Lipases from Different Organs. Pancreatic Enzymes. IX.** R. WILLSTÄTTER, F. HAUROWITZ, and F. MEMMEN (*Z. physiol. Chem.*, 1924, **140**, 203—222).—The comparative study of lipases from different organs (A., 1924, i, 695, 1145) has been extended to various species. In the present work, the gastric lipases from the dog, pig, horse, rabbit, cat, hen, and wild duck have been examined. The enzyme is extracted by desiccating the minced stomach with acetone and then extracting for two hours with *N*/40-ammonia. The greater part (80%) of the lipase is contained in the mucosa, and hence it is of advantage to extract this alone in place of the whole stomach. Purification may be effected by precipitation with acetic acid followed by electro-dialysis and treatment with kaolin. Gastric lipase is unstable in alkaline, but fairly stable in faintly acid solution. The crude



extracts of the enzyme give activity- $p_H$  curves which are characteristic for each species; the shape of these curves is, however, determined by the presence of an inhibitor which acts in the alkaline region and probably of an activator acting in the acid region. Thus the optimum for the crude enzyme from dogs and cats lies between  $p_H$  5.5 and 6.3 but passes into the alkaline region on purification. Further, purification of the enzyme results in a large (100%) apparent increase in the yield, despite the losses which necessarily attend these operations. Gastric lipase resembles pancreatic, but differs from hepatic, lipase in being a true lipase, *i.e.*, in hydrolysing both fats and esters of monohydric alcohols; it appears to differ from pancreatic lipase only in its stereochemical specificity.

E. S.

### **Tryptic Digestion with Low Concentrations of Enzyme. II.**

R. EHRENBERG (*Biochem. Z.*, 1924, **153**, 362—371).—Further evidence is brought forward in support of the author's view that part of the enzymic activity of dialysates obtained from trypsin-caseinogen digests is due to a substance derived from the caseinogen itself. During the process of tryptic hydrolysis the "carrier of enzymic activity" changes. (Cf. this vol., i, 103.) H. D. K.

### **Activation of Pancreatic Juice by Enterokinase. T. N.**

SETH (*Biochem. J.*, 1924, **18**, 1401—1416).—Enterokinase is a specialised proteolytic enzyme which acts primarily as a stimulus to the activation of trypsinogen by digesting a protective colloidal substance which is associated with trypsin in the zymogen state and masks the characteristic properties of trypsin. After initiation of activation by enterokinase, the process is carried to completion almost entirely by the liberated trypsin. The activation of trypsinogen is, therefore, essentially autocatalytic, except in the initial stages of the interaction between trypsinogen and enterokinase.

S. S. Z.

### **Proteolytic Enzyme in the Pods of *Vicia Faba*, L. P. W.**

DANCKWORTT and E. PFAU (*Arch. Pharm.*, 1924, **262**, 449—452).—The white spongy layer of the inner skin of the pod of the broad bean contains a proteolytic enzyme and a peroxydase. The rest of the pod contains some proteolytic enzyme, but both it and the peroxydase are absent from the seeds, leaves, and stem of the plant. Comparative tests were made on (i) the corresponding tissue in the pod of *Phaseolus vulgaris* (kidney bean), and on the latex from (ii) *Euphorbia lathyris*, (iii) *E. palustris*, (iv) *Chelidonium majus*, and (v) *Papaver rhæas*. Peroxydase was present in all these, whilst (iii) and (iv) contained in addition a proteolytic enzyme, and (iv) had an oxydase as well.

The peroxydase and proteolytic enzymes can be separated by selective adsorption; alumina takes up the proteolytic enzyme and animal charcoal the peroxydase.

W. A. S.

**Enzymes of *Utricularia vulgaris*. II. Relative Amounts of Proteolytic Enzymes in the Bladders and in the Stem.** A. N. ADOWA (*Biochem. Z.*, 1924, **153**, 506—509).—An extract of

the green bladders of the fully developed plant is about as active in the liquefaction of alkaline gelatin as a similar extract of a mixture of the red and blue bladders, and is far more active than an extract of the stem. Acid gelatin is more readily digested by extracts from the various portions of the plant than is alkaline gelatin.

H. D. K.

**Enzymes of the Skin. II.** J. WOHLGEMUTH. **Distribution of Enzymes in the Skin. The Presence of a Nucleotidase.** E. KLOPSTOCK (*Biochem. Z.*, 1924, **153**, 487—495).—To the list of enzymes previously found in human skin must be added trypsin (present only in minute quantity) and an active nucleotidase. The last is present in largest quantity in the skin of the sole of the foot in adults, and is also very active in the skin of suckling infants. Diastase is fairly evenly distributed in the skin from different parts of the body, but lipase and phenolase are more concentrated in the skin of the genital region.

H. D. K.

**Invertase and the Second Mode of Action of Hydrogen Ions.** H. P. BARENDRECHT (*Biochem. Z.*, 1924, **151**, 363—370).—The author's radiation hypothesis of the action of enzymes (A., 1920, i, 102, 195) is supported by an investigation of invertase in relation to the capacity of hydrogen ions and substrate to share the absorption of the specific radiation of the enzyme.

J. P.

**Biochemical Transformation of *as*-Dichloroacetone into Optically Active  $\alpha\gamma$ -Dichloropropan- $\beta$ -ol.** H. K. SEN (*Biochem. Z.*, 1924, **151**, 51—53).—Yeast in the presence of sugar reduces  $\alpha\gamma$ -dichloroacetone to lævorotatory  $\alpha\gamma$ -dichloropropan- $\beta$ -ol ( $[\alpha]_D - 8.7^\circ$ ).

J. P.

**Phytochemical Reduction of Methyl  $\alpha$ -Chloroethyl Ketone.** P. SANTOMAURO (*Biochem. Z.*, 1924, **151**, 48—50).—Despite its toxic nature, methyl  $\alpha$ -chloroethyl ketone is reduced by yeast in the presence of sugar to the corresponding lævorotatory chlorobutyl alcohol ( $\beta$ -hydroxy- $\gamma$ -chlorobutane).

J. P.

**Influence of Acidity on the Action of Yeast Extracts on Concentrated Solutions of Dextrose.** R. KUHN and G. E. VON GRUNDHERR (*Ber.*, 1924, **57**, [B], 1852—1854).—The differing results obtained by previous workers on the synthesis of disaccharides from dextrose by the aid of yeast extracts may probably be explained by the observation that with varying acidity of the solution two maxima for the rate of loss of reducing power are found. It appears therefore that the process is governed by at least two different enzymes which cause the formation of different products. This view is confirmed by the discovery of a yeast extract with a single optimal acidity. The yields of disaccharide vary unusually with different yeasts and also depend greatly on the concentration of the dextrose solution; at  $p_H$  5, the synthesis is most rapid in 40% solution.

H. W.

**Dried Yeast. II.** H. VON EULER and G. WESTLING (*Z. physiol. Chem.*, 1924, **140**, 164—176).—A comparison has been made between

the actions on dried and fresh yeast of certain substances which accelerate or inhibit alcoholic fermentation. The results show that the inhibitory action of phenol is much smaller with dried than with living yeast, whilst potassium formate, which strongly accelerates the action of living yeast, produces no change in that of dried yeast. The formation of hexosephosphates by dried yeast is inhibited by inorganic salts, the order of the inhibitory activity being  $\text{NH}_4\text{F} > \text{NaI} > \text{Na}_2\text{SO}_4$ . Neither the increase with time in the fermentative power of solutions containing dried yeast nor the simultaneous growth of yeast in such solutions is proof of the regeneration of the dried preparation; these solutions form an extremely favourable medium for the growth of yeast. E. S.

**Mechanism of Alcoholic Fermentation.** A. LEBEDEV (*Z. physiol. Chem.*, 1924, **141**, 61—62).—Polemical (cf. Hayduck, *ibid.*, **136**, 106). E. S.

**Carbohydrate and Fat Metabolism of Yeast. II. Influence of Phosphates on the Storage of Fat and Carbohydrate in the Cell.** I. S. MACLEAN and D. HOFFERT (*Biochem. J.*, 1924, **18**, 1273—1278).—Yeast incubated in a 4% oxygenated dextrose solution, frequently renewed, in the presence of phosphate shows an increase in the rate of formation of fat from the sugar, and the total amount of fat formed is somewhat higher than that produced in absence of phosphate. When laevulose is substituted for dextrose the rate is also increased and the total amount of fat formed is almost double that which is found in the absence of phosphate. When sodium hexosephosphate replaces the sugar and inorganic phosphate, no significant change in the formation of fat is observed. S. S. Z.

**Mechanism of Alterations in the Hydrogen-ion Concentration of Bacterial Cultures.** S. SIERAKOVSKI (*Biochem. Z.*, 1924, **151**, 15—26).—From the first to the fourth day of growth the  $p_{\text{H}}$  of most bacterial cultures approximates to 7.0 (6.8 to 7.6) irrespective of the original  $p_{\text{H}}$ , but later the cultures become alkaline. Bacterial growth is most rapid in cultures in which the initial  $p_{\text{H}}$  is near that to which the particular culture tends during the first few days, and attains greatest luxuriance in acid media, becoming progressively less vigorous in neutral and alkaline media, although the maximal growth is attained more quickly in alkaline than in acid media. The mechanism of the changes in  $p_{\text{H}}$  is discussed. The rate of development of alkalinity is directly correlated with the rate of evolution of carbon dioxide. J. P.

**Phosphorus Metabolism of certain Moulds, particularly *Aspergillus niger*.** R. SCHNÜCKE (*Biochem. Z.*, 1924, **153**, 372—423).—The moulds were grown in artificial culture media, acid potassium phosphate being used as the source of phosphorus, and various organic and inorganic compounds as sources of nitrogen. The uptake of phosphorus by *Aspergillus* is rapid at first, and the percentage of phosphorus in the young mycelium is high. The uptake rises to a maximum, which is maintained for a time. Then

inorganic phosphorus begins to be excreted by the fully developed mould and the percentage content of phosphorus eventually falls to a low value. Phosphorus uptake and percentage of this element in the dried mould vary with conditions of growth. With a large surface exposed to air and with ammonium sulphate in the medium there is increased production of phosphorus-free substances and the absolute and relative phosphorus content of the growth remains low. Changes in the phosphorus concentration in the medium scarcely affect the phosphorus content of the mycelium, in spite of the influence of such changes on the amount of growth. Phosphorus is not taken up specifically for spore formation, but is conveyed to the spores from the quantity already present in the rest of the plant.

*Oidium lactis*, *Penicillium W.II*, and *Dematium pullulans* differ from *Aspergillus* in that there is no excretion of phosphorus by the ageing mycelium. H. D. K.

**Acid Formation by *Aspergillus niger*.** K. BERNHAUER (*Biochem. Z.*, 1924, 153, 517—521).—Gluconic acid is produced during the fermentation of nutrient sucrose solutions by certain strains of this mould, giving yields as high as 70%. Gluconic acid does not appear to be an intermediate substance in the production of citric acid. The experimental conditions determine whether gluconic or citric acid will be the main product. It is possible to influence the nature of the products formed from sugar by growing the mould for a preliminary period on an unusual medium.

H. D. K.

**Formation of Methyl Ketones during the Oxidative Degradation of Triglycerides and Fatty Acids by Moulds with Reference to the Rancidity of Coconut Oil. I. Significance of Methyl Ketones in Butter Rancidity. II. Occurrence and Significance of Methyl Ketones as Odoriferous Substances in Roquefort Cheese.** M. STÄRKLE (*Biochem. Z.*, 1924, 151, 371—415).—The odour of rancid coconut oil is due to methyl ketones formed by moulds (*Penicillium* and *Aspergillus*) in the presence of water and nitrogen, the occurrence of those ketones already found by Haller and Lassieur (A., 1910, i, 355, 808) being confirmed, with the exception of methyl undecyl ketone, and the addition of methyl amyl ketone. The ketones are regarded as intermediate products formed from the ammonium salts of the corresponding higher fatty acids or fats, thus from hexoic, heptoic, octoic, nonoic, decoic, and dodecoic acids, methyl propyl, methyl butyl, methyl amyl, methyl hexyl, methyl heptyl, and methyl nonyl ketones, respectively, are derived. In addition to methyl ketone rancidity, coconut oil may also show a rancidity due to the formation of aldehydes from oleic acid. The supposed ester rancidity of butter is really due to the formation of ketones, and the odour of ripe Roquefort cheese is likewise ascribed to methyl ketones and not to butyric esters. J. P.

**Use of *Bacillus coli* in the Detection of Tryptophan and its Application to the Tubercle Bacillus.** MME. and E. WOLLMAN (*Bull. Soc. Chim. biol.*, 1924, 6, 869—872).—Tryptophan, in

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amounts as small as 1 part in 500,000 parts, can be detected by the production of indole by *Bacillus coli*, after 24 hours' incubation in a culture medium containing potassium dihydrogen phosphate and ammonium lactate. Tubercle bacilli grown on synthetic media, containing as sources of nitrogen only asparagine or ammonium lactate, showed, after acid hydrolysis or trypsin digestion, the presence of tryptophan.

E. M. C.

**Metabolism of Acid-fast Bacteria. III. Nutritional Needs of the Bacillus of Avian Tuberculosis; Utilisation of Simple Chemical Substances for its Growth.** S. KONDO (*Biochem. Z.*, 1924, **153**, 302—312).—Four strains were examined. As sole source of carbon in a synthetic medium containing sodium chloride, ammonium sulphate, magnesium sulphate, and a phosphate mixture of  $p_H$  7.1, sodium acetate alone gave good growth. Salts of propionic, butyric, oxalic, succinic, malic, tartaric, and citric acids were not utilised. One strain only was able to utilise lactic acid. Methyl, ethyl, and amyl alcohols, mannitol, dextrose, lævulose, and arabinose gave negative results. Glycerol was variable. As sources of nitrogen, ammonium salts and nitrates were satisfactory, but amino-acids (glycine, *D*-alanine, aspartic acid, leucine, and tyrosine) were not utilised unless sodium acetate was added as a second source of carbon. Urea and uric acid gave no growth.

H. D. K.

**Comparative Action of Bismuth on *Staphylococcus*, *Streptococcus*, and *Bacillus coli*.** P. LEMAY and L. JALOUSTRE (*Compt. rend.*, 1924, **179**, 1441—1442).—Potassium bismuth tartrate and sodium bismuthate were added to the cultures giving concentrations of 1/800,000 to 1/2500 (expressed as Bi). *Staphylococcus aureus* is destroyed after 12 hours by a concentration of 1/400,000, whilst the other two bacteria are not killed within 48 hours in a concentration of 1/2500.

A. E. C.

**Bactericidal Action of Tellurium- $\beta$ -diketones.** G. T. MORGAN, E. A. COOPER, and F. J. CORBY (*J. Soc. Chem. Ind.*, 1924, **43**, 304—306).—The tellurium- $\beta$ -diketones (T., 1920, **117**, 1456; 1921, **119**, 610; 1922, **121**, 922; 1923, **123**, 444; A., 1923, i, 517; 1924, i, 493, 495, 496, 591, 1044) are powerful germicides, acting in concentrations as low as 1 in 1,000,000 to 1 in 20,000,000; their action is most marked after 4 hours' contact with the organisms under examination. With protozoa, they are much less effective. The number and distribution of alkyl groups in the molecule largely affect the bactericidal power, the maximum activity being obtained when two methyl groups occupy the 2:6 positions respectively. Isomeric differences also influence this property, and the aromatic derivatives are of much the same order of activity as the aliphatic. The bactericidal power is definitely associated with the tellurium-carbon heterocyclic ring, and the presence of unsaturated tellurium is necessary for great activity. In the presence of serum, this property is destroyed, apparently due to colloidal, but not necessarily

to protein material, whereas their activity is largely retained in urine. The compound 2:4-dimethylcycloelluropentane-3:5-dione has been successfully used in treating cystitis and eye infections.

I. E. B.

### **Bactericidal Action of Quinones and Allied Compounds.**

G. T. MORGAN and E. A. COOPER (*J. Soc. Chem. Ind.*, 1924, **43**, 352—354).—The high germicidal power of *p*-benzoquinone is probably due to its property of dynamic isomerism and to the presence of nascent peroxide molecules in its aqueous solution; camphorquinone, which is fully saturated and does not therefore exhibit dynamic isomerism, is comparatively inactive. The introduction of substituents into the benzene ring generally results in a reduction in germicidal power except in the case of *m*-dichloroquinone, the abnormally high bactericidal power of which must be due to a specific action of the halogen in overcoming the effect of diminished tautomerism. Bromoanilic acid has a greater germicidal power than chloroanilic acid and the sodium salts in each case a much smaller power than the free acid.

[With A. W. BURT.]—The compounds tested are less active when examined by the inhibitory method, and the inhibitory power of benzophenone more closely approximates to that of its homologues. This is due to the fact that the quinones enter into chemical reaction with proteins, with the formation in many cases of red coloured compounds, the colour corresponding in intensity with the bactericidal power of the quinones, so that high concentrations of the quinones are necessary for disinfecting purposes in the presence of organic matter and, therefore, these substances are probably useless as internal germicides.

A. R. P.

### **Bio-assay of Pituitary Extracts. Action of the Standard Infundibular Powder on the Secretion of Urine.**

M. I. SMITH and W. T. McCLOSKEY (*J. Pharm. Exp. Ther.*, 1924, **24**, 371—389).—The standard desiccated and defatted infundibular powder suggested by the authors (*U.S. Public Health Repts.*, 1923, **38**, 493) has the same qualitative, and approximately the same quantitative effect on renal secretion as a 5% acidified aqueous extract of the fresh gland. In the anaesthetised rabbit, pituitary extract increases urinary flow for about half an hour; this is often preceded by brief urinary suppression, and followed by a more lasting diminution. In the non-anaesthetised rabbit and man, pituitary extract acts as an anti-diuretic.

H. J. C.

### **Dialysis of the Physiologically Active Constituents of the Infundibulum.**

M. I. SMITH and W. T. McCLOSKEY (*J. Pharm. Exp. Ther.*, 1924, **24**, 391—403).—Dialysis of pituitary solutions prepared from a standard desiccated and defatted infundibular powder (cf. preceding abstract) through collodion membranes of graded permeability showed that the uterine stimulating constituent diffused out quantitatively and at the same rapid rate as the pressor constituent. From measurements of the urine secreted after

injection of the dialysate into rabbits, it appears that the constituent affecting renal secretion also diffuses at approximately the same rate. The results support Abel's view of the chemical identity of the active constituents of the infundibulum. H. J. C.

**Intermediate Carbohydrate Metabolism and Insulin. Intermediate Sugar of the Liver and Musculature. VI.** T. BRUGSCH and H. HORSTERS (*Biochem. Z.*, 1924, **151**, 203—215).—The intermediate sugar formed in muscle- and liver-tissue of rabbits on simultaneous administration of insulin and glucose consists to a small extent of hexosediphosphate, and in large part of polysaccharides which yield on hydrolysis laevorotatory compounds. The formation of such intermediate sugars under the influence of insulin is supposed to differ only quantitatively from the normal process (cf. also Brugsch, Benatt, Horsters, and Katz, *ibid.*, **147**). J. P.

**Effect of Insulin and Muscle-tissue on Dextrose *in vitro*.** C. LUNDSGAARD and S. A. HOLBØLL (*J. Biol. Chem.*, 1924, **62**, 453—469).—Solutions of dextrose were treated with insulin and with mixtures of the latter with blood and muscle-tissue, dialysed through collodion, and the sugar in the dialysate was determined polarimetrically and by the method of Hagedorn and Jensen (*A.*, 1923, ii, 440). Neither insulin alone nor with the addition of blood caused any change in the rotatory power of the dextrose; with insulin and muscle-tissue there was observed a decrease in the rotatory power, which could be accounted for by a change in the equilibrium between  $\alpha$ - and  $\beta$ -glucose, without assuming the formation of  $\gamma$ -glucose. The muscle-tissue loses its activity after 2 hours. In all experiments the reducing power of the dextrose remained unaltered, indicating that neither insulin alone nor with blood or muscle-tissue is able, *in vitro*, to oxidise dextrose or to synthesise it into glycogen. C. R. H.

**Physiological Action of Insulin.** C. SERONO, E. TROCELLO, and A. CRUTO (*Rassegna Clin. Terap. Sci. aff.*, 1924, **23**, 53—60; from *Chem. Zentr.*, 1924, ii, 77; cf. *A.*, 1924, i, 1150).—Experiments were carried out to determine whether the action of insulin is connected with the physiological effect of derivatives of ammonia. Choline and neurine produce inappreciable changes in blood-sugar; muscarine, tetramethylammonium chloride, and picrotoxin cause hyperglycæmia. Insulin does not inhibit the action *in vitro* of certain enzymes which produce dextrose. The action of insulin *in vitro* and *in vivo* is antagonised by total pancreas extract and by pancreatic diastase. Insulin, however, only slightly inhibits the transformation *in vitro* of glycogen into dextrose by liver or pancreas extracts. It must therefore act as a kinase and not as an anti-enzyme. Insulin may be considered as the antagonistic hormone of the external secretion of the pancreas and of the digestive ferments, neutralising any excess of these enzymes in the portal blood or in the tissues generally. G. W. R.

**Mechanism of the Action of Insulin.** E. BISSINGER, E. J. LESSER, and K. ZIFP (*Klin. Woch.*, 1924, 2, 2233—2234; from *Chem. Zentr.*, 1924, ii, 77).—In perfusion experiments insulin does not inhibit the formation of sugar either in normal or pancreas-diabetic livers of frogs, nor does it antagonise the effect of adrenaline on sugar formation in the liver. After administration of insulin to mice, sugar disappears from all organs. Fresh formation of glycogen may take place if the tissue sugar is not too quickly oxidised.  
G. W. R.

**Blood-sugar Depressant Action of Plant Extracts and Oxydases. Detection of Enzymes in Insulin.** E. GLASER and L. WITTNER (*Biochem. Z.*, 1924, 151, 279—295).—Using Collip's method, blood-sugar depressant substances may be extracted from mushrooms and turnips, whilst the acid alcohol extract is inactive. Peroxydase from horseradish, tyrosinase from mushrooms, and catalase from sheep's liver all depress the blood-sugar and these enzymes are present in the extracts obtained from plants by Collip's procedure. Peroxydase or oxydase and aldehydase can be demonstrated in insulin, and since certain oxydases are known to inhibit the diastatic hydrolysis of starch, a correlation between insulin and oxidative enzymes is suggested.  
J. P.

**Biochemical Method for the Determination of Vitamins.** C. A. SAGASTUME and C. E. SPEGAZZINI (*Anal. Asoc. Quím. Argentina*, 1924, 12, 151—166).—The authors have investigated the method of Ganassini for the determination of vitamins (Funke, "Histoire et consequences pratiques de la découverte des vitamines," Paris, 1924, p. 16), depending on their effect on the activity of yeasts. The results obtained were contradictory and it is concluded that the proposed method is valueless for quantitative purposes.  
G. W. R.

**Effect of Fermentation on the Water-soluble Vitamin Content of [Beer] Wort.** H. W. SOUTHGATE (*Biochem. J.*, 1924, 18, 1248—1251).—When grown in beer wort, yeast abstracts almost quantitatively vitamin-B from the medium. The organism does not synthesise this vitamin during the process, but, if anything, actually uses up some of the principle which it has abstracted from the wort.  
S. S. Z.

**Connexion between the Water-soluble Growth Factors and Activators of the Degradation of Sugar. A Thermostable Biocatalyst in Yeast.** H. VON EULER and O. SWARTZ (*Z. physiol. Chem.*, 1924, 140, 146—163).—Experiments are being made to determine whether any relationship exists between the various active substances (co-enzyme, bios, growth factor, vitamin-B) which are present in yeast extracts. Wildier's bios (designated  $D_m$ ) has been found to possess great stability towards alkali ( $p_H$  12) at 100° and surpasses the co-enzyme in this respect; the growth factor (designated  $\bar{D}_r$ ), on the other hand, is much more sensitive to alkali. Extracts of dried yeast and of barley germ contain a biocatalyst



which accelerates the rate of fermentation of sucrose by living yeast and is little sensitive to alkalis ( $p_H$  12) at 100°. It is provisionally designated by the letter z. E. S.

**Dynamic Action of Ions on Growth on a Vitamin-rich Diet.** R. TSUKAMOTO (*Biochem. Z.*, 1924, **151**, 216—226).—In very young rats on a vitamin-rich diet deficiency of salts produces but a slight diminution in the rate of increase of body-weight. Absence of cell salts and the presence of sodium chloride likewise had little effect in young animals, but in older animals were followed by loss of weight. The rate of healing of injuries to bone and skin is not very markedly affected by salt deficiency. J. P.

**Nitrogenous Materials of Corn Offal. Comparative Study of their Biological Value as Factors of Existence, Growth, and Fertility.** L. RAUDOIN, J. ALQUIER, (MLLE.) ASSELIN, and (MLLE.) CHARLES (*Compt. rend.*, 1924, **179**, 1342—1345).—Experiments with guinea-pigs and rats show that although various kinds of corn offal all contain about 15% of nitrogen and give 4.5 cal./g., yet their values for supporting existence differ considerably; a similar variation occurs when the corn offal serves merely as the source of nitrogen in a diet of starch, calcium lactate, cellulose, butter fat, and lemon juice. Casein contains a factor necessary for reproduction which is lacking in bran or gelatin. F. M. H.

**Influence of the Parents' Diet on the Young. I. Influence of the Father's Diet.** V. KORENCHEVSKY and M. CARR (*Biochem. J.*, 1924, **18**, 1308—1312).—If the diet of male rats is deficient in fat-soluble factor a greater percentage of matings are unproductive and the litters begotten by such fathers are weaker than those from richly-fed fathers. The weight and calcium content of the skeletons of such offspring are not affected. S. S. Z.

**Influence of the Parents' Diet on the Young. II. Influence on the Young of an Excessive Amount of Fat-soluble Factor and Calcium in the Mother's Diet during Pregnancy.** V. KORENCHEVSKY and M. CARR (*Biochem. J.*, 1924, **18**, 1313—1317).—Young rats are less susceptible to nutritional disorders and rachitic changes in the skeleton induced by a diet deficient in the fat-soluble factor, if the mother during the period of gestation has her "normal" diet enriched with an excess of this vitamin. The administration of extra calcium to the mother's diet during this period has no such influence on the young unless the "normal" diet is deficient in this element. S. S. Z.

**Growth-promoting and Anti-rachitic Value of Cod-liver Oil when Injected Intraperitoneally.** K. M. SOAMES (*Biochem. J.*, 1924, **18**, 1349—1353).—By injecting intraperitoneally cod-liver oil into rats protection is afforded against a rickets-producing diet. Improved growth and calcification are also obtained on a diet deficient in the fat-soluble organic factor by this treatment. S. S. Z.

**Value of Egg-white as Sole Source of Nitrogen for Young Growing Rats.** M. A. BOAS (*Biochem. J.*, 1924, **18**, 1322).—Rats fed on the white from fresh English eggs grew normally and had good coats, whilst rats in the diet of which a commercial preparation of egg-white (Chinese) was employed ceased to grow after they had received the diet for from 4 to 6 weeks and typical symptoms of loss of hair etc., previously described by the author, appeared.

S. S. Z.

**Brown and White Bread in the Diet of the Rat.** G. A. HARTWELL (*Biochem. J.*, 1924, **18**, 1323—1326).—The rate of growth of young rats on a diet of bread (white or brown), butter, and salt mixture is slow. Male rats grow more rapidly on brown bread than on white. Female rats grow equally slowly on either diet. With both diets mothers yield litters of poor weight at birth, of which only a few are weaned.

S. S. Z.

**Comparison of the Values of Yeast and of Orange Juice with those of Marmite and of Decitrated Lemon Juice, respectively, in the Calcification of the Skeleton.** V. KORENCHESKY and M. CARR (*Biochem. J.*, 1924, **18**, 1319—1321).—The slight increase in the calcification obtained by the use of yeast instead of marmite is within the limits of the usual fluctuations observed. Neither orange juice nor decitrated lemon juice has any definite influence on calcification.

S. S. Z.

**Influence of Sunlight on the Growth-promoting and Anti-rachitic Properties of Cow's Milk.** E. M. LUCE (*Biochem. J.*, 1924, **18**, 1279—1288).—Sunlight of summer intensity in England has no significant effect in raising the growth-promoting value of cow's milk when the diet of the cow is deficient in fat-soluble vitamins. The degree of exposure to sunlight appears, however, to have a small effect in determining the anti-rachitic value of milk.

S. S. Z.

**Effect of Irradiation of the Environment with Ultra-violet Light on the Growth and Calcification of Rats Fed on a Diet Deficient in Fat-soluble Vitamins. Part Played by Irradiated Sawdust.** E. M. HUME and H. H. SMITH (*Biochem. J.*, 1924, **18**, 1334—1345).—Rats kept on a diet deficient in fat-soluble vitamins and housed in previously irradiated glass jars containing sawdust showed growth as good as that shown by directly irradiated animals. In the absence of sawdust, this growth does not take place. When the sawdust is replaced by a piece of deal board, partial growth takes place. The degree of calcification is directly proportional to the amount of growth.

S. S. Z.

**Effect on the Growth of Rats Receiving a Diet Deficient in Fat-soluble Vitamins of Exposing their Environment to the Emanation from Radium Bromide.** H. CHICK and M. TAZELAAR (*Biochem. J.*, 1924, **18**, 1346—1348).—Temporary ionisation of the air produced by emanation from radium bromide has no effect in promoting growth of rats subsisting on a diet deficient in the fat-soluble vitamins.

S. S. Z.

**Effect of Ultra-violet Radiations on Accessory Food Factors. I. Vitamin-A. II. Vitamin-B. III. Vitamin-C. IV. Vitamin-D.** J. ŠPINKA (*Biochem. Z.*, 1924, **153**, 197—241).

—Vitamin-A :—Butter exposed to the rays of a mercury quartz lamp becomes toxic to mice, and even if added to a normal diet will bring about the death of these animals in about 8 days. On a diet deficient in vitamin-A, control animals live, on an average, 50 days. Toxic substances aldehydic and ketonic in nature may be separated from the irradiated butter by steam distillation. In absence of air, exposure to the mercury lamp does not destroy the A factor in butter.

Vitamin-B :—This factor, defined as that which rapidly relieves acute symptoms of polyneuritis in pigeons (but does not cure alimentary dystrophy nor prevent further loss in weight), is not destroyed when its neutral or weakly acid solution is subjected to ultra-violet radiation.

Vitamin-C :—Fresh lemon juice containing this vitamin does not lose its anti-scorbutic value if the acid solution is irradiated by the mercury lamp, even in presence of air. If the solution, in presence of air, is diluted, or rendered less acid, it loses its activity on irradiation. This is doubtless due to oxidation either by the air or by the ozone produced during the exposure, since in absence of air irradiation of the same diluted or partly neutralised juice does not bring about the destruction of vitamin-C.

Vitamin-D :—This factor (which is taken to be that which cures alimentary dystrophy in pigeons on a polyneuritic diet) is remarkably resistant to irradiation, not only in presence or absence of air, but even if exposed to ultra-violet light after boiling for 6 hours in dilute alkaline solution.

H. D. K.

**Anti-rachitic Properties Imparted to Inert Fluids and to Green Vegetables by Ultra-violet Irradiation.** A. F. HESS and M. WEINSTOCK (*J. Biol. Chem.*, 1924, **62**, 301—313; cf. Steenbock and Black, A., 1924, i, 1272).—Irradiation with ultra-violet light was found to confer anti-rachitic properties on cotton-seed and linseed oils, wheat, and various green vegetables; in the case of the oils these properties were retained during 20 days' storage in the dark.

C. R. H.

**Dietary Requirements for Reproduction. III. Existence of Reproductive Dietary Complex (Vitamin-E) in Ethereal Extracts of Yellow Corn [Maize], Wheat Embryo, and Hemp-seed.** B. SURE (*J. Biol. Chem.*, 1924, **62**, 371—396).—A diet containing 50% of dried skimmed milk, 0.2% of ferric citrate, and the ordinary vitamins is sufficient for growth but not for reproduction. In order to obtain a normal reproductive cycle such a diet must be supplemented with an increased amount of vitamin-B and also with 5% of an ethereal extract of yellow maize, wheat embryo, or hemp-seed, or with cotton-seed oil or olive oil. The extra vitamin-B is concerned especially with the function of lactation; the substance contained in the oils appears to be a specific

reproductive vitamin, now designated vitamin-*E*. The conclusions of Anderegg (*ibid.*, 1924, 59, 587) against the existence of such a vitamin are criticised on the ground of the high fat content of his diets.  
C. R. H.

**Anaërobic Respiration in Plants.** C. NEUBERG and A. GOTTSCHALK (*Biochem. Z.*, 1924, 151, 167—168).—The anaërobic formation of alcohol in a sterile pulp of peas in the presence of dextrose proceeds with the intermediate formation of acetaldehyde.  
J. P.

**Is Carbon Dioxide a Climatic Factor in Plant Growth?** E. REINAU (*Z. Pflanz. Düng.*, 1924, 3A, 182—189).—After reviewing the evidence the author suggests that carbon dioxide is a climatic factor.  
O. O.

**Acidity of Plant Sap and Methods for its Determination.** A. ARLAND (*Z. Pflanz. Düng.*, 1924, 3A, 152—164).—Details are given for trustworthy determinations of  $p_H$  of sap, both electrometrically and colorimetrically.  
O. O.

**Diphenylamine Reaction in Problems of Plant Nutrition.** H. NIKLAS and F. VOGEL (*Z. Pflanz. Düng.*, 1924, 3A, 323—347).—The results of the diphenylamine test for nitrate in the tissue of sappy plants are shown to be correlated with the nitrogen supply of the soil. [Cf. *B.*, Mar. 6th.]  
E. M. C.

**Incrustive Substances of Plants.** V. E. SCHMIDT and G. MALYOTH (*Ber.*, 1924, 57, [B], 1834—1837; cf. A., 1921, i, 912; 1922, i, 206; 1923, i, 274, 884).—Chlorine dioxide solutions of concentration lower than 0.3% used alternately with sodium sulphite solution (2%) are without action on the skeleton substance of plants. Hydrolysis of the cell membrane is not effected by hydrochloric acid of concentration less than 2*N* whether the acid is used alone or alternately with sodium sulphite. Since the concentration of hydrochloric acid developed in the reaction with chlorine dioxide cannot exceed 0.015% the validity of the treatment of the cell membranes of plants with *N*/5-chlorine dioxide and 2% sodium sulphite solution alternately is fully established. The behaviour of galactose, lævulose, and the skeleton substance of *Fagus silvatica* and *Picea excelsa* is described in detail.  
H. W.

**Asparagine and Urea.** D. PRJANISCHNIKOV (*Biochem. Z.*, 1924, 150, 407—423).—In the plant, asparagine is formed in the same way, and serves the same purpose, as urea in the animal world. Asparagine formation is diminished and susceptibility to the toxic action of ammonia is increased in plants when carbohydrates are lacking. In the fungi, possessing no power of synthesising carbohydrates, urea may be formed. The ultimate fate of asparagine in the plant as a reserve source of nitrogen differs from that of urea in the animal, but the essential analogy between the two holds.  
J. P.

**Absorption of Salts by Plants. I. Mutual Influence of Ions.** H. LUNDEGÅRDH and V. MORÁVEK (*Biochem. Z.*, 1924, **151**, 296—309).—Various cations and anions in concentrations ranging from 0.01*N* to 0.0025*N* influence the rate of absorption of potassium, nitrate, and phosphate by plants. The action in this respect of the cations  $K^+$ ,  $Ca^{++}$ ,  $Mn^{++}$ ,  $Al^{+++}$ , and of the anions  $NO_3^-$ ,  $H_2PO_4^-$ ,  $PO_4^{---}$  is ascribed to valency and lyotropy. J. P.

**Rôle of Silica in Plant Growth. Its Assimilation and Physiological Relation to Phosphoric Acid.** D. R. NANJI and W. S. SHAW (*J. Soc. Chem. Ind.*, 1925, **44**, 1—6T).—Silica occurs in plant-tissues, especially in the leaves, in varying amounts, up to 80% of the total ash. About 90% of the total silica is present as free silicic acid, in which form it can be extracted with sodium hydrogen carbonate solution. A certain amount occurs in a form which is decomposable by acid and resists the action of sodium hydrogen carbonate. In the organic condition the silicic acid is present in an ester-like combination with certain carbohydrates, which is not affected either by sodium hydrogen carbonate or by hydrochloric acid. A method based on these observations is described, by means of which the amounts of silica in its various forms were determined in several samples of wheat and rice straw.

In order to test the validity of current views regarding the relationship between phosphoric acid and silica in plant growth (cf. Lemmermann and Wiessmann, A., 1922, i, 1103), determinations of the amounts of organic and inorganic phosphorus were made on each of the straws in which the silica content had been determined. The results show, in accordance with previous work, that when there is an abundant supply of silica in the absence of phosphoric acid, the former is capable of replacing the latter without any detrimental effect on growth. Contrary to previous opinion, it appears that conditions which are favourable for the assimilation of silica may be unfavourable for that of phosphoric acid. It was found that, on an average, 60—70% of the total phosphoric acid is in inorganic combination, as compared with 90% in the case of silica. W. F. F. R.

**Colorimetric Determination of Lycopin.** S. J. B. CONNELL (*Biochem. J.*, 1924, **18**, 1127—1128).—The lycopin is determined in a Stanford colorimeter against a standard solution made up of potassium dichromate and cobalt sulphate (free from nickel). The error is less than 1%. S. S. Z.

**Hemicelluloses. VI. Fermentative Fission of Salep Manna.** H. PRINGSHEIM and A. GENIN (*Z. physiol. Chem.*, 1924, **140**, 299—304).—Salep manna is hydrolysed practically quantitatively to mannose by malt extracts. Two enzymes evidently participate in the reaction, for if the malt extract has been kept for 6 months the hydrolysis stops at the stage of a *mannobiose*,  $[\alpha]_D^{25} + 12.8^\circ$  in water. This forms a *phenylhydrazone*, m. p.  $199^\circ$ , from which the disaccharose can be recovered in a crystalline condition by treatment with benzaldehyde. This mannobiose may be

identical with that obtained synthetically by Bourquelot and Herissey (A., 1920, i, 291).

The optimum acidity for the action of cellobiase (A., 1924, i, 1144) is at  $p_H$  6. E. S.

**Carbohydrate Enzymes of some Starch-free Monocotyledons.** R. E. CHAPMAN (*Biochem. J.*, 1924, **18**, 1388—1400).—The mature green leaf of the snowdrop (*Galanthus nivalis*) contains amylase, dextrinase, and invertase but no maltase or emulsin. That of the onion (*Allium cepa*) contains amylase, maltase, invertase, and emulsin, but no dextrinase. That of the leek (*Allium porrum*) contains dextrinase, maltase, invertase, and emulsin, but no amylase. That of the dock (*Rumex obtusifolius*) contains amylase, dextrinase, maltase, invertase, and emulsin. It is suggested that the failure of the snowdrop, onion, and leek to form starch in the mature green leaf is due to lack of the necessary enzymes.

S. S. Z.

**Constituents of the Sap of the Vine (*Vitis vinifera*, L.).** A. WORMALL (*Biochem. J.*, 1924, **18**, 1187—1202).—The sap contains 1.56 g. of solid matter per litre; one-third of this is inorganic and the remainder organic. The latter was found to consist mainly of dextrose, lævulose, a small amount of sucrose, and oxalic, tartaric, malic, and succinic acids. A small amount of an acid, m. p. 161—162°, which was not identified, was present. The mineral salts found were chlorides, sulphates, nitrites, nitrates, silicates, and phosphates of sodium, potassium, calcium, iron, magnesium, and to a lesser extent manganese and aluminium. A trace of a fat-like substance was isolated which may be a mixture of neutral fat and free fatty acid. A small amount of organic nitrogen, believed to be associated with the enzymes of the sap, is also present. Diastase, peroxydase, and, to a small extent, catalase were present, and maltase, invertase, lipase, protease, glycerophosphatase, and rennin were absent.

S. S. Z.

**A Protein from the Leaves of the Alfalfa Plant. A Protein from the Leaves of *Zea Mays*.** A. C. CHIBNALL and L. S. NOLAN (*J. Biol. Chem.*, 1924, **62**, 173—178, 179—181).—Cytoplasmic proteins have been obtained from the leaves of the alfalfa (lucerne) plant and of *Zea Mays* the properties of which are almost identical with those of spinacin (A., 1924, i, 1272), the chief characteristic being the ease with which they are precipitated from their solutions in acid by small amounts of salts.

C. R. H.

**Investigation of the Phosphorus Compounds in the Fruit of the Walnut (*Juglans regia*).** J. BIELECKI and J. SZTENCCEL (*Roczniki Chemji*, 1924, **4**, 63—71).—Crushed walnut kernels were extracted first with ether, then with alcohol, and the presence of lecithins in the extracts was confirmed. The residue was extracted with dilute hydrochloric acid and shown to contain a calcium-magnesium salt of inositolpentaphosphoric acid which yields

i-inositol on hydrolysis. The acid forms a *copper* salt,  $C_6H_{12}O_6(PO_4Cu)_6 \cdot 8H_2O$ , and a *lead* salt,  $C_6H_{12}O_6(PO_4Pb)_5 \cdot 3H_2O$ .  
G. A. R. K.

**Acetic Acid as a Hydrolysis Product of Pectin.** K. SMOLENSKI (*Roczniki Chemji*, 1924, 4, 72—74; cf. A., 1924, i, 16).—Both crude and purified pectin from sugar beet yield acetic acid on treatment with cold alkali or, more slowly, with dilute mineral acids. The quantity is roughly equivalent to half the alkali required to hydrolyse the two ester groups present in the pectin complex. It is suggested that the acid probably arises from the hydrolysis of an acetoacetic residue, and as a molecule of methyl alcohol is obtained at the same time, this may occur in the form of a methyl ester of the substituted acetoacetic acid; the possible connexion between these facts and the occurrence of acetoacetic acid in diabetic urine is discussed.  
G. A. R. K.

**Isolation and Identification of Quercetin in Apple Peels.** C. E. SANDS (*J. Agric. Res.*, 1924, 28, 1243—1246).—Quercetin was obtained by prolonged alcoholic extraction of apple peels which had previously been steam-distilled, dried, and extracted with light petroleum and ether.  
A. G. P.

**Chloride Content of the Leaf-tissue Fluids of Egyptian and Upland Cotton.** J. A. HARRIS, J. V. LAWRENCE, and Z. W. LAWRENCE (*J. Agric. Res.*, 1924, 28, 695—704; cf. A., 1924, i, 815).—Analyses of numerous samples of leaf-tissue fluids indicate that the Egyptian variety, Pima, has a higher chloride content (28—189%) than the Upland varieties Acala, Meade, and Lone Star. This is in agreement with figures showing osmotic pressure and electrical conductivity recorded in the former paper. A. G. P.

**Quantity of Chlorophyll in Marine Algæ.** V. LUBIMENKO (*Compt. rend.*, 1924, 179, 1073—1076).—The chlorophyll contents of various species of algæ from the Black Sea have been determined and compared with those of land plants from the same district by a spectrocoulometric method. Whilst the fresh leaves of *Ailanthus glandulosa* contained 0.46% and those of *Zostera marina* 0.293%, the values for the algæ investigated were 0.008 to 0.069%. The view that under low illumination chlorophyll may be partly replaced by phycoerythrin is opposed by the facts that the surface-dwelling *Laurentia coronopus* has the lowest amount of chlorophyll whilst *Phyllophora rubens* (a deep-water form) is much richer in the pigment. Marine algæ appear to be able to utilise luminous energy better than land plants.  
A. C.

**Toxicity and Nutritive Value of Ammonium Acetate for the Lower Fungi.** D. BACH (*Compt. rend.*, 1924, 179, 1085—1087; cf. A., 1924, i, 353).—Ammonium acetate is a good source of nitrogen for *Aspergillus repens*, De Bary, in a medium having  $p_H$  above 5.2; but below this value the medium becomes toxic. This is attributed, not to hydrogen ions, but to undissociated acetic acid. To obtain good results in media of ordinary concentration, it is necessary to keep within certain  $p_H$  limits, which,

for a particular organism, can only be stated with reference to a definite medium. The ammonium salts of formic, propionic, and butyric acids are also suitable sources of nitrogen. A. C.

**Influence of Alkaline-earth Salts on the Heat Coagulation of Plant Plasma.** VI. H. KAHN (*Biochem. Z.*, 1924, **151**, 102—111).—For calcium salts the order of anions in promoting heat coagulation is  $\text{CNS} > \text{NO}_3 > \text{Br} > \text{Cl} > \text{C}_2\text{H}_3\text{O}_2$ , for barium salts  $\text{CNS} > \text{Br} > \text{Cl}$ , for strontium salts  $\text{Br} > \text{NO}_3 > \text{Cl}$ , and for magnesium salts  $\text{Br} > \text{NO}_3 > \text{SO}_4 > \text{Cl} > \text{C}_2\text{H}_3\text{O}_2$ , the concentration being molar in each case. This action of the anions runs parallel to their respective powers of penetrating colloidal material. J. P.

**Effect of Methyl and Ethyl Alcohols on the Growth of Barley Plants.** A. N. PURI (*Ann. Bot.*, 1924, **38**, 745—752).—Ethyl alcohol is more toxic to barley plants than is methyl alcohol. The former favours the growth of ear shoots at the expense of leaves, whilst the latter has the reverse effect. The resistance of plants to ethyl alcohol increases with age. O. O.

**Chemical Study of the Development of the Wheat Grain.** H. E. WOODMAN and F. L. ENGLENDOW (*J. Agric. Sci.*, 1924, **14**, 563—586).—The data for fresh weight, dry matter, and water content are in general agreement with those of Brenchley and Hall (*J. Agric. Sci.*, 1908—1910, **3**, 195). The percentage of protein increased, whilst the non-protein nitrogen decreased throughout the ripening period. The function of asparagine in the nitrogen metabolism of plants is discussed. It is supposed that the nitrogen for protein synthesis enters the wheat kernel as asparagine resulting from the degradation of leaf proteins and that ammonia is split off to form the starting point for the synthesis of amino-acids. These may be formed by a reversal of the normal deamination process whereby, for example, lactic acid and ammonia may yield alanine, or by the addition of ammonia to unsaturated organic acids. The proteins appear in the grain during ripening in the following order: proteins soluble in sodium chloride solution (albumin, globulin, proteose), gliadin, and, finally, glutenin. A critical discussion of analytical methods is included. G. W. R.

**Influence of Soil Temperature and Moisture on the Chemical Composition of Wheat and Maize.** S. H. ECKERSON and J. G. DICKSON (*Phytopathology*, 1923, **13**, 50—51).—Wheat seedlings grown at a low soil temperature are high in available carbohydrates and low in available nitrogen; the cell walls are cellulosic even in the early stages and are soon impregnated with lignin. At a high soil temperature the reverse is the case as regards carbohydrates and nitrogen; the cell-walls are constituted of pectic materials, cellulose being absent until photosynthesis begins. For maize at high and low soil temperature the composition is the reverse of that for wheat. CHEMICAL ABSTRACTS.

**Replacement of Protein by Urea in Rations for Milch Animals.** A. MORGEN, C. WINDHEUSER, and E. OHLMER (*Landw. Versuchs-Stat.*, 1924, **103**, 1—40).—In continuation of earlier work



(cf. A., 1922, i, 293), experiments have been made on the yield and quality of the milk of sheep and goats as affected by the addition of urea or ammonium acetate to a basal ration either rich (ration A) or poor (ration B) in protein. Urea exerted only a slight favourable effect in a few cases even with the animals on ration B, whereas ammonium acetate increased the percentage of fat and of total solids in the milk in almost every case when fed with ration B and also acted favourably in about half the cases when fed with ration A. The failure of urea to act beneficially on the yield and quality of milk when added to a diet low in protein is not in agreement with the authors' previous experiments on the replacement of protein by urea nor with results obtained by other workers. It is thought that the somewhat long period (3 weeks) during which the animals were kept on ration B before introducing the urea may have affected the activity of the milk glands in such a way that they could not respond to a change in the diet, but this does not agree with the results obtained with ammonium acetate. C. T. G.

**Conservation and Transformation of Nitrogen in Stable Manure.** G. SANI and V. GRILLI (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 250—253; cf. Boullanger, A., 1912, ii, 381; Boullanger and Dugardin, A., 1912, ii, 971).—Treatment of stable manure with flowers of sulphur, either alone or, better, together with superphosphate, greatly diminishes the proportion of nitrogen lost and increases that present as ammonia and nitric acid. T. H. P.

**Nitrification of Phosphorus Nitride.** F. E. ALLISON (*J. Agric. Res.*, 1924, 28, 1117—1118).—The addition of phosphorus nitride to soil kept under conditions suitable for nitrification did not result in any significant production of nitrates. C. T. G.

**Decomposition of Urea in Soil.** F. LITTAUER (*Z. Pflanz. Düng.*, 1924, 3A, 165—179).—Two different soils, one loam and the other sandy, show markedly different effects on the rate of decomposition of urea. In addition to the soil type, temperature and soil moisture influence the velocity of decomposition. When mixed with the loam, urea (approx. 5%) was completely decomposed at 20° in 10 days and at 0° in 28 days. In the sandy soil at 20°, only 65% was decomposed in 10 days and at 0° only 20% in 28 days. The decomposition is so rapid in soils rich in bacteria that the ammonia produced may in some cases injure roots. O. O.

**Decomposition of Neutral Salts by Colloids.** W. HÜMMELCHEN and H. KAPPEN (*Z. Pflanz. Düng.*, 1924, 3A, 289—322).—Hydrated manganese dioxide and humic acid, prepared from sugar, decompose neutral salt solutions with the liberation of free acid. The action is similarly affected in both cases by time, concentration, volume of solution, amount of adsorbent, dilution, temperature, and the cation of the neutral salt. The decomposition differs from ionic exchange in permutites in being unaffected by subsequent dilution, in increasing with increasing temperature, and in the relative effects of different cations. Small quantities

of bases are completely and irreversibly adsorbed; with larger amounts the adsorption is incomplete and partly reversible, and is increased by the addition of neutral salts. The adsorption of acids is reversible and unaffected by neutral salts. The decomposition of neutral salts by manganese dioxide and humic acid respectively, differs only in the relative effects of different anions. No decomposition of neutral salts by silicic acid or ferric hydroxide can be detected by titration. The production of a small amount of alkali by cupric hydroxide is probably due to the displacement of adsorbed impurities. The decomposition of neutral salts is believed to depend on the adsorption of hydroxyl ions, and a subsequent chemical combination of the base. E. M. C.

**Heat of Wetting of Soil Colloids.** M. S. ANDERSON (*J. Agric. Res.*, 1924, 28, 927—935).—The heat of wetting of a number of soils and of colloidal material extracted from them has been determined, and it is shown that the amount of heat liberated from different soil colloids varies widely. Mineral powders ground to a degree of fineness comparable with that of the minerals in the soil showed no significant increase of temperature on wetting, indicating that the heat of wetting of a soil is almost entirely a function of the colloidal material present. Part of the colloidal material of soils is exceedingly difficult to isolate and this “unextractable” colloid usually has a lower heat of wetting than the more easily extracted portion. It is further shown that the process of extraction tends to alter the heat of wetting of the colloid. In spite of these difficulties, it is considered that a fair approximation to the colloid content may be obtained from the ratio of the heat of wetting of a soil to the heat of wetting of a sample of the colloidal material extracted therefrom. C. T. G.

**Electrical Charge on a Clay Colloid as influenced by Hydrogen-ion Concentration and by Different Salts.** W. C. DAYHUFF and D. R. HOAGLAND (*Soil Sci.*, 1924, 18, 401—408).—Cataphoresis experiments with a specially purified clay colloid showed that the charge on the colloid was influenced by the addition of various salts and by the hydrogen-ion concentration. Within the range  $p_H$  2.1—12.7 the colloid remained negatively charged. The nature and concentrations of cations present very largely governed the stability of the clay suspension. Modified explanations of the deflocculating action of alkaline substances are presented. A. G. P.

**Rôle of the Electro-negative Ions in the Reactions between Soils and Electrolytes.** N. M. COMBER (*Faraday Soc.*, Dec. 9, 1924. Advance Proof).—The author discusses the alleged adsorption of anions from solutions by soils. It is concluded that anions are only removed from solution when there are present in the soil available cations with which they can form insoluble compounds. The absorption is thus an ordinary chemical precipitation. The bearing of membrane equilibria on the reactions of soils with solutions is discussed. On account of the membrane effect of gels of

the soil and of root hairs, it is probable that differences in the concentrations of the different ions occur between the cell sap of the root hairs and the soil solution. The hydrogen-ion concentration will be greater within the root hair than in the soil solution whilst the reverse will hold in the case of the anions. The relative non-diffusibility of the aluminium ion may be a contributory cause of its toxicity.

G. W. R.

**Relation between the  $p_H$  Value, the Lime Requirement, and the Thiocyanate Colour of Soils.** S. J. SAINT (Faraday Soc., Dec. 9, 1924. Advance Proof).—The correlation between the  $p_H$  value, thiocyanate colour by the Comber test (*J. Agric. Sci.*, 1920, 10, 420) and the Hutchinson-McLennan lime requirement (A., 1914, ii, 784) is only approximate. Comparing heavy soils among themselves a fairly good correlation is shown between these three characters. A similar correlation is shown when light soils are compared among themselves. The effect of organic matter is to increase the Hutchinson-McLennan value and to decrease the thiocyanate colour. Differences in the thiocyanate coloration of soils may be caused by differences in the amounts of soluble iron and aluminium present.

G. W. R.

**Significance of the Hydrogen-ion Concentration for Micro-organisms and their Activity in the Soil.** A. RIPPÉL (*Z. Pflanz. Düng.*, 1924, 3A, 221—227).—A review of the literature leads to the conclusion that many microbiological changes can take place over a wide range of  $p_H$  on account of either the adaptability of the organisms or the existence of different species, which produce the same changes at different reactions.

E. M. C.

**Filtration and Other Errors in the Determination of the Hydrogen-ion Concentration of Soils.** W. R. G. ATKINS (*Sci. Proc. Roy. Dublin Soc.*, 1924, 17, 341—347).—The clear soil extract is best prepared by centrifuging, for the biological production of carbon dioxide may result if the subsidence method is used, and filtration may introduce serious errors. Ordinary filter-paper, and even acid-treated paper, may adsorb important amounts of acid. Washing an acid-treated paper does not diminish this power, and the fibres of such a paper act as if of a  $p_H$  of 4.8, and those of an untreated paper as of a  $p_H$  of 7.0—7.6. A large first filtrate (160 c.c.) should be discarded and a paper suitable to the soil used to minimise error from this source. Indicators of the Clark-Lubs series are satisfactory and should be used in their half-transformed condition. Bromocresol-green should, however, be substituted for methyl-red. Alcohol as a solvent should be avoided owing to its liability to undergo oxidation, producing traces of acetic acid.

D. G. H.

**Determination of the Hydrogen-ion Concentration of the Soil.** R. M. BARNETTE, D. J. HISSINK, and J. VAN DER SPEK (*Rec. trav. chim.*, 1924, 43, 434—446).—Experimental factors affect the determination of the hydrogen-ion concentration of soil suspensions; agitation of the solution and relatively rapid rate of

passing hydrogen through the suspension are recommended. Determinations carried out with filtrates show wide variations and cannot be duplicated with such accuracy as in the case of suspensions; moreover, filtrates are always less acid than the corresponding suspensions. Equilibrium with regard to hydrogen-ion concentration varies with the soil-water ratio; the thicker suspensions yield more constant values and are considered to approach more nearly the natural conditions of the soil. The theory of an electrical double layer around the adsorbing particles of clay and humus, which retains the adsorbed anions in its inner layer whilst the cations are fixed in the outer, previously put forward by the authors is now amplified. A soil suspension may contain particles the size of which varies over a wide range; some of these give rise to hydrogen ions which may exist in true solution or adsorbed on the surface of other particles. Such a system would give rise to a series of potential differences. The general conclusion is reached that the soil acids act as weak acids and that only a small part of the adsorbed hydrogen ions is concerned in the double layer phenomena.

H. J. E.

**Nature and Significance of Soil Acidity.** H. KAPPEN (*Z. Pflanz. Düng.*, 1924, **3A**, 209—218).—The progressive removal of bases and decomposition of zeolitic soil silicates gives rise to (1) "hydrolytic acidity," with adverse effects on plants and micro-organisms caused primarily by calcium shortage, (2) "exchange acidity," believed to be due to the direct exchange of aluminium ions, (3) "neutral salt decomposition" (cf. this vol., i, 218) in the case only of humus soils, and, finally, (4) the presence in uncultivated soils of water-soluble acids and acid salts.

E. M. C.

**Nature and Significance of Soil Acidity.** A. DENSCH (*Z. Pflanz. Düng.*, 1924, **3A**, 218—221).—The importance of soil acidity is frequently over-estimated, and the bad effect of a calcium carbonate deficiency is shown primarily in the physical state of the soil.

E. M. C.

**Determination and Nature of the Acidity of Moor Soils.** T. ARND (*Z. Pflanz. Düng.*, 1924, **3A**, 227—235).—Moor soils, treated with increasing amounts of calcium carbonate, showed increasing ammonification and denitrification up to the point of complete neutralisation, when nitrification began to appear. Their acidity, determined by the Tacke-Süchting method, is believed to be due to the dissociation of true acids, of which a portion is adsorbed by the humus colloids, and not to the phenomena of "exchange" or "hydrolytic" acidity.

E. M. C.

**Relation between the "Absolute Air Capacity" and Degree of Acidity of Forest Soils.** K. KVAPIL and A. NĚMEC (*Compt. rend.*, 1924, **179**, 1283—1284).—The "absolute air capacity" of a soil is defined as the percentage volume of pores in a soil which remain filled with air when the soil is saturated with water. In

plantations of conifers this capacity is lower than in those of deciduous trees and diminishes as the acidity of the soil increases.

T. H. P.

**Electrical Determination of Soil Alkali.** A. F. JOSEPH, F. J. MARTIN, and J. S. HANCOCK (*Cairo J. Sci.*, 1924, 12, 141—143).—Beam and Freak's conductometric method (A., 1914, ii, 828) for distinguishing between calcium sulphate and harmful alkalis in the soil is untrustworthy.

CHEMICAL ABSTRACTS.

**Base Exchange in Relation to the Problem of Soil Acidity.** G. W. ROBINSON and R. WILLIAMS (Faraday Soc., Dec. 9, 1924. Advance Proof).—The authors discuss the problem of soil acidity from the point of view of recent work on base exchange. From studies on base exchange in soils of North Wales, it is concluded that an appreciable degree of unsaturation is not necessarily inconsistent with fertility. The positive factor concerned in the need for liming may be the availability of the soil calcium, of which the Hissink method for the determination of exchangeable bases may give some indication. The use of dilute carbonic acid in the determination of the availability of calcium in soils is suggested. The topographical distribution of soil acidity is discussed. Open-textured soils in upland situations are most likely to become unsaturated and acid, whilst the soils of valley bottoms are less likely to develop unsaturation.

G. W. R.

**Base Exchange in Rothamsted Soils.** H. J. PAGE and W. WILLIAMS (Faraday Soc., Dec. 9, 1924. Advance Proof).—The results of studies on the content of exchangeable bases in the soils of the Broadbalk experimental field at Rothamsted lend support to the views of Hissink (A., 1923, i, 992) on base exchange. The amount and distribution of exchangeable bases in the soils are in close relationship with their known manurial treatment. On the assumption that soils which have long contained an excess of calcium carbonate have reached a state of equilibrium, the total amount of exchangeable bases present can be correlated with the amount of clay and very fine silt present. Measurements of  $p_H$  show that the reaction of the soil can be correlated with its state of saturation with basic cations. The complex aluminosilicic and humic acids of soils are not necessarily completely neutralised even when excess of calcium carbonate is present. Complete neutralisation could only be expected with a marked alkaline reaction of the equilibrium solution. The presence of adsorbed hydrogen ions in soils introduces an error in the determination of exchangeable bases in the presence of calcium carbonate. It is suggested that the amount of carbon dioxide given off when a soil is treated with sodium chloride solution in the presence of excess of calcium carbonate might be used as a measure of the degree of unsaturation.

G. W. R.

**Base Exchange in Soils.** D. J. HISSINK (Faraday Soc., Dec. 9, 1924. Advance Proof; cf. A., 1923, i, 992).—Theories of base

exchange and the results obtained with Dutch soils by the author's method for the determination of exchangeable bases are considered. The determination of the degree of unsaturation of soils is discussed. Electrometric titration is useless on account of the fact that the acids present in soils are very weak. Conductometric titration is, however, admissible. It has been found that in titrations with barium hydroxide solution the conductivity is proportional to the amount of barium hydroxide in solution. A modification of the conductometric method is therefore suggested, in which the same weight of soil is allowed to attain equilibrium with varying amounts of 0.1N-barium hydroxide solution. The excess of barium hydroxide is determined by titration, using phenolphthalein as indicator. By plotting the original amount of barium hydroxide used against the amount remaining in solution, curves are obtained, from which it is possible by extrapolation to obtain the amount of barium hydroxide required for neutralisation of the free soil acids. In Dutch soils, even in the presence of excess of calcium carbonate, the percentage saturation does not exceed 55.

G. W. R.

**Chemico-physical Influences of Quicklime and Calcium Carbonate on Mineral Soils.** E. RAMANN (*Soil Sci.*, 1924, **18**, 387—400).—A summary is given of results of experimental work to be recorded in detail elsewhere. The adsorption of commonly occurring substances by finely-divided quartz (0.002 mm. diameter) and the flocculation of suspensions is discussed. The process of base exchange was examined with the aid of artificial permutites and the effect of acid-reacting substances on this change is considered. In the light of these summarised results, the effects of quicklime and calcium carbonate on soils and the practice of marling receive considerable explanation.

A. G. P.

**Conversion of Quicklime into Calcium Carbonate in Soils.** E. BLANCK and W. LOHMANN (*Z. Pflanz. Düng.*, 1924, **3A**, 91—110).—In loams and sandy soils lime was converted quantitatively into calcium carbonate. The process occupied a considerable time and the rate of conversion depended primarily on the moisture content of the soil. The proportion of lime added did not affect the velocity of the action, which was, however, accelerated by frequent mixing of the soil.

A. G. P.

**Determination of the Different Forms of Manganese Present in Arable Soil.** G. BERTRAND (*Bull. Soc. chim.*, 1924, [iv], **35**, 1522—1527).—The importance of manganese in plant physiology has induced the investigations of methods of determining the different forms in which manganese is present in the soil, with a view to the accurate comparison of soils in respect of their manganese content. Manganese is present in soils: (1) as carbonate or phosphate, determined by extracting a dried sample of the soil with 1% acetic acid. The filtered solution is evaporated and the residue calcined. The residue is then dissolved in hydrochloric acid, converted into sulphate, dissolved in dilute nitric acid, and

the manganese determined colorimetrically (A., 1911, ii, 542); (2) in more or less complex organic form with vegetable debris or humic substances, determined by extracting the soil residue from (1) with dilute ammonia until the extract has only a straw colour. The filtrates are evaporated to dryness, calcined, and the residue treated as in (1); (3) as oxide, usually the larger proportion, which is less readily assimilated by plants, and is determined by calcining the residue from extractions (1) and (2), evaporating the calcined residue with hydrochloric acid, extracting repeatedly with water, and evaporating with sulphuric acid until fumes are produced; the manganese is determined colorimetrically as before; (4) as insoluble silicates. The manganese in this form is found indirectly from the total manganese, which is determined colorimetrically after converting it into sulphate. The distribution of manganese varies with the depth of the soil. R. B.

**Determination of Ammoniacal Nitrogen in Soils.** W. McLEAN and G. W. ROBINSON (*J. Agric. Sci.*, 1924, 14, 548—554).—The method is an adaptation of the method of Hissink (A., 1923, i, 992) for the determination of adsorbed bases in the soil. Good agreement is shown with the Matthews aëration method. The amount of ammoniacal nitrogen in any soil appears to be definite and not governed by the method of determination used. [Cf. B., 1925, 20.] G. W. R.

**Determination of Ammonia in Soils.** H. J. HARPER (*Soil Sci.*, 1924, 18, 409—417).—The sieved sample is extracted with ten times its weight of 10% potassium chloride solution (20% for neutral or alkaline soils). The ammonia in the extract is determined by distillation with magnesium oxide and subsequent nesslerisation or titration according to the quantity present. A. G. P.

**Determination of Sulphur in Soil.** M. I. WOLKOFF (*Soil Sci.*, 1924, 18, 371—377).—A mixture of soil, magnesium powder, and sodium peroxide is ignited in a Parr ignition bomb. The residue is extracted with water and evaporated with hydrochloric acid to remove silica. After solution in acid, the sulphate is precipitated, without the previous removal of iron and alumina, as barium sulphate, which is filtered after 24 hours on a Gooch crucible. A. G. P.

**Mechanical Composition Curves of Soils, Clays, and other Granular Substances.** G. W. ROBINSON (*J. Agric. Sci.*, 1924, 14, 626—633; cf. A., 1922, ii, 888).—A study of the mechanical composition curves of typical soils, clays, and other granular substances. The curves are smooth and, normally, of a sigmoid type. [Cf. B., 1925, 19.] G. W. R.

## Organic Chemistry.

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**Action of Iodine in Chloroform Solution on some Ethylenic Hydrocarbons.** J. BÖESEKEN and J. S. P. BLUMBERGER (*Rec. trav. chim.*, 1925, **44**, 96—98).—Iodine in chloroform solution slowly adds on to the ethylenic linking of an unsaturated hydrocarbon. The reaction is of the second order; the initial velocity is greater with an iodine solution which has been prepared for some days. Iodine acts on chloroform, and it is suggested that iodine chloride is formed and behaves catalytically. From a comparison of the rates of iodination of styrene,  $\alpha$ -phenyl- $\Delta^\alpha$ -,  $\Delta^\beta$ -, and  $\Delta\gamma$ -butenes, allylbenzene, and stilbene (which is not attacked), it is concluded that the immediate neighbourhood of the benzene nucleus causes a retardation, which is somewhat counteracted by substitution of an  $\omega$ -hydrogen atom by an aliphatic group. F. M. H.

**Polymerisation. X. Action of certain Silicates on Unsaturated Compounds.** S. W. LEBEDEV and E. P. FILONENKO (*Ber.*, 1925, **58**, [B], 163—168).—Unsymmetrical di- and tri-substituted derivatives of ethylene undergo polymerisation when preserved for longer or shorter periods in contact with Florida earth (cf. Gurvitsch, A., 1915, i, 933), whereas mono-, symmetrical di-, and tetra-substituted derivatives do not behave in this manner. Depolymerisation of the polymerised products can be effected frequently by the use of Florida earth at a higher temperature; the process usually proceeds smoothly, but is sometimes complicated by the formation of substances isomeric with the original material or containing a greater or smaller proportion of carbon.

The Florida earth ( $\text{SiO}_2$ , 55.28%;  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ , 21.05%;  $\text{CaO} + \text{MgO}$ , 4.29%;  $\text{K}_2\text{O} + \text{Na}_2\text{O}$ , 1.89%;  $\text{H}_2\text{O}$ , 17.88%) is activated by being heated at 275—325° until the loss of water is 12—12.3%; more strongly heated products are less active or inactive. Its activity is controlled by its ability to become moistened when treated with gaseous *isobutylene*. Polymerisation is observed when the following substances remain in contact with 25—100% of their weight of Florida earth:  $\beta$ -methyl- $\Delta^\alpha$ -propene;  $\beta$ -methyl- $\Delta^\alpha$ -butene; *as*-diphenylethylene;  $\beta\delta$ -dimethyl- $\Delta^\alpha$ -pentene;  $\beta$ -methyl- $\Delta^{\alpha\gamma}$ -butadiene;  $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene;  $\beta\epsilon$ -dimethyl- $\Delta^{\alpha\epsilon}$ -hexadiene;  $\beta$ -methyl- $\Delta^\beta$ -butene;  $\beta\delta$ -dimethyl- $\Delta^\beta$ -pentene;  $\beta\epsilon$ -dimethyl- $\Delta_{\beta\delta}$ -hexadiene. Polymerisation is not observed with ethylene, bromoethylene,\* propylene,  $\gamma$ -methyl- $\Delta^\alpha$ -butene,  $\Delta^{\alpha\epsilon}$ -hexadiene,\*  $\Delta^{\alpha\gamma}$ -butadiene,\*  $\Delta^\beta$ -butene, stilbene,\* ethyl cinnamate,\*  $\beta\gamma$ -dimethyl- $\Delta^\beta$ -butene,  $\beta$ -methyl- $\Delta^{\beta\gamma}$ -butadiene,\*  $\gamma$ -methyl- $\Delta^\alpha$ -butinene,\*  $\gamma\gamma$ -dimethyl- $\Delta^\alpha$ -butinene,\* and pyrrole\*; a tendency towards polymerisation is noticed with the substances marked with an asterisk.

H. W.

**True Acetylenic Compounds from Mixed Magnesium Derivatives of Acetylene.** M. LESPIEAU (*Compt. rend.*, 1924, **179**, 1606—1607).—Contrary to the views of Zalkind and Iocitsch,



the author considers the formation of true acetylenic compounds to be frequently due to reaction with the dimagnesium derivatives of acetylene. Three instances in favour of this are given. (I) The product formed when acetylene is passed into an ethereal solution of magnesium ethyl bromide (until the lower layer no longer increases) reacts with 1 mol. of chloroacetaldehyde to 1 mol. of dissolved magnesium to form a substance consisting mainly of the glycol,  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{C}\equiv\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$  (cf. A., 1922, i, 103). If half the quantity of chloroacetaldehyde is used, the same glycol is obtained together with the alcohol,  $\text{CH}_3\text{C}\equiv\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Cl}$ , b. p.  $60^\circ/12\text{ mm.}$ ,  $d_{21}^{25} 1.171$ ,  $n_D^{25} 1.475$ . Under similar conditions, dichloropropaldehyde yields the alcohol,  $\text{CH}_3\text{C}\equiv\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CHCl}\cdot\text{CH}_2\text{Cl}$ , b. p.  $91^\circ/12\text{ mm.}$ ,  $d_{23}^{25} 1.306$ ,  $n_D^{25} 1.500$ . (II) Chloromethyl ether, acting on a solution in which dipropargyl has been kept in contact with more than 2 mols. of magnesium ethyl bromide, yields the dimethyl ether of a glycol having 8 carbon atoms, together with the ether  $\text{CH}_3\text{C}\equiv\text{C}\cdot[\text{CH}_2]_2\cdot\text{C}\equiv\text{C}\cdot\text{CH}_2\cdot\text{OMe}$ . (III) In the action of magnesium pentamethylene bromide on  $\alpha\beta$ -dibromopropylene (A., 1924, i, 702), one of the chief products,  $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CHBr}\cdot\text{CH}_2$ , cannot be attributed to the monomagnesium derivative, as the latter ought to yield  $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_5\cdot\text{CBr}\cdot\text{CH}_2$ . A. C.

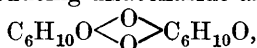
**Polymerisation Phenomena under the Simultaneous Action of Aluminium Oxide and Metallic Iron at High Temperatures and Pressures.** W. IPATIEV and N. KIJUKWIN (*Ber.*, 1925, 58, [B], 4—12).—Ethyl alcohol, when heated in an iron tube in the presence of aluminium oxide at  $530$ — $540^\circ$  under a maximal pressure of  $240$ — $260\text{ atm.}$ , is transformed into a mixture of hydrocarbons and oxygenated compounds. The former substances, which consist mainly of polymethylenes but contain also hexane and hexene, are produced by polymerisation of primarily formed ethylene under the influence of aluminium oxide. The oxygenated compounds include acetaldehyde, acetone, isopropyl alcohol, methyl ethyl ketone, methylethylcarbinol, and, probably, acetal. Their formation is attributable to catalytic decomposition of ethyl alcohol at the iron surface, with production of acetaldehyde and subsequent polymerisation of the latter under the influence of aluminium oxide. The primary products of the latter change appear most probably to be acetoin (which is readily reduced to methyl ethyl ketone and methylethylcarbinol) and ethyl acetate, which is transformed into acetic acid and thence into acetone, carbon dioxide, and water. The presence of carbon monoxide to only a small extent in the gaseous products of the change renders it unlikely that aldol, which is convertible at high temperatures into carbon monoxide and isopropyl alcohol, plays an important part in the change. H. W.

**Walden Inversion. XI. Substitution by Halogen of the Hydroxyl Group of Secondary Octyl Alcohols.** A. MCKENZIE and T. M. A. TUDHOPE (*J. Biol. Chem.*, 1924, 62, 551—556; cf. Levene and Mikeska, A., 1924, i, 940).—The action of thionyl chloride on *l*-sec.-octyl alcohol gives *d*- $\beta$ -chloro-octane,  $[\alpha]_D^{20} +33.7^\circ$ ;

with thionyl bromide and *d*-sec.-octyl alcohol, a partly racemised product having  $[\alpha]_D -26.1^\circ$  was obtained. The racemisation accompanying the change is therefore in the first case less and in the second more than that which attends the substitution of hydroxyl by halogen by means of the halogen acids (cf. Pickard and Kenyon, T., 1911, 99, 45). The action of silver acetate on *d*- $\beta$ -chlorooctane gave a partly racemised lævorotatory octyl acetate.

C. R. H.

**Unsaturated Reduction Products of the Sugars and their Transformations. IX. Anhydride of a Disaccharide from  $\delta$ -Hydroxy- $\delta$ -acetylbutyl Alcohol.** M. BERGMANN, A. MIEKELEY, and F. STATHER (*Ber.*, 1925, 58, [B], 82—85; cf. A., 1923, i, 1053; 1924, i, 5).—The conversion of  $\delta$ -hydroxy- $\delta$ -acetylbutyl alcohol into the non-reducing disaccharide anhydride,



when its aqueous solution is evaporated to dryness is due to the presence of an unstable acid which is somewhat volatile with steam. Its effect is nullified by neutralisation or by esterification with diazomethane. It appears to be destroyed by contact with animal charcoal, porous clay, or alkali hydroxide. The conversion of the alcohol into the disaccharide anhydride is a balanced action which is catalysed also by hydrochloric acid. The reverse change can be effected by 0.01*N*-hydrochloric acid.

H. W.

**Production of Glycerol by Fermentation.** Y. TOMODA (*J. Fac. Eng. Tokyo*, 1924, 15, 193—205).—Certain of the conditions necessary for the production of glycerol by the fermentation of sugar mashes are studied. Yeasts previously cultured give the best results, saké and wine yeasts being the most satisfactory, whilst soya bean yeast is decidedly inferior. The kind of sugar mash used is, in general, immaterial, but yeast nutrient (*e.g.*, ammonium sulphate) is added to mashes deficient in it. The sugar mash obtained from potatoes does not give satisfactory results. The effect of the addition to the fermentation medium of various solid salts has been investigated. Sodium hydrogen carbonate has but little effect even when added in quantity sufficient to form a saturated solution. Alkalis (*e.g.*, sodium carbonate), however, interfere, but, if added in small portions, 7% of sodium carbonate may be used without stopping the fermentation, contrary to the statement of Eoff, Linder, and Beyer (*J. Ind. Eng. Chem.*, 1919, 11, 843). This is probably due to the conversion of the carbonate into innocuous hydrogen carbonate by the carbon dioxide evolved during the fermentation. The hydrogen-ion concentration of the medium appears to be a deciding factor. The addition of sodium sulphite stimulates the production of glycerol (cf. Schweizer, A., 1919, i, 239; 1920, i, 757; Connstein and Lüdecke, A., 1919, i, 463; Neuberg and Reinfurth, A., 1920, i, 207), but retards the rate of the reaction. The addition of sodium hydrogen sulphite to the sulphite mash during the fermentation in quantities sufficient to keep the amount of free sulphite constant has a beneficial effect on the production

of glycerol, the yield of which reaches 39% of the sugar fermented, under these conditions.

L. F. H.

**Syntheses with  $\beta\beta$ -Dichlorodiethyl Ether.** L. H. CRETCHER and W. H. PITTENGER (*J. Amer. Chem. Soc.*, 1925, **47**, 163—166).—The following compounds have been prepared from di- $\beta$ -chloroethyl ether by treatment with the requisite alkoxide, primary base, or sodium salt of an organic acid in the presence of diethylamine:  $\beta$ -chloroethyl  $\beta$ -methoxyethyl ether, b. p.  $169^{\circ}/744$  mm.,  $d_{15}^{15}$  1.0562; di- $\beta$ -methoxyethyl ether, b. p.  $161.5^{\circ}/736$  mm.,  $d_{15}^{15}$  0.9514; di- $\beta$ -ethoxyethyl ether, b. p.  $187^{\circ}/735$  mm.,  $d_{15}^{15}$  0.9149; di- $\beta$ -propoxyethyl ether, b. p.  $219^{\circ}/737$  mm.,  $d_{15}^{15}$  0.8877; di- $\beta$ -butoxyethyl ether, b. p.  $250$ — $252^{\circ}/741$  mm.,  $d_{15}^{15}$  0.8847; 4- $p$ -tolylmorpholine, m. p.  $167^{\circ}$ ; 4- $\beta$ -naphthylmorpholine, m. p.  $239^{\circ}$ ;  $\beta$ -chloroethyl  $\beta$ -benzoxyethyl ether, b. p.  $191^{\circ}/25$  mm.,  $d_{15}^{15}$  1.1841; di- $\beta$ -benzoxyethyl ether, b. p.  $279$ — $281^{\circ}/24$  mm.,  $d_{15}^{15}$  1.1701.

G. S. W.

**Preparation of  $\beta$ -Chloropropionic Acid.** S. G. POWELL (*J. Amer. Chem. Soc.*, 1924, **46**, 2879).— $\beta$ -Chloropropionic acid, b. p.  $127^{\circ}/35$  mm., is obtained in 56% of the theoretical yield by the gradual addition of trimethylene chlorohydrin to concentrated nitric acid. After warming on the water-bath, the solution is diluted with water and extracted with ether.

R. B.

**Optimum Conditions for the Preparation of  $n$ -Valeric Acid from Magnesium Butyl Bromide and Carbon Dioxide.** H. GILMAN and H. H. PARKER (*J. Amer. Chem. Soc.*, 1924, **46**, 2816—2823).— $n$ -Valeric acid is obtained in 78% yield at  $0^{\circ}$  from carbon dioxide and 0.2 mol. of magnesium  $n$ -butyl bromide in 150—300 c.c. of ether. No increased yield is obtained at lower or at higher temperatures (cf. Bodroux, A., 1904, i, 276) and with increased concentration the yield decreases. The yield of  $n$ -valeric acid is practically independent of pressures up to 3 cm. of mercury, but decreased when the velocity of admission of the carbon dioxide increased above 500 c.c./min. The quantity of carbon dioxide above 45 litres (per 0.2 mol. of Grignard reagent) did not influence the yield, but with 30 litres or less a decrease in yield was observed. Similarly, an increased rate of admission shortened the time of reaction, or tended to increase the yield. Refluxing after addition of the carbon dioxide did not affect the yield, and the method of addition of carbon dioxide was also practically without influence. Spraying the magnesium butyl bromide into an atmosphere of carbon dioxide gave a slight improvement in yield, but much improved yields were obtained by this procedure in the preparation of pyrrole-2-carboxylic acid from magnesium pyrrol bromide and carbon dioxide (cf. Oddo, A., 1909, i, 672), probably owing to the decreased extent of side reactions between the  $R\cdot CO_2MgX$  compound and excess of Grignard reagent (cf. Grignard, A., 1904, i, 213). Even under the optimum conditions, the preparation of  $n$ -valeric acid is accompanied by the formation of small amounts of  $n$ -octane,  $n$ -butyl alcohol,  $n$ -butyl  $n$ -valerate, and tri- $n$ -butylcarbinol. Benzoic acid was similarly obtained from magnesium phenyl bromide in 72% yield; from the

corresponding iodide, the yield was only 32–35%. *cyclo*Hexane-carboxylic acid was obtained in 68% yield, but magnesium *cyclo*hexyl bromide and sulphur dioxide gave *cyclo*hexanesulphonic acid in only 28% yield, owing to oxidation to the sulphonic acid. R. B.

**Isolation of Lignoceric Acid from Arachis Oil.** A. HEIDUSCHKA and C. PYRIKI (*Pharm. Zentr.*, 1925, **66**, 1–3).—Arachis oil is saponified, the soap decomposed with boiling dilute hydrochloric acid, and the fatty acids obtained are washed with water. The acids are freed from palmitic and stearic acids by recrystallising twice from 96% alcohol, the resulting mixture of lignoceric and arachic acids having m. p. 71–72° and mol. wt. 342. Further repeated recrystallising from alcohol, or from acetone with a final crystallisation from alcohol (the quicker method), raised the mol. wt. to 367–369, but failed to raise the m. p. above 77·5° (corr.). Elementary analysis and mol. wt. agree with Kreilling's formula,  $C_{24}H_{48}O_2$ , but the m. p. found by Kreilling (81°) appears to be too high. Methods of separating lignoceric from arachidic acid through its salts were unsatisfactory owing to the small differences in their solubility. W. T. K. B.

**Heterogeneous Catalysis. II. Hydrogenation of Marine Oils.** A. S. RICHARDSON, C. A. KNUTH, and C. H. MILLIGAN (*Ind. Eng. Chem.*, 1925, **17**, 80–83).—When whale oil or menhaden oil is hydrogenated in the presence of a nickel catalyst the first stage is a conversion of the more highly unsaturated acids into less unsaturated acids without the formation of substantial quantities of completely saturated acids. At an iodine value of 84 nearly all the acids with more than two double bonds have disappeared and an abrupt change occurs. Below this point further hydrogenation results in the conversion of  $C_{20}$  and  $C_{22}$  acids containing two double bonds into corresponding acids with one double bond and in the formation of saturated acids. M. B. D.

**Steric Series. V. Transformation of *d*-Lactic Acid into *l*-Alanine.** K. FREUDENBERG and O. HUBER (*Ber.*, 1925, **58**, [B], 148–150).—Ethyl *d*-*p*-toluenesulphonoxypropionate, b. p. 158–160°/2 mm.,  $\alpha_{D}^{15} + 53\cdot5^\circ$ ,  $\alpha_{D}^{15} + 60\cdot7^\circ$  ( $l=1$ ) (cf. Freudenberg and Rhino, A., 1924, i, 1173), is converted by alcoholic ammonia into *p*-toluenesulphonoxypropionamide, ammonium *p*-toluenesulphonate, and partly racemised  $\alpha$ -aminopropionamide *p*-toluenesulphonate,  $[\alpha]_{D}^{17} + 3\cdot22^\circ$  (homogeneous *l*- $\alpha$ -aminopropionamide *p*-toluenesulphonate, prepared from natural *l*(+)-alanine, has m. p. 162°,  $[\alpha]_{D}^{17} + 5\cdot11^\circ$  in water). The transformation is therefore accompanied by a Walden inversion.

The suggestion that glyceraldehyde is an intermediate product of the conversion of dextrose into *l*(+)-lactic acid (Freudenberg and Brauns, A., 1922, i, 623) appears untenable, since it involves the assumption that the  $\beta$  and  $\epsilon$  carbon atoms of the carbohydrate pass through an inactive oxo stage from which an asymmetric group with reversed configuration is subsequently derived.

H. W.

**Unusual Type of Fatty Compound in a Product of Animal Origin [Caseinogen].** S. KON and C. FUNK (*Biochem. J.*, 1924, **18**, 1238—1239).—The compound is obtained by extracting caseinogen with boiling alcohol, from which it separates on cooling (yield about 1.5%). It melts at 55—55.5° after repeated crystallisation from ether and ethyl acetate and solidifies at 44.5°. The product is entirely neutral. On saponification, it yields only a fatty acid, m. p. 57.5—58°, solidifying at 55.5°, in slightly higher yield than the original substance. The substance is possibly the anhydride of a hydroxystearic acid. S. S. Z.

**Dissociation Constants of Dibasic Carboxylic Acids and the Normal Potential of the Quinhydrone Electrode in Absolute Methyl Alcohol.** L. EBERT (*Ber.*, 1925, **58**, [B], 175—184).—The value, 724.4 millivolts, has been determined for the oxidation-reduction potential of the quinhydrone electrode in absolute methyl alcohol at 18°. The value, 602 millivolts, is determined for the normal potential of the quinhydrone electrode towards the 3*M*-calomel electrode. The dissociation constants of suberic, succinic, tartaric, and fumaric acids have been measured. The greater differences between the first and second dissociation constants observed in methyl-alcoholic as compared with aqueous solution receive a satisfactory explanation on the basis of Bjerrum's theory (*A.*, 1923, i, 1059). Within the limits of mathematical accuracy, the distances of the carboxyl groups from one another are in agreement with the probable lengths of the molecules as deduced from Röntgen-ray measurements of diamond and Langmuir's capillary-chemical measurements. H. W.

**$\alpha$ -Ketopimelic Acid and  $\alpha$ -Ketosuberic Acid and their Behaviour towards Concentrated Sulphuric Acid.** F. ADICKES (*Ber.*, 1925, **58**, [B], 211—216).—Ethyl oxaloadipate, which is slowly transformed by semicarbazide hydrochloride into a substance,  $C_{13}H_{19}O_6N_3$ , m. p. 158—159° (decomp.) after softening at 154°, is converted by boiling hydrochloric acid partly into oxalic and adipic acids and partly into  $\alpha$ -ketopimelic acid, m. p. 93—94° after softening at 90° [*semicarbazone*, m. p. 196—197° or 194°, according to rapid or slow heating; oxime, m. p. 142° (decomp.); *phenylhydrazone*, m. p. 143—144° (decomp.); 2:4-dinitrophenylhydrazone, m. p. 190—191° (decomp.)]. Elimination of carbon dioxide under the influence of concentrated sulphuric acid occurs only to the extent of about 5% of that theoretically possible. When decomposed by heat, the acid gives approximately molecular quantities of carbon dioxide and water and very little carbon monoxide, but the formation of the expected cyclohexane-1:2-dione could not be established. In a similar manner, ethyl  $\alpha$ -oxalopimelate is hydrolysed by hydrochloric acid to oxalic, pimelic, and  $\alpha$ -ketosuberic acids. The latter substance, m. p. 123—124° after softening at 118°, gives a *semicarbazone*, m. p. 167—168° or 164—165°, according to the rate of heating, and a 2:4-dinitrophenylhydrazone, m. p. 173—174° (decomp.). When acted on by concentrated sulphuric acid, it gives 25% of the theoretically

possible quantity of carbon dioxide, whereas when heated it yields 1 mol. of water,  $\frac{1}{2}$  mol. of carbon dioxide, and very little carbon monoxide.

H. W.

**Keto-Enolic Desmotropy. IV. Ferric Chloride Reaction and Bromine Addition of Enols.** H. P. KAUFMANN and E. RICHTER (*Ber.*, 1925, 58, [B], 216—222).—The ability to add bromine is not characteristic of all enols, and may be suppressed by the presence of negative groups or steric influences. Similarly, all enols do not give characteristic colorations with ferric chloride. Thus the dienolic form of ethyl dibenzoylsuccinate ( $\alpha$ -ester), m. p. 85° (cf. Averbeck, *Diss.*, Jena, 1910), gives an intense coloration with ferric chloride but does not react with bromine. The semi-enolic forms of ethyl dibenzoylsuccinate could not be separated from one another; titration of the mixture with bromine indicates the presence of 22% of the  $\alpha\beta$ -ester. As judged by analogy with the diacetylsuccinates, the latter ester should be an intermediate phase in the transformation of all the isomeric dibenzoylsuccinates, but its rate of transformation appears to be so great that its presence in the equilibrium mixtures from the  $\beta$ -,  $\gamma$ -, and  $\alpha$ -esters cannot be experimentally established. Since the  $\alpha$ - and  $\gamma$ -forms of ethyl formylphenylacetate add bromine but only the  $\alpha$ -variety gives a coloration with ferric chloride, it is possible to examine their equilibrium in carbon disulphide and chloroform; in each solution very little  $\gamma$ -ester is present in the equilibrium mixture.

H. W.

**Formation of Citric Acid from Ketipinic Acid [Diketo-adipic Acid].** H. FRANZEN and F. SCHMITT (*Ber.*, 1925, 58, [B], 222—226).—Ethyl ketipinate is converted by an excess of aqueous potassium hydroxide solution into oxalic and citric acids, which are identified as their hydrazides or the benzylidene derivatives of the latter. It is suggested that citric acid may be formed in plants from sugar through saccharic acid and ketipinic acid which undergoes a type of benzilic acid transformation. Ketipinic acid is itself unstable and its presence in plants has never been established; diacetyl, which is readily obtained from it by loss of carbon dioxide, is frequently found in essential oils.

H. W.

**Trimethylenedithioglycollic [Trimethylenedithiolacetic] Acid.** K. ROTHSTEIN (*Ber.*, 1925, 58, [B], 53—56; cf. Tiberg, A., 1916, i, 789, 790).—*Trimethylenedithiolacetic acid*,

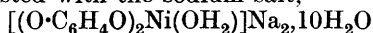


m. p. 71·6° (corr.),  $d_{20}^{20}$  1·492, is prepared by the action of trimethylene bromide on sodium thiolacetate in aqueous-alcoholic, alkaline solution. The following derivatives are described: *methyl ester*, b. p. 207—208°/15 mm.,  $d_4^{20}$  1·210; *ethyl ester*, b. p. 224—225°/23 mm.,  $d_4^{20}$  1·143; *amide*, m. p. 127°; *sodium salt*, *sodium hydrogen salt*,  $d_4^{20}$  1·568, *potassium salt*,  $d_4^{20}$  1·700, *dipotassium tetrahydrogen*, m. p. 147—149°; *dirubidium tetrahydrogen*, m. p. >160°; *tetracæsium decahydrogen salt*, m. p. about 130°; *barium* ( $+\frac{1}{2}\text{H}_2\text{O}$ ) and *magnesium* ( $+4\text{H}_2\text{O}$ ) salts.

H. W.

**Polymerisation of Formaldehyde in Presence of Inorganic Substances.** K. SHORT and W. F. SHORT (*Biochem. J.*, 1924, **18**, 1330—1333).—Magnesium, zinc, basic zinc carbonate, zinc oxide, magnesium oxide, magnesite, zinc oxide and magnesium oxide, and magnesite and basic zinc carbonate have a considerable catalytic action on the polymerisation of dilute solutions of formaldehyde to sugars in the presence of sunlight. The sugars thus formed are not by-products of the reaction in which methyl alcohol and formic acid are produced. S. S. Z.

**Reactivity of Organic Substances in Complex Combination.** H. REIHLEN, R. ILLEG, and R. WITTIG (*Ber.*, 1925, **58**, [B], 12—19).—Chromium acetylacetonate is converted by bromine in alcoholic solution into *chromium  $\gamma$ -bromoacetylacetonate*, whereas in the presence of chloroform it yields *chromium  $\alpha\gamma$ -dibromoacetylacetonate*. It thus appears that the additive and migrational powers of a double bond are not restricted by its presence in an internally-complex ring system. The ability of pyrocatechol to undergo the Tiemann-Reimer change when present in complex combination has been tested with the sodium salt,



(cf. Weinland and Döttinger, A., 1920, i, 545; Reichen, A., 1922, i, 1146). The yields of protocatechualdehyde are greater than those obtained with pyrocatechol if the duration of the action is not too short; the formation of resinous matter is repressed to a considerable extent and the by-products of the change (? trioxymethylene) differ in character from those produced normally. The corresponding potassium salt gives better yields, but its comparative instability renders it unsuitable for the authors' purpose. On the other hand, the salt,  $[Cr(O\cdot C_6H_4O)_3]K_3\cdot 2H_2O$  (cf. Weinland and Walter, A., 1923, i, 674), reacts much less readily with chloroform and gives only 60% of the normal yield of aldehyde, without production of resin. In all three cases, a limitation of the activity of the aromatic group is observed, since, if the period of action is restricted, the yields fall below those obtained with pyrocatechol. The improved yields, when observed, are due to restriction of subsequent resinification and not to facilitation of substitution in the nucleus.

The complex chromium chloroacetate reacts readily with potassium iodide, aniline, or methyl-alcoholic ammonia, whilst the halogen atom of the corresponding ferric salt is easily displaced by aniline; the products will be described subsequently. H. W.

**Relations between Rotatory Power and Structure in the Sugar Group. VI. Rotatory Powers of  $\alpha$ - and  $\beta$ -Forms of Methyl-*d*-xyloside and of Methyl-*l*-arabinoside.** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1925, **47**, 265—268).—Dextrorotatory *d*-xylose was methylated by anhydrous methyl chloride in the presence of hydrogen chloride;  $\beta$ -methyl-*d*-xyloside crystallised from ethyl acetate solution and  $\alpha$ -methyl-*d*-xyloside from the mother-liquor after concentration and addition of methyl ethyl

ketone. Methylation of dextrorotatory *l*-arabinose was carried out in a similar manner and the two isomerides were separated by fractional crystallisation from ethyl acetate. Rotatory powers were determined in dilute aqueous solution.  $\alpha$ -Methyl-*d*-xyloside has  $[\alpha]_D^{20} +153.9^\circ$ ;  $\alpha$ -methyl-*l*-arabinoside, m. p.  $131^\circ$ ,  $[\alpha]_D^{20} +17.3^\circ$ ;  $\beta$ -methyl-*d*-xyloside, m. p.  $157^\circ$ ,  $[\alpha]_D^{20} -65.5^\circ$ ;  $\beta$ -methyl-*l*-arabinoside, m. p.  $169^\circ$ ,  $[\alpha]_D^{20} +245.5^\circ$ .  
G. S. W.

**Relations between Rotatory Power and Structure in the Sugar Group. VII. Methyl Glycosidic Derivatives of the Sugars.** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1925, **47**, 268—280).—By consideration of the specific rotatory powers of the isomeric methyl derivatives of *d*-glucose, *d*-galactose, *d*-xylose, and *l*-arabinose, the average value of the methyl group was found to be  $a_{Me}=18,500$ . The specific rotatory power of methyl-*d*-lyxoside calculated from  $\alpha$ -*d*-lyxose, methyl-*d*-xyloside, and benzyl-*d*-lyxoside, gave the values  $[\alpha]_D +66^\circ$ ,  $61^\circ$ , and  $66^\circ$ , respectively. The rotation of other methyl derivatives obtained by calculation were  $\alpha$ -*d*-isorhamnose  $[\alpha]_D +105^\circ$ ;  $\beta$ -*d*-isorhamnose  $[\alpha]_D +1^\circ$ ;  $\alpha$ -methyl-*l*-fucoside  $[\alpha]_D -188^\circ$  and  $-190^\circ$  by different methods;  $\beta$ -methyl-maltoside  $[\alpha]_D +85^\circ$ ;  $\beta$ -methyl-lactoside  $[\alpha]_D +6^\circ$ ; methyl-*l*-sorboside  $[\alpha]_D -40^\circ$ .  
G. S. W.

**Glucosans.** J. KERB and E. KERB-ETZDORF (*Biochem. Z.*, 1924, **151**, 435—437; cf. A., 1924, i, 445).—A correction of Grafe and von Schröder (*Arch. klin. Med.*, **144**) in relation to a confusion of caramel substances with glucosans. Brigl's observation (A., 1922, i, 1117) that Pictet's supposed method of preparation of unimolecular  $\alpha$ -glucosan (A., 1920, i, 594) yields polymeric glucosans is confirmed.  
J. P.

**Constant of Hydrolysis of Sucrose.** H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1924, **179**, 1607—1609; cf. Cohen, A., 1897, ii, 484; Moran and Lewis, T., 1922, **121**, 1613).—The increase in the hydrolysis constant with the increase in the initial strengths of sucrose solutions has been investigated. Polarimetric measurements of the rate of hydrolysis by 0.1*N*-sulphuric acid were made on solutions of sucrose of 5 to 40% concentrations, at  $25^\circ$  using the green light of a mercury lamp ( $\lambda=5461$ ). The results confirm those of Moran and Lewis (*loc. cit.*), that the speed of hydrolysis increases more rapidly than the concentration of the sucrose. The value found for the relation  $(k_{40}-k_5)/k_5$ , 0.32, differs from that of Moran and Lewis (0.424), who used 0.1*N*-hydrochloric acid at  $25^\circ$ . Employing other substances the following values were found: hydrochloric acid, 0.55; hydrochloric acid and potassium chloride, 0.46; hydrobromic acid, 0.47; trichloroacetic acid, 0.33; oxalic acid, 0.20; formic acid, 0.17; acetic acid, 0.00. This shows that the increase of the speed of hydrolysis with the concentration of the sucrose depends on the catalyst used and the value  $(k_{40}-k_5)/k_5$  is lower the less the acid is dissociated.  
A. C.



**Chemical Analysis of Cotton. Oxycellulose.** I. C. BIRTEWELL, D. A. CLIBBENS, and B. P. RIDGE (*J. Text. Inst.*, 1925, 16, 13—52T).—By oxidation of bleached and scoured cottons, it is shown that oxycelluloses fall between two extreme types, one characterised by a great affinity for methylene-blue and having a high retentive power for alkalis and the other by a high reducing power as measured by its copper number and by suffering a considerable loss in weight when treated with alkali hydroxides. Both types of oxycellulose have a low viscosity in "cuprammonium" solution. Oxidation of cotton by alkaline hypobromite yields oxycellulose of the first type, oxidation by chlorine water yields the second type, and oxidation by sulphuric acid and potassium permanganate yields an intermediate oxycellulose. The type of oxycellulose produced by the action of a hypochlorite solution on cotton is dependent on the alkalinity or acidity of the solution. Under alkaline conditions, oxycellulose having a high methylene-blue absorption is formed; under acidic conditions, a highly reducing oxycellulose is produced. The behaviour of these types of oxycellulose towards the numerous reagents which are employed in the so-called "oxycellulose test" is described. [Cf. *B.*, 1925, 165.]

A. J. H.

**Wood Cellulose. III. Purity of Wood Cellulose.** T. OZAWA (*J. Chem. Ind. Japan*, 1924, 27, 884—891).—Acetolysis of bleached sulphite wood pulp gives cellobiose octa-acetate without producing dextrose as by-product, the maximum yield being 90%. Wood cellulose can therefore be regarded as the polymerised substance of cellobiose molecules which is decomposed by acetolysis in the same manner as starch by diastase. When wood pulp cellulose which has been treated with concentrated sodium hydroxide solution is methylated with methyl sulphate, heptamethylcellulose,  $C_{24}H_{33}O_{13}(OMe)_7$ , is produced. Pure wood cellulose is probably identical with cotton cellulose.

K. K.

**Synthesis of some Possible Precursors of Lysine.** C. S. MARVEL, D. W. MACCORQUODALE, F. E. KENDALL, and W. A. LAZIER (*J. Amer. Chem. Soc.*, 1924, 46, 2838—2842).—With a view to examine the synthesis of lysine (*l*- $\alpha$ -diaminohexoic acid) in the animal body from  $\alpha$ -substituted hexoic acids, a number of such derivatives have been synthesised. *Ethyl  $\delta$ -phenoxybutylmalonate*, b. p. 224—228°/20 mm.,  $n_D^{20}$  1.4879,  $d_4^{20}$  1.081, is obtained in 65—75% yield from ethyl malonate and  $\delta$ -phenoxybutyl bromide; the free acid, m. p. 152° (decomp.), on heating at 225° gives  $\epsilon$ -phenoxyhexoic acid, m. p. 69°, in 87—91% yield, which with 48% hydrobromic acid gives  $\epsilon$ -bromohexoic acid, m. p. 35°, b. p. 165—170°/20 mm. (yield 52—55%). The same acid was obtained by bromination of  $\epsilon$ -benzoylaminoxonitrile with bromine and phosphorus tribromide and hydrolysis with hydrobromic acid, and by the action of sodium cyanide on pentamethylene bromide, followed by hydrolysis with hydrobromic acid. On treatment with silver oxide,  $\epsilon$ -bromohexoic acid is converted into a mixture of  $\epsilon$ -hydroxyhexoic acid and its lactone (cf. Helferich and Malkomes, A., 1922,

i, 431).  $\delta$ -Phenoxybutylmalonic acid and bromine in dry ether give (yield 71%)  $\alpha$ -bromo- $\delta$ -phenoxybutylmalonic acid, m. p. 108—113° (decomp.), which at 150° gives carbon dioxide and  $\alpha$ -bromo- $\epsilon$ -phenoxyhexoic acid, m. p. 116—117° (yield 80%), which is converted by 45% hydrobromic acid into  $\alpha$ -dibromohexoic acid, m. p. 144—146°. R. B.

**Deamination of Aspartic Acid by Hydrolysis.** G. AHLGREN (*Compt. rend. Soc. Biol.*, 1924, 90, 1187—1190; from *Chem. Zentr.*, 1924, ii, 492—493).—Contrary to the general opinion that the deamination of amino-acids in the organism takes place by way of an oxidative process, the author holds that aspartic acid can undergo deamination through a hydrolytic process. This view is based on its reaction with methylene-blue in frog muscle. If the muscle is washed, aspartic acid is without action. Otherwise reduction takes place, but only to an equilibrium condition, as in the case of fumaric and malic acids. Complete reduction takes place with oxalacetic acid and with alanine. It is supposed that aspartic acid is changed into malic acid by a deaminase present in muscle which is readily removed by washing. G. W. R.

**Degradation of Histidine to *l*-Aspartic Acid.** W. LANGENBECK.—(See i, 306.)

**Peptide-like Compounds. III. Derivatives of *dl*-Serine. New Anhydrides of Glycylserine.** M. BERGMANN and A. MIEKELEY (*Z. physiol. Chem.*, 1924, 140, 128—145).—By treatment with diazomethane, *N*-benzoyl-*dl*-serine is converted into its methyl ester, which, with thionyl chloride, forms methyl 2-phenyloxazoline-4-carboxylate,  $n_D^{20}$  1.5504 (hydrochloride, m. p. 113—114°). The free acid, m. p. 159—160° after softening at 155°, is obtained by hydrolysis of the methyl ester with sodium hydroxide in aqueous-alcoholic solution. When treated with hydrochloric acid, or when kept in aqueous solution, 2-phenyloxazoline-4-carboxylic acid is transformed into *O*-benzoylserine, m. p. 149—150° (decomp.) (hydrochloride, m. p. 185—186°; picrate, m. p. 168—169°), which may be re-converted into *N*-benzoylserine by keeping for 12 hours in aqueous solution.

Glycyl-*dl*-serine methyl ester reacts with thionyl chloride to form a hydrochloride,  $C_6H_{11}O_3N_2Cl \cdot HCl$ , m. p. 160—161° (decomp.), which is converted by ammonia into anhydroglycyl-*dl*-serine anhydride I (annexed formula), which does not melt but darkens from 280° onwards. By treatment with aqueous sodium hydroxide, this is transformed into an isomeric compound which is termed anhydroglycyl-*dl*-serine anhydride II.

[With C. WITTE].—Thionyl chloride converts mandelamide into phenylchloroacetamide, m. p. 122°; ethyl lactate into a compound,  $CHMe(O \cdot SO \cdot Cl) \cdot CO_2Et$ , b. p. 95—96°/15 mm., and lactamide into a compound,  $CHMe \cdot CO \cdot NH \cdot SO \cdot O$ . E. S.

**Generation of Hydrocyanic Acid.** F. V. BICHOWSKY (*Ind. Eng. Chem.*, 1925, **17**, 57—58).—Moist carbon dioxide at a pressure less than atmospheric effects a quantitative liberation of hydrogen cyanide from sodium or calcium cyanide without the loss from polymerisation which occurs at atmospheric or higher pressure. A proper regulation of the added moisture, which no doubt plays an essential part in the reaction, is necessary. [Cf. *B.*, 1925, 129.]  
C. I.

**Catalytic Reduction of  $\beta$ -Methylbutyronitrile and of  $\alpha$ -Cyanocamphor.** H. RUPE and E. HODEL.—(See i, 275.)

**Reactions of the Alkyl- and Aryl-mercuric Hydroxides.** I. A. KOTEN and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 2764—2769).—Alkyl- and aryl-mercuric hydroxides react with an alcohol and carbon disulphide similarly to alkali hydroxides (cf. Maynard and Howard, *T.*, 1923, **123**, 960; Mills and Adams, *A.*, 1923, i, 970), giving in 70% of the theoretical yield, white, well-crystallised alkylmercuric xanthates,  $\text{RO}\cdot\text{CS}\cdot\text{SHgR}'$ , the reaction being catalysed by sodium hydroxide, which prevents the formation of mercaptans. The structure of these compounds is proved by their synthesis from alkyl- or aryl-mercuric chlorides and sodium xanthate. The xanthates decompose slowly on prolonged keeping, rapidly in sunlight, and with iodine in chloroform yield the corresponding alkyl- or aryl-mercuric iodide and yellow oils, probably possessing the structure  $[\text{RO}\cdot\text{CS}]_2$ . In the absence of alcohol, alkyl- or aryl-mercuric chlorides yield the corresponding mercaptans. The alkylmercuric hydroxides on treatment with carbon dioxide yield crystalline hydrogen carbonates, whilst the arylmercuric hydroxides are converted into normal carbonates. With carbon disulphide and alcohols, both the hydrogen carbonates and carbonates are converted into the alkylmercuric xanthates. The alkyl- or aryl-mercuric trinitrobenzoates on heating above their melting points behave like mercuric trinitrobenzoate (Kharasch, *A.*, 1922, i, 189), losing carbon dioxide and giving alkylaryl- or arylaryl-mercury compounds.  $(\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{CO}_2\text{HgR}' \rightarrow \text{CO}_2 + (\text{NO}_2)_3\text{C}_6\text{H}_2\cdot\text{HgR}'$ . The alkyl- or aryl-mercuric hydroxides do not react with ethyl malonate, ethyl acetoacetate, ethyl cinnamate, or phenols under the conditions used with mercuric oxide, and they cannot be used for the introduction of alkylmercury groups into organic compounds. The following compounds are described: *methylmercuric methyl xanthate*, m. p.  $59^\circ$ ; *methylmercuric ethyl xanthate*,  $\text{OEt}\cdot\text{CS}\cdot\text{S}\cdot\text{HgMe}$ , m. p.  $69^\circ$ ; *ethylmercuric ethyl xanthate*, m. p.  $53^\circ$ ; *n-propylmercuric ethyl xanthate*, m. p.  $38\text{--}39^\circ$ ; *n-butylmercuric ethyl xanthate*, oil; *p-tolylmercuric ethyl xanthate*, m. p.  $128^\circ$ ; *p-tolylmercuric methyl xanthate*, m. p.  $145^\circ$ ; *benzylmercuric ethyl xanthate*, m. p.  $74^\circ$ . *Methylmercuric mercaptan*, m. p.  $143^\circ$ , from methylmercuric hydrogen carbonate and carbon disulphide, is also obtained by passing hydrogen sulphide into an alcoholic solution of methylmercuric hydroxide. *Ethylmercuric mercaptan* has m. p.  $104^\circ$ . *p-Tolylmercuric mercaptan*, *methylmercuric hydrogen carbonate*, m. p.  $123^\circ$ ,

and *p*-tolylmercuric carbonate, decomp. above  $260^{\circ}$ , are described. *Ethylmercuric 2:4:6-trinitrobenzoate*, m. p.  $164^{\circ}$ , on heating at  $165^{\circ}$  yields *ethylmercuric-2:4:6-trinitrophenyl*, m. p.  $86^{\circ}$ . Similarly, *p*-tolyl mercuric-2:4:6-trinitrobenzoate, m. p.  $227^{\circ}$ , yields *p*-tolylmercuric-2:4:6-trinitrophenyl, m. p.  $192^{\circ}$  at  $220$ – $230^{\circ}$ . The mercury in the above compounds was determined by a modification of Rupp's method (A., 1908, ii, 1073). R. B.

**Mechanism of Catalytic Hydrogenation and Dehydrogenation.** N. ZELINSKI (*Ber.*, 1925, 58, [B], 185–187).—*cyclo*-Hexene, which is thermostable at temperatures below  $600^{\circ}$ , is quantitatively transformed in the presence of palladised asbestos (free from oxygen) at  $90^{\circ}$  into *cyclohexane* and benzene. The liquid hydrocarbon readily undergoes the same change at  $115$ – $120^{\circ}$ , or, more slowly, at the atmospheric temperature. It therefore appears probable that *cyclohexene* or *cyclohexadiene* is formed during the catalytic hydrogenation of benzene or dehydrogenation of *cyclohexane* and immediately undergoes disproportionation in the presence of the catalyst into benzenoid and saturated hydrocarbon. H. W.

**Reaction between Magnesium Organo Halides and Cupric Chloride.** H. GILMAN and H. H. PARKER (*J. Amer. Chem. Soc.*, 1924, 46, 2823–2827).—Continuing earlier work on the replacement of the group  $-\text{MgX}$  in the additive compounds formed in the Grignard reaction (A., 1923, i, 26; 1924, i, 382), the behaviour of cupric chloride towards these additive compounds has been examined. Coupling in accordance with the equation  $2\text{RMgX} + 2\text{CuCl}_2 = \text{R}\cdot\text{R} + \text{Cu}_2\text{Cl}_2 + 2\text{MgClX}$  takes place when the  $-\text{MgX}$  group is attached to an ethylenic carbon atom, to nitrogen, or to sulphur, but not to oxygen. Good yields are obtained only when the  $-\text{MgX}$  group is attached to sulphur, and the  $-\text{SMgX}$  grouping is better characterised by ethyl sulphate. Thus magnesium *p*-tolylthiol bromide and cupric chloride give *p*-tolyl disulphide in 67% yield, whilst bromomagnesium benzoate,  $\text{PhCO}_2\text{MgBr}$ , and bromomagnesium triphenylmethoxide,  $\text{Ph}_3\text{COMgBr}$ , yield no benzoyl peroxide or triphenylmethyl peroxide. Magnesium anilino-bromide,  $\text{NHPh}\cdot\text{MgBr}$ , with either cupric chloride or chromic chloride gives traces of azobenzene, probably by oxidation of hydrazobenzene first formed. With mercuric chloride, most of the aniline was again recovered and in addition a small quantity of a substance, m. p.  $191$ – $192^{\circ}$ , containing mercury and chlorine, was produced. Magnesium diphenylaminobromide and cupric chloride gave a small amount of *s*-diphenylbenzidine,  $(\text{NHPh}\cdot\text{C}_6\text{H}_4)_2$ , probably by rearrangement from tetraphenylhydrazine. With magnesium styryl bromide, *s*-diphenylbutadiene was formed in 17.6% yield, a 10% yield of the butadiene being obtained in the preparation of this Grignard reagent. R. B.

**Reaction of Bromonitromethane with Aromatic Compounds in the Presence of Aluminium Chloride.** M. L. SHERRILL (*J. Amer. Chem. Soc.*, 1924, 46, 2753–2758).—In view of

the formation of bromonitromethane from cyanogen bromide and sodium nitromethane (Scholl, A., 1897, i, 9) and the similarity between the halogenonitromethanes and the cyanogen halides, the behaviour of bromonitromethane in the Friedel-Crafts reaction has been examined (cf. Karrer, A., 1920, i, 389). With benzene, two simultaneous reactions appear to take place, the first proceeding normally with evolution of hydrogen bromide and the formation of phenylnitromethane (yield 8%) together with benzoic acid (14%) and benzaldehyde (23%) formed by decomposition of the latter. The second reaction gives bromobenzene (yield 27·7%), the bromination proceeding according to the equation  $\text{C}_6\text{H}_6 + \text{CH}_2\text{Br}\cdot\text{NO}_2 + \text{Al}_2\text{Cl}_6 \rightarrow \text{PhBr} + \text{MeNO}_2 + \text{Al}_2\text{Cl}_6$ , decomposition products only of the nitromethane being obtained. Condensation under diminished pressure (25 mm.) gave bromobenzene and phenylnitromethane in yields of 30–35% and 23·9%, respectively. Analogous reactions take place in carbon disulphide solution with bromobenzene, chlorobenzene, and anisole, the groups entering the para position in each case, and the yields of *p*-dihalogen compounds in the first two cases amount to 62%. In view of these results, bromonitromethane is regarded as an equilibrium mixture of two electromeric forms,  $\text{Br}^+\text{CH}_2^-\text{NO}_2 \rightleftharpoons \text{Br}^-\text{CH}_2^+\text{NO}_2$ , the one carrying the negatively charged bromine atom behaving as an alkyl halide in the Friedel-Crafts reaction, and the other behaving as a brominating agent. The instability of bromoisnitromethane (Hantzsch, A., 1899, i, 401) is readily interpreted on the same view. Bromonitromethane is best prepared by a slight modification of Scholl's method (A., 1896, i, 585).

R. B.

**Action of Iodine on Benzene.** N. D. COSTEANU (*Bul. Soc. Chim. România*, 1924, 6, 91–94).—When benzene is heated gradually to 600° with excess of iodine in a sealed tube, it yields a black, nacreous, infusible mass, which is not attacked by mineral acids and has a composition corresponding with the formula,  $\text{C}_{96}\text{H}_{23}\text{I}$ .

T. H. P.

**Nitration by means of a Mixture of Nitrosulphonic and Fuming Nitric Acids.** P. S. VARMA and D. A. KULKARNI (*J. Amer. Chem. Soc.*, 1925, 47, 143–147).—Nitrosulphonic acid was prepared by passing sulphur dioxide through cold fuming nitric acid until a 50% yield was obtained. By nitration with 18·5–22·0 g. of a solution of nitrosulphonic acid in fuming nitric acid, 5 g. of benzene gave a maximum yield of 5·1 g. of nitrobenzene. Dinitrobenzene, up to 20% of the theoretical, was obtained by prolonged nitration in the presence of traces of iodine. Considerable amounts of non-volatile residue were obtained by the action of the acid on *m*-xylene and mesitylene. Phenols and also aniline and methylaniline, alone and in the presence of diluents, were immediately charred. Nitrophenols gave good results, *o*-nitrophenol yielding 2:5-di- and 2:4:5-tri-nitrophenol and other products. Benzoic acid was nitrated smoothly to *m*-nitrobenzoic

acid. Dilution with acetone prevented charring in the nitration of *o*- and *p*-hydroxytoluic acids. G. S. W.

**Action of Hydrogen Sulphites and Sulphites on Nitro and Nitroso Compounds.** F. RASCHIG (*Schwefel-u. Stickstoffstudien*, 1924, 255—272; from *Chem. Zentr.*, 1924, ii, 1081—1082).—The action of sodium hydrogen sulphite on nitro compounds yields phenols and amines and their sulphonic acids, the sulphonic group in the *N*-monosulphonated amines,  $R \cdot NH \cdot SO_3H$ , being more firmly attached to nitrogen than this to carbon. When a *N*-solution of sodium nitrobenzenesulphonate reacts with a 5*N*-solution of sodium hydrogen sulphite, the latter substance disappears in 4 hours at the ordinary temperature; the first product appears to be a condensation product,  $R \cdot N(:O)(OH) \cdot SO_3Na$  or  $R \cdot N(O \cdot OH) \cdot SO_3Na$ .

Sulphuric acid appears after 10 hours, and the reaction is incomplete after 8 days. Free sulphurous acid is then present in place of the sulphite. If two-fifths of the sodium hydrogen sulphite is neutralised with sodium hydroxide, the reaction is much more rapid and after 6 hours only a little sodium hydrogen sulphite is present with the disulphonate,  $R \cdot N(SO_3Na)_2$ . A substance,  $C_6H_3(SO_3Na)_2 \cdot NH \cdot SO_3Na \cdot 5H_2O$ , has been qualitatively detected, in which two sulphonic groups occupy ortho-positions with respect to nitrogen. Aminophenolsulphonic acid is also formed. Dinitromesitylenesulphonic acid gives nitroaminomesitylenesulphonic acid and on warming a soluble trisulphonic acid, in which two sulphonic groups are attached to nitrogen, and, at the same time an amino-hydroxymesitylenesulphonic acid is formed.

*m*-Nitrosobenzenesulphonic acid similarly yields as a first reaction product a condensation product,  $SO_3Na \cdot C_6H_4 \cdot N(SO_3Na)_2$ , the liquid becoming acid during the reaction, which is thereby retarded. Treatment with hydrochloric acid gives metanilic acid. Phenylhydroxylamine-*m*-sulphonic acid yields benzidinedisulphonic acid, probably through the intermediate formation of the hydrazobenzenedisulphonic acid. Sodium phenylhydroxylaminesulphonate is prepared by reduction of sodium *m*-nitrobenzenesulphonate with zinc dust in alcoholic solution at 74—80°. Excess of potassium permanganate oxidises it back to nitrobenzenesulphonic acid, air only to the nitrososulphonic acid. R. B.

**Electrochemical Oxidation of Benzenesulphonic Acid, Toluene-*o*-sulphonic Acid, and Benzene-*p*-disulphonic Acid, and the Per-acids formed in the Process.** F. FICHTER and E. STOCKER (*Helv. Chim. Acta*, 1924, 7, 1064—1078).—Electrolytic oxidation of benzenesulphonic acid in *N*-solution with a lead oxide or platinum anode, and a current density of 0.05 amp./cm.<sup>2</sup>, gives the following products: (i) fumaric acid, or a mixture of fumaric and succinic acids, the latter produced only when no diaphragm is used; (ii) (a little) *p*-benzoquinone; (iii) pyrocatechol-4-sulphonic acid; (iv) phenol-*p*-sulphonic acid (traces only); (v) sulphuric acid. The pyrocatecholsulphonic acid (best yield, 9.5% of theory) was

separated as lead salt and conclusively identified by conversion into veratrolesulphonic acid. Phenol-*p*-sulphonic acid, when similarly oxidised, yields the same products, but pyrocatecholsulphonic acid, on further oxidation, affords no quinone.

It might be expected, as benzenesulphonic acid is readily soluble in water, and its solutions therein conduct electricity of themselves, that the oxidation should proceed regularly and should be easily controlled, but the meagre maximum yield (above) of the chief product shows that this is not so. It is found that carbon dioxide and sulphuric acid are produced even quite early in the oxidation, and that the solution also contains a powerful oxidising agent, which is neither quinone nor a persulphuric acid, being much less stable than either and insoluble in ether. Moreover, benzenesulphonic peroxide (Weinland and Lewkowitz, A., 1903, i, 808) is not in question, as it is decomposed by water into benzenesulphonic acid, sulphuric acid, and phenol. It appeared, therefore, that the peroxide-like substance might be the hitherto unknown *benzenepersulphonic acid*,  $\text{Ph}\cdot\text{SO}_4\text{H}$ . In an attempt to prepare this compound, benzenesulphonic anhydride (Meyer and Schlegel, A., 1913, i, 608) was treated with concentrated hydrogen peroxide; a vigorous action took place and a charred mass was obtained. When the reaction was carried out in a closed vessel or in acetic acid solution, the product was found to contain pyrocatecholsulphonic acid; in acetic acid solution the action was not so vigorous, but was accelerated by adding finely-divided palladium. Benzenesulphonic acid and hydrogen peroxide interact slowly to form what is presumably the above per-acid; the product liberated bromine from potassium bromide immediately. These observations indicate that the first stage in the electrolytic oxidation of benzenesulphonic acid is the formation of this very unstable per-acid; this yields then, first phenol-*p*-sulphonic acid, part of which is oxidised to *p*-benzoquinone and so to fumaric acid, whilst another part is oxidised to pyrocatecholsulphonic acid, and then to fumaric acid.

That it is the usually resistant sulphonic group which is attacked in the above oxidations shows how it is that toluene-*o*-sulphonic acid cannot be satisfactorily oxidised electrolytically to *o*-sulphobenzoic acid (cf. Fichter and Löwe, A., 1922, i, 242). Actually, when this oxidation is carried out, the products are mesaconic acid, toluquinone, and 5-sulphopyrocatechol-4-carboxylic acid (?), isolated as the barium salt.

When benzene-*p*-disulphonic acid is oxidised in the same way, it yields fumaric acid (a little), and pyrocatecholsulphonic acid. Phenol-2 : 5-disulphonic acid is oxidised electrolytically to the latter, so presumably is formed in the intermediate stage of the oxidation (cf. Fichter, Brändlin, and Hallauer, A., 1920, i, 428).

W. A. S.

**Velocity of Oxidation of Aromatic Ethylene Derivatives by Prileschaeff's Reagent.** J. BÖESEKEN and J. S. P. BLUMBERGER (*Rec. trav. chim.*, 1925, **44**, 90—95).—The activity of peroxybenzoic acid (Prileschaeff's reagent) varies with the age of the

specimen, and with the method of preparation used. The oxidation  $\text{PhCO}\cdot\text{O}_2\text{H} + >\text{C}\cdot\text{C}< \rightarrow \text{PhCO}_2\text{H} + >\overset{\text{O}}{\text{C}}\cdot\text{C}<$  is studied in chloroform or carbon tetrachloride solution for styrene, propenylbenzene, allylbenzene,  $\Delta^{1,2}$ ,  $\Delta^{2,3}$ , and  $\Delta^{3,4}$ -butenylbenzene, stilbene, and isostilbene, and is found to be of the second order. The velocity increases as the ethylenic linking approaches the benzene nucleus, whilst in styrene it is increased on replacement of an  $\omega$ -hydrogen atom by an aliphatic group, but decreased on replacement by a phenyl group. F. M. H.

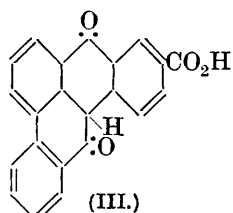
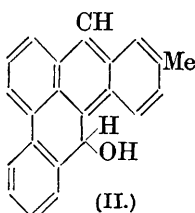
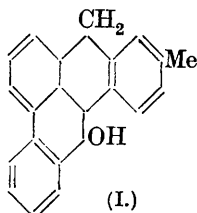
**1-Methyl- $\Delta^1$ -dihydronaphthalene.** K. VON AUWERS (*Ber.*, 1924, 58, [B], 151—156).—Dehydration of 1-methyl-*ac*-tetrahydro- $\alpha$ -naphthol followed by distillation under atmospheric pressure (cf. Auwers, A., 1918, ii, 343) leads to contamination of the product with a considerable quantity of 1-methylnaphthalene (identified as the picrate, m. p. 142°). This can be avoided if the dehydration is effected at as low a temperature as possible with phosphoric oxide, potassium hydrogen sulphate, formic acid, or an excess of magnesium methyl bromide and the product is distilled under diminished pressure or not at all. Its complete freedom from 1-methylnaphthalene cannot be placed beyond doubt. Oxidation with potassium permanganate in aqueous acetone shows it to be a mixture of 1-methyl- $\Delta^1$ -dihydronaphthalene and 1-methylene-1 : 2 : 3 : 4-tetrahydronaphthalene, from the latter of which 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene, identified as the semicarbazone, m. p. 219—223°, is produced. The former substance gives the normal oxidation products, 1 : 2-dihydroxy-1-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 75—76°, and  $\beta$ -o-acetylphenylpropionic acid, m. p. 69—70° (oxime, m. p. 123°; semicarbazone, m. p. 129—131°; ethyl ester, b. p. 160—163°/15 mm.,  $d_4^{20}$  1.091,  $n_D^{20}$  1.5277). H. W.

**Pyrogenic Decomposition of Naphthalene under the simultaneous Action of Oxides of Aluminium and Nickel.** W. IPATIEV and N. KIJUKWIN (*Ber.*, 1925, 58, [B], 1—3).—The action of hydrogen under high pressure at 450—480° on naphthalene in the presence of a catalyst consisting of equal parts of nickel and aluminium oxides results in the production of benzenoid hydrocarbons (ca. 30%), among which benzene, toluene, and *o*-xylene have been identified, and naphthalene (20%), the remainder being tetrahydronaphthalene. The last-named substance is regarded as the precursor of the benzenoid hydrocarbons. H. W.

**New Condensation Products from Anthracene and Phenanthrene.** A. SCHAARSCHMIDT, C. MAYER-BUGSTRÖM, and J. SEVON (*Ber.*, 1925, 58, [B], 156—160).—The action of a relatively large amount of aluminium chloride on a mixture of *m*-xylene and phenanthrene at 50° yields the compound, I or II, m. p. 218°, in the production of which atmospheric oxygen does not take part. It is oxidised by chromic acid in glacial acetic acid solution to the



carboxylic acid, III, m. p.  $282^{\circ}$ , which is reduced by zinc dust in ammoniacal solution to the corresponding dihydro derivative,  $C_{21}H_{23}\cdot CO_2H$ , m. p.  $168^{\circ}$ .



A partly completed investigation of the action of aluminium chloride on anthracene in the presence of aromatic hydrocarbons shows that one of the hydrogen atoms of anthracene is rendered so labile by the chloride that it can be removed by a current of air. The product, which contains combined benzenoid hydrocarbon, dissolves readily in aromatic hydrocarbons, yielding carmine-red solutions, whereas its solubility in glacial acetic acid is slight. It is suggested that it is a condensation compound of high molecular weight which is extensively dissociated in benzene solution into simpler residues containing tervalent carbon. Similar products are formed if condensation is effected with catalytic amounts of aluminium chloride in a stream of hydrogen chloride. With molecular amounts of aluminium chloride and hydrogen chloride, different products are formed.

H. W.

### Hydrogenation of Decacyclene (Trinaphthylenebenzene).

K. DZIEWOŃSKI and J. SUSZKO (*Roczniki Chemji*, 1924, 4, 207—219).—Reduction of decacyclene by means of hydriodic acid and a large proportion of red phosphorus at  $270$ — $280^{\circ}$  yields the following

hydrocarbons: (1) *Tri-dihydro-naphthylenebenzene* (*hexahydrodecacyclene*), (annexed formula) brown, amorphous mass, m. p.  $355$ — $365^{\circ}$ ; (2) *octahydrodecacyclene*,  $C_{10}H_{10}\cdot C_6(C_{10}H_8)_2$ , amorphous, reddish-brown mass, m. p.  $300$ — $310^{\circ}$ ; (3) *dodecahydrodecacyclene*,  $C_{10}H_{10}\cdot C_6(C_{10}H_{10})_2$ , dark red, microcrystalline powder, m. p.  $255$ — $265^{\circ}$ ; (4) *hexadecahydrodecacyclene*,  $C_{10}H_{10}\cdot C_6(C_{10}H_{12})_2$ , orange-yellow, microcrystalline powder, m. p.  $150$ — $160^{\circ}$ ; (5) *octadecahydrodecacyclene*,  $C_{10}H_{12}\cdot C_6(C_{10}H_{12})_2$ , lemon-yellow, microcrystalline powder, m. p.  $124$ — $128^{\circ}$ ; (6) *hexacosihydrodecacyclene*,  $C_{10}H_{14}\cdot C_6(C_{10}H_{14})_2$ , colourless or yellow, viscous oil. T. H. P.

**Reaction between Benzylideneaniline and Carbon Disulphide at High Temperature and Pressure.** L. A. BIGELOW (*J. Amer. Chem. Soc.*, 1925, 47, 193—198).—Phenylthiocarbimide, thiocarbanilide, stilbene, thiobenzanilide, and tetraphenylthiophen were identified among the products of the reaction between benzylideneaniline and carbon disulphide. A minimum temperature of

170° corresponding with a pressure of 19 atm. was required for the reaction.  
G. S. W.

**Interaction of Aniline and Calcium Hypochlorite.** F. RASCHIG (*Schwefel- u. Stickstoff-studien*, 1924, 79—82; from *Chem. Zentr.*, 1924, ii, 163—164).—The author discusses the reaction between calcium hypochlorite and aniline whereby the indophenol,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \diagup \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \end{smallmatrix}$ , is produced. It is suggested that chloroaniline forms, by loss of hydrochloric acid, phenyl nitride, which may have the constitution of phenyleneimine,  $\text{C}_6\text{H}_4 \cdot \text{NH}$ . This compound, being very reactive, yields *p*-aminophenol by addition of water. By further reaction with the hypochlorite, *p*-chloroaminophenol,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{NHCl}$ , is formed which forms with phenyleneimine the indophenol with elimination of hydrochloric acid. Phenyl nitride probably exists both as  $\text{C}_6\text{H}_5\text{N}$  and  $\text{C}_6\text{H}_4 \cdot \text{NH}$  since in the reaction above described azobenzene and benzoquinonephenyldi-imide,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NPh} \\ \diagup \text{N} \text{H} \end{smallmatrix}$ , are also formed.

G. W. R.

**Preparation and Reactions of Oximinoacetanilides.** P. KARRER, G. H. DIECHMANN, and W. T. HAEBLER (*Helv. Chim. Acta*, 1924, 7, 1031—1039; cf. *A.*, 1924, i, 722).—*p*-Oximinoacetamidophenyl allyl ether, m. p. 177—178°, is obtained by Sandmeyer's method from *p*-aminophenyl allyl ether, and by electrolytic reduction is converted into *glycine-p*-allyloxyanilide, m. p. 98—99°. Similarly, 4-aminoantipyrine yields the corresponding oximinoacetyl derivative, m. p. 190—194°, and this is reduced to 4-*glycyl*-amidoantipyrine, an amorphous substance giving oily salts, only the *picrolonate*, m. p. 225—226°, being obtained crystalline. The oximinoacetyl derivative of arsanilic acid is likewise readily obtained, and also, from 3-amino-4-hydroxyphenylarsinic acid, 3-oximinoacetamido-4-hydroxyphenylarsinic acid, which is reduced by stannous chloride in presence of a trace of potassium iodide to 3 : 3'-diglycyl-amido-4 : 4'-dihydroxyarsenobenzene, the hydrochloride of which is described.

When oximinoacetanilide is treated with warm thionyl chloride, cyanoformanilide is readily produced. Oximinoacetylthranilic acid, similarly treated, affords *cyanoformylanthranil*, m. p. 123°. This compound is hydrolysed when it is boiled with very dilute alcohol, and isatic acid is produced; more complete hydrolysis, which takes place when the boiling is prolonged, produces anthranilic acid. Oximinoacetanilide is converted, by treatment with chlorine in alcoholic hydrochloric acid solution, into Dimroth and Taub's oxanilhydroxamic chloride (*A.*, 1907, i, 97). From the corresponding amino compounds the following derivatives were prepared: *p*-oximinoacetamidoazobenzene, brown leaflets, m. p. 214°; *p*-toluene-3-azo-oximinoaceto-*p*-toluidide, m. p. 194°, and *o*-toluene-3-azo-oximinoaceto-*o*-toluidide.

W. A. S.

**Addition of Ethyl Sodioacetoacetate to Substituted Aromatic Mustard Oils [Thiocarbimides].** D. E. WORRALL (*J. Amer. Chem. Soc.*, 1924, **46**, 2834—2838).—Further examination of the reaction of substituted aromatic thiocarbimides with ethyl sodioacetoacetate shows that addition takes place rapidly with the *p*-substituted compounds, the anisyl and phenetyl compounds reacting more slowly than the other compounds examined. The speed of reaction diminishes through the series para  $\rightarrow$  meta  $\rightarrow$  ortho, but the ultimate yields are the same. The additive products on treatment with acid change to thioanilides, but in the cases of the *o*-toluidino, *o*- and *m*-anisidino derivatives these could not be obtained crystalline. No evidence was obtained of the "ketonic hydrolysis" previously described (A., 1918, i, 161), and in all cases "acid hydrolysis" took place with dilute alkali, the acids formed from the *o*- and *m*-toluidides being solids of low m. p. which spontaneously lose carbon dioxide, yielding amides of thionacetic acid. On repetition of the earlier work, the substance, m. p. 73—75°, obtained by "ketonic hydrolysis" of the product from *o*-tolylthiocarbimide could not be isolated and only thionaceto-*o*-toluidide, m. p. 91—92°, could be obtained, probably in an impure form. *m*-Tolylthiocarbimide and ethyl sodioacetoacetate yield *ethyl acetylthionmalono-m-toluidate*, m. p. 78—80°, which on hydrolysis gives *thionmalono-m-toluidic acid*, melting at the ordinary temperature and losing carbon dioxide to give *thionaceto-m-toluidide*, m. p. 42—43°. Similarly, from *m*-bromophenylthiocarbimide are obtained *ethyl acetylthionmalono-m-bromoanilate*, prisms, m. p. 81—82°, *thionmalono-m-bromoanilic acid*, m. p. 101° (decomp.), and *m-bromothionacetanilide*, m. p. 75—76°. *Ethyl acetylthionmalono-p-anisidate*, m. p. 97—98°, *thionmalono-p-anisidic acid*, m. p. 90—91° (decomp.), and *thionaceto-p-anisidide*, m. p. 114°; *ethyl acetylthionmalono-p-phenetide*, m. p. 87—88°, *thionmalono-p-phenetidic acid*, m. p. 105° (decomp.), and *thionaceto-p-phenetide*, yellow needles, m. p. 113—114° (Sachs and Loevy, A., 1904, i, 307); *ethyl acetylthionmalono-p-chloroanilate*, m. p. 77—79°, *thionmalono-p-chloroanilic acid*, m. p. 113—114° (decomp.), and *p-chlorothionacetanilide*, m. p. 141—142° (Sachs and Loevy, *loc. cit.*); *ethyl acetylthionmalono-p-iodoanilate*, needles, m. p. 63—65°, *thionmalono-p-iodoanilic acid*, m. p. 132—133° (decomp.), and *p-iodothionacetanilide*, m. p. 149°; *ethyl acetylthionmalono- $\alpha$ -naphthylamate*, prisms, m. p. 82—84°, *thionmalono- $\alpha$ -naphthylamic acid*, m. p. 56—57°, and *thionaceto- $\alpha$ -naphthylamide*, pale yellow needles, m. p. 111° (Jacobsen, A., 1887, 960), are similarly prepared. *Thionaceto-o-anisidide*, yellow plates, has m. p. 52—53°.

R. B.

**Identification of Amines. II. *m*-Nitrobenzenesulphonamides.** C. S. MARVEL, F. L. KINGSBURY, and F. E. SMITH (*J. Amer. Chem. Soc.*, 1925, **47**, 166—167).—*m*-Nitrobenzenesulphonamides were prepared either by treating *m*-nitrobenzenesulphonyl chloride with a slight excess of amine, the reaction being exothermic, or by warming a mixture of the sulphonyl chloride and amine in dilute sodium hydroxide solution. The derivatives of the following

amines were prepared: *diethylamine*, m. p.  $66^{\circ}$ ; *di-n-butylamine*, m. p.  $61^{\circ}$ ; *methylaniline*, m. p.  $100^{\circ}$ ; *ethylaniline*, m. p.  $100.5^{\circ}$ ; *n-propylaniline*, m. p.  $111.5^{\circ}$ ;  $\alpha$ -*naphthylamine*, m. p.  $166.5^{\circ}$ ;  $\beta$ -*naphthylamine*, m. p.  $165.5^{\circ}$ ; *o-chloroaniline*, m. p.  $153^{\circ}$ ; *p-chloroaniline*, m. p.  $119.5^{\circ}$ ; *p-bromoaniline*, m. p.  $120.5^{\circ}$ , and *n-butylaniline*, m. p.  $78.5^{\circ}$ .  
G. S. W.

**Mechanism of the Catalytic Reduction of Oximes and Nitriles and a New Method for the Preparation of Secondary Amines.** K. W. ROSENMUND and G. JORDAN (*Ber.*, 1925, 58, [B], 51—53).—Benzylamine is converted into dibenzylamine and ammonia to an extent greater than 90% when heated in boiling xylene in a current of hydrogen in the presence of palladised barium sulphate; if the hydrogen is replaced by air large quantities of benzylidenebenzylamine are produced, whilst in the presence of nitrogen the products are dibenzylamine and benzylidenebenzylamine (10—15%).  $\beta$ -Phenylethylamine gives di- $\beta$ -phenylethylamine in 88% yield. Benzene, toluene, and cumene are less suitable than xylene as solvents.

Gulevitch's criticisms (*A.*, 1924, i, 1285) of the "complex" theory of catalysis (cf. Rosenmund and Zetsche, *A.*, 1921, ii, 320, 392, 393, 631) are considered invalid, since the required condition of stability of the complex is not fulfilled in his crucial experiments.

H. W.

**Constitution of Organic Derivatives of Sulphurous Acid.** F. RASCHIG (*Schwefel- u. Stickstoff-studien*, 1924, 242—249; from *Chem. Zentr.*, 1924, ii, 1093—1094).—In the  $\omega$ -sulphonic acids formed from aldehyde-bisulphite compounds, the sulphur is linked directly to carbon, phenol and formaldehyde-bisulphite yielding the sulphonic acid,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$ . The compounds similarly obtained from amines such as aniline or methylamine are not true sulphonic acids, but are analogous in structure to formaldehyde-bisulphite itself, which has the structure  $\text{CH}_2\cdot\text{SO}_2\cdot\text{O}$  and contains the sulphur only loosely attached. One oxygen atom is readily removed by reduction, formaldehyde-bisulphite yielding "rongalite,"  $\text{CHNa}\cdot\text{SO}_2$ , in which the sodium is attached directly to carbon. All aldehyde- and ketone-bisulphite compounds contain the metal directly bound to carbon, and the power of the  $\text{SO}_2$ -group to make the hydrogen atoms attached to the neighbouring carbon atom replaceable by metals decreases with the distance of the carbon atom to which the hydrogen is attached from the  $\text{SO}_2$ -group. Benzophenone gives no bisulphite compound. The compound of phenanthraquinone with 1 mol. of sodium hydrogen sulphite is attributed to the addition of water to the ketonic oxygen atoms, giving the group  $\cdot\text{C}(\text{OH})_2$  in which a hydrogen atom of the hydroxyl groups is replaceable by metals. The third oxygen atom in sulphurous acid,  $\text{H}_2\cdot\text{SO}_2\cdot\text{O}$ , plays a part in the replacement of amino groups in aromatic amines by hydroxyl groups in the presence of sulphurous acid, naphthylamine yielding the intermediate compound,  $\text{H}_2\text{SO}_2\cdot\text{N}\cdot\text{C}_{10}\text{H}_7$ , which changes to  $\text{HSO}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$ . In alkaline solution, the tendency to replacement of the amino group by hydroxyl is greater than the tendency

to hydrolysis of the sulphonic group from nitrogen. In acid solution, the converse is true. The *N*-sulphonic acid of metanilic acid,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_3\text{H}$ , in alkaline solution yields phenol-*m*-sulphonic acid and aminosulphonic acid. Similarly, the formation of hyposulphurous acid by reduction of bisulphites with zinc is interpreted as reduction of the tautomeric form  $\text{H}_2\text{SO}_2\cdot\text{O}$  to  $\text{H}_2\text{SO}_2$  and inter-action of this with unchanged sulphurous acid yielding, by loss of water,  $\text{H}_2\text{SO}_2\cdot\text{SO}_2$ . The double linking of the two sulphur atoms is easily split by the action of aldehydes, yielding mixtures of the aldehyde compounds of sulphurous acid and hyposulphurous acid.

R. B.

**Nitro Derivatives of 2-Methylnaphthalene.** V. VESELY and J. KAPP (*Chem. Listy*, 1924, 18, 201—205; 244—249; cf. A., 1923, i, 911).—When 2-methylnaphthalene is nitrated to the mononitro stage four derivatives can be isolated or characterised. The crude mixture is reduced with alcoholic ammonium sulphide; 1-nitro-2-methylnaphthalene, the chief product and the only one isolated hitherto (cf. Schulze, A., 1884, 1183; Lesser, A., 1914, i, 33), remains unattacked. The mixture of amines obtained is semi-solid and when filtered affords 6(?)*-amino-2-methylnaphthalene*, m. p. 128° (*acetyl* derivative, m. p. 153°, *benzoyl* derivative, m. p. 182—183°); the corresponding 2-methyl-6(?)*-naphthol* has m. p. 125.5°. The residual oily amine is either acetylated or benzoylated and then fractionally crystallised from alcohol; it thus affords 4-*amino-2-methylnaphthalene*, m. p. 51—52°, as the *acetyl* derivative, m. p. 175—176°, or 8-*amino-2-methylnaphthalene* as the *benzoyl* derivative, m. p. 194—195°.

3-Methyl- $\alpha$ -naphthylamine was prepared for comparison as follows. 1-Acetamido-2-methylnaphthalene (Lesser, *loc. cit.*) is nitrated, and the resulting 4-nitro-1-acetamido-2-methylnaphthalene, m. p. 240—241°, hydrolysed to 4-nitro-2-methyl- $\alpha$ -naphthylamine, m. p. 184—185°, which, by displacement of the amino group in the usual way, affords 4-nitro-2-methylnaphthalene, m. p. 49—50°. Reduction now yields the desired amine, the *benzoyl* derivative of which has m. p. 188—189°. By the usual methods it affords 3-methyl- $\alpha$ -naphthol and 4-bromo-2-methylnaphthalene (*picrate*, m. p. 90—91°). 4-Nitro-2-methyl- $\alpha$ -naphthylamine, when reduced, affords 1:4-diamino-2-methylnaphthalene, m. p. 111—113°, which is converted by oxidation into 2-methyl- $\alpha$ -naphthaquinone (Fries and Lohmann, A., 1922, i, 29). 7-Methyl- $\alpha$ -naphthylamine (*acetyl* derivative, m. p. 175—176°) is converted in the usual way into 7-methyl- $\alpha$ -naphthol (Krollpfeiffer, A., 1923, i, 343) and its constitution thus established. It also affords 8-bromo-2-methylnaphthalene, an oil (*picrate*, m. p. 99—100°).

When 2-methylnaphthalene is dinitrated, "mixed acid" being used, it yields at least two dinitro derivatives. The 1:8(?), m. p. 209°, has already been described by Schulze and by Lesser (*loc. cit.*). The second product is 1:5-dinitro-2-methylnaphthalene, m. p. 131°. Its constitution was determined as follows. On reduction with alcoholic ammonium sulphide, it affords 1-nitro-(5)-*amino-2-methyl-*

*naphthalene*, m. p. 134—135° (*acetyl derivative*, m. p. 192°). This is converted into (5)-*bromo-1-nitro-2-methylnaphthalene*, m. p. 94° [cf. the product obtained by Lesser (*loc. cit.*), by brominating 1-nitro-2-methylnaphthalene], and, further, into (5)-*bromo-2-methyl- $\alpha$ -naphthylamine*, m. p. 53.5° (*acetyl derivative*, m. p. 184—185°), and so into (5)-*bromo-2-methyl- $\alpha$ -naphthol*, m. p. 78—79°. The latter affords 3-bromophthalic acid on oxidation. The bromine atom must therefore be in the 5- or in the 8-position in the original naphthalene nucleus. From the (5)-*bromo-2-methyl- $\alpha$ -naphthylamine* described above, the amino group was displaced. The product was different from the 8-bromo-2-methylnaphthalene previously described, and was therefore certified to be 5-bromo-2-methylnaphthalene (*picrate*, m. p. 91—92°). 1 : 5-Diamino-2-methylnaphthalene has m. p. 125—128°.

W. A. S.

**Diphenylmethane Series. Benzhydryltrimethylammonium Bromide.** M. SOMMELET (*Compt. rend.*, 1925, 180, 76—79; cf. A., 1923, i, 202).—Benzhydryltrimethylammonium bromide is obtained by heating a mixture of methyl bromide and benzhydryldimethylamine in benzene solution, or by mixing benzhydryl bromide with a benzene solution of trimethylamine. The crystals from a mixture of alcohol (95%) and ether contain 1 mol. of water, which can be removed by prolonged heating at 100°. When quickly heated at 130—140°, the compound decomposes with formation of benzhydryl ether and trimethylamine hydrobromide. This is shown to be directly due to the water of crystallisation, according to the equations, (i)  $\text{CHPh}_2 \cdot \text{NMe}_3 \cdot \text{Br} + \text{H}_2\text{O} = \text{CHPh}_2 \cdot \text{OH} + \text{NMe}_3 \cdot \text{HBr}$ , (ii)  $\text{CHPh}_2 \cdot \text{NMe}_3 \cdot \text{Br} + \text{CHPh}_2 \cdot \text{OH} = (\text{CHPh}_2)_2\text{O} + \text{NMe}_3 \cdot \text{HBr}$ . The quaternary bromide is particularly sensitive to compounds containing hydroxyl groups. With primary and secondary alcohols, it gives the benzhydryl ether, and with tertiary amyl alcohol it gives benzhydrol and its oxide. With ethyl lactate, a compound is formed which on hydrolysis yields *benzhydryl-lactic acid*,



m. p. 131°; *barium salt*,  $+5\text{H}_2\text{O}$ . The mechanism of the reaction of the quaternary bromide with alcohols is discussed. Benzhydryl bromide reacts with trimethylamine in cold alcoholic solution to form the ethyl ether of benzhydrol and trimethylamine hydrobromide. It is therefore likely that, before reacting with the alcohol, the quaternary compound dissociates into benzhydryl bromide and the tertiary amine. Simple decomposition into  $\text{CPh}_2$  and  $\text{NMe}_3 \cdot \text{HBr}$ , with formation of tetraphenylethylene (cf. Staudinger and Endle, A., 1913, i, 592), does not appear to take place when the quaternary bromide is heated alone at 250°. A. C.

**Synthesis of Fluorenylamines.** C. COURTOT and P. PETITCOLAS (*Compt. rend.*, 1925, 180, 297—299).—The extreme mobility of a halogen atom in the 1-position of indene and indane derivatives (cf. A., 1923, i, 1090; 1924, i, 279) is shown also by a halogen atom in the 9-position of fluorene. With anhydrous ammonia, 9-chlorofluorene reacts peculiarly, giving difluorenylamine (cf. Curtius and

Kof, A., 1912, i, 732), dibiphenylenethene, and traces of primary amine. With aliphatic or aromatic amines, however, the reaction is expressed by:  $C_{13}H_9Cl + 2NH_2R = C_{13}H_9 \cdot NHR + NH_2R \cdot HCl$ .

Fluorenylaniline, obtained from 9-chloro(or bromo)-fluorene and aniline, was prepared by Staudinger and Gaule (A., 1916, i, 852). *Fluorenyl-p-tolylamine*, similarly obtained, has m. p. 124°. *Fluorenyl-p-nitroaniline*, yellow needles, m. p. 225°, and *fluorenyl- $\alpha$ -naphthylamine*, flocks of pink needles, m. p. 172°, were also prepared.

Secondary fluorenylamines may be obtained also by reduction of the *N*-substituted ketimines of fluorenone (cf. Reddelien, A., 1910, i, 746) in alcoholic ammonia solution, this being sometimes preferable to the above method. Thus, 2-amino-9-chlorofluorene reacts in a complex manner with aniline, whereas reduction of the *anil* (orange needles, m. p. 141°) formed by condensation of 2-nitrofluorenone with aniline yields 2-aminofluorenylaniline, pale yellow, felted needles, m. p. 151—152°.

T. H. P.

**Catalytic Dehydration of Phenol-Alcohol Systems.** E. BRINER, W. PLÜSS, and H. PAILLARD (*Helv. Chim. Acta*, 1924, 7, 1046—1056).—When a mixture of phenol and methyl alcohol is passed over thorium oxide at 400—440°, some anisole is formed, but when the catalyst is aluminium oxide an oily product is obtained containing no anisole but a solid compound, now identified as hexamethylbenzene (cf. A., 1924, i, 503). Neither aluminium nor thorium oxide has any noteworthy effect on phenol alone at 415—420°, only a little diphenyl ether being formed, but when methyl alcohol alone is passed over aluminium oxide at the same temperature much dimethylether (yield, 40%) is produced, together with carbon monoxide and hydrogen. The gaseous products here are accompanied by traces only of formaldehyde, and indeed this compound is broken up under the conditions of the experiment. The production of hexamethylbenzene is thus evidently due to simultaneous dehydration and dehydrogenation and appears to take place according to the equation  $Ph \cdot OH + 7Me \cdot OH = C_6Me_6 + 7H_2O + CO + H_2$ . Actually, if an excess of methyl alcohol is used, the yield of hexamethylbenzene approaches 50% of the theoretical (calculated on the phenol introduced) and, in agreement with the equation proposed, much less hydrogen is obtained than would be yielded by the methyl alcohol used. The compound, precipitated by methyl alcohol and washed with ethyl alcohol, is nearly pure (m. p. 161°; corrected m. p. of a purified specimen, 163.5—164°). It is curious at first sight that only the hexamethyl derivative is produced, but a consideration of the thermochemistry of the possible reactions shows that in that which takes place the greatest amount of heat is generated. Remarkably enough, however, benzene itself will not react with methyl alcohol under the same conditions, although in this case even more heat should be set free.

Other phenols afford hexamethylbenzene when similarly treated; thus, *o*-cresol gives it in 24.7% yield (on the *o*-cresol introduced); *m*-cresol, 3.6%; *p*-cresol, 23.3%; 1:4:5-xylene, 54%; 1:3:5-xylene, 55.6%; resorcinol, 43%; and pyrogallol 1.2% (with much

tar).  $\beta$ -Naphthol yields a new *tetramethylnaphthalene*, m. p. 104—105° (*picrate*, m. p. 184—185°).

A mixture of phenol and ethyl alcohol yields, when passed over hot alumina, a complex mixture, consisting most probably of ethylated phenetoles. There is no formation of tetraethylbenzene, but this is not surprising, as ethyl alcohol itself yields diethyl ether and ethylene, and no hydrogen.

W. A. S.

**Action of Sodium Hypochlorite on *p*-Cresoldisulphonic Acid.** F. RASCHIG (*Schwefel- u. Stickstoff-studien*, 1924, 250—254; from *Chem. Zentr.*, 1924, ii, 1081).—*p*-Cresol-3: 5-disulphonic acid with sodium hypochlorite yields first a hypochlorous ester; the chlorine then becomes detached from the oxygen atom and enters the ring, 4 or 5 mols. of hypochlorite reacting with 1 mol. of disulphonic acid. With 4 mols. of hypochlorite the benzene ring is opened and a substance is produced in which the strong single linking between carbon and sulphur is converted into a weak double linking. The substance, which has the character of a hydroxy-acid and gives an odour of caramel on concentrating its solutions, appears to belong to the sugar group; it may have the

formula  $\text{CO}\cdot\text{C}(\text{SO}_3)\cdot\text{CH}(\text{OH})\cdot\text{CMe}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{SO}_3$ .

R. B.

**Preparation of *o*-Ethylthiophenol by Hydrogenation of Thionaphthen.** R. FRICKE and G. SPILKER (*Ber.*, 1925, 58, [B], 24—26).—Thionaphthen is converted by sodium and boiling ethyl alcohol mainly into *o*-ethylthiophenol, b. p. 210°/760 mm.,  $d^{15}_4$  1.037; the *mercuric* salt, m. p. 135°, *lead* salt, m. p. 147.5°, and the *methyl* ether, b. p. 229—230°/760 mm., are described. H. W.

**Action of Aromatic Alcohols on Aromatic Compounds in the Presence of Aluminium Chloride. III. Condensation of Benzyl Alcohol and Phenol.** R. C. HUSTON (*J. Amer. Chem. Soc.*, 1924, 46, 2775—2779; cf. A., 1917, i, 19; 1918, i, 299).—*p*-Benzylphenol (*p*-hydroxydiphenylmethane) and its methyl and ethyl ethers are readily obtained by the action of benzyl alcohol on phenol or the appropriate phenolic ether in the presence of aluminium chloride (0.5 mol.) at 20—30° in light petroleum, the yields varying from 43 to 57% of theory. In the condensation with phenol, the light petroleum may be replaced by carbon disulphide, but in the absence of any solvent, the reaction starts more slowly and the temperature rises to 65°, and lower yields are obtained. The use of 1 mol. of aluminium chloride does not increase the yield and in all cases a fraction, b. p. 180—230°/4 mm., was isolated from the crude product, which is probably a mixture of dibenzylphenols. Benzyl chloride itself with phenol and aluminium chloride at 35° gives a 36% yield of *p*-hydroxydiphenylmethane, but at this temperature no benzyl chloride was obtained by the action of aluminium chloride on benzyl alcohol, 96% of the alcohol being recovered unchanged. Above 40°, vigorous reaction set in and a complex mixture was obtained from which 25—30% of the theoretical amount of benzyl chloride was isolated.



No diphenyl ether was obtained by the action of aluminium chloride on phenol in light petroleum below 30° (cf. Merz and Weith, A., 1881, 264). *p*-Methoxydiphenylmethane has b. p. 133—135°/4 mm. (cf. Paterno, *J.C.S.*, 1872, 25, 702); the ethyl ether has b. p. 171—173°/12 mm. (cf. Klages and Allendorff, A., 1898, i, 433). R. B.

#### Action of Hydrobromic Acid on some Tertiary Alcohols.

P. RAMART (*Compt. rend.*, 1924, 179, 634—636; cf. Couturier, A., 1893, i, 244; Tissier, A., 1893, i, 542; Richard, A., 1911, i, 6).—Hydrobromic acid in glacial acetic acid acts on alcohols of the formula  $CPhAr(OH) \cdot CR_1R_2R_3$  as a dehydrating agent with formation of an unsaturated hydrocarbon in which one of the three alkyl groups has migrated to the other carbon atom. The hypothesis is put forward that the acid and alcohol yield the corresponding bromide with elimination of water, the bromine atom and an alkyl group then exchanging positions yielding an unstable bromide which loses a molecule of hydrogen bromide. H. J. E.

#### Order of Addition to Cyclic Double Linkings. II. S. S.

NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1924, 55, 47—69).—The existence of both *cis*- and *trans*-addition to aliphatic and alicyclic double bonds is discussed at length and it is suggested that the phenomenon of *trans*-addition, although incompatible with classical stereochemistry, is readily explained in the light of Werner's views. It is shown that *trans*-cyclohexanediols are obtained by the action of permanganate on the corresponding unsaturated hydrocarbons; the isomeric *cis*-compounds are prepared from the oxides obtained by the action of benzoyl peroxide on the unsaturated hydrocarbons (cf. A., 1923, i, 1081, 1082). G. A. R. K.

#### Reactivity of Organic Substances in Complex Combination.

H. REIHLEN, R. ILLIG, and R. WITTIG.—(See i, 232.)

#### Action of Grignard Reagents on Amino-acids. I. K.

THOMAS and F. BETZIECHE (*Z. physiol. Chem.*, 1924, 140, 244—260).—A number of amino-alcohols have been prepared by the action of Grignard reagents on esters of amino-acids. The yields obtained when the free esters were employed were practically identical with those obtained from the ester hydrochlorides; hence the direct employment of the more accessible hydrochlorides appears to be of advantage. In those cases where the amino-alcohols were difficult to separate from the product owing to their great solubility in water, they were not isolated in the free state, but were converted into benzoyl derivatives by benzylation of the aqueous solutions. The following new compounds were prepared:  $\beta$ -benz-amido- $\alpha\alpha$ -diphenylethan- $\alpha$ -ol, m. p. 182°;  $\delta$ -benz-amido- $\gamma$ -ethylbutan- $\gamma$ -ol, m. p. 104°;  $\gamma$ -amino- $\alpha$ -phenyl- $\beta$ -benzylpropan- $\beta$ -ol, m. p. 115—116°;  $\beta$ -amino- $\alpha\alpha$ -diphenylpropan- $\alpha$ -ol, m. p. 104—105° (hydrochloride, m. p. 210—215°);  $\delta$ -benz-amido- $\gamma$ -ethylpentan- $\gamma$ -ol, m. p. 104—105°;  $\delta$ -amino- $\delta$ -phenyl- $\gamma$ -ethylbutan- $\gamma$ -ol, m. p. 93—95° [hydrochloride, m. p. 214—215°; N-benzoyl derivative, m. p. 173° (corr.)];  $\gamma$ -amino- $\alpha\gamma$ -diphenyl- $\beta$ -benzylpropan- $\beta$ -ol, m. p. 125—126°;  $\beta$ -amino- $\alpha\alpha\gamma$ -triphenylpropan- $\alpha$ -ol hydrochloride, m. p. 227—228°;

$\gamma$ -amino- $\alpha\delta$ -diphenyl- $\beta$ -benzylbutan- $\beta$ -ol, m. p. 129—130°;  $\delta$ -amino- $\epsilon$ -phenyl- $\gamma$ -ethylpentan- $\gamma$ -ol, b. p. 145—148°/16—17 mm. (N-benzoyl derivative, m. p. 135°).  
E. S.

**Action of Grignard Reagents on Amino-acids. III. Deamination of Tertiary Amino-alcohols by Acetic Acid and Sodium Nitrite : Conversion into Carbonyl Compounds with Migration of Groups.** F. BETTZICHE (*Z. physiol. Chem.*, 1924, 140, 273—278).—A study of the action of nitrous acid on amino-alcohols has led to an interpretation of this reaction which is identical with that advanced by McKenzie and Roger (A., 1924, i, 650). Nitrous acid converts  $\beta$ -amino- $\alpha\alpha\beta$ -triphenylethan- $\alpha$ -ol into diphenylacetophenone,  $\beta$ -amino- $\alpha\alpha$ -diphenylethan- $\alpha$ -ol into deoxybenzoin,  $\beta$ -amino- $\alpha\alpha$ -diphenylpropan- $\alpha$ -ol into methyldeoxybenzoin, and  $\beta$ -amino- $\alpha\alpha\gamma$ -triphenylpropan- $\alpha$ -ol into benzyldeoxybenzoin.  
E. S.

**Action of Grignard Reagents on Amino-acids. IV. Acyl-amino-acids.** K. THOMAS and F. BETTZICHE (*Z. physiol. Chem.*, 1924, 140, 279—298).—When the benzoyl derivatives of amino-acid esters are treated with Grignard reagents (magnesium ethyl bromide, magnesium phenyl bromide) the benzamido groups are left intact and the esters are converted into benzoyl derivatives of the corresponding amino-alcohols. In some cases, the same products are obtained from the benzoyl derivatives of the acid chlorides, but the yields are considerably smaller. The hydrochloride of ethyl glycylglycine similarly reacts with magnesium phenyl bromide to form  $\beta$ -glycylamino- $\alpha\alpha$ -diphenylethan- $\alpha$ -ol. When hydrolysed with alkali, the benzoyl derivatives of the amino-alcohols yield benzoic acid and the free amino-alcohol; with acid hydrolysis, the latter is further decomposed with the elimination of ammonia (cf. preceding abstracts). The hydrolysis of  $\beta$ -glycylamino- $\alpha\alpha$ -diphenylethan- $\alpha$ -ol takes place in similar fashion. Acid hydrolysis of  $\delta$ -benzamido- $\gamma$ -ethylbutan- $\gamma$ -ol yields as main product a substance which retains the benzoyl group but has not yet been identified.  
E. S.

**Dimethyl and Diethyl Ethers of Phenolsulphonephthalein and of o-Cresolsulphonephthalein.** W. R. ORNDORFF and C. V. SHAPIRO (*J. Amer. Chem. Soc.*, 1924, 46, 2856—2860).—The colourless ethers obtained by the action of methyl and ethyl alcohols on phenolsulphonephthalein in the presence of hydrochloric or sulphuric acid, and previously regarded as monoalkyl ethers (A., 1923, i, 340), are now shown to be dialkyl ethers. Phenolsulphonephthalein dimethyl ether on heating at 180° in dry carbon dioxide melts to a red liquid which does not absorb ammonia and is reconverted into the colourless ether on keeping in methyl alcohol. Dilute sodium hydroxide hydrolyses it to phenolsulphonephthalein. The diethyl ether, m. p. 124—126°, does not absorb ammonia or hydrogen chloride, and on heating to 155° it melts to a red liquid which likewise does not absorb ammonia and in methyl alcohol undergoes alcoholysis to the colourless dimethyl ether. The colourless diethyl ether is hydro-

lysed by boiling with water. *o*-Cresolsulphonephthalein dimethyl ether, m. p.  $167^{\circ}$ , is converted on heating at  $190^{\circ}$  into a red liquid, which absorbs 1—2 mols. of hydrogen chloride, whereas the colourless ether absorbs neither hydrogen chloride nor ammonia. Hydrolysis in neutral, acid, or alkaline solution yields the original sulphonephthalein. The diethyl ether, m. p.  $131$ — $132^{\circ}$ , was obtained in the presence of sulphuric acid. Acid hydrolysis regenerates the original phthalein, but towards alkaline hydrolysis the diethyl ether is more stable. Heating at  $140^{\circ}$  in carbon dioxide gives a red liquid, which absorbs 2 mols. of hydrogen chloride and 3 mols. of ammonia; on keeping over potassium hydroxide and sulphuric acid, these products revert to the coloured diethyl ether. A quinonoid structure is attributed to the coloured ethers; the colourless forms are regarded as possessing the lactonic structure.

R. B.

**Naphthenic Acids. IV. Naphthenic Acids derived from Kubiki Kerosene Distillates.** Y. TANAKA and S. NAGAI (*J. Fac. Eng. Tokyo*, 1924, **16**, 1—10).—Substantially the same results as have already been published (cf. A., 1924, i, 168). W. A. S.

**Naphthenic Acids. V. Naphthenic Acids derived from Niitsu Petroleum.** Y. TANAKA, S. NAGAI, and S. ISHIDA (*J. Fac. Eng. Tokyo*, 1924, **16**, 11—18).—The crude acid mixture obtained by acidifying a waste lye from the refining of the "neutral distillate" from Niitsu petroleum contains 15.1% of organic acids. The isolated naphthenic acid mixture has  $d_4^{15}$  0.9937,  $n_D^{15}$  1.4917, acid value 223.9, and about 85% distils between  $180^{\circ}$  and  $230^{\circ}/8.9$ — $9.0$  mm., all the fractions having specific gravities greater than 0.99. The mixed methyl esters have  $d_4^{15}$  0.9631,  $n_D^{15}$  1.4792, and 73% distils between  $150^{\circ}$  and  $200^{\circ}/8.9$ — $9.0$  mm.; the fractions of b. p. above  $180^{\circ}$  have lower specific gravities than the earlier ones. The pure acids obtained by hydrolysing the methyl esters have  $d_4^{15}$  0.9902,  $n_D^{15}$  1.4887, acid value 226.1; 80% of this mixture distils between  $190^{\circ}$  and  $230^{\circ}/8.9$ — $9.0$  mm. The acids closely resemble those obtained from Kurokawa oil (cf. A., 1923, i, 464). W. A. S.

**Terpenes, Phytosterols, and Resins. III. Pyrogenic Decomposition of Abietic Acid.** K. A. VESTERBERG and E. BORGE (*Annalen*, 1924, **440**, 305—310).—Distillation of American colophony (abietic acid) (1 kg.) with pumice (50 g.) impregnated with nickel (5 g.) yielded a gas containing methane and carbon monoxide, with smaller quantities of heavier hydrocarbons, and an oil, b. p.  $300$ — $400^{\circ}$ , the main reaction being probably  $C_{20}H_{30}O_2 = C_{18}H_{26} + CH_4 + CO_2$ . The main fraction of the oil (b. p.  $335$ — $375^{\circ}$ ) afforded, on repeated fractionation under reduced pressure, retene, m. p.  $98^{\circ}$ , an octahydroretene,  $C_{18}H_{26}$ , b. p.  $323^{\circ}/758$  mm.,  $142$ — $143^{\circ}/1$  mm.,  $d_4^{20}$  0.9686,  $n_D^{20}$  1.5370,  $[\alpha]_D^{20}$   $-48.43^{\circ}$  in benzene (cf. Virtanen, A., 1920, i, 832) and a hydrocarbon, probably  $C_{18}H_{24}$ . It is concluded that the "diterebenthyl" present in resin oil is probably an octahydroretene (cf. Bruhn, *Chem. Zentr.*, 1900, **24**, 1105; Schultze, A., 1908, i, 356) and that the product of the action of

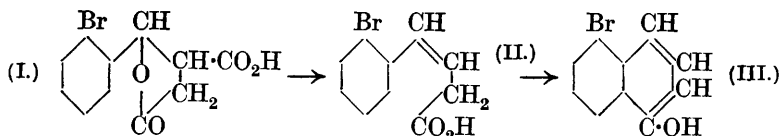
hydriodic acid on *d*-pimaric acid (Vesterberg, A., 1886, i, 1038) is probably a dodecahydrotetene, whilst the product similarly obtained from sandarak resin (Henry, T., 1904, 85, 1238) is probably an octahydrotetene.  
F. G. W.

**Nature of the Colophony extracted from the Firs of Bucovina.** O. CZERNY (*Bul. Soc. Chim. România*, 1924, 6, 94—96).—This colophony (cf. A., 1924, i, 659) contains 88.5% of acids and 4.6% of unsaponifiable residue, the deficit, 6.9%, being, according to Fahrion, hydroxy-acids;  $\alpha$ -,  $\beta$ -, and  $\gamma$ -abietic, sylvic, and  $\gamma$ -pinic acids are present.  
T. H. P.

**Two Photodimerides of  $\alpha$ -Phenylcinnamylideneacetone.** H. STOBBE and F. KUHRMANN (*Ber.*, 1925, 58, [B], 85—87).—The action of sunlight on  $\alpha$ -phenylcinnamylideneacetone dissolved in benzene or chloroform in the presence or absence of iodine yields two dimerides, *A* and *B* (m. p. 197° and 215°), the former of which has been shown to be 1:3-diphenylcyclobutane-2:4-di-*atrop*onitrile,  $\text{CN}\cdot\text{CPh}\cdot\text{CH}\cdot\text{CH}\begin{smallmatrix} \text{CHPh} \\ \text{CHPh} \end{smallmatrix}\text{CH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CN}$  (Stobbe and Barbaschinov, A., 1913, i, 178). It is found that the substance *A* is isomerised to *B* when warmed in the solid state or in glacial acetic acid solution, and that the latter compound is produced when the tetrabromide of *A* is dehalogenated with zinc dust and acetic acid. *B*, like *A*, is readily oxidised by cold permanganate to  $\alpha$ -truxillic acid and benzoyl cyanide and becomes depolymerised when gently heated; it does not, however, add bromine. The absorption curves of  $\alpha$ -phenylcinnamylideneacetone and the two dimerides are closely similar. It is suggested that the isomerism of *A* and *B* is of the *cis-trans* type, depending on a difference of location of the phenyl and cyano groups at one or both of the ethylenic linkings of the side chain.  
H. W.

**Naphthalene and the Centroid Structure.** R. C. FUSON (*J. Amer. Chem. Soc.*, 1924, 46, 2779—2788).—The centroid structure for naphthalene proposed by Huggins (A., 1922, i, 928, 997) requires the formation of peri-bridges in the naphthalene series between positions 1 and 5 and not between 1 and 8. Since the structures of 1:5- and 1:8-hydroxynaphthoic acid appear to rest on the assumption that naphtholactone is formed from the 1:8-isomeride, the synthesis of these two acids has been attempted by methods which would admit of no doubt as to their orientation. *o*-Bromophenylparaconic acid (I) on heating is converted by the Erdmann reaction (A., 1889, 150) into 5-bromo- $\alpha$ -naphthol (III), through the intermediate stage of *o*-bromo- $\beta$ -benzylidenepropionic acid (II). On methylation, the 5-bromo- $\alpha$ -naphthol is converted into 1:5-bromomethoxynaphthalene, from which 1:5-methoxynaphthoic acid is obtained by the Grignard reaction and found to be identical with the product obtained by methylating 1:5-hydroxynaphthoic acid. Consequently the accepted structures for 1:5- and 1:8-hydroxynaphthoic acids are correct, and the peri-bridge in naphtho-

lactone involves the 1:8-positions. The centroid structure for naphthalene is accordingly untenable.



*o*-Bromobenzaldehyde and succinic anhydride in the presence of anhydrous sodium acetate at 120–140° give in 50% yield *o*-bromophenylparaconic acid, m. p. 133–135°, which on heating at 250–300° yields 5-bromo- $\alpha$ -naphthol, m. p. 137°, identical with the product obtained by diazotising 5-bromo- $\alpha$ -naphthylamine hydrochloride and hydrolysing the diazonium sulphate with 10% sulphuric acid. Methyl sulphate converts the bromonaphthol into 1:5-bromomethoxynaphthalene, m. p. 67–68°, which with magnesium and ether yields a Grignard compound decomposed by carbon dioxide to give 5-methoxy- $\alpha$ -naphthoic acid, slightly yellow plates, m. p. 227–228.5°. The same compound was obtained by methylation of 1:5-hydroxynaphthoic acid, m. p. 231.5–233° (cf. Royle and Schedler, T., 1923, **123**, 1641) with methyl sulphate. R. B.

[Benzilic Acid Transformation.] A. SCHÖNBERG (*Ber.*, 1925, **58**, [B], 235; cf. A., 1923, i, 928; 1924, i, 1195).—A reply to Scheuing (this vol., i, 44). H. W.

**Formation of Camphor-sec.-tert.-nitrilic Chloride and Chlorocamphor-sec.-tert.-nitrilic Chloride from Camphorimide by Means of Phosphorus Pentachloride.** J. BREDT and A. IVANOV (*Ber.*, 1925, **58**, [B], 56–62).—Camphorimide is converted by phosphorus pentachloride in the presence of light petroleum at 110° mainly into camphor-sec.-tert.-nitrilic chloride,  $\text{CH}_2\text{—CH(CN)} > \text{CMe}_2$ , m. p. 92°, which is hydrolysed in cold alkaline solution to camphor-sec.-tert.-nitrilic acid, m. p. 151–152°. The chloride can also be prepared from the acid by the action of phosphorus pentachloride in the presence of octane at 0°. It is converted by ammonia in ethereal solution into the corresponding amide, m. p. 129–130° (monohydrate, m. p. 89–90°), and by aniline into the anilide, m. p. 200–201°. When heated with phosphorus pentachloride at 125°, it yields chlorocamphor-sec.-tert.-nitrilic chloride,  $\text{CH}_2\text{—CCl(CN)} > \text{CMe}_2$ , b. p. 152–153°/14 mm., which is also obtained when camphorimide is heated with an excess of phosphorus pentachloride in a sealed tube at 125°; it is transformed by warm, concentrated hydrochloric acid into chlorocamphorimide, m. p. 293° (decomp.). The product obtained by Mameli-Mannessier (A., 1914, i, 1127) by the action of phosphorus pentachloride on camphorimide is a mixture of camphor- and chlorocamphor-sec.-tert.-nitrilic chlorides. H. W.

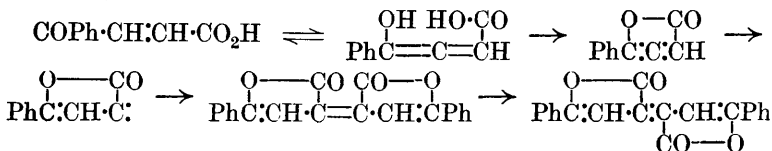
**Camphor-sec.-tert.-nitrilic and Chlorocamphor-sec.-tert.-nitrilic Acids.** J. BREDT (*Ber.*, 1925, 58, [B], 62—63; cf. Scheiber and Knothe, A., 1912, i, 542).—Chlorocamphor-sec.-tert.-nitrilic acid is converted above 180° into a mixture of camphanonitrile and chlorocamphorimide (cf. Bredt, Linck, and de Sousa, A., 1912, i, 411).  
H. W.

**Influence of Constitutional Variation on the Absorption and Stability to Hydrogen Ions of certain Halogenated Derivatives of Fluorescein.** W. C. HOLMES (*J. Amer. Chem. Soc.*, 1924, 46, 2770—2775).—The absorption maxima in dilute, slightly alkaline, aqueous, and alcoholic solutions of the dipotassium salts of fluorescein and a number of its halogen derivatives have been determined, using a Hilger wave-length spectrometer and a Nutting photometer. The nature of the halogen atom substituted within the phthalic anhydride residue exerts a definite influence on the displacement of the absorption maxima, but to a smaller extent than in the case of substitution in the resorcinol residues. The influence of substitution in the resorcinol nucleus is not constant under all conditions, but is modified by substitution in the phthalic anhydride residue, the effect being greater in fluoresceins thus substituted than in fluorescein itself. Moir's factors for the calculation of colour (A., 1923, ii, 48, 108) are therefore inadequate for accurate results. Substitution in the 1 and 8 (*h* and *i*) positions in the resorcinol residues is practically without effect on the absorption, and the hypsochromic effect predicted by Moir's factors is not observed, decaiodofluorescein having an absorption maximum of 549.5  $\mu\mu$ . Substitution within the resorcinol residues increases the stability of the dyes in aqueous solution towards hydrogen ions, whilst substitution in the phthalic acid residue produces the opposite result. The stability of the dyes towards acids is increased by the replacement of iodine by bromine or of bromine by chlorine.

R. B.

**Unsaturated Ketonic Acids. I. Constitution of the so-called "Pechmann Dyes" and the Mechanism of their Formation from  $\beta$ -Benzoylacrylic Acid.** M. T. BOGERT and J. J. RITTER (*J. Amer. Chem. Soc.*, 1924, 46, 2871—2878).—The yellow product obtained by Pechmann (A., 1882, 1074) by the action of alcoholic potassium hydroxide on the "Pechmann dye" from  $\beta$ -benzoylacrylic acid is a mixture of the bright yellow diphenacylfumaric acid,  $\text{COPh}\cdot\text{CH}_2\cdot\overset{\text{CO}_2\text{H}}{\underset{\text{CO}_2\text{H}}{\text{C}}}\cdot\text{CO}_2\text{H}$ , with colourless diphenacylmaleic acid,  $\text{COPh}\cdot\text{CH}_2\cdot\overset{\text{CO}_2\text{H}}{\underset{\text{CO}_2\text{H}}{\text{C}}}\cdot\text{CO}_2\text{H}$ , and the red substance obtained on dehydration with acetic anhydride is diphenacylmaleodilactone,  $\text{PhC}\cdot\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{CH}=\text{C}\cdot\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{CH}\cdot\text{CPh}$ , identical with the product obtained by Kugel by the oxidation of phenylcrotonolactone with ferric chloride (A., 1898, i, 198). Dehydration of diphenacylfumaric acid with glacial acetic acid (cf. Kugel, *loc. cit.*) or acetic anhydride yields the

dilactide,  $\text{PhC}:\text{CH}:\text{C}:\text{CO}\cdot\text{O}$   
 $\text{O}\cdot\text{CO}:\text{C}:\text{CH}:\text{CPh}$ , also obtained by Kugel. The *cis*-dilactone is the first product of the action of acetic anhydride on  $\beta$ -benzoylacrylic acid, longer heating yielding the *trans*-isomeride, which is the Pechmann dye. In view of these relations, the formation of the latter substance from  $\beta$ -benzoylacrylic acid is represented by the scheme :



the colour of the two dilactones being attributed to the presence of the indigo chromophore  $-\text{CO}:\text{C}:\text{C}:\text{CO}-$  in conjunction with unsaturated cyclic systems. In view of the appearance of symmetrical structure by the change from keto to enolic form, this view is not inconsistent with the fumaroid structure advocated for benzoylacrylic acid in its ketonic form (Rice, A., 1923, i, 218; 1924, i, 287) and it is supported by the formation of phenyl- $\gamma$ -crotonolactone,

$\text{PhC}:\text{CH}:\text{CH}_2$ , and not of dihydronaphthaquinone ( $\rightleftharpoons$  1:4-dihydroxynaphthalene) by dehydration of  $\beta$ -benzoylpropionic acid, and by the failure of  $\beta$ -benzoyl- $\alpha$ -methylacrylic acid to give a Pechmann dye. Diphenacylfumaric and diphenacylmaleic acids give blood-red solutions in cold dilute potassium hydroxide, the colour changing to pale yellow on warming owing to reconversion into the ketonic form. The two dilactones are converted into the corresponding acids by the action of alcoholic potassium hydroxide, the reverse change taking place with diphenacylmaleic acid alone on heating with acetic anhydride.  $\beta$ -( $\alpha$ -Naphthoyl)acrylic acid and acetic anhydride give *di- $\alpha$ -naphthacylfumarodilactone*, black needles with brilliant blue lustre, melting with decomposition at high temperatures.  $\beta$ -( $\beta$ -Naphthoyl)acrylic acid similarly yields *di- $\beta$ -naphthacylfumarodilactone*, dark red, glistening needles. R. B.

**Behaviour of certain Phenylhydrazones dissolved in Organic Solvents.** G. RASTELLI (*Gazzetta*, 1924, 54, 964—972).—The violet coloration appearing when benzaldehydephenylhydrazone is dissolved in chloroform (cf. Minunni and Rap, A., 1897, i, 40) is shown by a number of other aldehyde (but not ketone) hydrazones in this and other solvents, bromoform being the most effective in this respect. The appearance of the colour is not affected by light, but is accelerated by heating and prevented by the presence of moisture; oxygen seems to exert a positive catalytic effect, but the coloration is not due directly to oxidation products.

Cryoscopic measurements show that the molecular weight of benzaldehydephenylhydrazone in bromoform solution increases from about the normal value to about twice this value as the

violet colour develops. Further, with mixtures in varying proportions of chloroform (or bromoform) and the phenylhydrazone in benzene solution, the molecular freezing-point depression attains a minimum value when the two solutes are present in equimolecular proportions.

The conclusion is reached that the violet coloration is due to the formation of an unstable, additive compound containing 2 mols. of the hydrazone and 2 mols. of the solvent. The violet solution formed when a phenylchloroform solution of benzaldehydephenylhydrazone is cautiously heated deposits a compound, violet crystals, m. p. 65—67°, which very readily decomposes, containing 6.43% of nitrogen, the proportion required for an additive compound of the solvent (1 mol.) and solute (1 mol.) being 7.10%. T. H. P.

**Catalytic Reduction of Aromatic Aldehydes.** K. W. ROSENMUND and G. JORDAN (*Ber.*, 1925, **58**, [B], 160—162).—Hydrogenation of benzaldehyde, anisaldehyde, and *o*-chlorobenzaldehyde in glacial acetic acid solution in the presence of palladised barium sulphate with one molecular proportion of hydrogen yields a mixture of approximately equal parts of unchanged aldehyde, corresponding alcohol, and hydrocarbon, since aldehyde and alcohol are reduced at nearly equal rates. Addition of quinoline (cf. Rosenmund and Heise, A., 1921, ii, 631) diminishes the velocity of the second action to such an extent that the alcohols can be obtained in 62—75% yield. In the cases of piperonal and vanillin, the rates of the two reactions are sufficiently different to allow the preparation of either alcohol or hydrocarbon by the use of one or two molecular proportions of hydrogen; addition of quinoline is unnecessary.

H. W.

**Action of Grignard Reagents on Amino-acids. II. Conversion of  $\beta$ -Amino- $\alpha\alpha$ -diphenylethan- $\alpha$ -ol into Diphenylacetaldehyde.** K. THOMAS and F. BETZLECHE (*Z. physiol. Chem.*, 1924, **140**, 261—272).—Some examples of the conversion of amino-alcohols into carbonyl compounds by elimination of ammonia have been studied, but the evidence so far obtained is insufficient to permit any conclusion to be reached regarding the intermediate stage of the reaction. A migration of radicals similar to that which occurs during the analogous decomposition of glycols (Meerwein, A., 1920, i, 2) has not been observed with any of the amino-alcohols studied.

$\beta$ -Amino- $\alpha\alpha$ -diphenylethan- $\alpha$ -ol is converted into diphenylacetaldehyde by the action of boiling concentrated hydrochloric acid, but is unattacked by cold concentrated sulphuric acid. The similar conversion of  $\beta$ -amino- $\alpha\alpha$ -diphenylpropan- $\alpha$ -ol into diphenylacetone and of  $\beta$ -amino- $\alpha\alpha\beta$ -triphenylethan- $\alpha$ -ol into diphenylacetophenone is brought about by both reagents.  $\beta$ -Amino- $\alpha\gamma$ -triphenylpropan- $\alpha$ -ol yields triphenylacetone on treatment with cold concentrated sulphuric acid. Nitric acid has a more drastic action on the amino-alcohols; boiling sodium hydroxide has little, if any, action.

E. S.



**Chlorination of 1-Methylcyclohexan-4-one.** M. GODCHOT and P. BEDOS (*Compt. rend.*, 1925, **180**, 295—297).—Direct chlorination of 1-methylcyclohexan-4-one gives only a poor yield of 3-chloro-1-methylcyclohexan-4-one (cf. Kötze and Steinhorst, A., 1911, i, 210), together with considerable proportions of polychloro compounds; the highly stable *dichloro*-1-methylcyclohexan-4-one,  $C_7H_{10}OCl_2$ , m. p. 98—99°, was isolated. Chlorination by means of monochlorocarbamide (cf. Detœuf, A., 1922, i, 236, 327) yields 75% of 3-chloro-1-methylcyclohexan-4-one, which, when distilled under diminished pressure, separates into two isomerides, probably of *cis-cis*- and *cis-trans*-configurations: (1) b. p. 80—82°/12 mm.,  $d^{25}_4$  1.0994,  $n^{25}_D$  1.4705, and (2) b. p. 110—112°/12 mm.,  $d^{25}_4$  1.0749,  $n^{25}_D$  1.4649. At the ordinary temperature, each isomeride gradually undergoes partial transformation into the other, the form with the higher boiling point always predominating in the final mixture. This isomerisation doubtless takes place with intermediate formation of the enolic compound, the ease with which the latter arises being due to the presence in the molecule of a chlorine atom in the ortho position to the carbonyl group. Chlorocyclohexanone also forms an enolic modification spontaneously. T. H. P.

**Stereochemistry of Dicyclic Ring-systems. I. Decahydronaphthalene and its Derivatives.** W. HÜCKEL (*Annalen*, 1925, **441**, 1—48; cf. A., 1924, i, 31).—A decision is sought as to the planar or non-planar configuration of the cyclohexane ring (cf. Ingold, T., 1915, **107**, 1080; Sachse, A., 1890, 1386; Mohr, *ibid.*, 1919, ii, 229; 1922, i, 243; Böeseken, *ibid.*, 1924, i, 156; Eisenlohr and Polenske, *ibid.*, 1924, i, 1291), especially when combined with other rings. The existence of *cis*- and *trans*-forms of decahydronaphthalene (decalin) is placed beyond doubt.

*cis*- $\beta$ -Decalone (2-ketodecahydronaphthalene), synthesised by distillation of *cis*-cyclohexane-1-acetic-2-propionic acid (m. p. 109—110°; diethyl ester, b. p. 183°/20 mm.; *dianilide*, m. p. 163°) with acetic anhydride, has m. p. 109—110°, b. p. 128°/26 mm.,  $d^{20}_4$  1.0038,  $n^{20}_D$  1.49265 [*semicarbazone*, m. p. 182—183° (decomp.); *oxime*, b. p. 161—165°/16 mm.]. The same product obtained by oxidation of *cis*- $\beta$ -decalol (decahydro- $\beta$ -naphthol) has m. p. —14°. On reduction, the ketone gives *cis*- $\beta$ -decalol, m. p. 105°, which also results from the hydrogenation of *ar*- $\beta$ -tetralol by Willstätter's, Skita's, or Ipatiev's method, or of *ac*- $\beta$ -tetralol by Willstätter's method. *cis*- $\beta$ -Decalol (*phenylurethane*, m. p. 134°; *benzoate*, m. p. 57—58°) is practically odourless. *cis*- $\beta$ -Decaloneoxime is reduced by Skita's method or by sodium and alcohol to *cis*- $\beta$ -decalylamine (decahydro- $\beta$ -naphthylamine) (*acetyl* compound, m. p. 154—155°).

Hydrogenation of *ac*- $\beta$ -tetralol in the presence of nickel at 150—170° gives a liquid decalol of definite odour, from which an impure *cis*- $\beta$ -decalol, m. p. about 100°, is deposited on long standing. Pure *trans*- $\beta$ -decalol, m. p. 75°, is best obtained by reducing technical decalone with sodium and alcohol, the solid portion of the product being many times recrystallised from light petroleum,

in which the *cis*-isomeride is less soluble. Oxidation gives *trans*- $\beta$ -decalone, m. p. 6°, b. p. 241°/755 mm. or 126°/20 mm.,  $d_4^{15.7}$  0.9797,  $n_D^{19}$  1.48088, which has a faint odour, less sweet than that of the *cis*-compound. Technical decalone contains about 60% of *trans*- and 40% of *cis*-decalone. *trans*- $\beta$ -Decaloneoxime, m. p. 76°, is reduced in acetic acid by hydrogen and platinum black to *trans*- $\beta$ -decalylamine (acetyl compound, m. p. 128—129°).

[With E. BRINKMANN.]—In the  $\alpha$ - as in the  $\beta$ -series, catalytic hydrogenation of *ar*- and *ac*-tetralols leads only to one decalol, *cis*- $\alpha$ -decalol, m. p. 93° (*phenylurethane*, m. p. 118°), being obtained almost quantitatively from *ar*- $\alpha$ -tetralol, whilst *ac*- $\alpha$ -tetralol gives some 30% of *cis*-decalin. By oxidation of *cis*- $\alpha$ -decalol and purification of the resulting decalone *via* the semicarbazone with subsequent decomposition with oxalic acid, the product is impure *trans*- $\alpha$ -decalone, the solid portion of which, m. p. 33° (semicarbazone, m. p. 229—230°; oxime, m. p. 168°), is identical with Leroux's decalone (A., 1904, i, 236). If the ketone is isolated by means of its bisulphite compound, a pure *cis*- $\alpha$ -decalone, m. p. 2°, results. The *cis*-ketone is converted quantitatively into the *trans*-isomeride by long heating with oxalic or hydrochloric acid or with alcoholic sodium hydroxide, by distillation at ordinary pressure or after keeping several months. The oxime and the *benzylidene* compound (m. p. 91°) are *trans*-derivatives, as also is the *bis*- $\alpha$ -decalone,  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{C}(\text{OH})\text{---CH}\cdot\text{CH}_2\cdot\text{CH}_2$ , m. p. 151°, obtained from either *cis*- or *trans*- $\alpha$ -decalone by heating with sodium methoxide. Oxidation with nitric acid converts the decalones into *cis*- and *trans*-2-carboxycyclohexane-1-propionic acids respectively, m. p. 103° and 143°. The *trans*-acid is also obtained by the action of cold permanganate on *trans*- $\alpha$ -decalol. By oxidation with chromic acid or permanganate, the decalones both give  $\delta$ -ketosebacic acid, m. p. 116° [*semicarbazone*, m. p. 179—180° (decomp.)], which is reduced by Clemmensen's or Wolff's method to sebacic acid, m. p. 134° (dimethyl ester, m. p. 33°). *trans*- $\alpha$ -Decalol, m. p. 63°, b. p. 130°/28 mm., is obtained by alkaline reduction of *trans*- $\alpha$ -decalone, whilst reduction by Willstätter's method gives in addition a liquid decalol (*phenylurethane*, m. p. 134°). *trans*- $\alpha$ -Decalylamine (*decahydro- $\alpha$ -naphthylamine*), b. p. 128—129°/29 mm., from *trans*- $\alpha$ -decaloneoxime, has a much more unpleasant odour than  $\beta$ -decalylamine and more quickly absorbs carbon dioxide from the air. The benzoyl derivative (Leroux, m. p. 195°) is separable into two isomeric products, m. p. 194° and 112°. A pure acetyl compound, m. p. 127° (Leroux, 182°), is also described.

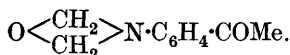
[With E. GOTH.]—Synthetic methods fail to give *cis*- $\alpha$ -decalone, but the *trans*-compound is synthesised as follows. *cis*-2-Carboxycyclohexyl-1-butyric acid, m. p. 92—94° (*monoanilide*, m. p. 125°; *dianilide*, m. p. 196—201°; *diethyl* ester, b. p. 185°/18 mm.,  $d_4^{20}$  1.0175,  $n_D^{20}$  1.45687), prepared by reduction by Skita's method of  $\gamma$ -o-carboxyphenylbutyric acid, is readily isomerised by hydrochloric acid at 200° to *trans*-2-carboxycyclohexyl-1-butyric acid,

m. p. 92—94° (mixed m. p. with *cis*-acid, 79—83°; *monoanilide*, m. p. 152°; *dianilide*, m. p. 210—213°; *diethyl ester*, b. p. 188°/21 mm.,  $d_4^{20}$  1.0118,  $n_D^{18}$  1.45537). Both the *cis*- and the *trans*-esters on treatment with sodium ethoxide give the same *ethyl trans- $\alpha$ -decalone- $\beta$ -carboxylate*, m. p. 76°, b. p. 171—172°/18 mm.,  $d_4^{25}$  1.0692,  $n_D^{18}$  1.49064, containing 40% of enol and 60% of ketone. This is also obtained by condensation of *cis*- or *trans- $\alpha$ -decalone* with ethyl oxalate at  $-10^\circ$  to  $-15^\circ$  (*ethyl  $\alpha$ -decaloneoxalate* forms with aniline a characteristic *pyrrolidone*,  $C_{24}H_{24}ON_2$ , m. p. 216—217°) and subsequent elimination of carbon monoxide at 160—180° in a vacuum (some *trans- $\alpha$ -decalone* is formed during distillation). The ethyl  *$\alpha$ -decalonecarboxylate* readily condenses with phenylhydrazine to form a *phenylpyrazolone*, m. p. 199—200°. Hydrolysis of the ester with methyl-alcoholic potassium hydroxide or, better, with sodium hexahydrophenoxide, gives *trans*-2-carboxy-*cyclohexyl*-1-butyric acid, whilst "ketonic hydrolysis" with 5% aqueous potassium hydroxide yields *trans- $\alpha$ -decalone*, m. p. 33°.

A detailed account is given of the work on *cis*- and *trans*-decalins briefly reported earlier (A., 1924, i, 31). Since hydrogenation of naphthalene or tetralin leads to a mixture of the two decalins, these are best prepared pure from *cis*- and *trans*-decalols (m. p. 105° and 75°) by oxidation to decalones and reduction by Clemmensen's method, or by dehydration to octalins and hydrogenation by Willstätter's method. The pure decalins differ by 8° in b. p. and are therefore separable by careful fractionation of technical decalin. *cis*-Decalin has m. p.  $-51^\circ$ , b. p. 193°,  $d_4^{20}$  0.893 to 0.898,  $n_D^{20}$  1.480 to 1.482, and is identical with Willstätter's decalin (A., 1924, i, 628). It is not converted into the *trans*-isomeride by passing it slowly with hydrogen over platinum black at 140—170°. *trans*-Decalin has m. p.  $-36^\circ$ , b. p. 185°,  $d_4^{20}$  0.8695 to 0.872,  $n_D^{20}$  1.4696 to 1.4713. C. H.

### Condensation of Formaldehyde with *p*-Aminoacetophenone.

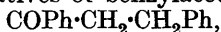
M. GRABOWSKA and S. WEIL (*Roczniki Farmacji*, 1924, 2, 130—133; from *Chem. Zentr.*, 1924, ii, 209).—When aqueous formaldehyde reacts with *p*-aminoacetophenone, a compound is obtained, m. p. 221°, probably



It evolves formaldehyde on being heated, leaving crystals, m. p. 194—195°, which, when heated with aqueous formaldehyde, give again the compound of m. p. 221°. G. W. R.

**Syntheses with Sodamide. XIII. Mono-, Di-, and Tri-allylacetophenones, Alkylallylacetophenones, and Allylisobutyrones.** A. HALLER, C. BAUER, and P. RAMART (*Ann. Chim.*, 1924, [x], 2, 269—281).—Allylacetophenone cannot be obtained by direct allylation of the sodium derivative of acetophenone, but the di- and tri-allylacetophenones and the alkylallylacetophenones are obtained by the action of allyl bromide or iodide on mono- or

di-allylacetophenone, or on alkylacetophenones in the presence of sodamide. Allyl derivatives of benzylacetophenone,



and of isobutyronone are similarly prepared.

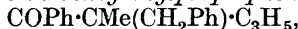
Allylacetophenone,  $\text{COPh}\cdot[\text{CH}_2]_2\cdot\text{CH}\cdot\text{CH}_2$ , obtained by Baeyer and Perkin's method (A., 1884, 63; T., 1885, 47, 242), has b. p. 128—130°/20 mm. *Diallylacetophenone*,  $\text{COPh}\cdot\text{CH}(\text{C}_3\text{H}_5)_2$ , b. p. 148—150°/18 mm.,  $d^{25}_D$  0.9745,  $n^{25}_D$  1.53023, on further treatment with allyl iodide yields *triallylacetophenone*,  $\text{COPh}\cdot\text{C}(\text{C}_3\text{H}_5)_3$ , b. p. 168—170°/18 mm.,  $d^{25}_D$  0.9815,  $n^{25}_D$  1.53659. Similarly, propiophenone with allyl iodide yields  $\alpha$ -allylpropiophenone,



b. p. 130—132°/16 mm.,  $d^{25}_D$  0.9759,  $n_D$  1.52447, which on further allylation gives  $\alpha\alpha$ -diallylpropiophenone,  $\text{COPh}\cdot\text{CMe}(\text{C}_3\text{H}_5)_2$ , b. p. 155—156°/14 mm., which does not yield an oxime, and is also obtained by the action of allyl iodide on propiophenone. Butyrophenone similarly yields  $\alpha$ -allylbutyrophenone,  $\text{COPh}\cdot\text{CHEt}\cdot\text{C}_3\text{H}_5$ , b. p. 138—140°/15 mm.,  $d$  0.9684,  $n_D$  1.52168 (oxime, liquid, b. p. 198°/15 mm.), together with a little  $\alpha\alpha$ -diallylbutyrophenone,  $\text{COPh}\cdot\text{CEt}(\text{C}_3\text{H}_5)_2$ , b. p. 160—162°/14 mm.,  $d^{25}_D$  0.9761,  $n_D$  1.52920, which yields no oxime.  $\alpha\alpha$ -Methylallylpropiophenone,



b. p. 255—256°/760 mm., 134—136°/16 mm.,  $d^{25}_D$  0.9682,  $n_D$  1.51856 (A., 1913, i, 485), yields no oxime but a crystalline hydrobromide, and on reduction with sodium and alcohol gives  $\alpha$ -phenyl- $\beta\beta$ -dimethyl- $\Delta$ -penten- $\alpha$ -ol, b. p. 133—134°/13 mm. (*phenylurethane*, m. p. 105—106°), together with  $\alpha$ -phenyl- $\beta\beta$ -dimethylpentan- $\alpha$ -ol, b. p. 141—142°/16 mm. (*phenylurethane*, m. p. 86°).  $\alpha\alpha$ -Methylallylbutyrophenone,  $\text{COPh}\cdot\text{CMeEt}\cdot\text{C}_3\text{H}_5$ , b. p. 140—142°/16 mm.,  $d^{25}_D$  0.9694,  $n_D$  1.51928, which yields no oxime, is obtained from  $\alpha$ -methylbutyrophenone or from  $\alpha$ -allylbutyrophenone.  $\alpha$ -Ethylallylbutyrophenone has b. p. 155—157°/14 mm.,  $d^{25}_D$  0.9705,  $n_D$  1.52194. Benzylpropiophenone, from propiophenone and benzyl chloride, similarly yields *benzylallylpropiophenone*,



b. p. 205—208°/17 mm., giving a crystalline bromine compound. *Benzylallylbutyrophenone*, similarly obtained, has b. p. 212—214°/20 mm.

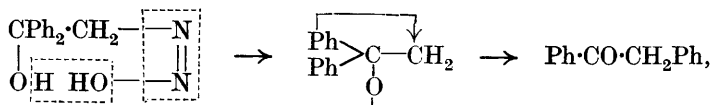
*iso*Butyronone and allyl iodide with sodamide in benzene yield a mixture of *allylisobutyronone*,  $\text{CMe}_2(\text{C}_3\text{H}_5)\cdot\text{CO}\cdot\text{CHMe}_2$ , b. p. 67.5—68.5°/14 mm., and *diallylisobutyronone*,  $[\text{CMe}_2(\text{C}_3\text{H}_5)]_2\text{CO}$ , b. p. 105—107°/13 mm., neither of which yields an oxime or a semicarbazone. The observed and calculated molecular refractions of the above substituted acetophenones show a remarkable concordance, whereas ethyl  $\alpha$ -benzoyl- $\Delta\gamma$ -pentenoate shows a pronounced exaltation.

R. B.

### Semipinacolic Deamination of certain Amino-alcohols.

A. ORÉKOV and M. ROGER (*Compt. rend.*, 1925, 180, 70—73).— $\beta$ -Hydroxy- $\beta\beta$ -diphenylethylamine,  $\text{CPh}_2(\text{OH})\cdot\text{CH}_2\cdot\text{NH}_2$ , when treated with nitrous acid, does not form diphenylethylene oxide,

$\overline{\text{CPh}_2 \cdot \text{CH}_2\text{O}}$ , as stated by Paal and Weidenkaff (A., 1906, i, 583). The product is stable towards acids, and its oxime, semicarbazone, and benzyl derivative are identical with those of deoxybenzoin. The change is represented by



and is an instance of semipinacolic deamination (cf. McKenzie and Roger, A., 1924, i, 650). It is pointed out that this reaction may be used to ascertain the migratory tendency of different radicals.  $\beta$ -Hydroxy- $\beta$ -phenyl- $\beta$ -anisylethylamine, when treated with nitrous acid, gives a crystalline substance, m. p. 98–99°, identified as *p*-methoxydeoxybenzoin (recently obtained by a different method), from which it is concluded that the anisyl has a greater migratory tendency than the phenyl radical, and that the formation of ketones of this type takes place without the intermediary formation of glycols or the corresponding oxides.

A. C.

#### Action of Nitric Acid on Derivatives of Benzophenone.

L. ELION (*Rec. trav. chim.*, 1925, **44**, 99–102).—The low stability towards nitric acid of 3 : 5-dibromo-4-aminobenzophenone (this vol., i, 44) as compared with 4 : 4'-tetramethyldiaminobenzophenone (cf. van Romburgh, A., 1888, 1196), and of 3 : 5-dibromo-4-aminobenzoic acid as compared with 3 : 5-dinitro-4-aminobenzoic acid (cf. A., 1923, i, 390), is attributed to the bromine atoms. This is confirmed by the fact that 3 : 5 : 3' : 5'-tetrabromo-4 : 4'-tetramethyldiaminobenzophenone, m. p. 165° (as prepared in 65% yield by reaction of the calculated amount of bromine with a dilute hydrochloric acid solution of Michler's ketone; cf. Nathan-son and Müller, A., 1889, 1188), is converted by boiling nitric acid (*d* 1.48) into 2 : 6-dibromo-4-nitrophenylmethylnitroamine, m. p. 91°, which oxidation serves to orient the bromine groups in the benzophenone. By the action of cold nitric acid, 3 : 5 : 3' : 5'-tetrabromo-4 : 4'-dimethyldinitroaminobenzophenone, decomp. *ca.* 235°, is obtained (yield 100%), and since with boiling acid it yields 2 : 6-dibromo-4-nitrophenylmethylnitroamine, it is regarded as an intermediate product in the formation of the latter. F. M. H.

#### Molecular Compounds of Aromatic Aminoketones. P.

PFEIFFER [with F. GOEBEL and O. ANGERN] (*Annalen*, 1924, **440**, 265–289).—4 : 4'-Tetramethyldiaminobenzophenone (Michler's ketone) forms *additive* compounds with one molecular proportion of *resorcinol* [greenish-yellow, m. p. 127–128° (decomp.)],  $\alpha$ -*naphthol* [similar, m. p. 87–88° (decomp.)], and  $\beta$ -*naphthol* (canary yellow, m. p. 106–107°). The following similar additive compounds are also described: *p*-methoxyphenyl *p*-dimethylaminostyryl ketone- $\alpha$ -*naphthol* (1 : 1), orange, m. p. 80°, and *di-p*-dimethylaminostyryl

*ketone-resorcinol* (2 : 1), dark-red, with green reflex, m. p. 105—107°. The melting points of mixtures of various aminoketones with hydrocarbons, phenolic ethers, and amines, from which no additive compounds could be isolated, are tabulated.

The intensity of colours of solutions of aminoketones in benzene, aniline, dimethylaniline, and guaiacol follow the order benzene < dimethylaniline < aniline, and benzene < dimethylaniline < phenol, this being the reverse of the colour-gradation of similar solutions of benzoquinone. Solutions of the aminoketones in alcohol are more deeply coloured than those in benzene and ether. It is concluded that the components of the additive compounds are linked together by the residual valency of the carbonyl group of the aminoketone, to which a hydrogen atom of the amino or hydroxyl group of the amine or phenol becomes attached. The strong colorations of solutions of aminoketones in organic acids are similarly explained.

The intensity of coloration of solutions of di-*p*-dimethylamino-styryl ketone in primary aliphatic alcohols decreases in the order : allyl, benzyl, methyl, ethyl, propyl, amyl, and hexyl alcohols, and in secondary and tertiary alcohols in the order : *isopropyl* alcohol, benzhydrol, *tert.*-butyl alcohol, and triphenylcarbinol. Colorations derived from aminoketones and phenols are more intense, and can be used for detecting phenols in commercial phenolic ethers. This effect, as well as that of the above-mentioned transference of a hydrogen atom, is ascribed to the greater residual affinity of the aromatic nucleus, compared with that of alkyl groups, for the oxygen or nitrogen atom, respectively, which tends to loosen the linking of the hydrogen atom.

F. G. W.

**Indones. VI. Methods of Preparation of Indones.** R. DE FAZI (*Gazzetta*, 1924, **54**, 996—1000).—In the preparation of indones by treating an aromatic ketone with the ester of an  $\alpha$ -brominated aliphatic acid in presence of zinc dust and thus obtaining the ester of a substituted lactic acid, the latter need not be isolated, since its ester gives a good yield of indone when treated with cold concentrated sulphuric acid :  $R \cdot CPh + CHBrR' \cdot CO_2Et + Zn = ZnBr \cdot O \cdot CPhR \cdot CHR' \cdot CO_2Et$ , and the latter  $+ H_2O = ZnO + HBr + OH \cdot CPhR \cdot CHR' \cdot CO_2Et \rightarrow OH \cdot CPhR \cdot CHR' \cdot CO_2H \rightarrow CPhR : CR' \cdot CO_2H \rightarrow C_6H_4 < \overset{CR}{CO} > CR'$ . This reaction appears to be a general one for  $\beta$ -phenyl-lactic esters containing a substituent,  $R'$ , in the  $\alpha$ -position. When no such group is present, the indone formed often undergoes rapid transformation into the corresponding truxone (cf. A., 1920, i, 316).

T. H. P.

**Migration of the  $\alpha$ -Naphthyl Radical.** E. LUCE (*Compt. rend.*, 1925, **180**, 145—148).—No migration of a radical occurs when silver nitrate or mercuric oxide reacts with the iodohydrins of *as*-phenyl- $\alpha$ -naphthylethylene (Acree, A., 1904, i, 743) and of *phenyl- $\alpha$ -naphthylpropylene*,  $CPh(C_{10}H_7) : CHMe$  (m. p. 55—61°, b. p. 232—236°/22—23 mm.), the reagents merely removing the elements of hypoiodous acid.  $\beta$ -Hydroxy- $\beta$ -phenyl- $\beta$ -1-naphthyl-

*ethylamine*,  $C_{10}H_7 \cdot CPh(OH) \cdot CH_2 \cdot NH_2$ , m. p.  $161^\circ$  [*hydrochloride*, m. p.  $244^\circ$  (decomp.), *chloroplatinate*, decomp. above  $187^\circ$ ], from magnesium  $\alpha$ -naphthyl bromide and  $\omega$ -aminoacetophenone hydrochloride, is converted by nitrous acid (cf. McKenzie and Roger, T., 1924, 125, 844) into *phenyl  $\alpha$ -naphthylmethyl ketone*, m. p.  $56.5\text{--}57^\circ$  (*oxime*, m. p.  $143\text{--}151^\circ$ ). The constitution of this substance follows from the synthesis of the other possible product (which would result if the phenyl radical migrated instead of the naphthyl), namely,  *$\alpha$ -naphthyl benzyl ketone*, m. p.  $64.5\text{--}65^\circ$ , prepared from phenylacetyl chloride and naphthalene, and also by oxidation of the product of interaction of magnesium  $\alpha$ -naphthyl bromide and phenylacetaldehyde.  *$\beta$ -Naphthyl benzyl ketone*, m. p.  $99.5^\circ$  (*picrate*), is also produced in the above Friedel and Crafts reaction. The compound previously described by Graebe and Bungener (A., 1879, 807) as  $\alpha$ -naphthyl benzyl ketone, m. p.  $57^\circ$ , was a mixture of the  $\alpha$ - and  $\beta$ -isomerides. G. M. B.

**Beckmann Transformation. II.** K. VON AUWERS and O. JORDAN (*Ber.*, 1925, 58, [B], 26—36; cf. A., 1924, i, 743).—Further examination of the oximes of a number of *o*-hydroxyphenyl ketones,  $OH \cdot C_6H_4 \cdot CR \cdot N \cdot OH$ , in which R is an alkyl group, confirms the validity of Meisenheimer's conception of the course of the Beckmann transformation (cf. A., 1922, i, 152; 1924, i, 432, 433). In cases in which R is an aryl radical, the relationships are less well defined and it is doubtful whether the transformation occurs entirely in a given direction; in any case, its course cannot be safely predicted in accordance with Beckmann's electrochemical conceptions (cf. A., 1923, i, 228), which require further development.

Oximation of 4(5-hydroxy)-*m*-xylyl methyl ketone leads to the production of the corresponding *n*-oxime, m. p.  $121\text{--}121.5^\circ$ , in addition to the *h*-oxime, m. p.  $143^\circ$ , described previously (A., 1916, i, 35). The former compound, in contrast to the latter, does not yield a nickel derivative. The *dibenzoates* of the *n*- and *h*-oximes have m. p.  $109\text{--}110^\circ$  and  $143\text{--}144.5^\circ$ , respectively. The *n*-oxime is converted by boiling, dilute sodium hydroxide solution into the *h*-oxime, which is stable under this treatment. The reverse transformation could not be effected by acids since the *h*-oxime is converted by cold formic acid, hydrogen chloride dissolved in glacial acetic acid, or concentrated aqueous hydrochloric acid into 1:3:5-trimethylbenzoxazole,  $C_6H_2Me_2 \cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ O \end{smallmatrix} > CMe$ , whereas the *n*-oxime is unaffected by acids. The *h*-oxime is converted by Beckmann's mixture at the atmospheric temperature quantitatively into 1:3:5-trimethylbenzoxazole, whereas the *n*-oxime remains for the most part unchanged. Phosphorus pentachloride in the presence of ether at  $0^\circ$  gives the oxazole in almost quantitative amount from the *h*-oxime, whereas a product containing phosphorus and a little oxazole derivative is obtained from the *n*-oxime. The *h*-oxime boils at  $180^\circ/10$  mm., almost without decomposition, but at  $180\text{--}210^\circ/760$  mm. it yields 1:3:5-tri-

methylbenzoxazole. The isomeric oxime is converted at 180—185°/10 mm. into the *h*-oxime. The *hydrochlorides* of the *h*- and *n*-oxime, m. p. 128—130° (decomp.), and 150° (decomp.) after softening at 145°, pass into 1:3:5-trimethylbenzoxazole when heated.

6-Hydroxy-*m*-tolyl methyl ketoxime, m. p. 145°, b. p. 168—170°/14 mm., 265—267°/760 mm. (cf. Anschütz and Scholl, A., 1911, i, 316), is transformed by potassium hydrogen sulphate at 150—160° or by phosphorus pentachloride in ethereal solution into 1:4-dimethylbenzoxazole. Phenyl 6-hydroxy-*m*-tolyl ketoxime, m. p. 134—135°, is converted by phosphorus pentachloride at -10° mainly into 1-phenyl-4-methylbenzoxazole, together with small amounts of *o*-benzamido-*p*-cresol and traces of a phosphoric ester; at the atmospheric temperature, the oxazole derivative is produced in relatively smaller amount, together with *p*-hydroxytoluanilide and a phosphoric ester, m. p. 187—189°, which has not been more closely examined. The hydrochloride of the oxime passes when heated into the oxazole derivative together with unchanged oxime, *o*-benzamido-*p*-cresol, and traces of *p*-hydroxytoluanilide. 2:2'-Dihydroxybenzophenone, m. p. 104—105°, is converted at 250° into 1-*o*-hydroxyphenylbenzoxazole, m. p. 120—121°, which is also prepared from phenyl salicylate and *o*-aminophenol at 200°.

H. W.

**Beckmann Transformation. III. K. VON AUWERS, M. LECHNER, and H. BUNDESMANN** (*Ber.*, 1925, 58, [B], 36—51).—The remarkable readiness with which the oxime of 4(5-hydroxy)-*m*-xylyl methyl ketone or its methyl ether is converted by acids into 4-amino-*m*-5-xyleneol or the corresponding methyl ether (von Auwers and Borsche, A., 1916, i, 34) has occasioned the examination of a lengthy series of ketoximes in similar circumstances. The oximes are boiled with hydrochloric acid (17—18%) during 1—1½ hours and the products are separated into regenerated ketone and basic substances by the usual methods. The oximes of the following ketones do not give any amine: *o*-hydroxy-, *o*-chloro-, *o*-iodo-, *o*-nitro-, *o*-amino-, 2-hydroxy-3-methyl-, 2-hydroxy-4-methyl-, 2-hydroxy-5-methyl-, and 2-hydroxy-3:5-dimethyl-, *m*-methyl-, *m*-methoxy-, *p*-methoxy-, 3:4-dimethyl-, 4-methoxy-3-methyl-, 4-hydroxy-3-methyl-, and 3:5-dimethyl-acetophenones, 2-hydroxy-5-methylpropiofenone. The percentage of amine yielded by the following ketoximes is placed in brackets after the name of the parent ketone: *o*-methylacetophenone (40); *o*-methoxyacetophenone (40); 2-methoxy-3-methylacetophenone (trace); 2:4-dimethylacetophenone (40); 2:4-dimethylpropiofenone (40); 2:4-dimethylbenzophenone (40); 4-methoxy-2-methylacetophenone (75); 4-hydroxy-2-methylacetophenone (80); 2-methoxy-4-methylacetophenone (80); 2:5-dimethylacetophenone (37); 2:5-dimethylbenzophenone (37); 2-methoxy-5-methylacetophenone (33); 2-methoxy-5-methylpropiofenone (33); 2:5-diethylacetophenone (35); 2:5-dipropylacetophenone (30); 3:5-dimethylacetophenone (25); 2-hydroxy-4:6-dimethylacetophenone

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(100); 2-methoxy-4:6-dimethylacetophenone (100). It appears, therefore, that under these conditions only those oximes which contain a substituent undergo the Beckmann transformation to a greater or less extent and that this rearrangement occurs when the substituent is an alkyl or methoxy group, but not when it is a halogen atom or a hydroxy, nitro, or amino group. The change does not depend on the nature of the second radical united to the C:N·OH group and is not affected by the electrochemical character of the substituent or by steric influences. It appears most probable that the course of the change depends on the amount of residual valency available at the carbon atom of the benzene nucleus which is attached to the C:N·OH group and that the tendency of this atom to unite with the nitrogen atom of the oximino group with production of an amine is greatest when the residual valency is greatest.

The following substances are described incidentally: *o*-methoxyacetophenoneoxime, m. p. 96—96·5°; *m*-methoxyacetophenoneoxime, b. p. 159°/9 mm.; *p*-methoxyacetophenoneoxime, m. p. 86—87°; 2-hydroxy-3-methylacetophenoneoxime, m. p. 132—133°; 2-methoxy-3-methylacetophenone, b. p. 115°/12 mm.,  $d_4^{25}$  1·0610,  $d_4^{20}$  1·060,  $n_D^{25}$  1·52441,  $n_D^{20}$  1·5240; 2-methoxy-3-methylacetophenoneoxime, m. p. 96—97°; 4-hydroxy-3-methylacetophenoneoxime, m. p. 92·5—93·5°; 4-methoxy-3-methylacetophenone, b. p. 145—146°/14 mm. (oxime, m. p. 101·5—102·5°); 4-hydroxy-2-methylacetophenoneoxime, m. p. 153—154°; 4-methoxy-2-methylacetophenoneoxime, m. p. 81·5—82° (corresponding semicarbazone, m. p. 194—195° after softening); 2-methoxy-5-methylacetophenoneoxime, m. p. 89—90°; 2-ethoxy-5-methylacetophenone, m. p. 44—45° (oxime, m. p. 107°; semicarbazone, m. p. 195—196°); isopropoxy-5-methylacetophenone, b. p. 136—137°/15 mm. (semicarbazone, m. p. 174—175°; oxime, m. p. 93°); 2-hydroxy-5-methylpropiophenoneoxime, m. p. 135° (corresponding semicarbazone, m. p. 211—212°); 2-hydroxy-3:5-dimethylacetophenone, m. p. 53—54°, b. p. 124·5—126°/16 mm. (oxime, m. p. 139·5—141°); 2-methoxy-3:5-dimethylacetophenone, b. p. 132—133°/14 mm. (oxime, m. p. 86—86·5°); *o*-methylacetophenoneoxime, m. p. 61·5—63°; *m*-methylacetophenoneoxime, m. p. 54—56° (sodium salt); 2:4-dimethylpropiophenone-*p*-nitrophenylhydrazine, m. p. 154—155°; *s*-*m*-xylylmethylcarbinol, b. p. 115—116°/12 mm.; 3:5-dimethylacetophenone, b. p. 236—237° (oxime, m. p. 114—114·5°; *p*-nitrophenylhydrazine, m. p. 179—180°); 2:5-dimethylbenzophenoneoxime, m. p. 135—135·5°; 2:5-diethylacetophenoneoxime, b. p. 168°/16 mm.; *p*-dipropylbenzene, b. p. 109°/22 mm.,  $d_4^{25}$  0·856,  $n_D^{25}$  1·48775,  $n_D^{20}$  1·4914; 2:5-dipropylacetophenone, b. p. 140—141°/14 mm. (oxime, b. p. 182°/18 mm.); *o*-chlorophenylmethylcarbinol, b. p. 115—116°/12 mm.; *o*-chloroacetophenone, b. p. 113°/18 mm.,  $d_4^{25}$  1·198,  $n_D^{25}$  1·54453,  $n_D^{20}$  1·5483 (oxime, m. p. 112—113°); *o*-iodoacetophenone, b. p. 139—140°/12 mm.,  $d_4^{25}$  1·746,  $n_D^{25}$  1·61634,  $n_D^{20}$  1·6173 (oxime, m. p. 130—132°); *o*-chlorobenzophenone, m. p. 52—56° (oxime, m. p. 125°); *o*-nitrobenzophenoneoxime, m. p. 122—123°.

H. W.

**Acid, Salt, Ester, and Adduct.** D. VORLÄNDER (*Ber.*, 1925, 58, [B], 118—143).—Observations on the liquid-crystalline properties of acids, salts, and esters have led the author to the conclusion that these are dependent on the linear form of the molecule and on the strain between the component parts, which diminishes in the order ester  $\rightarrow$  acid  $\rightarrow$  salt. Similarly, geometrical and energetic conceptions are derived from the study of additive compounds in which the strain exists between complete molecules. In the case of the  $\alpha$ -unsaturated phenolic ketones, it is shown that the free phenols, their alkali salts, and acyl and alkyl derivatives have the same structure, but differ from one another with regard to energy. Just as the liquid-crystalline properties of acids diminish in the order salt  $\rightarrow$  acid  $\rightarrow$  ester, so also the colour of the phenolic ketones decreases in the series alkali salt  $\rightarrow$  phenol  $\rightarrow$  ester. Chemically, the great strain between alkali metal and phenolic oxygen appears to be established by the greater difficulty with which the sodium salts of  $\alpha$ -unsaturated, phenolic ketones form additive compounds either at the double bond or the carbonyl group in comparison with the corresponding free phenols and their alkyl derivatives.

**$\alpha$ -Unsaturated Phenolic Ketones, their Acyl and Alkyl Derivatives** [with H. HIEMESCH, K. SCHOENEMANN, W. SCHADE, and K. KUNZE].—Phenyl *p*-hydroxystyryl ketone gives an unstable ammonium salt, methyl ether, m. p. 76° (*dibromide*, m. p. 140°), and benzoate, m. p. 104—105°. The same pyrazoline derivative, m. p. 146°, is obtained by the action of phenylhydrazine on the ketone in acetic acid solution or on its sodium salt. Reduction with sodium amalgam transforms the ketone into a substance,  $C_{15}H_{14}O_2$  or  $C_{15}H_{16}O_2$ , m. p. 81—83°, which appears to yield a diacetyl derivative. The *acetyl* compound, m. p. 90°, and *benzoyl* derivative, m. p. 142°, of *p*-hydroxyphenyl styryl ketone are described. *p*-Hydroxyphenyl *p*-hydroxystyryl ketone, m. p. 197°, yields a bluish-black *hydrochloride-A*, an *acetyl* derivative, m. p. 146°, and a *benzoyl* compound, m. p. 185°. *p*-Methoxyphenyl *p*-hydroxystyryl ketone, m. p. 180° (*hydrochloride-A*; acetate, m. p. 144°; benzoate, m. p. 141°), and *p*-hydroxyphenyl *p*-methoxystyryl ketone, m. p. 188—190° (*hydrochloride-A*; acetate, m. p. 101°; benzoate, m. p. 154°), are described. The green and yellow modifications of di-*p*-hydroxystyryl ketone described by Zincke and Mulhausen (*A.*, 1903, i, 265) are formed respectively by the decomposition of the coloured hydrohalides-*A* with water and by precipitation of the alkali salts of the ketone with acetic acid or carbon dioxide (the *hydrochloride* and *hydrobromide* are described). The yellow form can be preserved indefinitely, whereas the green modification is unstable, particularly in solution. Both varieties yield the same acetate, m. p. 166°, and benzoate, m. p. 208°, the differences in the rate of acetylation by cold acetic anhydride appearing to depend on the different solubilities in the reagent. Both varieties are remarkably stable towards light in the presence of uranyl acetate. Di-*p*-hydroxybenzylidenecyclopentanone exists similarly in a stable yellow form, m. p. above 300° (decomp.), and a less stable green

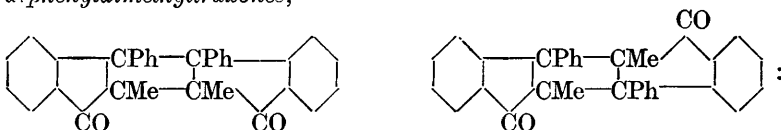
*modification* which passes into the yellow form below its melting point; the *hydrochloride-A*, *hydrobromide-A*, *diacetate*, m. p.  $240^{\circ}$ , *dibenzoate*, needles, m. p.  $236^{\circ}$  (corr.), leaflets, m. p.  $239^{\circ}$  (corr.), and *dicarbethoxy* derivative, m. p.  $188^{\circ}$  (corr.) or  $193^{\circ}$  (corr.), are described. The yellow *variety*, m. p. about  $293^{\circ}$  (corr., decomp.), and the green *modification*, m. p. about  $291^{\circ}$  (corr., decomp.), of *di-p-hydroxybenzylidenecyclohexanone* are less stable than the corresponding *cyclopentanone* derivatives and somewhat readily undergo interconversion; the *hydrochloride-A*, *hydrobromide-A*, *diacetate*, m. p.  $187^{\circ}$  (corr.), *dibenzoate*, m. p.  $222^{\circ}$  (corr.) and  $261^{\circ}$  (corr.), and *dicarbethoxy* derivative, m. p.  $136^{\circ}$  (corr.) and  $167^{\circ}$  (corr.), are described. *Dianisylidenecyclohexanone* (*monohydrochloride*) appears to exist only in the yellow form, m. p.  $166^{\circ}$  (corr.) and  $178^{\circ}$  (corr.). Reduction of *di-p-hydroxybenzylidenecyclohexanone* with sodium amalgam and alcohol in the presence of ammonium chloride yields *di-p-hydroxybenzylcyclohexanol*, m. p.  $185^{\circ}$  (corr.) [*triacetate*, m. p.  $133^{\circ}$  (corr.); *tribenzoate*, m. p.  $168^{\circ}$  (corr.)].  $\beta$ -Methylcyclohexanone does not condense with *p*-hydroxybenzaldehyde in the presence of alkali, but in alcoholic solution saturated with hydrogen chloride yields *di-p-hydroxybenzylidenemethylcyclohexanone*, which exists in a stable yellow and a less stable green form, m. p.  $236^{\circ}$  (corr.); the *monohydrochloride-A*, *disodium salt*, *diacetate*, m. p.  $180^{\circ}$  (corr.), and *dibenzoate*, m. p.  $195$ – $196^{\circ}$  (corr.), are described. *Dianisylidene- $\beta$ -methylcyclohexanone*, m. p.  $114^{\circ}$ , is prepared by methylating the corresponding hydroxy compound or by the condensation of anisaldehyde with methylcyclohexanone in the presence of hydrogen chloride; in the presence of alkali in the latter reaction, *anisylidene- $\beta$ -methylcyclohexanone*, m. p.  $96$ – $97^{\circ}$ , is produced. The latter substance condenses with *p*-hydroxybenzaldehyde in the presence of hydrogen chloride to yield *p-hydroxybenzylideneanisylidene- $\beta$ -methylcyclohexanone*, which exists only in a yellow form, m. p.  $199^{\circ}$  (corr.) [*hydrochloride-A*; *sodium salt*; *acetate*, m. p.  $172^{\circ}$  (corr.)]. Salicylaldehyde condenses with *cyclopentanone* and *cyclohexanone* in alkaline solution to give *disalicylidenecyclopentanone*, m. p.  $193^{\circ}$  (decomp.), and *disalicylidenecyclohexanone*, m. p.  $150^{\circ}$ , whereas in an acid medium dilactones appear to be produced (cf. Borsche and Seyer, A., 1912, i, 891).

**Sodium salts** [with H. HIEMISCH].—The *sodium* salts of the following compounds are prepared by adding a solution of sodium ethoxide to an ethyl-alcoholic solution of the phenolic ketone or, preferably, by treatment of an absolute ethereal solution of the ketone with sodium methoxide dissolved in methyl alcohol: *p*-hydroxybenzoic acid,  $C_7H_4O_3Na_2$ ; methyl *p*-hydroxybenzoate, *p*-hydroxycinnamic acid,  $C_9H_6O_3Na_2$ ; methyl *p*-hydroxycinnamate; *p*-hydroxyphenyl styryl ketone; *p*-methoxyphenyl *p*-hydroxystyryl ketone; phenyl *p*-hydroxystyryl ketone; *p*-hydroxyphenyl *p*-hydroxystyryl ketone; *di-p*-hydroxystyryl ketone; *p*-hydroxybenzylidene-*p*-anisylidenemethylcyclohexanone; *di-p*-hydroxybenzylidenemethylcyclohexanone; *di-p*-hydroxybenzylidenecyclohexanone; *di-p*-hydroxybenzylidenecyclopentanone; *disalicylidenecyclohexanone*.

**Adducts of Di-*p*-hydroxybenzylidene Derivatives of Ketones with Hydrogen Chloride and Bromide** [with H. HIEMISCH, K. SCHOENEMANN, and W. SCHADE].—The capacity of the dry hydroxyketones or their monohydrohalides to add hydrogen chloride or hydrogen bromide has been examined. The green form of di-*p*-hydroxystyryl ketone or its monohydrohalide absorbs more hydrogen halide than the yellow variety; the final product corresponds approximately with the addition of 2HCl or 2HBr. The yellow modification of di-*p*-hydroxybenzylidenecyclopentanone adds 2 mols. HCl, whereas the green variety adds only 1 mol. Either form combines with 2 mols. HBr; the *monohydrobromide* is prepared by passing hydrogen bromide into the ketone dissolved in alcohol or glacial acetic acid. The yellow variety of di-*p*-hydroxybenzylidenecyclohexanone gives a *dihydrochloride* and *dihydrobromide*, whereas the green modification absorbs 1 or 2 mols. HBr; the salts are unusually stable towards water.

**Action of Hydroxylamine on Phenyl *p*-Hydroxystyryl Ketone and Phenyl *p*-Methoxystyryl Ketone** [with K. SCHOENEMANN].—Phenyl *p*-hydroxystyryl ketone is transformed by hydroxylamine in alkaline solution into 3-phenyl-5-*p*-hydroxyphenyl-4 : 5-dihydroisooxazole,  $\text{N} \equiv \text{CPh} \text{---} \text{O} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OH}) \text{---} \text{CH}_2$ , m. p. 147° (acetate, m. p. 104°; benzoate, m. p. 158—160°; methyl ether, m. p. 103°), whereas in glacial acetic acid solution 3-phenyl-5-*p*-hydroxyphenylisooxazole, m. p. 165—166°, is produced in varying and small yield; the constitution of the latter substance is established by its conversion into the known 3-phenyl-5-*p*-methoxyphenylisooxazole, m. p. 120°. Phenyl *p*-methoxystyryl ketone and hydroxylamine in alkaline solution give mainly ill-defined products with smaller amounts of 3-phenyl-5-*p*-methoxyphenylisooxazole and 3-phenyl-5-*p*-methoxyphenyl-4 : 5-dihydroisooxazole. H. W.

**Indones. VII. Constitution and Synthesis of Truxones.** R. DE FAZI (*Gazzetta*, 1924, **54**, 1000—1009).—Under the influence of the ultra-violet rays emitted by a quartz mercury vapour lamp, 3-phenyl-2-methylindone in benzene solution gives rise to two *diphenyldimethyltruxones*,



(1) white crystals, m. p. 307—308°; (2) pale canary-yellow prisms, m. p. 259—260°. These compounds combine with neither chlorine nor bromine, but react with concentrated sulphuric acid to form 3-phenyl-2-methylindone. When the latter is exposed in benzene solution to the action of ordinary sunlight, the truxone of m. p. 307—308° is formed together with what appears to be a third *isomeride*, yellow crystals, m. p. 174—176°.

3-Phenyl-2-methylindoneoxime undergoes no change when exposed in benzene solution to ultra-violet light, but under similar

conditions the phenylhydrazone yields a compound, red laminae, m. p. 73—75°, which may possibly be the isophenylhydrazone.

A third *diphenyltruxone*,  $C_{30}H_{20}O_2$ , yellow needles, m. p. 184—185°, is obtained when the colourless isomerides formed by treating ethyl  $\beta\beta$ -diphenyl-lactate with concentrated sulphuric acid (cf. A., 1920, i, 316) is exposed in benzene solution to ultra-violet light. The existence of a fourth isomeride appears probable.

Truxones derived from monosubstituted indones are indifferent towards concentrated sulphuric acid, which, however, readily converts those from disubstituted indones into the indones themselves. This difference in behaviour is shown in more marked degree by the indones, which, in the absence of an alkyl or a phenyl group in the 2- or 3-position, are converted into truxones as soon as they are formed.

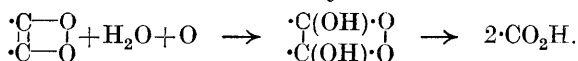
T. H. P.

**Acid Character of Ketoximes.** P. PFEIFFER, G. ARM-BRUSTER, P. BACKES, and H. OBERLIN (*J. pr. Chem.*, 1924, [ii], 108, 341—355).—Certain oximes of the hydrochalkone group are abnormally weak acids. The relationship of this property to constitution has been investigated by comparison of the following five oximes. Condensation of alcoholic *o*-vanillin and *p*-methoxyacetophenone in presence of sodium hydroxide gives *p*-hydroxyphenyl 2 : 3-dimethoxystyryl ketone (4'-hydroxy-2 : 3-dimethoxychalkone) (yield 61%), m. p. 143°, which forms a sodium salt, and an acetyl derivative, m. p. 113.5°; methylation yields *p*-methoxyphenyl 2 : 3-dimethoxystyryl ketone, m. p. 102—103°, or this may be prepared by condensation of *o*-vanillin methyl ether and *p*-methoxyacetophenone (yield 91%). Its acetic acid solution is reduced by hydrogen in presence of catalytic platinum, forming *p*-methoxyphenyl  $\beta$ -2 : 3-dimethoxyphenylethyl ketone, m. p. 53—54° (yield 60%); oxime (a), m. p. 123—128°; *p*-methoxyphenyl  $\beta$ -*p*-methoxyphenylethyl ketoxime (b); phenyl  $\beta$ -*p*-methoxyphenylethyl ketoxime (c); *p*-methoxyphenyl  $\beta$ -phenylethyl ketoxime (d); and phenyl  $\beta$ -phenylethyl ketoxime (e). The solubilities of these ketoximes per 100 mols. of aqueous sodium hydroxide at the ordinary temperature are 0.2, 0.4, 0.5, 0.6, and 0.6 mol., respectively, whence it appears that the small solubility in alkali is not due to the methoxy groups. For phenyl benzyl ketoxime and the oxime, m. p. 78—79°, of phenyl  $\delta$ -phenylbutyl ketone (m. p. 45—46°, b. p. 160°/3 mm.), prepared by catalytic reduction of cinnamylideneacetophenone) the solubilities are 4.7 mol. and nil, respectively. By comparison with (e), it is concluded that solubility in alkali is increased by diminution of the number of methylene groups between the phenyl and ketoximino groups and *vice versa*. The solubilities of acetophenoneoxime, phenyl ethyl ketoxime, phenyl propyl ketoxime, and phenyl butyl ketoxime are 93, 60, 30, and 11; hence the acidity is greatly increased by elimination of the second phenyl group, whilst it is decreased by lengthening the aliphatic chain. *o*-Vanillin and acetophenone yield phenyl 2-hydroxy-3-methoxystyryl ketone, m. p. 111° (yield 36%); potassium salt; acetyl derivative, m. p. 124.5°.

F. M. H.

**Quinhydrones.** P. PFEIFFER [with F. GOEBEL and O. ANGERN] (*Annalen*, 1924, **440**, 241—264).—The influence of substituents on the colour of quinhydrones is in the same order as that observed among other substituted chromophores, supporting the view that quinhydrones are additive compounds held together by residual valencies of the nuclei, rather than by those of the substituent groups (cf. Willstätter and Piccard, A., 1908, i, 475). The colours of phenol quinhydrones show no parallelism with the halochromy of quinones with acids. Analogy between quinhydrones and additive compounds of ketones of the type  $R \cdot CO \cdot CH : CH \cdot CO \cdot R$  having been established (Pfeiffer and Böttler, A., 1919, i, 62; Pfeiffer and Flater, A., 1922, i, 341), the following additive compounds of the type  $R \cdot CH : CH \cdot CO \cdot CH : CH \cdot R$  were obtained from ketones: *distyryl ketone-resorcinol* (1 : 1), yellow, m. p.  $95^\circ$ ; *distyryl ketone- $\alpha$ -naphthol* (1 : 2), canary yellow, m. p.  $68^\circ$ ; *dimethoxystyryl ketone-resorcinol* (1 : 2), orange, m. p.  $88-90^\circ$ ; *dimethoxystyryl ketone- $\alpha$ -naphthol* (2 : 3), m. p.  $69^\circ$  (cf. K. H. Meyer, A., 1910, i, 179); *dimethoxystyryl ketone- $\beta$ -naphthol* (2 : 3), yellow, m. p.  $73-74^\circ$ ; *perchloroindone-acenaphthene* (1 : 1), orange, m. p.  $132-133^\circ$  after softening at  $129^\circ$ ; *perchloroindone-fluorene* (1 : 1), orange, m. p.  $100-102^\circ$ ; *perchloroindone-durene* (1 : 1), golden-yellow, m. p.  $70-71^\circ$  (decomp.); *perchloroindone-scatole* (1 : 1), reddish-brown, m. p.  $119-121^\circ$ ; *perchloroindone- $\alpha$ -naphthol*, crystallising with benzene (0.5 mol.), dark red, or with acetic acid (0.5 mol.), red, m. p.  $108-109^\circ$ ; *perchloroindone- $\beta$ -naphthol* (1 : 1) ( $+0.5C_6H_6$ ), orange, m. p.  $88-91^\circ$  after sintering; and *perchloroindone- $\alpha$ -naphthol methyl ether* (1 : 1), brownish-yellow, m. p.  $100-103^\circ$ . Colours of solutions of the above ketones and of dicinnamylideneacetone and dibromoindone in benzene, anisole, phenol, aniline, and dimethylaniline are in the same order of intensity, but with gradation less marked, as those of quinones in the same solvents. It is concluded that the formation of quinhydrones from quinones depends rather on the above unsaturated ketonic grouping than on the six-membered ring structure. Pure perchloroindone has m. p.  $151-152^\circ$ . F. G. W.

**Oxidation of *o*-Quinones.** G. CHARRIER and A. BERETTA (*Gazzetta*, 1924, **54**, 988—995).—Oxidation by means of alkaline permanganate solution of most *o*-quinones, including those derived from heterocyclic hydrocarbons, results in addition of two hydroxyl groups to the quinone grouping, followed by scission of the peroxide linking and formation of two carboxyls :



By this method of oxidation, *o*-benzoquinone gives oxalic acid;  $\beta$ -naphthaquinone, phthalonic acid; acenaphthenequinone, naphthalic, 2 : 6-dicarboxyphenylglyoxylic, and hemimellitic acids; phenanthraquinone, diphenic acid; 2-phenylnaphthatriazolequinone, 1-phenyl-4-*o*-carboxyphenyl-1 : 2 : 5-triazole-3-carboxylic acid, and 2-*p*-chlorophenylnaphthatriazolequinone the corresponding *p*-chloro compound. The last three quinones yield, respectively,



**Trihydroxymethylanthraquinones. V. Synthesis of Morindone.** R. A. JACOBSON and R. ADAMS (*J. Amer. Chem. Soc.*, 1925, **47**, 283—290).—3 : 4-Dimethoxyphenyl-2'-hydroxy-*m*-tolylmethane-2-carboxylic acid (cf. preceding abstract) is converted by cold 85% sulphuric acid into 5-hydroxy-1 : 2-dimethoxy-6-methyl-9-anthrone, which was oxidised to 5-hydroxy-1 : 2-dimethoxy-6-methylanthraquinone, m. p. 138.5—139°, by chromic oxide in glacial acetic acid. This compound was converted into 5-acetoxy-1 : 2-dimethoxy-6-methylanthraquinone, m. p. 185—185.5°, by acetic anhydride and finally demethylated with hydrobromic acid, giving 1 : 2 : 5-trihydroxy-6-methylanthraquinone, orange-red needles, m. p. 281—282°, which was shown to be identical with natural morindone. The synthesis of 1 : 2 : 8-trihydroxy-7-methylanthraquinone, which was partly accomplished by Simonsen (*T.*, 1924, **125**, 721) from hemipinic anhydride and *o*-cresol, has been completed. 3 : 4-Dimethoxy-2-(2-hydroxy-3-methylbenzoyl)benzoic acid, when heated with boric acid in concentrated sulphuric acid, gives the required substance, m. p. 287—288°. 3 : 4-Dimethoxy-2-(4'-methoxy-3'-methylbenzoyl)benzoic acid, obtained by condensation of hemipinic anhydride with *o*-tolyl methyl ether, is not identical with the benzoylbenzoic acid obtained by condensation of opianic acid with *o*-tolyl methyl ether and subsequent oxidation with potassium permanganate.  
G. S. W.

**Diazo-, Diaminodihydroxy-, and Tetrahydroxy-phenanthraquinones.** K. BRASS and G. NICKEL (*Ber.*, 1924, **58**, [B], 204—211).—In continuation of previous work (A., 1924, i, 407, 408), 2 : 7-dinitrophenanthraquinone has been reduced by sodium hyposulphite to 2 : 7-diaminophenanthraquinone, which does not melt below 360°; the corresponding *monoxime* and *phenazine* derivatives, m. p. 325°, after softening at 320°, are described. The base is diazotised in concentrated sulphuric acid solution with nitrosylsulphuric acid and the tetrazonium compound is converted by bromine in potassium bromide solution into the relatively stable *phenanthraquinone-2 : 7-tetrazonium perbromide*, from which 2 : 7-diazidophenanthraquinone, m. p. 248° (decomp.), is obtained by the action of ammonia (10%); it yields a *quinoxaline* derivative, C<sub>20</sub>H<sub>10</sub>N<sub>8</sub>, m. p. 210° after softening at 200°. The azide decomposes explosively when treated with concentrated sulphuric acid, but is converted by 75% acid into 2 : 7-diamino-3 : 6-dihydroxyphenanthraquinone together with much 2 : 7-diaminophenanthraquinone and insoluble by-products; with less concentrated acid, the diaminodihydroxy compound is not formed, the main product being 2 : 7-diaminophenanthraquinone. 2 : 3 : 6 : 7-Tetrahydroxyphenanthraquinone is prepared from 2 : 7-diamino-3 : 6-dihydroxyphenanthraquinone in the usual manner.

4 : 5-Diaminophenanthraquinone is converted in the manner described for the 2 : 7-compound through the unstable *tetrazonium perbromide* into 4 : 5-diazidophenanthraquinone, m. p. 160° (*quinoxaline* derivative, m. p. 190°). The diazide is converted by moderately dilute sulphuric acid into 4 : 5-diamino-1 : 8-dihydroxy-



*phenanthraquinone* in small yield. Insoluble products of high molecular weight are mainly formed; regeneration of 4:5-diaminophenanthraquinone is not observed. H. W.

### Oxidations with Ozone. II. Preparation of Camphor.

E. BRINER, T. EGGER, and H. PAILLARD (*Helv. Chim. Acta*, 1924, 7, 1018—1022; cf. A., 1924, i, 290).—When borneol is treated with ozone in the manner described in the former paper (*loc. cit.*) camphor is obtained. The proportion of ozone actually utilised in oxidation reaches 92.7% under the most favourable conditions, viz., in hexane solution at  $-80^{\circ}$  with ozone of 8.5% strength by volume. At higher temperatures, although the borneol is satisfactorily oxidised, much ozone is lost, partly by decomposition in the apparatus and partly because further oxidation takes place, mainly to camphoric acid. The loss of ozone in bubbling through the solvent depends mainly on the temperature and to a lesser degree on the concentration of the ozone. Thus with 4.1% (vol.) ozone 33—39% is decomposed in bubbling through carbon tetrachloride at  $20^{\circ}$ , but only 6.4% in the same solvent at  $-20^{\circ}$  and only 1.9% in hexane at  $-70^{\circ}$ ; with 13.2% (vol.) ozone the figures are 42.1, 8.7, and 2.1%, respectively.

*iso*Borneol is oxidised just as readily, the yield (on the ozone) being about 10% less. Camphene gives no camphor when oxidised in solution (cf. Harries and Palmen, A., 1910, i, 497) nor when it is vaporised; Nordheim's statement (D.R.-P. 64180) is thus not confirmed.

Camphor was satisfactorily determined in such mixtures as were obtained in the above experiments by Fuller's method (*J. Ind. Eng. Chem.*, 1911, 3, 791) using hydroxylamine. W. A. S.

**Conversion of Camphor into Fenchone.** L. RUZICKA (*Annalen*, 1924, 440, 322).—Reply to Nametkin (A., 1924, i, 1084). F. G. W.

**Influence of Constitution on the Rotatory Power of Optically Active Substances. XVIII. Anomalous Rotation-dispersion of Ketones.** H. RUPE and E. KOPF (*Annalen*, 1924, 440, 215—241).—*cis-trans*-Borneolcarboxylic acid (Bredt, A., 1906, i, 680; 1909, i, 498) has  $[\alpha]_D^{20} + 45.00^{\circ}$  in alcohol. The ethyl ester, amorphous, liquid above  $30^{\circ}$ , has  $d_4^{20}$  1.0578,  $[\alpha]_D^{20} + 44.88^{\circ}$ . Bornylenecarboxylic acid (Rupe and Brin, A., 1924, i, 753) has  $[\alpha]_D^{20} + 139.89^{\circ}$  in alcohol,  $147.54^{\circ}$  in benzene. The ethyl ester has  $d_4^{20}$  0.9834,  $[\alpha]_D^{20} + 118.09^{\circ}$ .  $\alpha$ -Bornylene ethyl ketone (3-propionylbornylene), b. p.  $112.5^{\circ}/10$  mm.,  $d_4^{20}$  0.9501,  $[\alpha]_D^{20} + 148.51^{\circ}$  (semicarbazone, m. p.  $207-208^{\circ}$ ; oxime, m. p.  $107^{\circ}$ ), was obtained by the action of zinc ethyl on bornylenecarboxylic chloride in ether or benzene.  $\alpha$ -Bornylene methyl ketone (3-acetylbornylene), similarly prepared using zinc methyl, has b. p.  $103^{\circ}/11$  mm.,  $d_4^{20}$  0.9561,  $[\alpha]_D^{20} + 148.66^{\circ}$  (semicarbazone, m. p.  $217^{\circ}$ ; phenylhydrazine, unstable, m. p.  $99^{\circ}$ ; hydrobromide, m. p.  $63.5^{\circ}$ , b. p.  $87-94^{\circ}/10$  mm.; benzylidene derivative, m. p.  $77.5^{\circ}$ , b. p.  $216-218^{\circ}/11.5$  mm.,  $[\alpha]_D^{20} + 175.5^{\circ}$  in alcohol). The above ketones were accompanied by bimolecular

products, b. p. 214—220°/12 mm. (*phenylhydrazones*, m. p. 181° and 185°, respectively). 3-Camphanecarboxylic acid has  $[\alpha]_D^{20} +56.00^\circ$  in alcohol; the *ethyl* ester has b. p. 110°/10 mm.,  $d_4^{20}$  0.9785,  $[\alpha]_D^{20} +58.92^\circ$  (liquid) and 59.03° in benzene.  $\alpha$ -Camphanyl *ethyl ketone* (3-propionylcamphane), prepared similarly to the bornylene derivative, has b. p. 113°/11 mm.,  $d_4^{20}$  0.9448,  $[\alpha]_D^{20} +39.86^\circ$  (*semicarbazone*, m. p. 222°; *oxime*, m. p. 92.5°).  $\alpha$ -Camphanyl *methyl ketone* (3-acetylcamphane) was prepared by the action of zinc methyl on camphanecarboxylic chloride (*a*) and also by reducing  $\alpha$ -bornylene methyl ketone with hydrogen in presence of nickel (*b*). The product from (*a*) had b. p. 100—100.5°/10 mm.,  $d_4^{20}$  0.9517,  $[\alpha]_D^{20} +30.55^\circ$ , and deposited needles, m. p. 23—24°,  $d_4^{20}$  0.9493,  $[\alpha]_D^{20} +9.89^\circ$  (supercooled), rotation-dispersion anomalous (*semicarbazone*, m. p. 236°; *oxime*, m. p. 95.5°); that from (*b*) yielded crystals of different form, m. p. 25°, b. p. 100.5—100.7°/10 mm.,  $d_4^{20}$  0.9539,  $[\alpha]_D^{20} +82.14^\circ$ , rotation-dispersion normal, and a liquid,  $d_4^{20}$  0.954,  $[\alpha]_D^{20} +58.35^\circ$ . The differences are ascribed to the varying configuration of the carbon atom, which becomes asymmetric on passing from bornylene to camphane. In the ketone of m. p. 23—24°, the rotation of the new asymmetric carbon atom is assumed to be of opposite sign to that of the carbon atom originally asymmetric, whilst in the compound of m. p. 25°, the rotations of both asymmetric carbon atoms are of the same sign. The liquids are mixtures of the optical isomerides, in proportions calculable from the optical data. Both ketones gave the same *benzylidene* derivative, m. p. 100°,  $[\alpha]_D^{20} +76.74$ —78.10° in benzene. Camphanylcarbinol (Rupe and Brin, *loc. cit.*) has  $d_4^{20}$  0.9601,  $[\alpha]_D^{20} +19.73^\circ$ .

Whilst the rotation-dispersions of carboxylic acids (and their esters) derived from bornylene and camphane are normal, those of the ketones, especially the methyl and phenyl ketones, are anomalous in many cases, the benzylidene derivatives of the methyl ketones being again normal. The effect is ascribed to the residual valency of the R·CO· group, which disappears by conjugation of partial valencies (Thiele) in the benzylidene derivatives. F. G. W.

**Catalytic Reduction of  $\beta$ -Methylbutyronitrile and of  $\alpha$ -Cyanocamphor.** H. RUPE and E. HODEL (*Helv. Chim. Acta*, 1924, 7, 1023—1030; cf. A., 1923, i, 1199).—When  $\beta$ -methylbutyronitrile is catalytically reduced it behaves like its analogues previously described (*loc. cit.*) and yields ammonia and the secondary amine, diisoamylamine, the *hydrochloride* of which has m. p. 289°.  $\alpha$ -Cyanocamphor behaves differently; the products obtained are (i) ammonia, (ii) a little  $\alpha$ -methylcamphor, and (iii)  $\alpha$ -camphomethylaminomethylenecamphor,  $C_8H_{14} \begin{array}{c} \text{C:CH}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH} \\ \diagup \quad \quad \quad \diagdown \\ \text{CO} \quad \quad \quad \text{CO} \end{array} C_8H_{14}$ , prisms, m. p. 152° with previous softening. This compound, which behaves as a secondary base, cannot be reduced further. When treated with hot dilute hydrochloric acid, it is broken up, yielding hydroxymethylenecamphor and  $\alpha$ -camphomethylamine, b. p. 126—128°/11 mm. (with partial decomposition), the *hydrochloride*, *chloroaurate* (decomp. 198°), and *phenylthiocarbimide* derivative

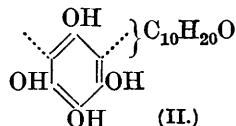
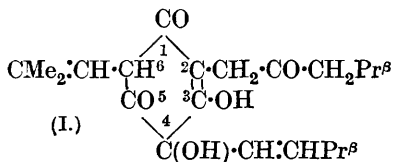
(m. p. 136°) of which are described. This compound decomposes when it is distilled with steam, or even under diminished pressure, into ammonia and methylenecamphor; when the crude distillation product, containing unchanged camphomethylamine, is treated with hydrochloric acid, some *isodi*(camphomethyl)amine (Rupe and Kusssmaul, A., 1920, i, 622) is separated as hydrochloride.

The formation of the  $\alpha$ -camphomethylaminomethylenecamphor is evidently due to the camphoraldehyde originally formed in the first stage of the reduction (cf. the theory already put forward, *loc. cit.*) reacting, but as hydroxymethylenecamphor, with the camphomethylamine simultaneously produced.

Aminomethylenecamphor is not reducible by the catalytic method used in the above investigations (cf. Rupe and Kusssmaul, *loc. cit.*).  
W. A. S.

**Chemical Nature of the Resin Acids of Hops. I. H. WIELAND** [with W. SCHNEIDER and E. MARTZ] (*Ber.*, 1925, 58, [B], 102—112).—Humulon,  $C_{21}H_{30}O_5$  (cf. Wöllmer, A., 1916, i, 494), is hydrolysed by aqueous-alcoholic sodium hydroxide solution to acetic acid, *isobutaldehyde*,  $\gamma$ -methyl- $\Delta^5$ -pentenoic acid and humulic acid,  $C_{15}H_{22}O_4$ , m. p. 92°, b. p. 130—131°/1 mm. The acid enolic group of humulon is retained in humulic acid. One of the three unsaturated linkings of humulon is removed in the  $\gamma$ -methyl- $\Delta^5$ -pentenoic acid, whereas that of the enolic group and the third linking remain in humulic acid as proved by its hydrogenation to dihydrohumulic acid,  $C_{15}H_{24}O_4$  (cf. Wöllmer, *loc. cit.*). Drastic reduction of humulic acid by Clemmensen's method gives an unsaturated *hydrocarbon*,  $C_{15}H_{28}$ , b. p. 122—123°/13—14 mm., which has not been obtained quite pure; the union of the carbon atoms with one another and the presence of a ring in humulic acid is thereby established. Catalytic hydrogenation of humulon yields  $\beta$ -methylbutane and a compound,  $C_{16}H_{24}O_5$ , which is regarded as a substituted quinol, since it is readily oxidised to humuloquinone,  $C_{16}H_{22}O_5$  (*semicarbazone*, m. p. 184—186°), which is decomposed by alkali hydroxide mainly into carbon dioxide and dihydrohumulic acid. Oxidation of the quinone by hypobromite gives carbon dioxide and *isohumulic acid*, m. p. 143° (*monoanil*, m. p. 90°; *disemicarbazone*, m. p. 170—171°), which exhibits all the reactions of a derivative of 1 : 3 : 4-triketocyclopentane.

The properties of humulon are most satisfactorily explained if the formula (I) is assigned to it, in which some uncertainty exists with regard to the distribution of the residue,  $C_{10}H_{18}O$ , at the carbon



atoms 2 and 6. Replacement of the group  $C_5H_9$  by hydrogen renders it possible for the ring to become aromatic with the pro-

duction of humuloquinol (II). Decomposition of humulon by alkali hydroxide causes opening of the ring at the carbon atom 4, which becomes part of a carboxyl group, whilst the residue undergoes ring closure to humulic acid, which is thus a cyclopentane derivative,  $\left\{ \begin{array}{l} \text{CH(OH)}-\text{CH} \\ \text{C(OH)}=\text{C} \end{array} \right\} \text{CO} \text{C}_{10}\text{H}_{18}\text{O}$ ; in dihydrohumulic acid, the complex  $\text{C}_{10}\text{H}_{18}\text{O}$  is hydrogenated. This conception is strongly supported by the conversion of humuloquinone into dihydrohumulic acid. The constitution,  $\left\{ \begin{array}{l} \text{C(OH):C} \\ \text{CO}-\text{CH} \end{array} \right\} \text{CO} \text{C}_{10}\text{H}_{18}\text{O}$ , is assigned to isohumulic acid.

H. W.

**Phosphoric Derivatives of the Inositol of *Hevea brasiliensis*.** A. CONTARDI (*Annali Chim. Appl.*, 1924, 14, 281—289).—The latex of *Hevea brasiliensis* contains a considerable proportion of quebrachitol. The latter remains unchanged when heated for 10 hours with dilute sulphuric acid (1 : 10) under a pressure of 20 atm., but, when heated with concentrated nitric acid, is converted into leuconic acid, water, carbon dioxide, and oxalic acid. Esterification of quebrachitol by means of phosphoric acid yields *quebrachitolpentaphosphoric acid*,  $[\alpha] -23.28^\circ$ , which resembles phytic acid, and may be obtained also by displacing the acetyl groups of penta-acetylquebrachitol; its *barium* salt,  $\text{C}_7\text{H}_9\text{O}_2\text{P}_5\text{Ba}_5 + 5\text{H}_2\text{O}$ , and its *magnesium* salt ( $+5\text{H}_2\text{O}$ ) were prepared.

Demethylation of quebrachitol and esterification with phosphoric acid of the *l*-inositol thus obtained, yields a new *phytic acid*,  $[\alpha] -16.15^\circ$ , the *barium* salt of which,  $\text{C}_6\text{H}_6(\text{PO}_4)_6\text{Ba}_6 + 3\text{H}_2\text{O}$ , is described.

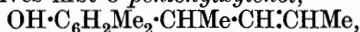
T. H. P.

**Pyrogallolbenzein and its Hydrochloride.** W. R. ORNDORFF and C. WANG (*J. Amer. Chem. Soc.*, 1925, 47, 290—292).—Pyrogallolbenzein was prepared by heating together pyrogallol and benzenyl chloride and decomposing the hydrochloride formed by repeated boiling with water. The product, crystallised from ethyl alcohol-benzene, corresponded with the formula  $\text{C}_{19}\text{H}_{12}\text{O}_5$ . From methyl alcohol, the compound crystallised with  $3\text{H}_2\text{O}$ . A crystalline hydrochloride,  $\text{C}_{19}\text{H}_{12}\text{O}_5 \cdot \text{HCl} \cdot 3\text{H}_2\text{O}$ , was obtained; an anhydrous hydrochloride was obtained by treating pyrogallolbenzein with dry hydrogen chloride (cf. Doebner and Förster, A., 1890, 899).

G. S. W.

**Preparation of Chromans.** L. CLAISEN (D.R.-P. 394797; from *Chem. Zentr.*, 1924, ii, 1134).—In the chroman synthesis described in D.R.-P. 374142, the butadienes can be replaced by  $\beta\gamma$ -unsaturated secondary or tertiary alcohols or pinacones. As intermediate products, *o*-alkenylphenols are formed, which with suitable condensing agents or at higher temperatures isomerise to chromans. Thus  $\alpha\alpha$ -dimethylallyl alcohol ( $\gamma$ -methyl- $\Delta^2$ -buten- $\gamma$ -ol), b. p.  $98-99^\circ$  (from ethyl acrylate and magnesium ethyl iodide), with *p*-cresol and formic acid yields 2 : 2 : 6-trimethylchroman, b. p.  $242-245^\circ$ ; with *as-m*-xyleneol, 2 : 2 : 6 : 8-tetramethylchroman,

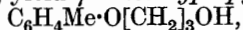
b. p. 250—253°, is similarly obtained.  $\alpha\alpha\beta$ -Trimethylallyl alcohol ( $\beta\gamma$ -dimethyl- $\Delta^2$ -buten- $\gamma$ -ol), b. p. 118—119° (from ethyl methylacrylate and magnesium methyl iodide), with *p*-cresol gives 2 : 2 : 3 : 6-tetramethylchroman, b. p. 256—258°, also obtained by heating *p*-cresol with pinacone, formic acid, potassium hydrogen sulphate, and potassium sulphate. *as-m*-Xylenol and pinacone similarly give 2 : 2 : 3 : 6 : 8-pentamethylchroman, b. p. 260—264°.  $\alpha\gamma$ -Dimethylallyl alcohol ( $\Delta^2$ -penten- $\delta$ -ol), b. p. 120—122°, from crotonaldehyde and magnesium methyl iodide, with *as-m*-xylenol and formic acid gives first *o*-pentenylxylenol,



b. p. 262—264°, converted by boiling over potassium sulphate into 2 : 4 : 6 : 8-tetramethylchroman, b. p. 247—248°. Similarly, *p*-cresol gives *o*-pentenyl-*p*-cresol,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CHMe}$ , b. p. 252—257°, which on heating with potassium hydrogen sulphate changes into 2 : 4 : 6-trimethylchroman. R. B.

**$\beta$ -Toloxypropionic Acids and the Corresponding Chromanones.** S. G. POWELL and N. G. JOHNSON (*J. Amer. Chem. Soc.*, 1924, 46, 2861—2863).—By methods analogous to those previously described (A., 1924, i, 287; cf. also Arndt and Källner; Krollpfeiffer and Schultze, A., 1924, i, 411)  $\beta$ -*m*-toloxy- and  $\beta$ -*p*-toloxypropionic acids have been prepared and converted into the corresponding chromanones.  $\beta$ -*p*-Toloxypropionic acid yields 6-methylchromanone (Auwers and Krollpfeiffer, A., 1915, i, 442), whilst the product from  $\beta$ -*m*-toloxypropionic acid is regarded as 7-methylchromanone and not as 5-methylchromanone, since  $\beta$ -*m*-anisoxypropionic acid yields 7-methoxychromanone (Pfeiffer and Oberlin, A., 1924, i, 413).

Trimethylenechlorohydrin and *m*-cresol in aqueous sodium hydroxide give in 80% yield  $\gamma$ -*m*-toloxypropyl alcohol,



b. p. 146—147°/13 mm., oxidised to  $\beta$ -*m*-toloxypropionic acid, m. p. 105° (yield 41%), by potassium permanganate in the presence of magnesium sulphate. The *amide* has m. p. 108°. Phosphoric oxide in benzene converts the acid into 7-methylchromanone, b. p. 138°/13 mm. (*oxime*, m. p. 98—99°).  $\gamma$ -*p*-Toloxypropyl alcohol, m. p. 21—22°, b. p. 171°/39 mm., similarly obtained, yields  $\beta$ -*p*-toloxypropionic acid (*amide*, m. p. 128°), converted by phosphoric oxide in benzene into 6-methylchromanone. Attempts to obtain  $\beta$ -*o*-toloxypropionic acid in this way failed. R. B.

**Dibenzohomopyran.** A. SIEGLITZ and H. KOCH (*Ber.*, 1925, 58, [B], 78—82).—*o*-Nitrophenyl benzyl ether, m. p. 29°, b. p. 210°/10 mm., is reduced by alcoholic ammonium sulphide solution to *o*-aminophenyl benzyl ether, m. p. 39—40° (*hydrochloride*, m. p. 193°; *acetyl* derivative, m. p. 113—114°; *benzoyl* compound, m. p. 92°), which could not be transformed into dibenzopyran. *o*-Iodophenyl *o*-iodobenzyl ether, m. p. 94°, is dehalogenated by copper powder without yielding a homogeneous product. *o*-Nitrophenyl  $\beta$ -phenylethyl ether, b. p. 221—223°/14 mm., m. p. 38—39°,

is reduced similarly to *o*-aminophenyl  $\beta$ -phenylethyl ether, b. p. 198°/13 mm. (acetyl derivative, m. p. 83°; benzoyl compound, m. p. 113—114°), which is converted by diazotisation and treatment of the diazonium compound with aqueous sulphuric acid into a mixture of dibenzohomopyran,  $\begin{matrix} \text{C}_6\text{H}_4\text{---O} \\ \text{C}_6\text{H}_4\text{---CH}_2 \end{matrix} > \text{CH}_2$ , m. p. 116°, and *o*-hydroxyphenyl  $\beta$ -phenylethyl ether, m. p. 49° (benzoate, m. p. 78—79°). Dibenzohomopyran is converted by concentrated hydriodic acid and red phosphorus at 220—250° followed by oxidation of the product with chromic acid into phenanthraquinone.

*o*-Nitrophenyl benzyl sulphide, b. p. 230°/12 mm., m. p. 82—83°, is reduced to *o*-aminophenyl benzyl sulphide, m. p. 45° (acetyl derivative, m. p. 57°; benzoyl compound, m. p. 67—68°). H. W.

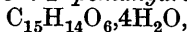
### Action of Ammonia on *o*-Hydroxyphenyl-1 : 3-diketones.

G. WITTIG (*Ber.*, 1925, 58, [B], 19—24; cf. A., 1924, i, 412).—6-Acetylaceto-*o*-cresol, m. p. 85—86°, prepared by the action of sodium on ethyl acetate and 6-acetyl-*o*-cresol, is converted by acetic anhydride and sodium acetate into 3-acetyl-2 : 8-dimethyl chromone, m. p. 121·5—122·5°. It is transformed by ammonia in absolute ethyl-alcoholic solution into a mixture of 3-amino-2 : 8-dimethylchromanone,  $\text{Me}\cdot\text{C}_6\text{H}_3\begin{matrix} \text{O---CHMe} \\ | \\ \text{CO}\cdot\text{CH}\cdot\text{NH}_2 \end{matrix}$ , m. p. 100·5—101°,

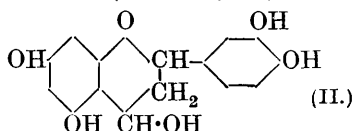
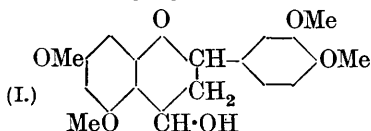
(which is converted by cold 2*N*-hydrochloric acid into 2 : 8-dimethylchromone and by boiling 2*N*-sodium hydroxide solution into 3-methylsalicylic acid) and (?) 2-amino-2 : 8-dimethylchromanone, m. p. 119—120°, which gives 2 : 8-dimethylchromone when boiled with dilute acids. Boiling aqueous ammonia (25%) converts 6-acetylaceto-*o*-cresol into an additive compound of 3-amino-2 : 8-dimethylchromanone and 2 : 8-dimethylchromone, m. p. 98·5—99°, which is also obtained from its components dissolved in a mixture of benzene and light petroleum. Attempts to acetylate or benzoylate 3-amino-2 : 8-dimethylchromanone were unsuccessful. The action of semicarbazide hydrochloride and sodium acetate on 6-acetylaceto-*o*-cresol or 3-amino-2 : 8-dimethylchromanone in alcoholic solution yields a mixture of the semicarbazone of 6-acetylaceto-*o*-cresol, m. p. 196—197° (decomp.), and 3 : 2'-hydroxy-m'-tolyl-5-methylpyrazole, m. p. 133—133·5°, the chromanone ring undergoing an unusual fission. The additive compound (see above) is transformed similarly into a mixture of 6-acetylaceto-*o*-cresol-semicarbazone, pyrazole derivative, and 2 : 8-dimethylchromone. 6-Acetylaceto-*o*-cresol is converted by diethylamine exclusively into 2 : 8-dimethylchromone whereas 3-acetyl-2 : 8-dimethylchromone is unchanged by this reagent. H. W.

**Constitution of Catechin. VII. 4 : 5 : 7 : 3' : 4'-Penta-hydroxyflavan.** M. NIERENSTEIN (*J. Amer. Chem. Soc.*, 1924, 46, 2793—2798).—5 : 7 : 3' : 4'-Tetramethoxyflavone (Kostanecki and Tambor, A., 1904, i, 426), on reduction with zinc and alcoholic potassium hydroxide, is converted (yield 67%) into 4-hydroxy-5 : 7 : 3' : 4'-tetramethoxyflavan (I), m. p. 159—160° (acetyl deriv-

ative, m. p. 171°), which on demethylation with hydriodic acid (*d* 1.94) yields 4 : 5 : 7 : 3' : 4'-pentahydroxyflavan (II),

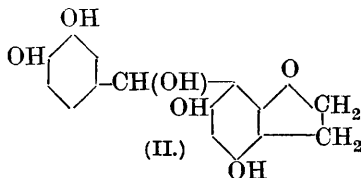
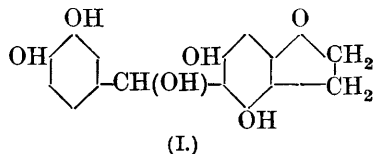


m. p. 212—214° (penta-acetyl derivative, m. p. 167°), one of the structures proposed for catechin by Perkin (T., 1902, 81, 1172;



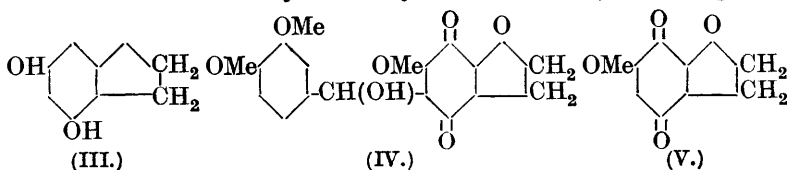
1905, 87, 405; cf. Freudenberg, Orthner, and Fikentscher, A., 1924, i, 660). Since, however, this pentahydroxyflavan resists reduction with hydriodic acid, it differs fundamentally from catechin and resembles quercetin, a similar difference from catechin and resemblance to quercetin appearing in its failure to give the phloroglucinol test. The catechins cannot therefore be regarded as intermediary between the flavones, anthocyanins, and tannins. In view of the identity of the m. p. of 4 : 5 : 7 : 3' : 4'-pentahydroxyflavan and Freudenberg's *dl*-catechin (212—214°) and also of 4 : 5 : 7 : 3' : 4'-penta-acetoxyflavan and penta-acetyl-*dl*-catechin (166°) and penta-acetyl-*dl*-epicatechin (167°), it is suggested that Freudenberg is possibly working with some products of the 4 : 5 : 7 : 3' : 4'-pentahydroxyflavan series, which are not present in catechins from authentic *Acacia catechu* heartwood. Acacatechin is readily converted into epicatechin by dilute pyridine, and this is possibly why Freudenberg finds practically the same m. p. for penta-acetyl-*dl*-catechin and -*dl*-epicatechin, pyridine being used in both acetylations. Acetic acid and pyridine readily convert penta-acetylacacatechin into penta-acetylepicatechin. R. B.

**Constitution of Catechin. VIII.  $\alpha$ -3 : 5 : 3' : 4'-Penta-hydroxy-4-benzyl-1 : 2-dihydrocoumarone.** H. F. DEAN and M. NIERENSTEIN (*J. Amer. Chem. Soc.*, 1924, 46, 2798—2806).— $\alpha$ -3 : 5 : 3' : 4'-Pentahydroxy-4-benzyl-1 : 2-dihydrocoumarone (I) and  $\alpha$ -3 : 5 : 3' : 4'-pentahydroxy-6-benzyl-1 : 2-dihydrocoumarone (II) have now been synthesised. These substances are entirely

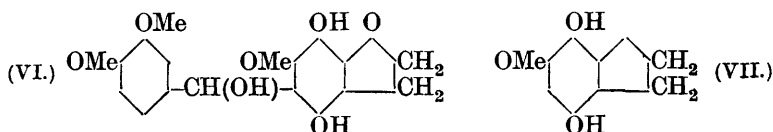


distinct from catechin and, like 3 : 5-dihydroxy-1 : 2-dihydrocoumarone (III), do not give the specific catechin test with pine-wood and hydrochloric acid, probably owing to the greater stability of the coumaran ring as compared with that of the chroman ring in catechin. The constitution of these two substances is established by the behaviour of their tetramethoxy derivatives on oxidation : (I) is converted into a quinone (IV), whilst (II) yields veratralde-

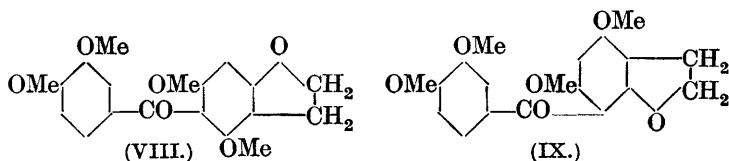
hyde and a quinone (V) identical with that obtained by the oxidation of 3:5-dimethoxy-1:2-dihydrocoumarone (cf. Koenig and



Kostanecki, A., 1907, i, 62). On reduction, these quinones yield the colourless substances (VI) and (VII), which both contain a hydroxyl group in position 6, thereby invalidating Nierenstein's suggestion that hydroxyl in this position has chromophoric properties (A., 1912, i, 203; 1913, i, 501).



3 : 5-Dimethoxycoumaran-2-one yields a *hydrazone*, m. p. 157—159°, which on reduction with sodium ethoxide (cf. Wolff, A., 1920, i, 764) gives 3 : 5-dimethoxy-1 : 2-dihydrocoumarone, m. p. 109°, converted by reduction with sodium and alcohol and methylation with methyl sulphate into 1 : 3 : 5-trimethoxy-2-ethylphloroglucinol. On boiling with acetyl chloride in 80% acetic acid, the dimethoxy compound gives (yield 67%) 3 : 5-dihydroxy-1 : 2-dihydrocoumarone (III), m. p. 176—178° (*diacetyl* derivative, m. p. 177°), whilst on oxidation with chromic acid in glacial acetic acid it is converted into 5-methoxy-1 : 2-dihydro-3 : 6-quinocoumarone (V), m. p. 168—170° (decomp.), which gives no azine with tolylene-3 : 4-diamine, and with zinc dust and acetic acid yields 3 : 6-dihydroxy-5-methoxy-1 : 2-dihydrocoumarone (VII), m. p. 191—192° (*diacetyl* derivative, m. p. 207—209°). Veratroyl chloride and 3 : 5-dimethoxy-1 : 2-dihydrocoumarone with aluminium chloride in chloroform give a mixture of 3 : 5 : 3' : 4'-tetramethoxy-4-benzoyl-1 : 2-dihydrocoumarone (VIII), m. p. 148° [*phenylhydrazone*, m. p. 218—222° (decomp.)] and 3 : 5 : 3' : 4'-tetramethoxy-6-benzoyl-1 : 2-dihydrocoumarone (IX), m. p. 132—133° [*phenylhydrazone*, m. p.



204—207° (decomp.)], which are separated by exhaustive extraction first with light petroleum and then with benzene. 3:5:3':4'-Tetramethoxy-4-benzoyl-1:2-dihydrocoumarone on reduction with zinc and sodium hydroxide gives, in practically theoretical yield, *α*-hydroxy-3:5:3':4'-tetramethoxy-4-benzyl-1:2-dihydrocoumarone,



m. p. 124—126° (*acetyl* derivative, m. p. 147—148°), which by reduction with sodium and alcohol, methylation with methyl sulphate, and oxidation with alkaline potassium permanganate is successively converted into 2:4:6:3':4'-pentamethoxy-3-ethyl-diphenylmethane and 2:4:6:3':4'-pentamethoxydiphenylmethane-3-carboxylic acid (T., 1920, 117, 971). Oxidation of the  $\alpha$ -hydroxytetramethoxy compound gives 64% of the theoretical yield of  $\alpha$ -hydroxy-5:3':4'-trimethoxy-4-benzyl-1:2-dihydro-3:6-quinocoumarone (IV), m. p. 272—275° (decomp.) (*acetyl* derivative, m. p. 297—299°), reduced by zinc and acetic anhydride to  $\alpha$ :3:6-trihydroxy-5:3':4'-trimethoxy-4-benzyl-1:2-dihydrocoumarone (VI), m. p. 197—202° (decomp.). On demethylation with *acetyl* chloride and acetic acid the  $\alpha$ -hydroxytetramethoxy compound is converted into  $\alpha$ :3:5:3':4'-pentahydroxy-4-benzyl-1:2-dihydrocoumarone (I), m. p. 200—201° (*penta-acetyl* derivative, m. p. 157—158°), which is remarkably resistant to alkali. Similarly, 3:5:3':4'-tetramethoxy-6-benzyl-1:2-dihydrocoumarone, on reduction with zinc and sodium hydroxide, yields  $\alpha$ -hydroxy-3:5:3':4'-tetramethoxy-6-benzyl-1:2-dihydrocoumarone, m. p. 127—128° (*acetyl* derivative, m. p. 136—137°), which on demethylation gives  $\alpha$ :3:5:3':4'-pentahydroxy-6-benzyl-1:2-dihydrocoumarone (II), m. p. 187—188° (*penta-acetyl* derivative, m. p. 151—152°). R. B.

**Preparation of *Bz*-Hydroxycoumarone Compounds.** A. SONN and E. PATSCHKE (*Ber.*, 1925, 58, [B], 96—98).— $\beta$ -Hydroxy-ethyl 3-hydroxy-5-methoxyphenyl ether, b. p. 153°/14 mm. (*phenyl-urethane*, m. p. 92°), is prepared by the action of ethylene chlorohydrin on resorcinol monomethyl ether in the presence of alcoholic sodium ethoxide; ring closure to a hydroxycoumarone could not be smoothly effected. The *oxime* of 6-hydroxycoumaran-3-one, m. p. 158—159° (decomp.) after darkening at 110°, is reduced by sodium amalgam in the presence of alcohol and glacial acetic acid to 3-amino-6-acetoxycoumaran, m. p. 105—106°, which, when heated at 120° and ultimately at 140—150°, or, preferably, boiled in concentrated aqueous solution, yields 6-hydroxycoumarone, m. p. 56°; the latter substance is converted by hydrogen in the presence of spongy platinum into 6-hydroxycoumaran, which is characterised as the *benzoate*, m. p. 69—72°.

6-Methoxycoumaran-3-one yields a *semicarbazone*, m. p. 212° (decomp.). 3:6-Diacetoxycoumaran yields an uncrystallisable oil when hydrogenated. H. W.

**Sulphur Compounds of Kimmeridge Shale Oil.** I. F. CHALLENGER, J. R. A. JINKS, and J. HASLAM (*J. Chem. Soc.*, 1925, 127, 162—166).—The oil distilled from Kimmeridge shale (Dorset) contains 5—8% of sulphur. 2-Methylthiophen, thiophen, ketones, unsaturated hydrocarbons, and toluene are present, but no alkyl sulphides, thioalcohols, or polymethylene sulphides (cf. Scheibler, A., 1916, i, 65; 1917, i, 153; 1920, i, 74). C. H.

**Aconite Alkaloids.** New Alkaloid from *Aconitum Napellus*. H. SCHULZE and G. BERGER (*Arch. Pharm.*, 1924, 262, 553—563; cf. A., 1906, i, 599).—"Aconitin pur. amorph. Merck," which

contains all the alkaloids in *Aconitum Napellus* other than aconitine, has been investigated. The remaining aconitine was separated as the *perchlorate* (discolours at 208°, sinters at 215°, decomp. 226°), which is sparingly soluble in water. Picroaconitine was not detected. The chief component, about 47% of the whole of the rest of the mixture—part of which is soluble, as free base, in ether, and the rest in chloroform, but from the latter no crystalline products could be obtained—is termed *neopelline*. It was not obtained crystalline. The formula,  $C_{28}H_{33}O_5(OMe)_3 \cdot NMe, 3H_2O$ , is assigned to it as a result of analyses carried out on the partly purified amorphous material. When it is boiled with 2*N*-potassium hydroxide it yields benzoic and acetic acids, and *neoline*,  $C_{23}H_{39}O_6N$ , a gum (*hydrobromide*, colourless needles, m. p. 210—215° after sintering,  $[\alpha]_D^{28} - 43.17^\circ$ ), the *acetyl* derivative of which affords a *chloroaurate*, m. p. 145° (after sintering at 124°). W. A. S.

**Conversion of Alkaloids of the "Aporphine" Series into those of the Chelidonine Series.** S. OSADA (*Arch. Pharm.*, 1924, 262, 501—517).—Gadamer (A., 1924, i, 1227) calls the hypothetical parent of apomorphine and its analogues "aporphine." The molecules of these compounds contain a six-membered heterocyclic ring, but those of the chelidonium alkaloids, which are similar in other respects, contain, it appears (*loc. cit.*), a seven-membered ring. The ring in the former can be disrupted by treating the compound with, *e.g.*, ethyl chloroformate (Gadamer and Knoch, A., 1921, i, 579). The secondary amines eventually obtained in this way should, possibly, condense with formaldehyde to yield analogues of the chelidonium alkaloids.

Although the ring scission is readily brought about, the hydrolysis of the compounds obtained is not easy (*cf.* Gadamer and Knoch, *loc. cit.*). More easily removable groups cannot be introduced, because, *e.g.*, corydine methyl ether is not attacked by thionyl chloride, carbonyl chloride, or phosphorus trichloride. It was found, however, that 0.5*N*-alcoholic potassium hydroxide will bring about the hydrolysis of the carbethoxy and other derivatives when other reagents (including lipase) fail, and the conversions described below were effected by this means, at the temperatures indicated.

Ethyl bulbocapninecarboxylate methyl ether (Gadamer and Knoch, *loc. cit.*) thus affords (at 150—160°) *methyl-β-8-(3:4-di-methoxy-5:6-methylenedioxy)phenanthrenylethylamine (hydrochloride*, m. p. 190—192°), and *benzyl bulbocapninecarboxylate methyl ether*, m. p. 92°, is hydrolysed in a similar way, at 125—135°, yielding the same product. Bulbocapnine methyl ether interacts with benzenesulphonyl chloride to produce *benzenesulphobulbocapnine methyl ether*, m. p. 125—126°, but this is only hydrolysed at such a temperature that decomposition in other ways takes place.

*Ethyl corydinecarboxylate methyl ether*, m. p. 95°, is prepared either from corydine methyl ether or from ethyl corydinecarboxylate (Gadamer and Knoch, *loc. cit.*). When hydrolysed (at 140—150°) it affords *methyl-β-8-(3:4:5:6-tetramethoxy)-phenanthrenylethyl-*

*amine (hydrochloride, m. p. 205—206°). Benzyl corydinecarboxylate is amorphous, and its methyl ether is a syrupy mass; this, when hydrolysed as above, affords the same base. Benzenesulphocorydine, m. p. 161°, reacts with methyl sulphate to yield benzenesulphocorydine methyl ether, m. p. 132—133°, which also is hydrolysed, but less readily than the above compounds, to give the same base.*

Neither base condenses in the expected fashion when treated with methylal; an unrecognisable tarry mass is the only product. When tetrahydroisoquinoline was prepared by a similar method (cf. Pictet and Spengler, A., 1911, i, 807), a much poorer yield than that claimed was obtained, and an attempt to obtain *N*-methyltetrahydroquinoline from methyl- $\beta$ -phenylethylamine gave, not the expected product, but a base not yet identified (*hydrochloride, m. p. 185°, mercury double salt, m. p. 154—155°, chloroaurate, m. p. 120—121°*). The methyl- $\beta$ -phenylethylamine was prepared either by Johnson and Guest's method (A., 1909, i, 784), this being the better, or *via benzylidene- $\beta$ -phenylethylamine, m. p. 36° (methiodide, m. p. 145—147°)*.  
W. A. S.

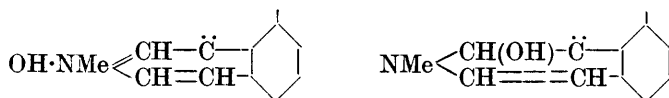
**Chelidonium Alkaloids. III (contd.).** J. GADAMER and collaborators (*Arch. Pharm.*, 1924, 262, 452—500; cf. A., 1924, i, 1227). (ii) **Bromochelidonine and the Oxidation of Chelidonine with Mercuric Acetate.** K. WINTERFELD.—Bromochelidonine, m. p. 230—231° (no decomp.),  $[\alpha]_D^{15} +135^\circ$ , is best obtained by Wintgen's method (A., 1901, i, 743). It is not oxidised by mercuric acetate under the same conditions as chelidonine, and differs in this respect so much from the latter as to suggest that the bromine atom had entered where oxidation takes place, and that possibly differences of behaviour in other directions might throw light on the constitution of the alkaloid. This expectation, however, has not been fulfilled; indeed, it has been found that the bromo derivative can be oxidised by mercuric acetate if the treatment be carried out in a hot mixture of alcohol and chloroform, not in 30% acetic acid alone (see below). This and other evidence indicates that the bromine atom is in position 7 (see formula II, A., 1924, i, 1227). It should be noted that the methylenedioxy groups in this formula are not definitely located, but that they are probably in the 2:3 and 5:6 positions, respectively); thus, the optical activity is of the same order as that of chelidonine, and the bromine atom is not very mobile, as it resists the action of sodium amalgam or moist silver oxide. When bromochelidonine is treated with acetic anhydride, it behaves like its parent, affording, in the cold, the *O*-acetyl derivative, m. p. 150—152°,  $[\alpha]_D^{15} +131^\circ$ , and, at the b. p., the *N*-acetyl derivative, m. p. 170—172°, optically inactive. The former is also obtained when *O*-acetylchelidonine is brominated, and is easily hydrolysed by dilute alcoholic potassium hydroxide. In the formation of the latter, dehydration and ring scission and re-formation have taken place, as with chelidonine (*loc. cit.*), the formula of the compound being  $C_{22}H_{18}O_5NBr$ . This is confirmed by the facts that the compound is also obtained when the *O*-acetyl derivative is boiled with acetic anhydride, but it contains only one acetyl group, and that it is remarkably resistant to hydro-

lysis; the absence of other characteristic reactivity also agrees with the explanation put forward. When the *N*-acetyl derivative is heated with alcoholic hydrochloric acid for a long time it is hydrolysed and converted into *anhydrobromochelidonine*, a strongly basic, viscous substance (formula analogous to IV, A., 1924, i, 1228). When treated with methyl iodide this affords *methylanhydrobromochelidonine*, the *methiodide* of which, like the corresponding derivative of chelidonine itself, does not break down when heated with potassium hydroxide, and trimethylamine is produced only when the compound is treated with sodium amalgam, the nitrogen-free product of this action being a mixture of brominated and unbrominated compounds  $C_{19}H_{13}O_4Br$  and  $C_{19}H_{14}O_4$ (!).

When bromochelidonine is oxidised with mercuric acetate (see above) it affords *didehydrobromochelidonine*, which is isolated as a yellow *hydrobromide*,  $[\alpha]_D +307^\circ$ . This is reduced by zinc and sulphuric acid to a mixture of chelidonine and (a little) bromochelidonine. Here is further evidence that the bromine atom is in position 7, for only there would the ethylenic linking render it labile. *Didehydrobromochelidonine cyanide*, m. p. 178—183° (decomp.),  $[\alpha]_D +157^\circ$ , is a colourless substance, resembling its unsubstituted analogue described below. *Anhydrodidehydrobromochelidonine (dihydrobromo- $\psi$ -chelerythrine)*, produced in a manner similar to that which affords its prototype (see below), has m. p. 206—207° (decomp.), and when oxidised yields *bromo- $\psi$ -chelerythrine*, which resembles its unsubstituted congener, but neither it nor any of its salts was obtained in a crystalline form.

Gadamer (*loc. cit.*) has observed that when chelidonine is oxidised with mercuric acetate in 30% acetic acid solution, much mercurisation takes place; this action is avoided if the oxidation be carried out on the *O*-acetyl derivative. *O*-Acetylchelidonine is dimorphous; the common form, m. p. 161—163° (cf. *loc. cit.*), is converted into another form, m. p. 184—186°, when it is slowly heated, or recrystallised from ethyl alcohol. The product obtained when *O*-acetylchelidonine is oxidised (at room temperature for 14 days) is *didehydrochelidonine* (isolated as *hydrobromide*, a yellow substance,  $[\alpha]_D +412^\circ$ ), the acetyl group also having been removed. This compound, being optically active, must contain the ethylenic linking between carbon atoms 11 and 12. Chelidonine is reproduced when the didehydro compound is reduced with zinc and dilute sulphuric acid. *Didehydrochelidonine cyanide*, m. p. 194—196°,  $[\alpha]_D +151—153^\circ$ , is colourless, and is only slowly acted on by silver nitrate or hydrochloric acid; in this and other respects it resembles chelerythrine and cotarnine cyanides (cf., e.g., Karrer, A., 1917, i, 349). The free base, a gum, is tertiary, for when treated with methyl iodide it eventually affords the *chloroaurate*,  $C_{20}H_{17}O_5N, MeCl, AuCl_3$ , m. p. 176° (decomp.). When didehydrochelidonine is boiled with aqueous alcohol for some time, a feebly basic substance is produced, namely, *anhydrodidehydrochelidonine* or *dihydro- $\psi$ -chelerythrine*, m. p. 187—188°, and this is oxidised, best by mercuric acetate in chloroform-alcohol solution, to  *$\psi$ -chelerythrine*, m. p. 239—242° (the red *hydrochloride* is described), the colourless *cyanide* (m. p. 237.5—238°) of

which corresponds in its properties with Karrer's chelerythrine cyanide (*loc. cit.* above). This second oxidation, with the production of a carbinol base, such as is  $\psi$ -chelerythrine, cannot be explained unless Gadamer's second formula (II, *loc. cit.*) is taken as a basis. The salts and the carbinol base are then represented by the following formulæ, in which only the 7-ring and the adjacent benzene nucleus are shown :

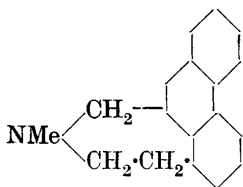


This carbinol base is surprisingly apt to form ethers of the annexed general formula, and if no alcohol is present it will even form an (unstable) ether with itself. The bearing of these observations on the behaviour of sanguinarine when recrystallised (cf., *e.g.*, Karrer, *loc. cit.*), and on the possible identity of  $\psi$ -chelerythrine and sanguinarine, is discussed (see below).

(iii) **Chelerythrine and Sanguinarine.** A. STICHEL.—It has hitherto been said that sanguinarine contains one methoxyl group, but repeated analyses, by various workers, have failed to furnish results in satisfactory agreement with this statement. Moreover, there is confusion in the descriptions of the alkaloid and its salts. It is now suggested that the  $\psi$ -chelerythrine described above is the true sanguinarine, which thus contains no methoxyl group, and that the substance previously described as sanguinarine is an ether-like compound of chelerythrine and (true) sanguinarine. The supposition has proved to be correct. When the mixture obtained by concentrating the mother-liquor from the technical isolation of chelidonium—this mixture containing chiefly chelerythrine and sanguinarine, but also all the other alkaloids present in *Chelidonium majus*—is dissolved (hydrochlorides) in water and precipitated with potassium cyanide, a mixture of ( $\psi$ )-cyanides and bases is obtained from which the latter are removed as acetates. By repeated treatment, a pure mixture of cyanides is produced, and when this is fractionally crystallised from a mixture of chloroform and alcohol it eventually affords pure chelerythrine cyanide (m. p. 256°). Eventually a second fraction, representing the sanguinarine, with a methoxyl-content of only 4%, can be obtained. Further separation is only effected when the *d*-tartrate of this partly purified sanguinarine is fractionally crystallised; the remaining chelerythrine then forms the less soluble salt, whilst from the more soluble hydrogen *d*-tartrate completely pure sanguinarine (entirely free from methoxyl) is obtained. The base (alcoholate) has m. p. 195–197°, and the cyanide, m. p. 238°, is identical with  $\psi$ -chelerythrine cyanide.

Karrer's "chelalbines" (A., 1923, i, 357) are alkylidihydrochelerythrines, as has been suggested by Gadamer (*loc. cit.*, 1920). The following are described: *methyldihydrochelerythrine*, m. p. 206°;

*ethylidihydrochelerythrine*, m. p. 209°; *phenyldihydrochelerythrine*, m. p. 230° (the *chloroaurate* is described). The latter is oxidised by potassium permanganate, chromic acid, or auric chloride to *phenylchelerythrine*, m. p. 201°, of which the *chloroaurate* is described.



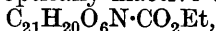
After preliminary trials with oxidation products formed in the purification, the mixture of chelerythrine and sanguinarine described above was distilled with zinc dust. A base, m. p. 136°, to which the annexed formula is ascribed, is thus obtained. It yields a yellow *hydrochloride*, a *picrate*, m. p. 235°, and a *chloroaurate*, m. p. 196°. W. A. S.

**Chelidonium Alkaloids. III (contd.).** J. GADAMER and collaborators (*Arch. Pharm.*, 1924, 262, 578—612; cf. preceding abstract). (iv) **Oxychelidonine.** M. THIESSEN.—The residues from the technical extraction of chelidonine from *Chelidonium majus* contain, besides the substances described below, a crystalline compound, which is identical with the oxychelidonine,  $C_{20}H_{17}O_6N$ , m. p. 285°,  $[\alpha]_D +102.5^\circ$ , obtained by Gadamer as one product when chelidonine was oxidised with mercuric acetate. Wintgen's "oxychelidonine" (A., 1901, i, 743) appears to be an oxide. The analytical figures obtained—on the "natural" oxychelidonine—were in fair agreement with the formula given, except those of the methylimino group determination (here only about half the expected percentage was found, but this is probably because the compound forms no salts, not even a chloroaurate), and the molecular-weight determination (this was carried out cryoscopically, but difficulties were encountered because the compound is so sparingly soluble). Two methylenedioxy groups are present. No acetyl derivative is formed, either in the cold (when the hydroxy group should be attacked; it must still be present, as the compound is optically active) or at the b. p. of acetic anhydride. These results suggest that the methylene group lying between the methylimino group and the carbinol group ( $C_{13}$  in the formula II, A., 1924, i, 1227) has been oxidised to a carbonyl group. Oxychelidonine affords no oxime, neither can it be reduced by Clemmensen's method. It is oxidised to some extent by potassium permanganate in acetone, but the only recognisable product is oxalic acid. When chelidonine is oxidised under the same conditions, oxychelidonine and didehydrochelidonine are formed. Oxychelidonine does not combine with bromine. Didehydrochelidonine might be expected to afford equimolecular proportions of chelidonine and oxychelidonine when treated with warm concentrated sodium hydroxide solution (Cannizzaro's reaction) but actually is unaffected. Sanguinarine, however, when so treated, yields a product that appears to be *oxy-sanguinarine*,  $C_{20}H_{13}O_5N$ , m. p. above 285°. Oxychelidonine is not converted into sanguinarine when it is exposed to the action of hydrochloric acid in chloroform for several weeks.

(v). **Minor Alkaloids of *Chelidonium majus*.** K. WINTER-FELD.—The mixture of bases, a dark-coloured, viscous mass,

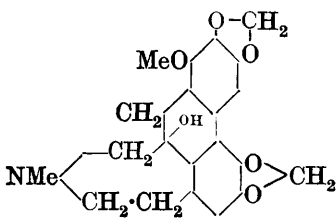
obtained as a by-product in the technical extraction of chelidonine, was examined, more especially to see whether sanguinarine were present (cf. Gadamer, *loc. cit.*). The procedure adopted consisted in first fractionally crystallising the picrates from alcohol, then fractionally precipitating as perchlorates such mixtures as were not separated into individual bases by this means, and finally, there being still a portion unresolved, the thiocyanates were prepared and fractionally extracted with alcohol. In this way, the following were isolated: protopine (chiefly from the picrate, m. p. 248°, insoluble in alcohol), allocryptopine, homochelidonine, traces of chelidonine and of sanguinarine (?), and, from the picrate fraction melting at 160—166°, a new base, *methoxychelidonine* (?),  $C_{21}H_{21}O_6N$ , m. p. 221° (see below); the latter was separated also in the perchlorate fractionation, and here, in the more sparingly soluble perchlorate, another new *alkaloid*, m. p. 198—199° (see below) was found. The final separation, as thiocyanates, yielded no new alkaloid, and only a small proportion of the material remained as a gum.

The first new product, methoxychelidonine, forms stout, colourless prisms,  $[\alpha]_D +115.8^\circ$ . It contains two methylenedioxy groups, one methoxyl group, and one methylimino group. The *hydrochloride* and *chloroaurate*, m. p. 237—238°, are described. The *O-acetyl* derivative, m. p. 147°,  $[\alpha]_D +55.5^\circ$ , prepared in the cold, like that of chelidonine, is amorphous, but yields a crystalline *chloroaurate*, m. p. 136—137° (decomp.), and when treated with ethyl chloroformate (Gadamer and Knoch, *loc. cit.*) it affords (like *O-acetylchelidonine*) an optically inactive *urethane*,



m. p. 107°. In its general properties the new base closely resembles chelidonine, from which, indeed, it differs only in the possession of the methoxyl group. By analogy with narcotine and hydrastine

this group is provisionally located and to the compound the annexed formula is assigned.



The second compound, needles, m. p. 198—199°,  $[\alpha]_D -40.7^\circ$ , has the empirical formula  $C_{19}H_{24}ON_2$ . It gives no colour reactions with the usual reagents. It is the first alkaloid from such a source with two nitrogen

atoms in the molecule and the only chelidonium alkaloid to be laevorotatory. The *dichloroaurate* has m. p. 122—124° (decomp.). The compound is unaffected by mercuric acetate; it contains no methoxyl, methylenedioxy, or methylimino group; the oxygen atom forms part of a hydroxyl group which is not phenolic. The *O-acetyl* derivative is a gum,  $[\alpha]_D -12.5^\circ$ , and affords a *dichloroaurate*, m. p. 147° (decomp.). The hydroxyl group is also the point of attack when the compound is treated with ethyl chloroformate, *i.e.*, no ring-scission takes place; the viscous product,  $[\alpha]_D -15.25^\circ$ , of this action yields a *dichloroaurate*, m. p. 142° (decomp.). These derivatives are both readily hydrolysed

to the parent base. Both nitrogen atoms are tertiary. The viscous *dimethiodide* gives a viscous *dimethochloride*,  $[\alpha]_D -103.15^\circ$ , of which the *dichloroaurate* has m. p.  $123-124^\circ$  (decomp.). The dimethochloride is decomposed only by hot alcoholic potassium hydroxide; volatile bases and a *compound*, the *chloroaurate* of which has m. p.  $118-120^\circ$ , are then produced. W. A. S.

**Syntheses in the Quinine Series. IV. Aliphatic Quinotoxins, Monocyclic Quinaketones, and Carbinols.** L. RUZICKA, C. F. SEIDEL, and F. LIEBL (*Helv. Chim. Acta*, 1924, 7, 995—1012; cf. A., 1921, i, 584, 585).—In continuation of the earlier work (*loc. cit.*), ethyl quinate was condensed, in benzene solution by sodium ethoxide, with the lactam of  $\epsilon$ -aminohexoxic acid; the amorphous product (yield only about 5%) is hydrolysed by hydrochloric acid to 6-methoxy-4-quinolyl  $\epsilon$ -aminoamyl ketone, an oil affording a *dipicrolonate*, m. p.  $229-230^\circ$ . When ethyl cinchonate is condensed, as above, with ethyl  $\epsilon$ -aminohexoate 4-quinolyl  $\epsilon$ -amino- $\alpha$ -carbethoxyamyl ketone, a viscous mass, is produced (yield, 17%); the *picrolonate* has m. p.  $187^\circ$  (decomp.). This ketone is hydrolysed by 20% hydrochloric acid to 4-quinolyl  $\epsilon$ -aminoamyl ketone (*loc. cit.*). When the condensation is carried out on ethyl  $\epsilon$ -benzamido-hexoate 4-quinolyl  $\epsilon$ -benzamido- $\alpha$ -carbethoxyamyl ketone, also gummy in nature (*picrate*, m. p.  $153-154^\circ$ ), is produced (yield, 17%), but with the benzoylmethylamino ester a superior yield (45%) is obtained, the product, 4-quinolyl  $\epsilon$ -benzoylmethylamino- $\alpha$ -carbethoxyamyl ketone, being a yellow, amorphous mass [*picrolonate*, m. p.  $110^\circ$  (decomp.), and *picrate*, m. p.  $105^\circ$  (decomp.)], and suffering only partial hydrolysis when heated with 10% hydrochloric acid on the steam-bath, giving 4-quinolyl  $\epsilon$ -benzoylmethylaminoamyl ketone, a viscous mass, b. p. about  $250^\circ$  (in high vacuum). When the hydrolysis is carried out at  $140^\circ$  with 20% hydrochloric acid, 4-quinolyl  $\epsilon$ -methylaminoamyl ketone (*loc. cit.*) is obtained. Ethyl quinate and ethyl  $\epsilon$ -benzoylmethylamino-hexoate afford 6-methoxy-4-quinolyl  $\epsilon$ -benzoylmethylamino- $\alpha$ -carbethoxyamyl ketone (yield, 35%), which, when hydrolysed, produces 6-methoxy-4-quinolyl  $\epsilon$ -methylaminoamyl ketone [*dipicrate*, m. p.  $145^\circ$  (decomp.)].

Ethyl cinchonate and ethyl  $\delta$ -benzoyl-ethylamino-hexoate afford 4-quinolyl  $\delta$ -benzoyl-ethylamino- $\alpha$ -carbethoxybutyl ketone, a viscous oil, which is hydrolysed by hot 20% hydrochloric acid to 4-quinolyl  $\delta$ -benzoyl-ethylaminobutyl ketone, b. p.  $260^\circ$  (in a high vacuum), the *picrate* of which has m. p.  $90-91^\circ$ . 4-Quinolyl  $\delta$ -ethylaminobutyl ketone is more readily obtained *via* the lactam (*loc. cit.*) than by debenzoylating the above compound.

Attempts were made to convert the above "aliphatic quinotoxins" into "monocyclic quinaketones" by the methods already described (*loc. cit.*); all the products were unstable, thus resembling their analogues prepared from natural alkaloids. 4-Quinolyl  $\epsilon$ -methylaminoamyl ketone (cf. above and *loc. cit.*) is thus converted first into 4-quinolyl  $\alpha$ -bromo- $\epsilon$ -methylaminoamyl ketone (*dihydrobromide*, m. p.  $136^\circ$ ), which, when treated with alcoholic



sodium ethoxide at  $-10^{\circ}$  (see below) gives 4-quinolyl *N*-methyl-2-piperidyl ketone, an oil (hydrochloride, m. p.  $159-160^{\circ}$ ; monopicrolonate, m. p.  $188-189^{\circ}$ ; dipicrate, m. p.  $145^{\circ}$ ). When this is reduced in cold alcohol with aluminium and sodium hydroxide (cf. Rabe and Kindler, A., 1918, i, 303), it affords 4-quinolyl-*N*-methyl-2-piperidylcarbinol, m. p.  $113^{\circ}$  [dipicrate, m. p.  $110^{\circ}$  (decomp.), dipicrolonate, m. p.  $179-180^{\circ}$  (decomp.)], whilst when the reduction is carried out with aluminium amalgam a pinacone (?), yielding a di(?)picrate, m. p.  $125-150^{\circ}$  (decomp.), is obtained.

When the dihydrobromide of 4-quinolyl  $\alpha$ -bromo- $\delta$ -methylaminobutyl ketone is treated with aqueous sodium hydroxide, the expected product is not obtained (*loc. cit.*); if, however, alcoholic sodium ethoxide at  $-10^{\circ}$  be used, a superior yield is obtained and the product, although containing a considerable proportion of a compound giving the hydrochloride of m. p.  $185^{\circ}$  already described, yet contains also another substance, the hydrochloride of which is more soluble in alcohol and has m. p.  $100^{\circ}$ ; this is considered to be the expected 4-quinolyl *N*-methyl-2-pyrrolidyl ketone. 4-Quinolyl  $\alpha$ -bromo- $\delta$ -ethylaminobutyl ketone dihydrobromide (*loc. cit.*), when similarly treated, affords 4-quinolyl *N*-ethyl-2-pyrrolidyl ketone, an oil [dipicrolonate, m. p.  $170-172^{\circ}$  (decomp.)]; this ketone gives only an amorphous product when it is reduced with aluminium and alcoholic sodium hydroxide. 6-Methoxy-4-quinolyl *N*-methyl-2-pyrrolidyl ketone is similarly prepared from the corresponding "aliphatic quinatoxin" (*loc. cit.*); it is an oil and affords a monopicrolonate, m. p.  $155-157^{\circ}$ , and a dipicrolonate, m. p. about  $155^{\circ}$  (decomp.). This compound also yields no crystalline product when reduced with aluminium and alcoholic sodium hydroxide. 4-Quinolyl  $\epsilon$ -aminoamyl ketone is converted by bromine into 4-quinolyl  $\alpha$ -bromo- $\epsilon$ -aminoamyl ketone (dihydrobromide, m. p.  $185^{\circ}$ ), and this, when treated as above, affords 4-quinolyl 2-piperidyl ketone, an oil the phenylhydrazone of which was prepared and isolated as dipicrate, m. p.  $179-180^{\circ}$  (decomp.).

Ethyl nicotinate and *N*-methyl-2-piperidone (lactam of  $\delta$ -methylaminovaleric acid) afford (yield, 30%), when condensed as described above, 3-pyridyl 3-*N*-methyl-2-piperidonyl ketone, an oil [picrolonate, m. p.  $204-205^{\circ}$  (decomp.)]; when this is heated with concentrated hydrochloric acid, 3-pyridyl  $\delta$ -methylaminobutyl ketone, the dihydrochloride, and dipicrolonate, m. p.  $153^{\circ}$  (decomp.), of which are described, is obtained.

Ethyl 2-phenylcinchonate condenses with *N*-methyl-2-piperidone to afford 2-phenyl-4-quinolyl 3-*N*-methyl-2-piperidonyl ketone, m. p. about  $135^{\circ}$  (picrate, m. p.  $174^{\circ}$ ). When this is heated with concentrated hydrochloric acid, 2-phenyl-4-quinolyl  $\delta$ -methylaminobutyl ketone, an oil (dihydrochloride, m. p.  $110-120^{\circ}$ ), is obtained.

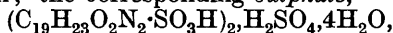
A selection of the above compounds was submitted to examination as to their action on protozoa (trypanosomes, spirochaetes, etc.); although they differed in potency, none was as active as quinine.

*N*-Methyl-2-piperidone is easily obtained by catalytically reducing 1-methyl-2-pyridone, using the method of Willstätter and Waldschmidt-Leitz (A., 1921, ii, 185).

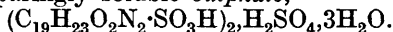
Rabe's criticism (A., 1922, i, 360) of Ruzicka's nomenclature is based on a misunderstanding.

W. A. S.

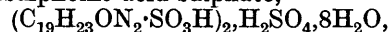
**Cinchona Alkaloids. VI. Action of Sulphuric Acid on Hydrocinchonine, Hydroquinine, Hydroquinidine, and Quinine. *apo*Quinine.** G. GIEMSA and K. BONATH (*Ber.*, 1925, 58, [B], 87—96).—Hydroquinine is converted by sulphuric acid ( $d$  1.84) at 100° during 8—10 hours into *hydrocupreinesulphonic acid*,  $C_{19}H_{23}O_2N_2 \cdot SO_3H$ , m. p. 270°,  $[\alpha]_D^{25} -93.3^\circ$  in ammoniacal, alcoholic solution; the corresponding *sulphate*,



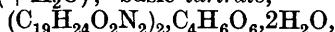
m. p. 231°, and the *nitrate* are described. Similarly, hydroquinidine hydrochloride yields *hydrocupreidinesulphonic acid*, m. p. 282°, which gives a sparingly soluble *sulphate*,



*Hydrocinchoninesulphonic acid sulphate*,



$[\alpha]_D^{18} +139^\circ$  in water, is obtained from hydrocinchonine. The action of sulphuric acid on quinine follows a somewhat different course, since in addition to sulphonation a molecule of sulphuric acid becomes combined at the vinyl group with the production of the *compound*,  $C_{19}H_{21}O_2N_2 \cdot SO_3H \cdot H_2SO_4 \cdot 1.5H_2O$ , m. p. 255—256°, which gives a *sulphate*,  $(C_{19}H_{21}O_2N_2 \cdot SO_3H \cdot H_2SO_4) \cdot H_2SO_4 \cdot 5H_2O$ , and a corresponding *hydrochloride* ( $+4H_2O$ ). Hydrolysis of *hydrocupreinesulphonic acid* or its *sulphate* by hydrochloric acid ( $d$  1.126) at 100° yields *hydrocupreine*, m. p. 186°,  $[\alpha]_D^{25} -159.2^\circ$  in alcoholic solution, the identity of which is confirmed by the preparation from it and from authentic *hydrocupreine* of the following salts: *hydrochloride*,  $C_{19}H_{24}O_2N_2 \cdot 2HCl \cdot H_2O$ ; *basic sulphate*; *normal sulphate*; *nitrate* ( $+H_2O$ ); *basic tartrate*,



m. p. 242°; *succinate*, m. p. 251°. *Hydrocupreidine*, m. p. 193°,  $[\alpha]_D^{20} +242.5^\circ$  in ethyl alcohol (the *hydrochloride* is described), and *hydrocinchonine*, m. p. 268°,  $[\alpha]_D^{25} +196.5^\circ$ , are similarly obtained by hydrolysis of the corresponding *sulphonic acids*. The product obtained from quinine is hydrolysed to 9:6'-*dihydroxyrubyl-3-ethosulphuric acid*,  $C_{19}H_{22}O_2N_2 \cdot H_2SO_4$ , m. p. 234°,  $[\alpha]_D^{25} -102.8^\circ$ , in ethyl alcohol (for nomenclature see Rabe, A., 1922, i, 360), which gives a *hydrochloride*,  $(C_{19}H_{22}O_2N_2 \cdot H_2SO_4)_2 \cdot 3HCl \cdot 9H_2O$ . *Hydrocupreine* obtained by means of sulphuric acid from *hydroquinine* is reconverted into the latter substance by methylation with *nitrosomethylurethane* and *methyl-alcoholic potassium hydroxide*.

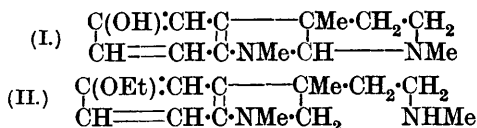
*apo*Quinine is converted by ethyl sulphate and alcoholic sodium hydroxide solution into *ethylapoquinine*, m. p. 183°. In contrast to *cupreine*, it is not hydrogenated in the presence of nickel. It is therefore considered improbable that *apoquinine* and *cupreine* are optical isomerides.

H. W.

**Synthesis of  $\psi$ -Ephedrine.** E. SPÄTH (*Ber.*, 1925, 58, [B], 197—199).—As a result of the criticism of Fourneau and Puyal (A., 1923, i, 238) and Fourneau and Kanao (A., 1924, i, 978), the author has repeated and confirmed the observations of Späth and

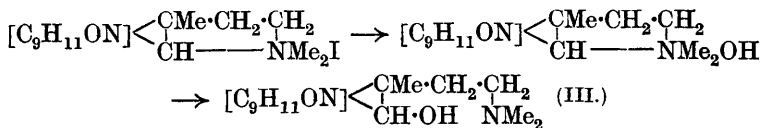
Göhring (A., 1921, i, 45) on the hydrochlorides of *d*-, *l*-, and *r*- $\psi$ -ephedrine and the chloroaurate of  $\psi$ -ephedrine. H. W.

**Physostigmine [Eserine]. III.** E. STEDMAN and G. BARGER (*J. Chem. Soc.*, 1925, 127, 247—258).—Earlier work (T., 1923, 123, 758; 1924, 125, 1373; Straus, A., 1914, i, 78; 1915, i, 448; M. and M. Polonovski, A., 1918, i, 504; 1923, i, 700, 940) has established the presence in eseroline of a 5-hydroxy-1:3-dimethylindoline nucleus, and the present investigation confirms the structure (I) suggested to the authors by Robinson. Eserine is the methylcarbamido derivative (NHMe·CO·O· for ·OH) and eserethole the ethyl ether of eseroline.

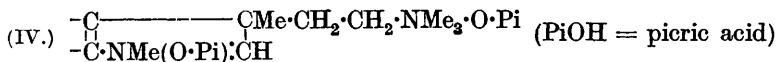


Eserethole, reduced with zinc and hydrochloric acid (Polonovski) or by Willstätter's method, yields a dihydro compound (II) (oxalate, m. p. 204°), which is a secondary base (the product formed by methylation gives a *dipicrate*, m. p. 204°) evidently produced by the opening of the ring containing the more strongly basic nitrogen atom. The point of rupture is determined by the fact that etheserolene (from exhaustive methylation of eserethole) gives on reduction a substance identical with that formed by the exhaustive methylation of dihydroeserethole (Polonovski).

Another compound in which the pyrrolidine ring has been opened is Polonovski's eseretholemethine (III), which is shown to be produced by a tautomeric change from eserethole methohydroxide:



Treatment of eseretholemethine methiodide with picric acid gives a diquaternary picrate (IV), m. p. 170°, with elimination of water, thus indicating the pseudobasic function of the oxygen atom, although reclosure of the pyrrolidine ring is precluded. Eseretholemethine is further characterised as a 2-hydroxyindoline deriv-



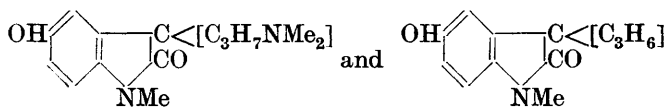
ative by oxidation with ammoniacal silver nitrate or alkaline ferricyanide to the indolinone, *dehydroeseretholemethine* (*picrate*, m. p. 199°; *methiodide*, m. p. about 131°; a *picrate*, m. p. 211°, probably derived from the corresponding indoline formed by reduction during isolation, is also described). Exhaustive methylation of dehydroeseretholemethine gives trimethylamine and

5-ethoxy-1 : 3-dimethyl-3-vinylindolin-2-one, m. p.  $62^{\circ}$  (*picrate*, m. p.  $103^{\circ}$ ), which is reduced by hydrogen and colloidal palladium to the 3-ethyl compound,  $C_{14}H_{19}O_2N$ , m. p.  $68^{\circ}$ . The behaviour of eseretholemethine is thus in accord with the suggested structure for eserine. Polonovski's structure (A., 1924, i, 980) for eserethole fails to explain the easy degradation of eseroline methiodide to physostigmol and cannot be built up from known naturally-occurring substances as can the authors' structure from tryptophan.

Eserethole is unattacked by dilute nitric acid; concentrated nitric acid gives *trinitroeserethole*, m. p.  $152^{\circ}$ . Oxidation with permanganate in acetone at  $-10^{\circ}$  converts eserethole into an oily product,  $C_{15}H_{20}O_2N_2$  (*picrate*, m. p.  $166^{\circ}$ ; *methiodide*, m. p.  $198-199^{\circ}$ ). Etheserolene, contrary to Polonovski's statement, forms a *picrate*, m. p.  $98^{\circ}$ .

The results of exhaustive methylation of esoline ethyl ether (T., 1923, 123, 758) are further detailed. The two products are (a) a substance,  $C_{16}H_{28}ON_2$  (*dipicrate*, m. p.  $156^{\circ}$ ; *methiodide*, m. p.  $169-170^{\circ}$ ), and (b) a substance,  $C_{18}H_{30}O_2N_2$  (*dipicrate*, m. p.  $199^{\circ}$ ; *methiodide*, m. p.  $141^{\circ}$ , and at  $100^{\circ}$  a second *methiodide*, m. p.  $188^{\circ}$ ). The substance (b) is not, as at first supposed, the ethyl ether of the hypothetical esoline base. C. H.

**Oxyeserine and its Derivatives.** M. and M. POLONOVSKI (*Compt. rend.*, 1925, 180, 73-76; cf. A., 1918, i, 505).—The bases designated  $\psi$ -geneserines are formed by the oxidation of the groups  $\cdot NMe \cdot CH \cdot$  to  $\cdot NMe \cdot CO \cdot$ , and should be termed oxyeserines, bringing them into line with oxyhydrastine etc.  $\psi$ -Geneserolimethine,  $C_{14}H_{20}O_2N_2$ , is basic and forms a *hydrochloride* without loss of water. It differs from the bases of the eserine series in giving no diacid salts nor di-iodomethiodides, the hydroindolic nitrogen having entirely lost its basic character. The final result of exhaustive methylation of these bases is *methiodo-o-methyl- $\psi$ -geneserolimethine*, m. p.  $275^{\circ}$ , which when heated at  $200^{\circ}$  with sodium hydroxide yields  $\psi$ -geneseroline,  $C_{12}H_{13}O_2N$ , m. p.  $224^{\circ}$ ,  $[\alpha]_D -85^{\circ}$  (in 95% alcohol). It is phenolic and dissolves in alkalis, but unlike etheseroline it is insoluble in acids, and in all its properties appears similar to the *N*-methyloxindoles. The following formulæ are therefore suggested for  $\psi$ -geneserolimethine and  $\psi$ -geneseroline respectively, with alteration of the names to oxyeserolimethine and



oxyeserolene etc. It is pointed out that in the breaking down of the eserine molecule the loss of two carbon atoms and the formation of a true indole (physostigmol) only takes place on starting from a closed basic nucleus (eseroline, eserethole). Starting from a methiodide of an open methine base (eseretholemethine etc.) there is no loss of carbon and degradation by Hofmann's method still leads to a dihydroindole derivative (etheserolene, oxyeserolene). The

fact that physostigmol is obtained and not an allylindole is in favour of a methylpyrrolidine rather than of a pyridine structure. A. C.

**Laudanidine.** E. SPÄTH and E. BERNHAUER (*Ber.*, 1925, 58, [B], 200—204).—Laudanidine, m. p. 184—185°,  $[\alpha]_D^{25}$  —100.6° in chloroform, isolated from opium by Hesse, is converted by diazomethane into 1-*laudanidine*, m. p. 87—88°, the identity of which is established by admixture with an equal weight of *d*-laudanidine and identification of the product so formed with *r*-laudanidine (Späth, A., 1921, i, 50). Since laudanidine when ethylated and then oxidised yields 4-methoxy-3-ethoxybenzoic acid (Späth, *loc. cit.*), it is established that laudanidine is the racemic form of laudanidine.

A convenient method for the preparation of 4-methoxy-3-ethoxybenzoic acid consists in the ethylation of isovanillin to 4-methoxy-3-ethoxybenzaldehyde, m. p. 50—51° (oxime, m. p. 98—99°), and oxidation of the latter with potassium permanganate in aqueous, alkaline solution. 4-Methoxy-3-ethoxybenzamide has m. p. 196—197°.

H. W.

**Preparation of a Reduction Product of Anhydrolupinine.** KALLE & Co. A.-G., E. BARTHOLOMÄUS, and O. SCHAUMANN (D.R.-P. 396508; from *Chem. Zentr.*, 1924, 95, ii, 1409).—Anhydrolupinine or its salts on treatment with hydrogen in acetic acid solution in the presence of platinum black, or chlorolupinine on reduction with sodium and alcohol, yield a colourless oil, *lupinane*, b. p. 89—91°, probably  $C_9H_{16}NMe$  (*picrate*, m. p. 185°); it is stated to have therapeutic properties.

R. B.

**Chemical Constitution of Spermine. I. Isolation of Spermine from Animal Tissues and Preparation of its Salts.** H. W. DUDLEY, M. C. ROSENHEIM, and O. ROSENHEIM (*Biochem. J.*, 1924, 18, 1263—1272).—Spermine has been isolated from the following animal organs: testis, ovary, pancreas, muscle, liver, brain, spleen, thymus, and thyroid. It has been prepared by precipitating extracts of the organs with phosphotungstic acid and extracting the phosphotungstates with acetone, which leaves the bulk of the base behind, or by continuously extracting the extracts with butyl alcohol, precipitating with phosphotungstic acid in butyl alcohol, and treating the phosphotungstates as above or by steam distillation from strongly alkaline solution. The phosphate,  $C_{10}H_{26}N_4 \cdot 2H_3PO_4 \cdot 6H_2O$ , lenticular crystals, has m. p. 230—234°. The *picrate*,  $C_{10}H_{26}N_4 \cdot 4C_6H_3O_7 \cdot N_3$ , forms yellow needles, m. p. (decomp.) 248—250° (darkening at 242°). The *hydrochloride*,  $C_{10}H_{26}N_4 \cdot 4HCl$ , forms prismatic needles, m. p. 310° after turning brown at 300—302°. The *picrolonate*, pale yellow needles, has m. p. 288—289° (decomp.). The *chloroaurate*,  $C_{10}H_{26}N_4 \cdot 4HCl \cdot 4AuCl_3$ , forms golden-yellow leaflets, m. p. about 225° (decomp.). The *chloroplatinate*,  $C_{10}H_{26}N_4 \cdot 2H_2PtCl_6$ , red prisms, has m. p. 242—245° (decomp.). *Benzoylspermine*,  $C_{10}H_{22}N_4 \cdot Bz_4$ , obtained by treating the phosphate with sodium hydroxide and benzoyl chloride, forms fine needles, m. p. 155°. *Sperminephenylcarbimide*, prepared from the hydrochloride by adding sodium hydroxide and phenylcarbimide, forms colourless needles, m. p. 179—180°. The free base, which is volatile with

steam and can be distilled in a vacuum, is prepared by adding potassium hydroxide to a concentrated solution of the hydrochloride or to a suspension of the phosphate in water and extracting with chloroform; it forms needles, m. p. 55–60°. The *arsenate* resembles closely the phosphate in crystalline form and solubility. The *oxalate* crystallises in leaflets, m. p. 225°. The *sulphate*, *nitrate*, *acetate*, and *carbonate* crystallise well, but are very hygroscopic. The free base and the hydrochloride are optically inactive. S. S. Z.

### Bromination and Iodination of some Derivatives of Pyrrole.

A. P. TERENTJEV and W. W. TSCHELINZEV (*Ber.*, 1925, **58**, [B], 66–71; cf. Pieroni, A., 1923, i, 613).—Pyrrole-2-aldehyde reacts very readily with bromine in the presence of light petroleum, yielding a mixture of mono- and di-bromopyrrolealdehydes which are extraordinarily unstable; in aqueous solution, dibromomaleinimide is ultimately formed. The primary action consists doubtless in the substitution in positions 3 or 4 without alteration of the aldehyde group. Iodination of pyrrole-2-aldehyde in very dilute, faintly alkaline, aqueous solution gives *tetraiodopyrrole-2-aldehyde*, m. p. 137°. 2-Acetylpyrrole is transformed under similar conditions into 3:4-di-iodo-2-acetylpyrrole, m. p. 157°, the constitution of which is established by its oxidation with ice-cold nitric acid (*d* 1.48) to *di-iodomaleinimide*, m. p. 255°. 2-Propionylpyrrole yields, similarly, 3:4-di-iodo-2-propionylpyrrole, m. p. 148°, or, in more concentrated solution and in the presence of a greater excess of alkali hydroxide and halogen, 3:4:5-tri-iodo-2-propionylpyrrole, m. p. 193°. Iodination of 2-benzoylpyrrole occurs with greater difficulty and appears to yield primarily a moniodo derivative which could not be isolated in the homogeneous form; at higher temperatures, (?) 3:4-di-iodo-2-benzoylpyrrole, m. p. 168–169°, and (?) 3:4:5-tri-iodo-2-benzoylpyrrole, m. p. 215°, are produced. Oxidation of the latter compound with fuming nitric acid yields 4-iodo-3-nitropyrrole, m. p. 195°. H. W.

**Magnesylypyrrole and its Use in the Synthesis of Pyrrole Compounds.** B. ODDO (*Mem. R. Accad. Lincei*, 1923, [v], **14**, 510–623).—The volume of ethane developed in the reaction between magnesylethane and the magnesyl derivatives of tripyrrole and tri-indole proves that each of these compounds contains only one secondary nitrogen atom.

Magnesylyndole forms, with pyridine and quinoline, compounds similar to those given by magnesylypyrrole (A., 1904, i, 920; 1907, i, 549, 668; 1909, i, 672). Magnesylcarbazole gives a definite compound with 1 mol. of ether.

Sulphur converts magnesylyndole and magnesyl-2-methylindole into crystalline compounds, di-indolyl sulphide and  $\alpha\alpha'$ -dimethyldi-indolyl sulphide, respectively; liquid sulphur dioxide converts the former into di-indolyl sulfoxide (cf. A., 1919, i, 134; 1920, i, 691).

3-Ethylindole, b. p. 276–277° (picrate, m. p. 144.5°), is obtained in the same way as 3-methylindole (A., 1911, i, 486). 1-Methylindole and 1:3-dimethylindole, b. p. 225–232° (picrate, m. p.

140°), are also obtained similarly to 3-methylindole by shortening the period of heating.

Phyllopyrrole is synthesised in small yield by the action of methyl iodide on the magnesyl derivative of 2 : 5-dimethyl-3-ethylpyrrole, but the principal product of this reaction is a pyrrolenine.

2-Benzyl pyrrol ketone, b. p. 335—340° (partial decomp.), m. p. 95° (*phenylhydrazone*, m. p. 133°, and *silver* derivative described), is prepared by the action of phenylacetyl chloride on magnesylpyrrole. The following are obtained similarly : 2 : 3 : 5-trimethyl-3-benzoylpyrrole, m. p. 172—173° (cf. A., 1910, i, 426); 4-(6-methoxyquinolyl) 2-pyrrol ketone, m. p. 139°; 4-(6-methoxyquinolyl) 2-(3 : 5-dimethylpyrrol) ketone, m. p. 165° (cf. A., 1918, i, 38); 2-methyl-3-chloroacetylindole, m. p. 201°; acetylcarbazole, m. p. 70°; *propionylcarbazole*, m. p. 90° (alcoholic potassium hydroxide gives carbazole and propionic acid; *picrate*, m. p. 140°; nitric acid gives *nitropropionylcarbazole*, m. p. 233°); benzoylcarbazole, m. p. 98° [boiling aqueous alkali gives carbazole and benzoic acid (cf. A., 1911, i, 486)].

Carbonyl chloride converts magnesylpyrrole into 2 : 2'-dipyrrol ketone, m. p. 160—161° (silver derivative described), which is also obtained by the action of pyrrole-2-carboxylic chloride on magnesylpyrrole. Ethyl nitrate reacts with magnesyl-2-methylindole to give a very small yield of 3-nitro-2-methylindole. At 260° carbon dioxide and magnesylpyrrole give pyrrole-3-carboxylic acid, m. p. 161° (cf. A., 1909, i, 672). In the absence of solvent at high temperature, magnesylcarbazole and carbon dioxide give carbazole-carboxylic acid, m. p. 275—276°, with slight blackening; silver and barium derivatives are described (cf. A., 1911, i, 486; 1912, i, 649).

The action of ethyl chloroformate on magnesylscatole at 140° gives only ethyl 3-methylindole-1-carboxylate, but at 250° a small yield of ethyl 3-methylindole-2-carboxylate, m. p. 134°, is obtained. By the action of the appropriate chloroformic ester on magnesylpyrrole the following are obtained, usually in 85—90% yield : methyl pyrrole-2-carboxylate, m. p. 73° (ammonia gives the amide, m. p. 176°); methyl pyrrole-1 : 2-dicarboxylate, m. p. 141°; ethyl pyrrole-1-carboxylate, b. p. 235°, m. p. 38°; *n*-propyl pyrrole-2-carboxylate, b. p. 164—165°/50 mm.; *isobutyl* pyrrole-2-carboxylate, b. p. 119—122°/70 mm.; *isoamyl* pyrrole-2-carboxylate, b. p. 186—190°/100 mm. Ethyl indole-2-carboxylate, m. p. 107°; ethyl 3-methylindole-1-carboxylate and ethyl 2-methylindole-3-carboxylate, m. p. 135°, are obtained by the action of ethyl chloroformate on the magnesyl derivatives of indole, scatole, and 2-methylindole, respectively. In this way magnesylcarbazole gives ethyl diphenylcarbamate, m. p. 77.5°.

Besides 3 : 3'-di-indyl (silver derivative; osazone, m. p. 158°; quinoxaline, m. p. 163°), the action of oxalyl chloride on magnesylindole gives 2 : 2-di-indyl, m. p. 273° (osazone, m. p. 170°, decomp.; quinoxaline, m. p. 154°, decomp.), and 1 : 2-bisindyl, m. p. 320°.

Malonyl chloride converts magnesylindole into *di-indolylmethane*, m. p. 287°. This substance is an equilibrium mixture of keto- and mono-enolic forms, the proportion of the former of which increases

with rising temperature. A silver derivative is described; phenylhydrazine gives 1-phenyl-3 : 5-di-indylpyrazole, m. p. 236° (decomp.); hydroxylamine gives 3 : 5-di-indylisooxazole, m. p. 219° (decomp.); hydrolysis of the product from the action of semicarbazide results in 3 : 5-di-indylpyrazole, m. p. 229° (decomp.); hydrolysis by alkali gives indole-3-carboxylic acid and 3-indolyl methyl ketone. Di-(2-methylindolyl)methane, m. p. 219°, is obtained similarly from magnesyl-2-methylindole. In the same way as the preceding one, this compound gives 1-phenyl-3 : 5-di(2-methylindyl)pyrazole, m. p. 192° (decomp.); 3 : 5-di(2-methylindyl)isooxazole, m. p. 174°; 3 : 5-di(2-methylindyl)pyrazole, m. p. 247° (decomp.). Di-indolylethane, m. p. 287° (silver derivative and dioxime, m. p. 305°, decomp.) and di(2-methylindolyl)ethane, m. p. 297° (decomp.) (dioxime, m. p. 267°), are obtained by the action of succinyl chloride on magnesylindole and magnesyl-2-methylindole, respectively.

Ethyl pyrrole-2-glyoxylate, m. p. 44·5°, is obtained by the action of ethoxalyl chloride on magnesylpyrrole; it is readily hydrolysed to the corresponding acid, m. p. 113° (decomp.).

Ethyl pyrrolylacetate (A., 1912, i, 804) gives pyrrolylphenylpyrazolone, m. p. 193°, and semicarbazone, m. p. 90°; alcoholic ammonia transforms it into the amide, m. p. 184°.

The paper contains a full bibliographical record of previous work. R. E. E.

### Preparation of Aldehydes and Ketones of the Pyrrole Series.

KALLE & Co., A.-G., and H. FISCHER (D.R.-P. 395092; from *Chem. Zentr.*, 1924, 95, ii, 1405—1406).—Aldehydes and ketones of the pyrrole series are obtained by the action of cyano compounds on pyrrole and indole derivatives in the presence of hydrogen chloride, the imino-hydrochloride formed intermediately being decomposed on boiling with water. Substitution in the  $\alpha$ -position predominates. Thus ethyl 2 : 4-dimethylpyrrole-3-carboxylate with acetonitrile in absolute alcohol gives an orange iminohydrochloride, yielding ethyl 5-acetyl-2 : 4-dimethylpyrrole-3-carboxylate, m. p. 140°, on treatment with water; with hydrogen cyanide ethyl 2 : 4-dimethyl-3-aldehydopyrrole-5-carboxylate, m. p. 165°, is obtained. 2 : 4-Dimethylpyrrole and chloroacetonitrile yield 5-chloroacetyl-2 : 4-dimethylpyrrole, m. p. 136°. Ethyl 3-carbethoxy-2 : 5-dimethylpyrrole-4-

glyoxylate,  $\text{NH} \begin{smallmatrix} \text{CMe}:\text{C}:\text{CO}:\text{CO}_2\text{Et} \\ \text{CMe}:\text{C}:\text{CO}_2\text{Et} \end{smallmatrix}$ , m. p. 102°, is similarly obtained

from ethyl pyrrole-3-carboxylate and ethyl cyanoformate. 2-Methylindole with chloroacetonitrile similarly yields 3-chloroacetyl-2-methylindole, m. p. 207°, and with hydrogen cyanide, 2-methylindole-3-aldehyde, m. p. 198° (cf. Plancher and Ponti, A., 1907, i, 341).

R. B.

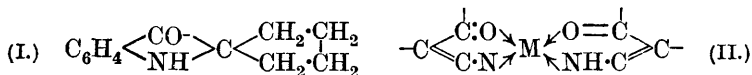
**Metabolism of Tryptophan. I. Synthesis of Racemic Bz-3-Methyltryptophan.** W. ROBSON (*J. Biol. Chem.*, 1924, 62, 495—514).—With the object of carrying out metabolism experiments to elucidate the mechanism of the formation of kynurenic acid from tryptophan, Bz-3-methyltryptophan has been synthesised. In preparing 5-methylindole by the method of Raschen (A., 1887, 956)

m\*



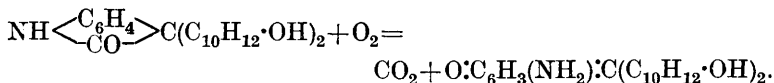
it was found that on saturating an alcoholic solution of pyruvic acid *p*-tolylhydrazone with dry hydrogen chloride, simultaneous esterification and ring closure occurred with direct formation of ethyl 5-methylindole-2-carboxylate; the yield of 5-methylindole itself was much improved by heating the dry ammonium salt of 5-methylindole-2-carboxylic acid instead of the free acid. 5-Methylindole gives, by Ellinger and Flamand's modification (A., 1907, i, 153) of the Tiemann and Reimer reaction, 5-methylindole-3-aldehyde, m. p. 148°, in small yield, with formation of 3-chloro-6-methylquinoline as a by-product. The aldehyde was also obtained in about the same yield by the method of Majima and Kotake (A., 1923, i, 156). Ethyl 3-aldehydo-5-methylindole-2-carboxylate, m. p. 189°, was obtained from ethyl 5-methylindole-2-carboxylate by the method of Adams and Levine (A., 1924, i, 51), and on hydrolysis gave ethyl 3-aldehydo-5-methylindole-2-carboxylate, m. p. 254—255° (decomp.). On heating this acid, a trace only of 5-methylindole-3-aldehyde was obtained. 5-Methylindole-3-aldehyde was condensed with hydantoin to give 5-methylindolylidenehydantoin, m. p. 295—298°; on reduction, this gave 5-ethylindolylhydantoin, m. p. 206—207°, which on hydrolysis with barium hydroxide gave Bz-3-methyltryptophan, m. p. 259—263°. C. R. H.

**Co-ordinated Compounds of the Alkali Metals.** N. V. SIDGWICK and S. G. P. PLANT (*J. Chem. Soc.*, 1925, 127, 209—211).—When  $\psi$ -indoxylspirocyclopentane (I) (Perkin and Plant, T., 1923, 123, 676) is heated with aqueous sodium, potassium, or lithium hydroxide at 200—210° in a closed tube, there results a compound of the type MB,HB [HB=(I); M=Na, K, or Li]. The sodium derivative, m. p. 204°, and the potassium derivative, m. p. 80—90°, are soluble in toluene, decomposed at once by water regenerating (I), and give by distillation in a vacuum (I) and a solid residue, which is



probably the simple metal salt of (I). The lithium compound, m. p. 170°, is less stable and cannot be purified. The co-ordination formula (II) is suggested for the compounds MB,HB. C. H.

**Dithymolisatin Colouring Matter.** CÂNDEA (*Bul. Soc. Chim. România*, 1924, 6, 113).—When oxidised in alkaline solution, dithymolisatin yields a red colouring matter:

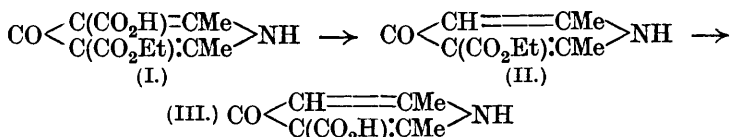


The course of the reaction may be followed by measuring the volume of carbon dioxide liberated. T. H. P.

**Synthesis of 4-Methyl-3-ethylpyridine and a New Parvoline [2:6-Dimethyl-3-ethylpyridine].** E. KOENIGS and F. K. HOFFMANN (*Ber.*, 1925, 58, [B], 194—197; cf. A., 1921, i, 595).—3-Ethylpyridine methiodide is converted at 300° into 2-methyl-5-ethyl-

pyridine and a small proportion of 4-methyl-3-ethylpyridine, b. p.  $198^{\circ}$  (picrate, m. p.  $144^{\circ}$ ). Under similar conditions, 5-ethyl-2-vinylpyridine methiodide is transformed into a saturated base,  $C_{10}H_{13}N$ , b. p.  $106-107^{\circ}/30$  mm. (picrate, m. p.  $164^{\circ}$ ; chloroplatinate, m. p.  $104-105^{\circ}$ ; additive compound with mercuric chloride, m. p.  $137^{\circ}$ ). 2-Methyl-5-ethylpyridine methiodide gives 2:6-dimethyl-3-ethylpyridine, b. p.  $83-85^{\circ}/23$  mm.,  $d^{18}_4$  0.9120 (picrate, m. p.  $162^{\circ}$ ; chloroplatinate, m. p.  $178^{\circ}$ ), the constitution of which is established by its oxidation to pyridine-2:3:6-tricarboxylic acid, identified as the calcium salt. H. W.

**Structure of Dehydracetic Acid.** C. F. RASSWEILER and R. ADAMS (*J. Amer. Chem. Soc.*, 1924, 46, 2758—2764).—The ethyl 4-lutidone-3:5-dicarboxylate obtained by Conrad and Guthzeit (A., 1886, 333) on partial hydrolysis with 4*N*-alcoholic potassium hydroxide (2 equivalents) yields ethyl hydrogen 4-lutidone-3:5-dicarboxylate, m. p.  $181-184^{\circ}$  (I). On distillation at 30 mm., the hydrogen ester affords carbon dioxide and ethyl 4-lutidone-3-carboxylate, m. p.  $161-162^{\circ}$  (II), which on hydrolysis yields an acid (III) identical with that obtained from dehydracetic acid by treatment with sulphuric acid and then with ammonia, relations which are only in harmony with this synthesis if dehydracetic acid possesses the Feist formula.



Some ethyl 4-lutidone-3:5-dicarboxylate is formed in the above hydrogen ester decomposition, and also a liquid fraction consisting mainly of ethoxylutidine. Some 4-lutidone is present in the residue after distillation. 4-Lutidone-3-carboxylic acid, m. p.  $158-159^{\circ}$  (decomp.), on heating at  $270^{\circ}$  yields 4-lutidone. 4-Lutidone-3:5-dicarboxylic acid has m. p.  $275-277^{\circ}$  (decomp.) (cf. Conrad and Guthzeit, A., 1887, 500). R. B.

**Fission of the Pyridine Nucleus During Reduction. II. Preparation of Glutardialdoxime.** B. D. SHAW (*J. Chem. Soc.*, 1925, 127, 215—216).—That pyridine is reduced by sodium and alcohol first to 1:4-dihydropyridine (cf. A., 1924, i, 1343) is confirmed by the formation of glutardialdoxime, m. p.  $175^{\circ}$ , in good yield when hydroxylamine hydrochloride is added to the reduction liquor and the solution boiled for a few minutes. The pyridine is purified with permanganate and dried over calcium carbide; the alcohol is distilled through a column packed with calcium carbide. Amyl alcohol gives a slightly higher yield. C. H.

**Preparation of Hydroxy Derivatives of Pyridine, Quinoline, and their Homologues.** A. E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1924, 55, 7—18).—Quinoline reacts with carefully dried potassium hydroxide at about  $230^{\circ}$ , giving a good yield of 2-hydroxyquinoline, hydrogen being evolved. On raising the

temperature to 300°, a second hydroxyl group is introduced, apparently in position 4. The action of potassium hydroxide is thus similar to that of sodamide. Sodium hydroxide does not react under these conditions; barium oxide, especially when partly hydrated, reacts at a lower temperature (150°), but the yield of 2-hydroxyquinoline is less and some diquinoline is formed; in addition to this there is, in all cases, evidence of the formation of indole. Pyridine gives 2-pyridone when heated with potassium hydroxide; quinaldine does not react, but an evolution of hydrogen is observed with lepidine. The reaction is inhibited by traces of moisture.

G. A. R. K.

**Preparation of Readily Soluble Compounds of C-Substituted Dialkyl- and Arylalkyl-barbituric Acids.** F. HOFFMANN-LA ROCHE & Co., A.-G. (D.R.-P. 398851; from *Chem. Zentr.*, 1924, ii, 1409).—Readily soluble salts of C-substituted dialkyl- and arylalkyl-barbituric acids are obtained by treating the free acids with alkylamines, and these salts are more stable than the sodium salts in aqueous solution. They show a pronounced increase in the hypnotic effect, as compared with the free acids, without a corresponding increase in toxicity, and in consequence of their solubility in water can be used for injections. The following compounds are described: Diethylamine diethylbarbiturate; diethylamine diallylbarbiturate, fibrous needles; dimethylamine phenylethylbarbiturate, dense prisms; monomethylamine diethylbarbiturate; choline diethylbarbiturate.

R. B.

**Phenylethylethylbarbituric Acid and Related Derivatives.** A. W. DOX (*J. Amer. Chem. Soc.*, 1924, 46, 2843—2846).—In view of the tetanic effect which accompanies the hypnotic action of benzyloethylbarbituric acid (A., 1922, i, 681; Shonle and Moment, A., 1923, i, 248), substitution of phenyl on a  $\beta$ -carbon atom in the alkyl side-chain has been investigated in the hope that the compounds obtained would show greater similarity to phenylethylbarbituric acid in accordance with the alternation of properties in an homologous series. Phenylethylbarbituric acid, isomeric with "luminal," is physiologically inactive, but  $\beta$ -phenylethylethylbarbituric acid is a powerful hypnotic when administered intravenously, although much less so when administered orally. The convulsive symptoms observed with benzyloethylbarbituric acid were absent and the evidence is accordingly in favour of the recurrence of physiological character with substitution of the phenyl group on alternate carbon atoms.  $\beta$ -Phenylethyl bromide, b. p. 79—81°/4 mm. (cf. Grignard, A., 1904, i, 498), obtained in 71% yield by the action of hydrobromic acid and sulphuric acid on  $\beta$ -phenylethyl alcohol, with ethyl sodiomalonate gives, together with some styrene, (yield 68%) ethyl  $\beta$ -phenylethylmalonate, b. p. 142—143°/2 mm., 296—298°/741 mm.,  $d^{25}_4$  1.0580; the ester amide forms needles, m. p. 98°, and the diamide has m. p. 232°. With ethyl bromide and sodium ethoxide, ethyl  $\beta$ -phenylethyl malonate gives, in 89% yield, ethyl  $\beta$ -phenylethylethylmalonate, b. p. 148—150°/2 mm., 314—316°/741 mm.,  $d^{25}_4$

1.0382; the free acid has m. p. 125—126°, decomp. 160°. With carbamide or substituted carbamides, the two malonic esters described above yield the following substituted barbituric acids: 5-β-phenylethylbarbituric acid (yield 95%), m. p. 212—213°, 1-phenyl-5-β-phenylethylbarbituric acid (yield 75%), m. p. 164°; 5-β-phenylethyl-5-ethylbarbituric acid (yield 90%), m. p. 168°; 1-phenyl-5-β-phenylethyl-5-ethylbarbituric acid (yield 20%), m. p. 110°; and 1-benzyl-5-β-phenylethyl-5-ethylbarbituric acid (yield 53%), m. p. 141—142°. R. B.

**Preparation of Pyrazolone Derivatives.** FARBENFABR. VORM. F. BAYER & CO., H. HAHN, and L. SCHÜTZ (D.R.-P. 396507; from *Chem. Zentr.*, 1924, ii, 1408).—Hydroxypyrazolones are treated with basic alkyl halides of the general formula,  $R_2N \cdot CH_2 \cdot CH_2 \cdot X$ , in the presence of alkaline solvents, or the hydroxypyrazolone is first converted into the halogenalkyl ether by the action of alkylene dihalides, and this converted into the aminoalkyl ether by treatment with secondary aliphatic amines. Thus 3-hydroxy-1-phenyl-4-dimethyl-5-pyrazolone with diethylaminoethyl chloride in the presence of alcoholic sodium ethoxide yields the β-diethylaminoethyl ether (annexed formula), a yellow oil, b. p. 210—215°/10 mm. (*hydrochloride*, m. p. 157°). The β-diethylaminoethyl ether of 3-hydroxy-4-diallyl-5-pyrazolone, a yellow oil, b. p. 228—235°/10 mm., is similarly obtained. The sodium salt of hydroxydiethylpyrazolone on heating with dimethylaminoethyl chloride at 120° is converted into 3-β-dimethylaminoethoxy-4-diethyl-5-pyrazolone, yellow oil, b. p. 220—225°/10 mm., crystallising in the cold, a strongly basic ether which has therapeutic use. In addition to antipyretic properties, pyrazolones containing basic alkyl groups attached to carbon show vascular contractive properties. R. B.

**Preparation of Homologues of 2-Aminopyridine.** CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING), H. HORSTERS, and M. DOHRN (D.R.-P. 398204; from *Chem. Zentr.*, 1924, ii, 1409).—Pyridine homologues on amination with sodamide, or with sodium and gaseous ammonia in diluents of high b. p., such as xylene, cumene, or mesitylene, at temperatures above 150°, yield homologues of 2-aminopyridine which are of therapeutic importance or are used for the preparation of therapeutic agents. 2-Methyl-5-ethylpyridine yields 6-amino-2-methyl-5-ethylpyridine, m. p. 51°, b. p. 110—112°/4 mm. 2-Amino-4-ethylpyridine, b. p. 134—139°/16 mm., is similarly prepared, whilst 4 : 4'-dipyridyl with sodamide in cumene at 200° yields 2 : 2'-diamino-4 : 4'-dipyridyl, pale yellow needles, m. p. 183°. R. B.

**Iodination of 2-Aminopyridine.** O. MAGIDSON and G. MENSCHIKOFF (*Ber.*, 1925, 58, [B], 113—118).—2-Acetamido-1-methylpyridinium iodide is converted by boiling hydriodic acid into a mixture of 5-iodo-2-aminopyridine periodide,  $C_5H_5N_2I_2$ , m. p. 144—146°, and 1-methyl-2-pyridoneimide hydriodide, m. p. 148—

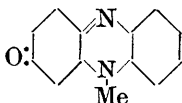
149° (cf. Tschitschibabin, A., 1921, i, 450). The direct iodination of 2-aminopyridine is effected more readily with hydrogen peroxide and hydriodic acid, or, preferably, with iodide-iodate or a solution of iodine in aqueous potassium iodide. In all cases, a relatively stable periodide is formed which is decomposed by boiling alkali hydroxide solution. 5-Iodo-2-aminopyridine has m. p. 129°; the corresponding *hydriodide* and *picrate*, m. p. 240° (decomp.), are described. The introduction of a second atom of iodine could not be effected. 5-Iodo-2-aminopyridine is converted by sulphuric acid ( $d$  1.84) and nitric acid ( $d$  1.4) at 0° into 5-iodo-2-nitroaminopyridine, m. p. 189° (decomp.). 5-Iodo-2-pyridone, m. p. 183—189°, is prepared by the action of nitrous acid on 5-iodo-2-aminopyridine or by the direct iodination of 2-pyridone, which proceeds with considerable difficulty. Diazotisation of 5-iodo-2-aminopyridine in the presence of hydrochloric acid ( $d$  1.19) yields 2-chloro-5-iodopyridine, m. p. 99°, which is notable for the absence of basic properties; it is transformed by sodium methoxide solution into 5-iodo-2-methoxypyridine, b. p. 231° (*picrate*, m. p. 147°). The position of the halogen atom in the latter compound (and hence in 5-iodo-2-aminopyridine) is established by the conversion of the silver salt of 5-nitro-2-pyridone successively into 5-nitro-2-methoxypyridine, m. p. 110°, 5-amino-2-methoxypyridine, and 5-iodo-2-methoxypyridine, b. p. 85°/22 mm., identical with the product described above. H. W.

**Chemistry of Furfuraldehyde. Preparation of the Furan Analogue of Benzoflavine or Dimethylldiaminofurylacridine Hydrochloride.** S. A. MAHOOD and C. R. HARRIS (*J. Amer. Chem. Soc.*, 1924, **46**, 2810—2813; cf. Renshaw and Naylor, A., 1922, i, 566).—Furfuraldehyde condenses with *m*-tolylenediamine sulphate in alcoholic solution, yielding tetraminoditolylfurylmethane sulphate, hydrolysed by 6*N*-hydrochloric acid at 140° to diamino-dimethylfuryldihydroacridine (yield 60%), from which 2:8-di-amino-3:7-dimethyl-5-furyl-5:10-dihydroacridine, isolated as the *additive* compound,  $3C_{19}H_{18}ON_3 \cdot 3HCl \cdot ZnCl_2$  (?), is obtained on oxidation with 30% ferric chloride in the presence of zinc chloride. The zinc content is variable, but the nitrogen content on a zinc chloride-free basis is constant. R. B.

**Reduction of Dialkylxydihydropyrazines.** P. KARRER and C. GRÄNACHER (*Helv. Chim. Acta*, 1924, **7**, 1062—1064).—When 2:5-dibenzoyloxydihydropyrazine (cf. A., 1924, i, 212) is reduced with sodium and hot amyl alcohol it yields piperazine and some  $\beta$ -hydroxyethylamine (?). This result is interesting in connexion with the conclusion (Abderhalden) that a diketopiperazine ring structural arrangement is present in proteins. W. A. S.

**Syntheses of Quinone-imide Dyes. V. The Use of Hydroxy-*p*-benzoquinone.** F. KEHRMANN and F. CHERPILLOD (*Helv. Chim. Acta*, 1924, **7**, 973—980; cf. Kehrman and Messinger, A., 1891, 746).—When hydroxy-*p*-benzoquinone (Willstätter and

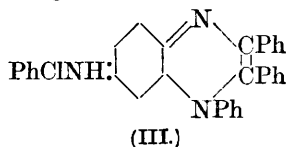
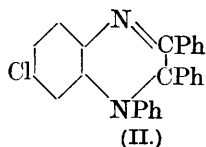
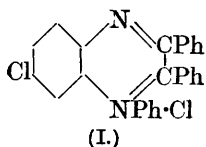
Muller, A., 1911, i, 728) is treated in cold acetic acid solution with *o*-phenylenediamine, 2-hydroxyphenazine, golden-yellow crystals, m. p. 253—254°, is produced (yield : 87%). The compound forms a dark red *hydrate*, being precipitated in this form when its solution in sodium hydroxide is acidified. The *acetyl* derivative forms yellow crystals, m. p. 152°; when it is treated with methyl sulphate, followed by hot water, the product is a mixture of two isomerides, which are separated by fractional precipitation of the perchlorates. The sparingly soluble perchlorate is that of *N*-methylaposafranine (annexed formula), dark red leaflets, m. p. 185° (the *chloride* and *chloroplatinate* are described); the other is that of *methylprasindone* (?), the *nitrate* and *chloroplatinate* of which are described, but the base itself was not isolated.



Hydroxybenzoquinone also interacts with *o*-tolylenediamine (1 : 3 : 4), only one of the possible isomerides, and that in meagre yield, being formed. This, a *hydroxymethylphenazine*, forms orange-red crystals, m. p. 248°, and yields an *acetyl* derivative, m. p. 207°. With 1 : 2-naphthylenediamine 3-hydroxynaphthaphenazine, red needles, decomp. 285—287°, is produced, accompanied by an azine-like by-product. The 3-position is assigned to the hydroxy group because of the great similarity between the compound and the corresponding *isorosindone*. The *acetyl* derivative forms yellow needles, m. p. 216.5°. With *o*-aminodiphenylamine, a poor yield of *aposafranine* (A., 1895, i, 527) accompanied by a little fluorindene, is obtained. The product of the interaction of hydroxybenzoquinone and *o*-aminophenol is mainly triphendioxazine, but a little phenazoxone (cf. Kehrmann and Saager, A., 1902, i, 235) is also formed. Hydroxybenzoquinone and aniline yield a mixture of dianilinobenzoquinone, anilinohydroxybenzoquinoneanilide (Zincke and Hagen, A., 1885, 787), and anilinohydroxybenzoquinone (Kehrmann and Bahatryan, A., 1899, i, 31).

W. A. S.

**Syntheses of Quinone-imide Dyes. VI. Certain aposafranine Analogues of the Stilbazonium Series.** F. KEHRMANN and E. FALKE (*Helv. Chim. Acta*, 1924, 7, 981—984; cf. A., 1891, 945).—Benzil condenses with 5-chloro-2-aminodiphenylamine hydrochloride in hot alcoholic solution to form 3-chlorophenylstilbazonium chloride (I). The corresponding perchlorate forms



citron-yellow needles and when it is treated in aqueous solution with sodium hydroxide a yellow precipitate of the  $\psi$ -base (II) is separated. When the chloride is boiled with aniline the compound (III), which is the analogue of *aposafranine*, is produced. This substance forms dark-violet bronze needles but when it is treated with sodium hydroxide it also yields a yellow  $\psi$ -base resem-

bling II. The chlorophenylstilbazonium chloride likewise reacts with dimethylamine at 150—180°, giving the *dimethylamino* analogue, the *perchlorate* of which is described. W. A. S.

**Syntheses of Quinone-imide Dyes. VII. 1-Amino-phenazine.** F. KEHRMANN and P. PRUNIER (*Helv. Chim. Acta*, 1924, 7, 984—991).—3 : 5-Diamino-*o*-benzoquinone (Nietzki and Moll, A., 1893, i, 699; see also below) reacts with *o*-phenylenediamine in dilute acetic acid solution at 30—40° to produce 1 : 3-*di*-aminophenazine, red leaflets, m. p. 255° (decomp.). The *mono-perchlorate*, when treated with cold acetic anhydride, affords 3-amino-1-acetamidophenazine, the *perchlorate* of which is described. When the aminoacetamidophenazine is dissolved in cold sulphuric acid (*d* 1.68) and treated with sodium nitrite followed by alcohol, the amino group is removed and 1-acetamidophenazine, yellow needles, is produced. This undergoes hydrolysis when it is heated with sulphuric acid (*d* 1.68) at 40°, yielding 1-aminophenazine, dark red leaflets, m. p. 172°.

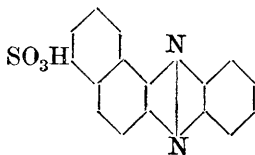
Di-iminopyrocatechol similarly reacts with *o*-aminodiphenylamine, yielding solely Kehrman and Kramer's *isophenosafraanine* (A., 1900, i, 61; 1901, i, 52).

The constitutional formulæ of the above compounds and their congeners are discussed.

The product obtained by nitrating diacetylpyrocatechol is not dinitrodiacetylpyrocatechol, as Nietzki and Moll supposed, but *dinitromonoacetylpyrocatechol*, m. p. 120°. This compound resembles picric acid; it forms yellow, crystalline salts when treated with sodium and potassium acetates. When it is boiled with acetic anhydride and a little zinc chloride, the true *diacetyl* compound, m. p. 112—114°, is obtained. Nietzki and Moll's prescription was followed in converting the above product into 3 : 5-diamino-*o*-benzoquinone. It was found that the final oxidation must be carried out with care.

W. A. S.

**Preparation of Azine Derivatives.** AKT.-GES. F. ANILIN-FABRIKATION, W. HERZBERG, W. BRUCK, G. HOPPE, and H. OHLENDORF (D.R.-P. 394195; from *Chem. Zentr.*, 1924, ii, 1135—1136).—Naphthaphenazine- and dinaphthazine-sulphonic acids on heating with sodium or potassium hydroxide are converted into the corresponding hydroxy derivatives without the azine ring being attacked. If one of the hydroxyl groups is ortho to the



azine nitrogen atom condensation occurs simultaneously.  $\alpha$ -Naphthaphenazine-4-sulphonic acid (annexed formula), yellow powder, from *o*-phenylenediamine and 1 : 2-naphthaquinone-5-sulphonic acid, with 30% sodium hydroxide at 210—220° under pressure yields 4-hydroxy- $\alpha$ -naphthaphenazine, yellow needles, m. p. about 250°. Similarly,  $\alpha$ -naphthaphenazine-3-sulphonic acid, yellow, from *o*-phenylenediamine and 1 : 2-naphthaquinone-6-sulphonic acid, with potassium hydroxide at 250° yields 3-hydroxy- $\alpha$ -naphthaphenazine, bright yellow needles, m. p. about

280° (red sodium salt).  $\alpha\beta$ -Naphthaphenazine-1-sulphonic acid, similarly prepared, with potassium hydroxide at 200°, yields a substance, greenish-yellow needles, m. p. 210°.  $\alpha\alpha'\beta\beta'$ -Dinaphthazine-2 : 3'-disulphonic acid (Meigen and Norman, A., 1900, i, 702) with potassium hydroxide at 260° yields the yellow potassium salt (?) of 3-hydroxy- $\alpha\alpha'\beta\beta'$ -dinaphthazine-3-sulphonic acid, and 3 : 3'-dihydroxy- $\alpha\alpha'\beta\beta'$ -dinaphthazine, brownish-yellow. 5-Hydroxy- $\alpha\alpha'\beta\beta'$ -dinaphthazine-5'-sulphonic acid, orange-red, from 2-hydroxy-1 : 4-naphthaquinone and 1 : 2-diaminonaphthalene-4-sulphonic acid, with potassium hydroxide at 240° yields 5 : 5'-dihydroxy- $\alpha\alpha'\beta\beta'$ -dinaphthazine, yellow (potassium salt, reddish-brown), together with an isomeric red dihydroxydinaphthazine.  $\alpha\alpha'\beta\beta'$ -Dinaphthazine-1 : 1'-disulphonic acid, obtained by oxidising 2-amino-naphthalene-8-sulphonic acid with sodium hypochlorite, with potassium hydroxide at 240° yields a substance, orange-yellow needles, m. p. above 300°. R. B.

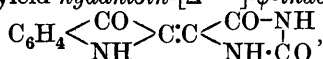
**Reduction of the Carbocyanines.** (MISS) F. M. HAMER (*J. Chem. Soc.*, 1925, **127**, 211—214).—König's method (A., 1923, i, 1188; 1924, i, 669) for the synthesis of 1 : 1'-dimethylcarbocyanine iodide does not give more than 20% of the yield claimed. The relationship of the carbocyanines to the methylenediquinaldine dialkylhalides (T., 1923, **123**, 246) has now been further demonstrated by the reduction of 1 : 1'-dimethyl-, 1 : 1'-diethyl-, and 6 : 6'-dimethyl-1 : 1'-diethyl-carbocyanine halides with hydriodic acid at about 180° to the corresponding methylenediquinaldine dialkyl iodides. *p*-Dimethylaminobenzylidenequinaldine ethiodide, m. p. 259—263° (decomp.) (König and Treichel, A., 1921, i, 738), prepared in much improved yield by increasing the time of heating, is similarly reduced to *p*-aminobenzylquinaldine ethiodide, m. p. m. p. 200—201° (softens at 198°), the two methyl groups being eliminated during the reduction. C. H.

**Condensation Reactions of Cyclic Ketones. I. Action of Isatin and Isatin  $\alpha$ -Chloride on certain Hydantoins.** A. J. HULL and H. R. HENZE (*J. Amer. Chem. Soc.*, 1924, **46**, 2806—2810).—In view of the activity of acenaphthenequinone, phenanthraquinone, and isatin towards certain compounds possessing the linking  $X\cdot CH_2\cdot CO$  (cf. A., 1908, i, 673; 1910, i, 278; 1911, i, 333; 1917, i, 663) the interaction of isatin and isatin  $\alpha$ -chloride with hydantoin, 3-phenyl-2-thiohydantoin, and phenylhydantoin has been examined, with a view to obtain further information regarding the activity of cyclic ketones towards the grouping  $-CO\cdot CH_2\cdot NH-$ . Deeply coloured brown or red condensation products were obtained, the  $\alpha$ -compounds analogous to indigotin being more deeply coloured than the  $\beta$ -compounds analogous to indirubin. Parabanic acid could not be condensed with hydantoin, but its inactivity is to be attributed to the amidic character of both carbonyl groups as well as to the absence of the activating phenyl group.

Isatin and hydantoin in the presence of acetic acid and sodium acetate at 150° give hydantoin- $[\Delta^{5:3'}]$ -oxindole, 
$$\begin{array}{c} C_6H_4\cdot C=C\cdot CO\cdot NH \\ | \\ NH-CO\cdot NH-CO\cdot \end{array}$$



reddish-brown, m. p. above  $300^{\circ}$ . Similarly, isatin  $\alpha$ -chloride and hydantoin at  $160^{\circ}$  yield *hydantoin*- $[\Delta^{5:2'}]$ - $\psi$ -*indoxyl*,



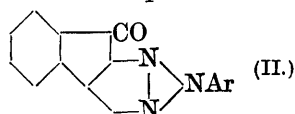
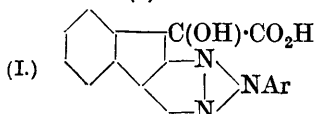
chocolate-brown, m. p. above  $300^{\circ}$ ; isatin and 3-phenyl-2-thiohydantoin at  $160^{\circ}$  yield 3-*phenyl-2-thiohydantoin*- $[\Delta^{5:3'}]$ -*oxindole*, reddish-brown, m. p. about  $300^{\circ}$ ; 3-phenyl-2-thiohydantoin and isatin  $\alpha$ -chloride yield 3-*phenyl-2-thiohydantoin*- $[\Delta^{5:2'}]$ - $\psi$ -*indoxyl*, dark red, m. p. above  $300^{\circ}$ ; and isatin and 3-phenylhydantoin yield 3-*phenylhydantoin*- $[\Delta^{5:3'}]$ -*oxindole*, yellowish-red, m. p. about  $300^{\circ}$ . The reduction and hydrolysis of these products are under investigation in view of their possibilities for the synthesis of amino-acids.

R. B.

**Degradation of Histidine to *l*-Aspartic Acid.** W. LANGENBECK (*Ber.*, 1925, 58, [B], 227—229).—The relationship of natural, dextrorotatory *l*-histidine to *l*-aspartic acid is established by the observation that its methyl ester is transformed by benzoyl chloride into the substance,  $\text{CO}_2\text{Me}\cdot\text{CH}(\text{NHBz})\cdot\text{CH}_2\cdot\text{C}(\text{NHBz})\cdot\text{CH}\cdot\text{NHBz}$ , which is converted by ozone into methyl dibenzoylasparagine. The latter substance is hydrolysed to *l*-benzoylaspartic acid, m. p.  $179^{\circ}$ ,  $[\alpha]_{\text{D}}^{18} + 38.4^{\circ}$  in 2*N*-sodium hydroxide solution, which is identical with the product of the benzylation of *l*-aspartic acid. The possibility of a Walden inversion during the changes is excluded, since the groups attached to the asymmetric carbon atom are not involved. Racemisation does not appear to occur during the process.

H. W.

**Phenylene-2-aryltriazoxyleneglycollic Acids.** G. CHARRIER and M. GALLOTTI (*Gazzetta*, 1924, 54, 982—988).—The action of dilute alkali hydroxide solution on 2-aryl- $\alpha\beta$ -naphthatriazole-*o*-quinones (cf. A., 1924, i, 1351) proceeds similarly to that on phenanthraquinone or benzil, yielding phenylene-2-aryltriazoxyleneglycollic acids (I). These acids are colourless compounds which are



rapidly turned bright yellow in the light and decompose on melting; they readily undergo oxidation to pale yellow compounds, which are probably the corresponding ketonic derivatives (II). Their sodium salts are phototropic, form slightly fluorescent solutions which froth intensely when shaken, and, when heated, yield deep orange-yellow, crystalline sublimates, apparently analogous to dibiphenylene-ethene. Oxidation of phenylene-2-aryltriazoxyleneglycollic acids by an acetic acid solution of hydrogen peroxide gives 2-aryltriazoxyphenyldicarboxylic acids,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}_2\text{N}_3\text{Ar}\cdot\text{CO}_2\text{H}$  (cf. A., 1924, i, 329).

[With C. VITALE].—*Phenylene-2-phenyltriazoxyleneglycollic acid*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C(OH)} \diagdown \\ \diagdown \text{C}_2\text{N}_3\text{Ph} \end{array} \text{C(OH)}\cdot\text{CO}_2\text{H}$ , prepared from 2-phenyl- $\alpha\beta$ -naphthatri-

azolequinone, has m. p. about  $135^{\circ}$  (decomp.), and its sodium salt ( $+4\text{H}_2\text{O}$ ), m. p. about  $200^{\circ}$ . *Phenylene-2-p-chlorophenyltriazoyle-glycollic acid*,  $\text{C}_{16}\text{H}_{10}\text{O}_3\text{N}_3$ , has m. p.  $197-198^{\circ}$  (decomp.); its sodium salt ( $+4\text{H}_2\text{O}$ ) has m. p.  $252^{\circ}$  (decomp.). T. H. P.

**Bile Pigments. XV. Bilirubin Dimethyl Ester.** W. KÜSTER, R. HAAS, and H. MAURER (*Z. physiol. Chem.*, 1924, **141**, 40—54).—The difficulties previously encountered (A., 1922, i, 885) in attempts to prepare bilirubin dimethyl ester have now been overcome. When chloroform solutions of bilirubin are shaken with aqueous solutions of amino-acids (glycine, alanine, histidine) molecular compounds consisting of 1 mol. of bilirubin with 2 mols. of monoamino-acid (or 1 mol. of histidine) are formed. These compounds slowly decompose into their components in chloroform solution, a process which is accelerated by the addition of calcium chloride, and differ from bilirubin in their inability to combine with ammonia. The amino-acids evidently protect the "sensitive" points of the molecule which are attacked by diazomethane, for the bilirubin-glycine thus prepared undergoes esterification to dimethylbilirubin-glycine when its chloroform solution is treated with diazomethane. This ester yields *dimethylbilirubin*,  $\text{C}_{35}\text{H}_{40}\text{O}_6\text{N}_4$ , when kept for 4 days in chloroform solution over calcium chloride or when heated at  $120^{\circ}$  in an atmosphere of hydrogen; the product obtained by the latter method, however, retains 3 mols. of chloroform and alcohol, respectively, when treated with these solvents. Dimethylbilirubin exists in two isomeric forms, an enolic form, m. p.  $204-205^{\circ}$  after sintering at  $165-167^{\circ}$ , which has an orange colour and gives a green coloration with ferric chloride in dilute alcoholic solution, and a keto form, m. p.  $168-169^{\circ}$  after sintering at  $144^{\circ}$ , which is reddish-brown in colour and gives a deep red coloration with aluminium chloride but does not react with ferric chloride. Separation of the two forms is effected by fractional crystallisation from methyl alcohol. Dimethylbilirubin may be prepared more simply by treating a suspension of bilirubin in chloroform with diazomethane; this method is only completely successful, however, when the bilirubin has been prepared by the chloroform extraction method. The preparation of two isomeric dimethylbilirubins explains older observations on bilirubin (e.g., A., 1917, i, 421). Biliverdin forms a compound with one molecule of glycine. E. S.

**Porphyrins. XII. Ætioporphyrin from Urinoporphyrin.** H. FISCHER and J. HILGER (*Z. physiol. Chem.*, 1924, **140**, 223—243).—When a pyridine solution of the methyl ester of urinoporphyrin is heated with methyl-alcoholic potassium hydroxide and magnesium oxide, the potassium salt of a phyllin, which can be readily reconverted into the original porphyrin, separates. On distillation in a vacuum, this potassium salt gives a sublimate which yields *ætiourinoporphyrin* on removal of magnesium by treatment with acid. Spectroscopic results indicate that coproporphyrin is similarly converted into an identical ætioporphyrin. Ætiourinoporphyrin has been found to be identical with ætioporphyrin from hæmatoporphyrin; it is evidently formed from urinoporphyrin by

the elimination of eight carboxyl groups and hence no hydroxyl groups are present in the latter substance. Coproporphyrin is similarly considered to contain four carboxyl groups. Alternative structures are advanced for aetioporphyryn, which the authors consider probably possesses the formula  $C_{32}H_{36}(\text{or } 38)N_4$  instead of that ( $C_{31}H_{36}N_4$ ) proposed by Willstätter. The corresponding structures of urinoporphyryn and coproporphyrin are also given.

E. S.

**Action of Hydroxylamine and of Hydrazine on the Aryl Monothioamides of Ethyl Acetylmalonate. II.** D. E. Worrall (*J. Amer. Chem. Soc.*, 1924, **46**, 2832—2834; cf. A., 1922, i, 874).—A further series of isooxazoles and pyrazoles has been obtained by the action of hydroxylamine and hydrazine on the thioamides of ethyl acetylmalonate recently described (A., 1924, i, 208). The compounds in both series form salts with both acids and bases, contain a reactive methylene group, and are readily acetylated or benzoylated.

The following compounds are described: 3-o-toluidino-5-ketooxazole, m. p. 146—147°; 3-m-toluidino-5-ketooxazole, decomp. 160—161°; 3-o-anisidino-5-ketooxazole, decomp. 173—174°; 3-m-anisidino-5-ketooxazole, m. p. 136°; 3-p-anisidino-5-ketooxazole, softens at 120°, decomp. 146°; 3-p-phenetidino-5-ketooxazole, decomp. 150°; 3-m-bromoanilino-5-ketooxazole, decomp. 180—185°; 3-p-chloroanilino-5-ketooxazole, softens at 160°, decomp. 186°; 3-p-iodoanilino-5-ketooxazole, decomp. 173°; 3- $\alpha$ -naphthylamino-5-ketooxazole, decomp. 148—149°; 3- $\beta$ -naphthylamino-5-ketooxazole, decomp. 146°. 3-o-Toluidino-5-ketopyrazole, softens at 200°, decomp. 223—224°; 3-m-toluidino-5-ketopyrazole, decomp. 250—251°; 3-o-anisidino-5-ketopyrazole, m. p. 199.5—200°; 3-m-anisidino-5-ketopyrazole, m. p. 212.5—213°; 3-p-anisidino-5-ketopyrazole, decomp. 205—206°; 3-p-phenetidino-5-ketopyrazole, decomp. 198—199°; 3-m-bromoanilino-5-ketopyrazole, decomp. 271°; 3-p-chloroanilino-5-ketopyrazole, decomp. 249°; 3-p-iodoanilino-5-ketopyrazole, decomp. 222—223°; 3- $\alpha$ -naphthylamino-5-ketopyrazole, m. p. 214—215°; and 3- $\beta$ -naphthylamino-5-ketopyrazole, decomp. 239—240°.

R. B.

**Tetrahydrobenzisooxazoles.** K. VON AUWERS, T. BAHR, and E. FRESE (*Annalen*, 1925, **441**, 54—67; cf. A., 1924, i, 572).—In connexion with researches on the constitution of indazole and anthranil the preparation and properties of the tetrahydrobenzisooxazoles (I and II) were investigated. The condensation of

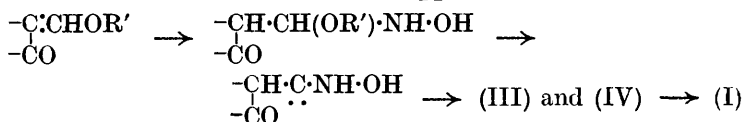


2-hydroxymethylenecyclohexanone with hydroxylamine hydrochloride gives, in 75% yield, a mixture of the two isomerides ( $R=H$ ), the 4:5-compound (I) forming 75—80% of the product or 85% in the presence of excess of hydrochloric acid. In alkaline solution, the amount of 3:4-derivative (II) is further decreased,

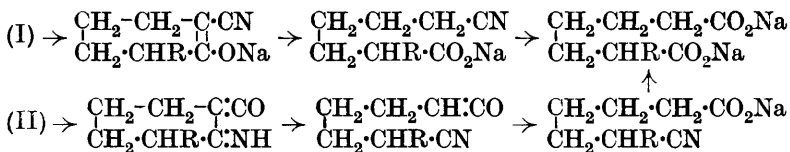
with formation of 2-cyanocyclohexanone and other products. No oxime of the hydroxymethylene-ketone can in any case be isolated. 6-Methyl-2-hydroxymethylenecyclohexanone condenses best with hydroxylamine hydrochloride in alcoholic solution, the yield being 80% of a mixture containing 7—8 parts of (I) ( $R=Me$ ) to 1 part of (II). In dilute alkali the yield is 70% and the proportions are 5 : 1, whilst in 30% sodium hydroxide solution only 25% is obtained, the ratio being 3 : 1. In the last case, much methylcyclohexanone and its oxime are formed. The attempt to increase the proportion of (II) by using the ethoxymethylene derivative results in a mixture of (III) and (IV) :



The course of the reaction thus appears to be :



( $R'=H$  or  $Et$ ), for in neutral solution the free hydroxymethylene-ketone yields a solid oxime (probably IV), which very readily loses water and forms the 4 : 5-isooxazole. Separation of the isomeric isooxazoles is very difficult in the case of the lower homologues, but the 3 : 4-compounds may be obtained pure by destruction of the isomeride by repeated treatment with sodium ethoxide. All four substances are colourless liquids, distilling in a vacuum unchanged. Their salts with mineral acids are hydrolysed on dilution. The 4 : 5-compounds (I) are decomposed in the cold by sodium methoxide, giving the enolic form of the cyanoketone; in warm alcohol, this decomposition proceeds further to the seminitrile of a pimelic acid, and on long boiling to the pimelic acid itself, thus providing a useful method for the preparation of these open-chain compounds. The 3 : 4-derivatives are more slowly attacked but give similar end-products :



The general behaviour of the tetrahydrobenzisooxazoles is not appreciably different from that of the corresponding dialkylisooxazoles.

The mixed 4 : 5- and 3 : 4-tetrahydrobenzisooxazoles (tetramethyleneisooxazoles) (I and II,  $R=H$ ), formed by the interaction of 2-hydroxymethylenecyclohexanone and hydroxylamine hydrochloride in the cold, distil at 90—95°/14 mm. or 100°/20 mm. When the product is treated in ether below 25° with alcoholic sodium methoxide or ethoxide, sodiocyanocyclohexanone (see

following abstract) is precipitated and the unchanged tetrahydrobenz-3:4-isooxazole (tetrahydroanthranil, II), b. p. 87—88°/14 mm., may be isolated from the filtrate. It forms a mercuric chloride compound, m. p. about 104—106° (not completely clear). Tetrahydrobenz-3:4-isooxazole, b. p. 90—92°/13 mm., obtained about 90% pure by repeated fractional distillation, forms a mercuric chloride compound, which begins to melt at 135°.

*Methyltetrahydrobenz-4:5-* and *-3:4-isooxazoles* (I and II, R=Me), prepared similarly from 6-methyl-2-hydroxymethylencyclohexanone in 75—84% yield, distil at 86—91°/10 mm. In concentrated sodium hydroxide, the reaction gives 2-methylcyclohexanone, an oxime of this (b. p. 108—110°/15 mm., liquid at the ordinary temperature), 25% of the mixed isooxazoles, and 5-aminomethyltetrahydrobenz-3:4-isooxazole (see following abstract). The mixed isooxazoles from the acid condensation, when treated with alcoholic mercuric chloride, deposit, on addition of water, the crystalline compound,  $(C_8H_{11}ON)_2 \cdot HgCl_2 \cdot H_2O$ , m. p. 66°, derived from the 4:5-isomeride (I), from which the latter is obtained pure, b. p. 85—86°/11 mm., by acidification and steam distillation. The 3:4-isomeride (II), b. p. 90—91°/10 mm., is isolated as in the case of the lower homologue.

6-Methyl-2-ethoxymethylencyclohexanone, b. p. 117—119°/13 mm., obtained in 80% yield by an application of Claisen's method (A., 1918, ii, 382), reacts with free hydroxylamine to give the oxime of 6-methyl-2-formylcyclohexanone (III) or of 6-methyl-2-formylcyclohexenol (IV), b. p. 140—144°/11 mm. The free hydroxymethylencetone similarly yields an oxime (probably IV), m. p. 66—68° (oily dibenzoyl derivative described), which is readily dehydrated to the 4:5-isooxazole.

$\alpha$ -Methylpimelic acid, m. p. 55—57°, results when either of the isomeric methylisooxazoles is heated under reflux for several days with 20% alcoholic sodium hydroxide. C. H.

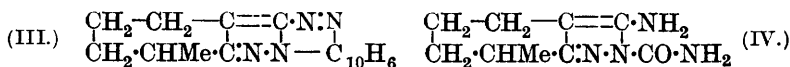
### Cyanocyclohexanones and their Transformation Products.

K. VON AUWERS, T. BAHR, and E. FRESE (*Annalen*, 1925, 441, 68—100).—2-Cyanocyclohexanone and 2-cyano-6-methylcyclohexanone are obtained very easily from the corresponding tetrahydrobenz-4:5-isooxazoles (preceding abstract) by the action of alcoholic alkali at any temperature up to 40°. Both are colourless, practically odourless oils, which, unlike 2-cyanocyclopentanone (Best and Thorpe, T., 1909, 95, 710), are soluble in sodium hydroxide or carbonate, although in the free state they contain only 10.5% and 1.7% of enol, respectively. Alkylation with alkyl halides and sodium ethoxide yields both C- and O-derivatives, the proportions depending on the halogen and alkyl groups used. Cyanocyclopentanone yields only C-derivatives (Best and Thorpe, *loc. cit.*). The cyanoketones give oximes readily convertible by traces of alkali into C-aminotetrahydrobenzisooxazoles (cf. Obrégia, A., 1892, 324; Hanriot, *ibid.*, 1891, 1108; Burns, *ibid.*, 1893, i, 314). That these products are amino rather than imino compounds is indicated by their stability to hot alkali, their con-

densation with aldehydes to azomethines, their dialkylation, and the strongly acid nature of their acetyl derivatives. The oximes of 2-cyano-2-alkylcyclohexanones do not undergo a change into iminoisooxazolines. By treatment with ammonia in ether, the cyanoketones are converted into aminocyanocyclohexenes, the intermediate additive product being isolable. Towards semicarbazide, the two cyanoketones behave rather differently. 2-Cyanocyclohexanone yields a semicarbazone, whilst the 6-methyl compound gives also the dicyclic aminopyrazolecarbonamide, which is hydrolysable to 3-amino-7-methyl-4 : 5 : 6 : 7-tetrahydroindazole. Under other conditions, the methylcyanoketonesemicarbazone is converted into the 3 : 3'-bisindazyl (I), the constitution of which is indirectly confirmed by the synthesis of the 2 : 2'-isomeride, which has different properties. The 3-amino-7-methyltetrahydroindazole results directly from methylcyanocyclohexanone and hydrazine, and it is probable that the products obtained by Meyer (A., 1914, i, 996) from semicarbazide or hydrazine and aliphatic  $\alpha$ -cyanoketones are aminopyrazoles, not iminopyrazolines. Like 3-aminoindazole (Bamberger and Wildi, A., 1907, i, 164), the tetrahydro derivative is easily oxidised to an azo compound. Diazotisation in concentrated acid solution leads to a diazonium salt which couples readily; in dilute acid intramolecular coupling occurs, with formation of the substance (II). The tendency of the



cyclic NH group to take part in further cyclisations is also shown in the product of coupling with  $\beta$ -naphthol, which readily anhydrides to a triazine derivative (III).

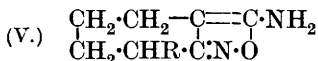


2-Cyanocyclohexanone, b. p. 132°/10 mm.,  $d_4^{20}$  1.070,  $n_{\text{D}}^{20}$  1.47932, prepared from its sodium derivative (preceding abstract) by acidification, becomes yellow in air, acquiring a sweet, unpleasant odour and eventually depositing a white, insoluble polymeride or condensation product, which is more quickly formed in alkaline solution. The oxime, m. p. 117—118.5°, p-nitrophenylhydrazone, m. p. 163—165°, and semicarbazone, m. p. 165°, are described. The last, heated with hydrochloric or oxalic acid, loses carbon dioxide and ammonia and gives 3 : 3'-ditetrahydroindazyl (as I), m. p. 265—266° (picrate, m. p. 237—238°). 2-Cyano-6-methylcyclohexanone, b. p. 127—129°/11 mm., 138—140°/18 mm.,  $d_4^{20}$  1.040,  $n_{\text{D}}^{20}$  1.47305 (oxime, m. p. 115—116°), does not change on keeping. The semicarbazone cannot be obtained, the only products being 3-amino-7-methyl-4 : 5 : 6 : 7-tetrahydroindazole-2-carboxylamide (IV), m. p. 142.5—143.5°, and 3 : 3'-di(7-methyl-4 : 5 : 6 : 7-tetrahydroindazyl) (I), m. p. 229—231°.

The following alkylated cyanocyclohexanones are described, the C- and O-derivatives being separated by means of semicarbazide.

2-Cyano-2-methylcyclohexanone, b. p. 94°/18 mm. (semicarbazone, m. p. 206—207°, oxime, m. p. 87°), has a weak camphor smell and is converted by long shaking with 10% sodium hydroxide into  $\epsilon$ -cyanoheptanoic acid, b. p. 183—184°/14 mm.,  $d_4^{20}$  1.022,  $n_D^{17.6}$  1.44940. The isomeric 1-cyano-2-methoxy- $\Delta^1$ -cyclohexene is only obtained in small quantity. 2-Cyano-2-ethylcyclohexanone, b. p. 114—115°/15 mm., 129°/25 mm.,  $d_4^{20}$  1.008,  $n_D^{18.6}$  1.46851 (semicarbazone, m. p. 195°; oxime, m. p. 117°). 1-Cyano-2-ethoxy- $\Delta^1$ -cyclohexene, b. p. 133—135°/16 mm., 142—145°/24 mm.,  $d_4^{20}$  1.021,  $n_D^{18.3}$  1.49741. 2-Cyano-2-propylcyclohexanone, b. p. 122°/13 mm.,  $d_4^{20}$  0.997,  $n_D^{20}$  1.46721 (semicarbazone, m. p. 212—213°). 1-Cyano-2-propoxy- $\Delta^1$ -cyclohexene, b. p. 137—139°/13 mm.,  $d_4^{20}$  0.991,  $n_D^{21}$  1.49053. 2-Cyano-2-allylcyclohexanone, b. p. 120—121°/13 mm.,  $d_4^{20}$  1.017,  $n_D^{18.6}$  1.48147 (semicarbazone, m. p. 197°). 2-Cyano-2-benzylcyclohexanone, m. p. 56—57° (semicarbazone, m. p. 201°).

C-Aminotetrahydroanthranil (V, R=H), m. p. 130° (p-nitrobenzylidene derivative, m. p. 216—217°; acetyl derivative, m. p.



82—83°), may be obtained by adding sodium hydroxide to 2-cyanocyclohexanone oxime, or more conveniently from the sodiocyanoketone and hydroxylamine hydrochloride with excess of sodium hydroxide (yield 89%). With methyl bromide and methyl alcohol at 100° it gives C-dimethylaminotetrahydroanthranil (hydrobromide, m. p. 95—96°; picrate, m. p. 154—155°). C-Amino-7-methyltetrahydroanthranil (V, R=Me), m. p. 66—70° (hydrochloride, m. p. 78°; p-nitrobenzylidene derivative, m. p. 215—216°; benzoyl derivative, m. p. 95—97°), is similarly prepared from 2-cyano-6-methylcyclohexanone.

2-Amino-1-cyano- $\Delta^1$ -cyclohexene, m. p. 94—95° (hydrochloride hygroscopic; acetylation product, m. p. 160—161°), forms as a solid white mass when cyanocyclohexanone is shaken with dilute ammonium carbonate. If ammonia is passed into an ether solution of the cyanoketone, 1-amino-2-cyanocyclohexanol, m. p. 78—79°, is precipitated, which is gradually converted into the cyclohexene when ground with water. 2-Cyano-6-methyl-1-aminocyclohexanol, m. p. 68—70°, similarly prepared from 2-cyano-6-methylcyclohexanone, decomposes very quickly. 2-Amino-1-cyano-6-methyl- $\Delta^1$ -cyclohexene, m. p. 87—88°, b. p. 150°/10 mm.,  $d_4^{20}$  0.9704,  $n_D^{20.5}$  1.50225 (hydrochloride hygroscopic; very stable benzoyl derivative, m. p. 201°), is obtained in 82% yield by adding 10% aqueous ammonia to a solution of 2-cyano-6-methylcyclohexanone in a little alcohol.

3-Amino-7-methyl-4 : 5 : 6 : 7-tetrahydroindazole, a yellowish syrup, b. p. about 190°/15 mm., setting to a resinous mass, is obtained from the carboxylamide (IV) by boiling with acids or alkalis or, less conveniently, by the action of hydrazine hydrate on 2-cyano-6-methylcyclohexanone or on 2-amino-1-cyano-6-methyl- $\Delta^1$ -cyclohexene. It combines with auric, platonic, and mercuric chlorides and with silver nitrate, and forms also a picrate, m. p. 205°, hydro-

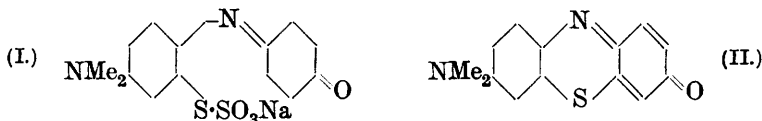
*chloride*, m. p. 226—228° (rapid heating), *p*-nitrobenzylidene derivative, m. p. 177°, and *dibenzoyl* derivative, m. p. 194°. The *diacetyl* compound, m. p. 122·5—123·5°, is hydrolysed slowly by cold alkali and more quickly by boiling dilute acetic acid to a *monoacetyl* derivative, m. p. 212—213°. Oxidised with ferricyanide, the amine gives in 80% yield 3 : 3'-azo-7-methyltetrahydroindazole, an orange-red powder, m. p. 185—191° (decomp.), which regenerates the amine on reduction with stannous chloride.

2 : 3-endo-Azo-7-methyl-4 : 5 : 6 : 7-tetrahydroindazole ("7-methyl-tetrahydroindazoletriazolene," II), m. p. 137—145° (decomp.), is precipitated in 72% yield when the amine is diazotised in 2*N*-hydrochloric acid. In ice-cold 20% acid a soluble diazonium salt is formed, which couples with  $\beta$ -naphthol to give an azo compound,  $C_{18}H_{18}ON_4$ , carmine-red needles from alcohol, m. p. 208°. The alcoholic solution on evaporation deposits yellow crystals of 7-methyltetrahydroindazolophthatriazine (III), m. p. 152—154°. 3 : 3'-Di(7-methyl-4 : 5 : 6 : 7-tetrahydroindazolyl) (I), m. p. 229—231° (*picrate*, m. p. 212—213°; *monoacetyl* compound, m. p. 195—196°; *diacetyl*, m. p. 105—120°), is formed when 3-amino-7-methyltetrahydroindazolecarboxylamide is heated at 100° with dilute hydrochloric acid, acetic acid, or oxalic acid, or in 66% yield, together with hydrazodicarboxylamide, by heating 2-cyano-6-methylcyclohexanone in alcohol with semicarbazide hydrochloride and sodium acetate. Methylation with methyl iodide gives a *dimethyl* derivative, m. p. 156—160° (*picrate*, m. p. 214°, or with  $1H_2O$  189—191°). 2 : 2'-Di(7-methyl-4 : 5 : 6 : 7-tetrahydroindazolyl), m. p. 272—273°, is synthesised by the action of bromine on the silver salt of 7-methyltetrahydroindazole in ether. There is also formed in small quantities a substance which is probably 3-bromo-7-methyl-tetrahydroindazole. C. H.

**Organic Thiosulphates.** G. HELLER (*J. pr. Chem.*, 1924, [ii], 108, 257—274).—2-Amino-5-dimethylaminophenyl hydrogen thiosulphate,  $NH_2 \cdot C_6H_3(NMe_2) \cdot S \cdot SO_3H$ , blue crystals, m. p. 194—195° (decomp.), is obtained by the reduction of *p*-nitrosodimethylaniline hydrochloride in acetic acid solution with sodium thiosulphate. The *methyl* ester, colourless prisms, m. p. 236—238°, is produced by the action of methyl sulphate and sodium hydroxide. Ammonia and carbon disulphide afford Losanitsch's salt which is converted by alkali into 5-dimethylamino-1-thiolbenzthiazole, yellow needles, m. p. 230°; the latter is amphoteric in character, as it gives salts with mineral acids, and *silver*, *lead*, *copper*, and *mercury* salts. The *benzoyl* derivative forms yellow needles, m. p. 119—120°. 5-Dimethylamino-1-thiolbenzthiazole is capable of tautomerism; on treatment of the *potassium* salt with methyl iodide, the *N-methyl ether methiodide*,  $NMe_3 \cdot C_6H_3 \langle \begin{smallmatrix} NMe \\ S \end{smallmatrix} \rangle CS$ , star-shaped needles, m. p. 187° (decomp.), is produced, whilst the silver salt yields the *S-methyl ether methiodide*,  $NMe_3 \cdot C_6H_3 \langle \begin{smallmatrix} N \\ S \end{smallmatrix} \rangle C \cdot SMe$ , rosettes, m. p. 205°. By oxidation with hydrogen peroxide, the corresponding



*disulphide* is produced as red crystals, m. p.  $161^{\circ}$ ; the colourless *hydrochloride* on reduction gives the thiol compound. By the action of potassium cyanide on the *sodium* salt of the amino-dimethylphenyl hydrogen thiosulphate, or on the free acid, 5-dimethylamino-1-iminobenzthiazole (needles, m. p.  $176-177^{\circ}$ ), is produced, not easily hydrolysed or reduced; it yields an amorphous red *nitrosoamine*. The *monobenzoyl* derivative (green needles) melts at  $218-219^{\circ}$ . By the interaction of the hydrogen thiosulphate with 80% formic acid, 5-dimethylaminobenzthiazole, colourless plates, m. p.  $79^{\circ}$ , is produced. By the action of alkaline sodium hypochlorite solution and phenol on the thiosulphate, *sodium* 4-dimethylaminoindophenyl-2-thiosulphate (I) is produced as green

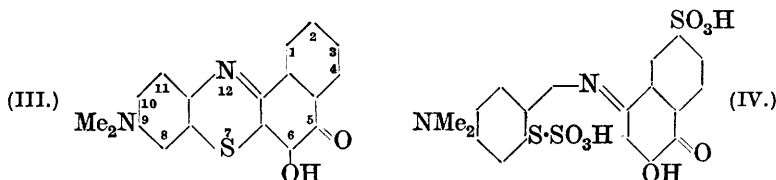


needles, the free *indophenol* being generated as red needles, hydrolysed by mineral acids. By the action of 20% sodium hydroxide, for 3 days, 9-dimethylaminophenthiazine (II), green needles, is produced. This compound exhibits fluorescence in various solvents.

4-Dimethylamino-2'-chloroindophenyl hydrogen 2-thiosulphate is produced by the action of alkaline sodium hypochlorite and *m*-chlorophenol on the thiosulphate, as the *sodium* salt (green crystals); the free acid forms red needles.

By addition of potassium 2-naphthaquinone-4-sulphonate to an alkaline solution of the thiosulphate, with warming, 9-dimethylamino-6-hydroxy-5-keto-7 : 12-naphthaphenthiazine (III) is formed as bluish-violet needles, sintering at  $160^{\circ}$ , decomp.  $305-308^{\circ}$ ; the *hydrochloride* (blue rosettes) on reduction with stannous chloride yields the *leuco* compound, which is readily oxidised by air in alkaline solution.

By addition of potassium 1 : 2-naphthaquinone-4 : 6-disulphonate to an alkaline solution of the thiosulphate, 4'-dimethylamino-3-hydroxyindonaphthyl-7-sulphonic acid hydrogen 2'-thiosulphate (IV)



separates out as the *dipotassium* salt (deep blue crystals). The ring is closed on heating with alkali. Interaction between the thiosulphate and potassium 1 : 2-naphthaquinone-4 : 6-disulphonate, in alkaline solution, yields *potassium* 9-dimethylamino-6-hydroxy-5-keto-7 : 12-naphthaphenthiazine-2-sulphonate (bluish-violet), the free *dye* being liberated with acid as violet crystals.

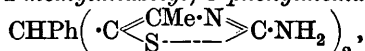
2-Amino-5-diethylaminophenyl hydrogen thiosulphate melts at  $228-230^{\circ}$ . The *methyl* ester (m. p.  $199^{\circ}$ ) and a *methylated acid* (m. p.

189°, decomp.) are formed by the action of methyl sulphate in alkaline solution. The free acid reacts with potassium 1 : 2-naphthaquinone-4-sulphonate to give 9-diethylamino-6-hydroxy-5-keto-7 : 12-naphthaphenthiazine (green needles, sintering at 215°). 5-Amino-2-ethylamino-*p*-tolyl hydrogen 4-thiosulphate is produced from nitroso-ethyl-*o*-toluidine by the above method, as colourless prisms, m. p. 232° (decomp.). By the action of sodium thiosulphate on an acetic acid solution of *p*-benzoquinone, 2 : 4-dihydroxyphenyl hydrogen thiosulphate, isolated as the potassium salt (colourless needles), is produced. This on oxidation yields the corresponding *p*-benzoquinone derivative.  $\beta$ -Naphthaquinone yields potassium 1 : 2-dihydroxynaphthyl 4-thiosulphate, which on oxidation yields potassium 1 : 2-naphthaquinonyl 4-thiosulphate as yellow needles. On heating with water, a substance is produced insoluble in organic solvents, and on shaking the potassium salt with aniline, 4-anilino- $\beta$ -naphthaquinone is obtained.  $\alpha$ -Naphthaquinone yields potassium 1 : 4-dihydroxynaphthyl 2-thiosulphate, which on oxidation yielded potassium 1 : 4-naphthaquinonyl 2-thiosulphate (yellow prisms). A. E. C.

**Constitution of the Two Isomeric "Dehydrothio-*m*-xylicidines."** R. ANSCHÜTZ and G. SCHULTZ (*Ber.*, 1925, 58, [B], 64—66; cf. A., 1889, 612).—"isoDehydrothio-*m*-xylicidine," m. p. 120—121° (acetyl derivative, m. p. 201—202°), prepared by the action of sulphur on *m*-xylicidine and separated from the isomeric "dehydrothio-*m*-xylicidine," m. p. 107°, by treatment with a mixture of benzene and light petroleum, is shown to be  $\mu$ -6-amino-*m*-tolyl-*m*-xylothiazole,  $C_6H_2Me_2 \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ S \end{smallmatrix} > C \cdot C_6H_3Me \cdot NH_2$ ,

since it is transformed by molten potassium hydroxide into 6-amino-3 : 5-dimethylthiophenol and 2-amino-*m*-toluic acid. Under similar conditions, "dehydrothio-*m*-xylicidine" yields 6-amino-3 : 5-dimethylthiophenol and 4-amino-*m*-toluic acid (the sulphate is described) and hence is  $\mu$ -4-amino-*m*-tolyl-*m*-xylothiazole. H. W.

**Thiazoles. VI. New Group of Dyes from Poison Gases through the 2-Aminothiazoles as Intermediates. Preparation of Thiazole Dyes of Doebner Violet Type.** M. T. BOGERT and M. CHERTCOFF (*J. Amer. Chem. Soc.*, 1924, 46, 2864—2871; cf. this vol., i, 80).—2-Amino-4-methylthiazole (2 mols.), benzaldehyde (1 mol.), and hydrochloric acid ( $\frac{2}{3}$  mol.) at 145° give, in 55% yield, di(2-amino-4-methylthiazolyl)-5-phenylmethane,



m. p. 180° (decomp.). 2-Amino-4-phenylthiazole (acetyl derivative, m. p. 212—213°, 2-*p*-nitrobenzylidene derivative, m. p. 156·8°), and diazotised *p*-nitroaniline give *p*-nitrobenzeneazo-2-amino-4-phenylthiazole, green needles, m. p. 179·6°, dyeing red shades on wool. *p*-Benzene-*p*-sulphonylazo-2-amino-4-phenylthiazole, a red solid, is similarly obtained with diazotised sulphanilic acid. 2-Amino-4-phenylthiazole and benzaldehyde in the presence of hydrochloric acid at 145° give, in 95% yield, di(2-amino-4-phenylthiazolyl)-5-

*phenylmethane* [sinters at  $181^{\circ}$ , softens at  $207^{\circ}$ , m. p.  $221^{\circ}$  (decomp.)], yielding only benzoic acid on oxidation. The *carbinol*, reddish-black, m. p.  $197.3^{\circ}$  (decomp.), obtained by dissolving the base in alcoholic hydrochloric acid, and oxidising with lead peroxide and acetic acid, yields a dark green *oxalate*,  $2C_{25}H_{18}N_4S_2 \cdot 3C_2H_2O_4$ , dyeing bluish-green shades on wool or on cotton. Similarly, *p*-chlorobenzaldehyde yields *di*(2-amino-4-phenylthiazolyl)-5-*p*-chlorophenylmethane, colourless prisms (sinters at  $148^{\circ}$ , m. p.  $203^{\circ}$ ). *Di*(2-amino-4-phenylthiazolyl)-5-*o*-nitrophenylmethane, orange-yellow needles, m. p.  $231.6^{\circ}$  (decomp.); *di*(2-amino-4-phenylthiazolyl)-5-*m*-nitrophenylmethane (+ 1 mol. benzene, lost at  $100^{\circ}$ ), pale yellow rhombs, m. p.  $202.3^{\circ}$  (decomp.); *di*(2-amino-4-phenylthiazolyl)-5-*p*-nitrophenylmethane, greenish-yellow needles, m. p.  $238.5^{\circ}$  (decomp.); *di*(2-aminophenylthiazolyl)-5-*p*-dimethylaminophenylmethane, colourless needles, m. p.  $235.8^{\circ}$  (decomp.); *di*(2-amino-4-phenylthiazolyl)-5-*p*-hydroxyphenylmethane, colourless needles, sinter and change colour at  $248^{\circ}$ , m. p.  $252.4^{\circ}$  (decomp.), and *di*(2-amino-4-phenylthiazolyl)-5-*o*-hydroxyphenylmethane, colourless rhombs, sintering and colouring at about  $148.5^{\circ}$ , m. p.  $222.5^{\circ}$  (decomp.), are similarly obtained. The oxalates of the corresponding dyes contain 3 mols. of oxalic acid. Fusion of the *o*-hydroxyphenylmethane with potassium hydroxide yields ammonia and benzoic acid, whilst the corresponding triphenylmethane derivative is more stable. Piperonaldehyde did not condense with 2-amino-4-phenylthiazole in alcoholic solution.

R. B.

**Action of Nitrous Acid on Azoxyphenols.** D. BIGIARI and A. ANGELI (*Atti R. Accad. Lincei*, 1924, [v], **33**, 319—322).—When a concentrated ethereal solution of  $\beta$ -*p*-azoxyphenol is saturated at  $0^{\circ}$  with the mixture of nitrogen oxides from arsenious oxide and nitric acid, *m*-nitro- $\beta$ -*p*-azoxyphenol, m. p.  $174^{\circ}$ , is produced (cf. Valori, A., 1915, i, 903). In the same way,  $\beta$ -*m*-azoxy-2-hydroxytoluene and *p*-nitrophenol yield, respectively, benzene- $\beta$ -*m*-azoxy-2-hydroxy-3-nitrotoluene, m. p.  $121^{\circ}$ , and 2 : 4-dinitrophenol (cf. A., 1898, i, 133). Nitrous acid from sodium nitrite, however, reacts with none of these three (cf. A., 1922, i, 878); moreover,  $\alpha$ -*p*-azoxyphenol, which gives only a mononitro derivative with the latter reagent, is converted by the mixture of nitrogen oxides into benzene- $\alpha$ -*p*-azoxy-3 : 5-dinitrophenol, m. p.  $197^{\circ}$  (cf. A., 1915, i, 903). Azoxyphenols are usually oxidised by nitrous acid. Thus *pp'*-dihydroxyazobenzene gives, not only a dinitroazoxyphenol, but also nitrophenol by oxidative fission (cf. A., 1923, i, 715). Benzeneazo- $\alpha$ -naphthol is likewise oxidised to a *substance*, m. p.  $231^{\circ}$ , containing 10% of nitrogen. Benzene- $\alpha$ -azoxyquinol gives benzene- $\alpha$ -azoxy-*p*-benzoquinone. The mechanism of the formation of nitro derivatives by means of nitrous acid is discussed.

W. E. E.

**Nitroazobenzenes.** G. CHARRIER and A. BERETTA (*Gazzetta*, 1924, **54**, 977—982).—*p*-Nitroazobenzene, prepared by Bamberger and Hübner (A., 1904, i, 115) by the action of aniline on *p*-nitro-nitrosobenzene, may be obtained in good yield by the interaction

of nitrosobenzene and *p*-nitroaniline, and gives *p*-aminoazobenzene when reduced by sodium sulphide in alcoholic solution.

The action of nitrosobenzene on *o*-nitroaniline gives, however, not *o*-nitroazobenzene, but *o*-nitro-*p'*-nitrosodiphenylamine, m. p. 175°, owing to the semidine transposition of the original additive compound:  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2 + \text{NO} \cdot \text{Ph} \rightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NPh} \cdot \text{OH} \rightarrow \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}$ . This compound forms a cherry-red solution in concentrated sulphuric acid and intense orange-red solutions in alkali hydroxides; it yields *op'*-dinitrodiphenylamine when oxidised by means of hydrogen peroxide, and *opp'*-trinitrodiphenylamine when heated with nitric acid (*d* 1.2).

*m*-Nitroazobenzene, prepared by the action of *m*-nitroaniline on nitrosobenzene, has the properties given by Bamberger and Hübner (*loc. cit.*) and gives a good yield of *m*-aminoazobenzene when reduced by means of sodium sulphide. T. H. P.

**Hydrogenation in the Naphthalene Series. Properties of Derived Azo Dyes.** F. M. ROWE and V. J. TARBETT (*J. Soc. Dyers and Col.*, 1925, 41, 5—10).—Some azo compounds containing at least one tetrahydronaphthalene nucleus were prepared and their dyeing properties compared with those of related azo dyes.  $\alpha$ -Naphthaleneazo-*ar*-tetrahydro- $\alpha$ -naphthylamine, brownish-red needles, m. p. 144—145°;  $\alpha$ -*ar*-tetrahydronaphthaleneazo- $\alpha$ -naphthylamine, red needles, m. p. 135°, and a less soluble by-product, yellowish-orange needles, m. p. 118°;  $\alpha$ -*ar*-tetrahydronaphthaleneazo-*ar*-tetrahydro- $\alpha$ -naphthylamine, brownish-red needles, m. p. 141°, and a less soluble by-product, dark red needles, m. p. 172°, were prepared by the usual methods. 4- $\alpha$ -Nitro-*ar*-tetrahydronaphthalene-azosalicyclic acid, yellowish-red needles, m. p. 215° (decomp.), is a bright orange-brown dye for chrome-mordanted wool. The dyeing properties are described of the compounds obtained as follows: chromotropic acid (1:8-dihydroxynaphthalene-3:6-disulphonic acid) coupled with diazotised *ar*-tetrahydro- $\alpha$ -naphthylamine; diazotised sulphanilic acid coupled with *ar*-tetrahydro- $\alpha$ -naphthylamine; diazotised *ar*-tetrahydro- $\alpha$ -naphthylamine-4-sulphonic acid coupled with *ar*-tetrahydro- $\alpha$ -naphthylamine; diazotised 4-nitro-*ar*-tetrahydro- $\alpha$ -naphthylamine coupled with H-acid in acid solution and the product coupled in alkaline solution with diazotised *ar*-tetrahydro- $\alpha$ -naphthylamine;  $\alpha$ -naphthol-3:6-disulphonic acid coupled with diazotised  $\alpha$ -*ar*-tetrahydronaphthaleneazo-*ar*-tetrahydro- $\alpha$ -naphthylamine,  $\alpha$ -*ar*-tetrahydronaphthaleneazo- $\alpha$ -naphthylamine,  $\alpha$ -naphthaleneazo-*ar*-tetrahydro- $\alpha$ -naphthylamine and  $\alpha$ -naphthaleneazo- $\alpha$ -naphthylamine. [Cf. *B.*, 1925, 165.] A. J. H.

**Halogenated Aromatic Hydrazines. I. 3:4-Dibromophenylhydrazine.** E. VOTOČEK and P. JIRŮ (*Chem. Listy*, 1924, 18, 153—158; cf. *A.*, 1924, i, 887, and *A.*, 1923, i, 961).

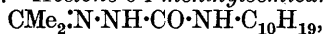
W. A. S.

**4-*p*-Tolylsemicarbazide and certain Derivatives.** A. S. WHEELER and R. W. BOST (*J. Amer. Chem. Soc.*, 1924, 46, 2813—2816).—4-*p*-Tolylsemicarbazide,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , obtained

by heating *p*-tolylcarbamide with hydrazine hydrate in absolute alcohol (cf. Curtius and Burkhardt, A., 1899, i, 137), *m*. p. 157—158° (remaining opaque), decomp. 274° (cf. Pinner, A., 1888, 687), has been condensed with ketonic compounds, yielding 4-*p*-tolylsemicarbazones of acetone (decomp. 205°); acetophenone, *m*. p. 165°; benzophenone, *m*. p. 162°, *p*-benzoquinone, *m*. p. 165°, and camphor, *m*. p. 225—229°. *p*-Tolylcarbamide, *m*. p. 184° (cf. Cosack, Ber., 1879, 12, 1450), was obtained by Davis and Blanchard's method (A., 1923, i, 902). R. B.

**2-Phenylsemicarbazide.** R. C. GOODWIN and J. R. BAILEY (*J. Amer. Chem. Soc.*, 1924, 46, 2827—2832).—Neutral hydrolysis of acetone-2-phenylsemicarbazone gives 1-phenylsemicarbazide,  $\text{NHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , and not 2-phenylsemicarbazide as stated by Arnold (A., 1897, i, 409). The latter compound is readily obtained by acid hydrolysis (1 mol. of hydrochloric acid), alkaline hydrolysis effecting a third decomposition into ammonia and acetonephenylhydrazine. 2-Phenylsemicarbazide reacts normally with benzaldehyde (cf. Rolla, A., 1908, i, 473) and with cyclohexanone (the 2-phenylsemicarbazone having *m*. p. 177°), but not with terpene ketones. With dextrose, it afforded phenylglucosazone. It is hydrolysed to phenylhydrazine on boiling the aqueous solution of its hydrochloride, but is comparatively stable to steam distillation in alkaline solution. Acetone-2-phenylsemicarbazone is obtained in 77% yield by the action of potassium cyanate in aqueous acetic acid on acetonephenylhydrazine. R. B.

**Action of Amines on Semicarbazones. II.** F. J. WILSON and A. B. CRAWFORD (*J. Chem. Soc.*, 1925, 127, 103—109; cf. T., 1922, 121, 866).—Acetone- $\delta$ -1-menthylsemicarbazone,



*m*. p. 128°,  $[\alpha]_D^{20} -64\cdot93^\circ$ , formed by the interaction of acetone-semicarbazone and *l*-menthylamine at 165°, gives on hydrolysis  $\delta$ -menthylsemicarbazide, *m*. p. 138°,  $[\alpha]_D^{20} -77\cdot94^\circ$  (hydrochloride, *m*. p. 203—204°,  $[\alpha]_D^{20} -65\cdot18^\circ$ ; benzylidene derivative, *m*. p. 111°,  $[\alpha]_D^{20} -47\cdot18^\circ$ ). Acetone- $\delta$ -3-carbethoxyphenylsemicarbazone, *m*. p. 146°, obtained in 80% yield from ethyl *m*-aminobenzoate and acetonesemicarbazone, is hydrolysed by dilute hydrochloric acid to  $\delta$ -3-carbethoxyphenylsemicarbazide, *m*. p. 119° (hydrochloride, *m*. p. 172°; benzylidene derivative, *m*. p. 144°). Acetone- $\delta$ -4-carbethoxyphenylsemicarbazone, *m*. p. 194°, and the corresponding benzophenone compound, *m*. p. 168°, are similarly prepared. The former is accompanied by two unidentified substances, *m*. p. 130° and 210°. Hydrolysis of the two semicarbazones results in complete decomposition.

In the ortho series, aminodiketotetrahydroquinazolines are produced. Methyl *o*-aminobenzoate reacts with benzophenonesemicarbazone at 210° to give 3-diphenylmethylenamino-2:4-diketotetrahydroquinazoline, *m*. p. 240°, which is hydrolysed by dilute hydrochloric acid to the 3-amino compound (Kuncell, A., 1910, i, 438) and benzophenone. Methyl *o*-aminobenzoate and acetonesemicarbazone give, in place of the expected isopropylidene-

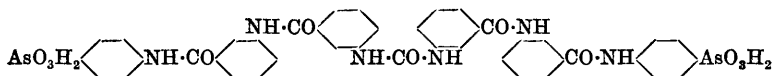
amino compound, as main product 3-amino-2 : 4-diketotetrahydroquinazoline itself. This, boiled with undried acetone, is converted into its isopropylidene derivative, m. p. 212°, which reacts with acetonesemicarbazone at 190° to form dimethylketazine and the aminodiketotetrahydroquinazoline in accordance with the authors' views on the course of the original condensation. C. H.

**Organic Compounds of Arsenic. II. Derivatives of the Arsenic Analogue of Carbazole.** J. A. AESCHLIMANN, N. D. LEES, N. P. McCLELAND, and G. N. NICKLIN (*J. Chem. Soc.*, 1925, 127, 66—69).—*o*-Aminodiphenyl, prepared from diazoaminobenzene, when diazotised and coupled with sodium arsenite gives *diphenylarsinic acid*, m. p. 205° (*diphenyl-o-arsenious chloride* and *oxide* are described), which is readily converted by warm concentrated sulphuric acid into *oo'-diphenyllylenearsinic acid*,  $\text{C}_6\text{H}_4 > \text{AsO}_2\text{H}$ , m. p.

290°. By reduction with sulphur dioxide in the presence of hydrochloric acid, it yields *oo'*-diphenylenechloroarsine, m. p. 161°, b. p. about 230°/25 mm. The corresponding *iodoarsine*, m. p. 166°, *oxide*, m. p. 178° (+EtOH), and *cyanide*, m. p. 178°, are described. *oo'*-Diphenyleneiodoarsine reacts with magnesium methyl iodide to give *oo'*-diphenylenemethylarsine,  $\text{C}_6\text{H}_5\text{CH}_2\text{AsMe}_2$ , m. p. 46°, which forms a *methiodide*, m. p. 190°. The simple diphenylenearsine could not be isolated owing to its ready oxidisability.

**Trypanocidal Compounds.** R. ADAMS and J. R. JOHNSON (U.S. Pat. 1501894).—Interaction, in boiling alcoholic solution, of *p*-aminophenylarsinic acid, pyruvic acid, and aldehydes yields the following *products*: with benzaldehyde, m. p. 186—187° (decomp.); with anisaldehyde, m. p. 164—165° (decomp.); with *o*-methoxybenzaldehyde, m. p. 173—176° (decomp.); with *p*-chlorobenzaldehyde, m. p. 163—165°; with *p*-bromobenzaldehyde, m. p. 150—155°; with piperonal, m. p. 176—178°; with *o*-nitrobenzaldehyde, m. p. 176—180°. CHEMICAL ABSTRACTS.

**Trypanocidal Action and Chemical Constitution. I. Arylamides of *p*-Aminophenylarsinic Acid.** H. KING and W. O. MURCH (*J. Chem. Soc.*, 1924, 125, 2595—2611).—The authors have prepared a series of compounds of the type



analogous to the Bayer trypanocides (cf. Fourneau and others, A., 1924, i, 382), the two main features of which are the presence of amide linkings and the great number of sulphonic acid groups, which confer solubility. The compounds of the type indicated above exhibit colloidal properties in their salt formation and are sparingly soluble. They are totally devoid of trypanocidal action.

The most active compounds obtained were *m'*-aminobenzoyl-*p*-aminophenylarsinic acid and *p''*-aminobenzoyl-*m'*-aminobenzoyl-*p*-aminophenylarsinic acid, one-third of the toxic dose of the former causing a temporary disappearance of trypanosomes (*T. equiperdum*) from the blood-stream when injected into mice. Tables are shown of the maximum tolerated doses of the compounds prepared. These arsinic acids cannot be characterised by m. p., as these are indefinite. They can readily be compared by their lithium, magnesium, calcium, and barium salts, of which tables are given. The nitroarsinic acids were reduced by ferrous chloride and alkali at 0°, and the complex carbamides prepared by treating the aminophenylarsinic acid with carbonyl chloride in toluene in the presence of sodium acetate. The following derivatives of *p*-aminophenylarsinic acid are described: benzoyl, *o'*-, *m'*-, and *p'*-nitrobenzoyl, *o'*-, *m'*-, and *p'*-aminobenzoyl, *p'*-carbethoxyaminobenzoyl, *o''*-, *m''*-, and *p''*-nitrobenzoyl-*o'*-aminobenzoyl, *o''*-, *m''*-, and *p''*-aminobenzoyl-*o'*-aminobenzoyl, *o''*-, *m''*-, and *p''*-nitrobenzoyl-*m'*-aminobenzoyl, *o''*-, *m''*-, and *p''*-aminobenzoyl-*m'*-aminobenzoyl, the *s*-carbamides of *m''*-aminobenzoyl-*m'*-aminobenzoyl, *m''*-aminobenzoyl-*o'*-aminobenzoyl, *o''*-aminobenzoyl-*m'*-aminobenzoyl, *o''*-aminobenzoyl-*o'*-aminobenzoyl; *s*-diphenylcarbamide-4:4'-diarsinic acid, 1:2:3-benzotriazone-3-phenyl-*p*-arsinic acid; *p*-carbethoxyaminobenzoic acid (m. p. 208—209°), methyl (m. p. 161—162°), ethyl (m. p. 131—132°), and *n*-butyl (m. p. 89—90°) esters, acid chloride, *n*-butyl-*p*-nitrobenzoate (m. p. 35—36°). *p*-Carbethoxyaminobenzoyl chloride is a useful reagent for the identification of alcohols, giving solid esters of moderately high m. p.

I. E. B.

**Reactions of Alkyl- and Aryl-mercuric Hydroxides.** I. A. KOTEN and R. ADAMS.—(See i, 236.)

**Anhydride Structure of Proteins.** E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1924, **141**, 62).—Correction of a printer's error in the formula for *OO'*-dibenzoylglycine anhydride (A., 1924, i, 1361).

E. S.

**Hydrolysis of Peptones, Albumoses, and Proteins with Hydrochloric Acid.** I. S. YAITSCHNIKOV (*J. Russ. Phys. Chem. Soc.*, 1924, **54**, 814—817).—The action of *N*-hydrochloric acid on peptone, protalbumose, albumin, casein, and edestin has been followed at 10°, 37°, and 100°. Except in the initial period, and also in the last stages, the hydrolytic process is similar to that observed with enzymes and conforms with the Schütz-Borisov formula  $k = x/t^{\frac{1}{2}}$ ; in some cases (edestin at 70°, peptone and casein at 100°)  $x/t = K_p$ .

G. A. R. K.

**Separation of Proteoses Derived from Egg-albumin.** G. V. RUDD (*Austral. J. Exp. Biol. Med. Sci.*, 1924, **1**, 179—185).—The proteoses which result from the peptic digestion of egg-albumin are divided into primary proteoses which are precipitated by half-saturation, and secondary proteoses precipitated by complete saturation with ammonium sulphate. The primary proteoses are sub-divided into hetero-proteoses, insoluble, and proto-proteoses,

soluble in water; the secondary proteoses into  $\alpha$ -deutero-proteoses, insoluble, and  $\beta$ -deutero-proteoses, soluble in alcohol (67% vol.). The smallest fraction was that of the proto-proteoses. C. R. H.

**Proteoses, Peptones, and Polypeptides.** G. V. RUDD (*Austral. J. Exp. Biol. Med. Sci.*, 1924, **1**, 187—190).—A neutralised peptic digest of egg-albumin was extracted for 24 hours with butyl alcohol. The total peptides extracted amounted to 27% of the original albumin; those which were soluble in butyl alcohol contained 12.09% total N and 3.37% amino-N; the fraction which separated from the alcohol contained 12.95% total N and 5.76% amino-N; both fractions contained traces only of cystine. The extracted aqueous solution, on fractionation by the author's method (see preceding abstract), was found to be poor in hetero-proteose and  $\alpha$ -deutero-proteose. The results indicate that "proteoses" may be largely a mixture of relatively simple peptides. C. R. H.

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## Biochemistry.

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**Method of Measuring Respiration and Glycolysis.** O. WARBURG (*Biochem. Z.*, 1924, **152**, 51—63).—The manometric method of measuring respiration of cells and tissues already described (*ibid.*, 1923, **142**, 317) has been improved, and is now applicable to determining the oxygen consumption in the presence of free carbon dioxide and glycolysis in the presence of oxygen. The principle involved is discussed mathematically, the method and apparatus are described, and the degree of accuracy is given.

J. P.

**Normal Presence of Carbon Monoxide in the Blood.** M. NICLOUX (*Compt. rend.*, 1924, **179**, 1633—1636).—Contrary to the views of Buckmaster and Gardner (A., 1910, ii, 50), carbon monoxide is found in the blood of animals (even newly born), as well as in that of fishes. The results of three series of experiments are given in support of this: (1) No carbon monoxide is removed from blood at 40° in a vacuum, but in the presence of phosphoric acid at 100° the gas obtained shows the eudiometric characteristics of carbon monoxide, and, brought into contact with a weak solution of hæmoglobin, gives the two absorption bands of CO-hæmoglobin. (2) The gas displaced from blood *in vitro* by shaking it with nitrogen dioxide gives the same absorption bands when submitted to the blood test. (3) Expired air (man or dog), after breathing pure oxygen, is shown similarly to contain carbon monoxide.

A. C.

**Influence of Narcotics on the Rate of Sinking of Blood Corpuscles.** W. BAUMECKER (*Biochem. Z.*, 1924, **152**, 64—78).—Methyl, ethyl, propyl, butyl, and amyl alcohols, and ethyl-urethane diminish, whilst chloral hydrate and ethyl ether increase

the rate of sinking of corpuscles in citrate blood. The inhibiting substances act in concentrations much below that at which their narcotic action on isolated muscle is apparent, and the former action is maximal at the concentration at which the latter action commences. Chloral hydrate, on the other hand, still increases the rate of sinking at concentrations above the limiting concentration for narcosis. The narcotics are supposed to act in such a way that diminution in the rate of sinking is associated with stabilisation of the plasma, and *vice versa*. J. P.

**Chemistry of the Blood during Activity of the Digestive Glands.** K. ONOHARA (*Biochem. Z.*, 1924, 154, 263—277).—Changes in the total solids, chloride, and sugar content of the blood have been followed in dogs for 3 hours after the ingestion of food. Meat, fat, and carbohydrate were investigated separately. The dogs were fed (1) normally, (2) direct into the stomach by gastric fistula, (3) by the mouth, but food recovered from oesophageal fistula ("sham feeding"). When fed by methods (1) or (2), if the secretion of the gastric glands were stimulated by ingestion either of carbohydrate or protein, the blood tended to become more dilute and the sodium chloride content tended to rise. Method (3) gave no change in the sodium chloride content. When fat was fed there was little stimulation of the glands, and the tendency was for the blood to become more concentrated. H. D. K.

**Chemistry of the Blood during Sleep.** K. GOLLWITZER-MEIER and C. KROETZ (*Biochem. Z.*, 1924, 154, 82—89).—During sleep the sensitivity of the respiratory centre is diminished, acidosis occurs, and liquid rich in sodium chloride and phosphate but poor in proteins passes from tissues to blood. P. W. C.

**Problem of Permeability.** P. GYÖRGY (*Biochem. Z.*, 1924, 152, 281—283).—In agreement with the results of Rona, Petow, and Wittkower (A., 1925, i, 94), the distribution of calcium and phosphate ions between serum and blood-corpuscles is unequal and remains so even on hæmolysis of the latter and the interposition of a semi-permeable membrane. The hypothesis of a cell membrane impermeable to calcium as a cause of the unequal ionic distribution is abandoned. J. P.

**Precipitation Curves of Serum Proteins.** P. RUSZCZYNSKI (*Biochem. Z.*, 1924, 152, 250—256).—A study of the extent to which the proteins of human and horse sera are precipitated by concentrations of ammonium sulphate varying from zero to 75%. J. P.

**Colloidal Composition of Blood-serum. Significance of Cholesterol.** H. HANDOVSKY (*Münch. med. Woch.*, 1924, 71, 708—709; from *Chem. Zentr.*, 1924, ii, 485).—Large variations in composition are found between the sera of individual animals. Calf sera are poorer in protein and in globulin than the sera of adult animals and are even occasionally free from euglobulin. The tendency is for the albumin to be higher in summer and the globulin in winter. The amount of cholesterol extractable directly from

native serum is not dependent on the total content of cholesterol. There is a connexion between the euglobulin and the cholesterol contents. Only from sera poor in euglobulin and rich in albumin is much cholesterol extractable by shaking out. The cholesterol thus removable may be influenced by the addition of certain salts and dextrose, and also by their intravenous injection. A portion of the cholesterol is protected by euglobulin and is thus not extractable.

G. W. R.

**Precipitin Reactions of Serum Proteins.** L. HEKTOEN and W. H. WELKER (*J. Infect. Dis.*, 1924, **35**, 294—304).—The euglobulin, pseudoglobulin, and albumin of ox, dog, horse, and human sera are distinct for each species. Precipitin sera produced by injecting blood, serum, or albuminous urine may contain specific precipitins for the corresponding serum proteins, and also for hæmoglobin if present in the antigen. Thus, each protein exists as an independent, antigenic unit in the blood or serum.

CHEMICAL ABSTRACTS.

**Determination of Blood Urea-Nitrogen.** W. G. KARR (*J. Lab. Clin. Med.*, 1924, **9**, 329—333).—After precipitation of protein by tungstic acid, the filtrate is digested with Folin's phosphate buffer solution and with Folin's urease solution, or urease paper. After dilution, and admixture with Nessler's reagent, to known volume, the colour is compared with that of a standard containing ferric, cobalt, and nickel chlorides which has previously been calibrated against a urea solution. CHEMICAL ABSTRACTS.

**Apparatus for the Determination of Blood Nitrogen by Folin's Method.** D. P. OSBORN (*J. Lab. Clin. Med.*, 1924, **9**, 788—789).

CHEMICAL ABSTRACTS.

**Micro-determination of Organic Substances.** M. BÁLINT and P. RUSZCZYNSKI (*Biochem. Z.*, 1924, **152**, 246—249).—An attempt to utilise oxidation by alkaline permanganate for the determination of the serum proteins. The solution after remaining in contact with the permanganate for 18 to 20 hours is acidified, treated with potassium iodide, and the residual iodine determined by thiosulphate. A control is necessary. Accurate quantitative results are obtained only with difficulty. J. P.

**Micro-determination of Blood-sugar.** E. DINGEMANSE (*Biochem. Z.*, 1924, **154**, 483—485).—The modification of the Hagedorn and Jensen technique suggested by Dresel and Rothmann (*A.*, 1924, ii, 632), in which filter-paper and a torsion balance are used instead of a pipette for measuring the blood, has been found to be very satisfactory. H. D. K.

**Ammonia Content and Ammonia Formation of Blood.** I. J. K. PARNAS and J. HELLER (*Biochem. Z.*, 1924, **152**, 1—28).—A vacuum steam distillation method is described whereby the ammonia present in 1—2 c.c. of blood may be determined in a few minutes, keeping the blood at 25°, and by means of which the ammonia content of, and the ammonia formation in, rabbit's blood

has been investigated. In normal males less than 0.05 mg.% is found, whilst rather higher amounts are present in the blood of pregnant females and starving animals. The ammonia content of isolated blood increases from minute to minute, due to the formation of ammonia, principally in the erythrocytes, from a component (other than urea) of the residual nitrogen fraction. This ammonia formation, which is optimal at the  $p_H$  of gas-free blood, is independent of a supply of oxygen, and is not affected by hæmolysis, but is slowed by diluting the blood. It is not appreciably inhibited by the addition of ammonia, nor is it increased by adding urea. J. P.

**Calcium Ionisation in the Blood.** P. GYÖRGY (*Biochem. Z.*, 1924, 152, 284—285).—A reply to Holló (*ibid.*, 150, 496). J. P.

**Calcium Studies on Men. III. Calcium Content of Human Blood under Pathological Conditions.** W. H. JANSEN (*Deut. Arch. klin. Med.*, 1924, 144, 14—18; from *Chem. Zentr.*, 1924, ii, 486).—For normal adults the average concentration of calcium in total blood is 11.5 mg.%, and in serum 10.5 mg.%. Diseases are mentioned in which the calcium content is subnormal. G. W. R.

**Simple Clinical Micro-method for Determining Sodium in Blood-serum.** F. LEBERMAN (*Biochem. Z.*, 1924, 152, 345—354).—The sodium is precipitated as acid sodium pyroantimonate and the turbidity of the suspension is compared with a series of standards. The method can be applied to 0.1 c.c. of blood-serum, and is capable of determining amounts of sodium between 0.05 and 2.0 mg. J. P.

**Lactic Acid Content of Blood in High Altitudes. II. Influence of Muscular Work.** F. LACQUER (*Pflüger's Archiv*, 1924, 203, 35—41; from *Chem. Zentr.*, 1924, ii, 486).—No marked differences in the lactic acid content of blood during rest or exercise were observed at 2400 metres as compared with low altitudes. At 2400 metres, even for vigorous muscular work, the oxygen supply of the body is adequate. G. W. R.

**Nature and Variations of the Aldehyde contained in the Blood.** R. FABRE (*Compt. rend.*, 1925, 180, 83—85).—Experiments showing the presence of aldehydes in the blood have usually been carried out on blood distillates, and the aldehydes may have been formed during the heating. The following experiment shows that they are present in the original blood. After removal of protein by means of sodium tungstate and sulphuric acid, the clear filtrate from 2 litres of blood is kept under a bell jar in the presence of Nessler's reagent. The latter rapidly becomes cloudy and a precipitate due to volatile ketones is formed (cf. Bougault and Gros, A., 1922, ii, 666); this is dissolved by addition of hydrochloric acid, the residual cloudiness being due to a mercury compound of volatile acetaldehyde. Determinations of acetaldehyde by the method of Bougault and Gros on human and animal blood show values of 0.32 to 0.81 mg. per litre of blood. The blood of a dog contained 0.32 mg. of acetaldehyde; after depancreatisation this value rose to

5.02 mg., and fell almost to zero after the animal had received insulin.  
A. C.

**Ionic Reaction of the Blood of certain Invertebrates.** M. DUVAL (*Compt. rend.*, 1924, 179, 1629—1631).—The  $p_H$  values of the blood of various invertebrates have been determined electrometrically (Hasselbach electrode) and colorimetrically. The blood of the crustaceans had only a faint blue tint which did not hinder the colorimetric measurements; the blood of the crustaceans and molluscs studied has  $p_H$  about 7.7 and is more alkaline than that of the mammals (about 7.4). The internal fluid of sea animals is less alkaline than the surrounding sea-water ( $p_H$  8.15), and never exceeds  $p_H$  7.8; that of the echinoderms and worms is less alkaline than that of the crustaceans and molluscs, the blood reaction of which appears to be independent of the nature of the exterior medium. The crayfish, the marine crustaceans, and the edible snail have the same blood alkalinity ( $p_H$  7.7—7.8). The blood reaction of the edible snail was found to be the same during hibernation as in activity as stated by Damboviceanu (*Compt. rend. Soc. Biol.*, 1923, 89, 261).  
A. C.

**Determination of Small Amounts of Glycogen in Solution.** S. E. DE JONGH and J. PLANELLES (*Biochem. Z.*, 1924, 154, 167—170).—A micro-determination of glycogen in solution by adding an equal volume of alcohol, shaking with ether, and comparing the turbidity of the aqueous layer with that of a standard, is described. The method is applied to protein-free blood filtrates. The limiting concentration is 1/128,000.  
P. W. C.

**Calcium Content of Bile.** J. DITTRICH (*Z. ges. exp. Med.*, 1924, 41, 355—357; from *Chem. Zentr.*, 1924, ii, 489).—The calcium content of the bile of normal rabbits shows great variations amongst individuals. After intravenous injection of 30 c.c. of 1.3% calcium chloride solution the concentration of calcium is increased by 100%, although the total amount secreted in a given time is definitely lowered. If a chologogue is administered simultaneously there is a fourfold increase in the amount of calcium excreted, whilst the concentration is nearly doubled. Intravenous injection of lecithin is without effect. Bile has only a slight solvent action on calcium carbonate.  
G. W. R.

**Total Bile. VII. Calcium Content.** D. R. DRURY (*J. Exp. Med.*, 1924, 40, 797—815).—The calcium content of the bile of dogs is constant unless the secretory output fluctuates widely. During fasting, however, the content is markedly increased, whereas a large amount of bile is accompanied by relatively large amounts of calcium. Intravenous or oral administration of calcium does not affect the biliary output of calcium. "White bile" contains but little calcium. The greater portion of the bile calcium is evidently secreted by the liver itself.  
CHEMICAL ABSTRACTS.

**Iodine Content of Goat's Thyroid.** R. ARNOLD and E. GLEY (*J. Physiol. Pathol. gén.*, 1923, 21, 498—504; from *Chem. Zentr.*, 1924, ii, 483—484).—From 1.93 to 8.06 mg. of iodine (average

6.35 mg.) per gram of dry tissue are found. There are appreciable differences between the two lobes. No correlation is found between the iodine content and the weight of the gland. G. W. R.

**Protein in Exhumed Bone Tissue and its Antigenic Properties.** M. KERNBACH (*Compt. rend. Soc. Biol.*, 1924, 90, 1075—1077; from *Chem. Zentr.*, 1924, ii, 484).—In bones of men and horses exhumed after many years a protein was found having the antigenic properties of the ossein of fresh bones. G. W. R.

**Hæmoleucolysin of the Pancreas and its Relation to Delezenne and Fournau's Lysocithin.** S. BELFANTI (*Biochem. Z.*, 1924, 154, 148—166).—During insulin extraction, a very toxic acid fraction is obtained, soluble in 95% alcohol, insoluble in water, called "substance Y" (*Rend. Ist. Lomb. Sci. Lett.*, 1924, 57). This is divided by ether-precipitation of the alcoholic solution into a very toxic, ether-soluble substance and an alkaline portion soluble in water and insoluble in ether, chloroform, or acetone. The latter (hæmoleucolysin) gives neither Millon nor biuret tests but contains a higher percentage of nitrogen and phosphorus than "substance Y" and has a powerful destructive action on both red and white corpuscles. By chemical and biological tests this substance is shown to be similar in many respects to lysocithin prepared by the action of cobra venom on lecithin (A., 1913, i, 141; 1914, i, 781). The hæmolytic action in the body is supposed to be restrained by formation of inactive compounds with substances of the serum, the latter lowering or preventing hæmolytic action. P. W. C.

**Water-Salt Content of the Human Organism in Relation to the Acid-Base Economy. II. Physiological Ionic Equilibrium and Mineral Metabolism.** C. OEHME [with H. PAAL] (*Arch. exp. Path. Pharm.*, 1924, 104, 115—147).—A study has been made of the effect on the retention of ions and water of the addition of hydrochloric acid, sodium hydrogen carbonate and other salts to diets identical as regards their content in fat, water, and chlorides but differing in other respects. E. S.

**Unusual Type of Fatty Compound in a Product of Animal Origin.** S. KON and C. FUNK.—(See i, 230.)

**Effect of Hydrogen-ion Concentration on the Precipitation of Colloidal Benzoin and Gold Solutions by Cerebrospinal Fluid.** I. W. SHAFFER (*J. Lab. Clin. Med.*, 1924, 9, 757—765).—The curves obtained indicate that there are two substances in the fluid which cause the precipitation of colloidal solutions, "A" acting as a precipitant when  $p_H < 4.8$  (benzoin) or 6.9 (gold), and "B" having much higher optimal  $p_H$  precipitation values.

CHEMICAL ABSTRACTS.

**Uric Acid Content of Cerebrospinal Fluid.** A. BERNHARD (*J. Lab. Clin. Med.*, 1924, 9, 753—757).—The uric acid content of the spinal fluid of children is higher than of adults. In seven infectious diseases the uric acid was greatly increased whilst the sugar was decreased.

CHEMICAL ABSTRACTS.

**Wool-fat. VIII. Instability of Wool-fat.** I. LIFSCHÜTZ (*Z. physiol. Chem.*, 1924, **141**, 146—152).—Wool on the surface of the sheep's fleece contains less "fat" than that near the roots, and the composition of the fat varies. Thus, the fat from the surface wool contains a much larger proportion of fatty acids and soaps; it also contains oxycholesterol in place of the ischolesterol present in the fat near the roots. These changes are apparently brought about by hydrolysis and oxidation under the influence of moisture, air, and light. E. S.

***Petromyzon fluviatilis* L. I. Detection of Adenine, Xanthine, Methylguanidine, Leucine, Tyrosine, Fatty Acids of the  $C_nH_{2n}O_2$  Series, and Lactic Acid. II. Detection of Neosine, the Chief Extractive of *Petromyzon*, and of Betaine, Choline, and Crangitine.** O. FLÖSSNER and F. KUTSCHER (*Z. Biol.*, 1924, **82**, 302—305, 305—309).—In addition to the substances mentioned in the title, traces of histidine were detected in a hot phenol-water extract of raw tissue. The substances were isolated as chloraurates and chloroplatinates. O. O.

**Skin Secretion of *Triton taeniatus* (Small Water Newt).** S. MAKI (*Arch. exp. Path. Pharm.*, 1924, **104**, 100—114).—The poison contained in the secretion from the skin of *Triton taeniatus* is readily destroyed by heat and is adsorbed by animal charcoal. It possesses hæmolytic properties, but is less active in this respect than the secretion from *T. cristatus*. Its toxicity is greater for warm- than for cold-blooded animals; no action on bacteria, yeast, or germinating beans could be detected. The action of the secretion on isolated organs has been investigated. E. S.

**Dependence of Diuresis on the Salt Content and Hydrogen-ion Concentration of the Water Ingested.** E. STARKENSTEIN (*Arch. exp. Path. Pharm.*, 1924, **104**, 6—22).—The diuretic action of mineral waters is a function of their content in salts and carbon dioxide; the latter favours, whilst the former inhibit, the excretion of the water. The effect of the carbon dioxide does not result from an increased resorption, but is due to the increased hydrogen-ion concentration of the water. E. S.

**Excretion of Creatinine and Creatine by Sheep in Normal and Fasting Conditions.** A. PALLADIN (*Pflüger's Archiv*, 1924, **203**, 93—99; from *Chem. Zentr.*, 1924, ii, 492).—The creatinine and creatine metabolism in sheep, and apparently in ruminants generally, is similar to that of other animals. In the normal urine, creatinine alone is excreted, and its excretion is unaltered or increased in the beginning of a fasting period, when creatine also appears in the urine, and persists during fasting and for some days after starvation is ended. G. W. R.

**Origin of Lactose and Lactosuria in Cows.** A. CAMPUS (*Nuovo Ercolani*, 1920, **25**, [12], 154—157, 161—170; [13], [14]).—The maximum urinary lactose of pregnant cows occurs at calving. The urinary lactose output cannot be correlated with the subsequent

milk production, although when suckling is suspended after calving the amount of urinary lactose is directly proportional to the yield of milk.

CHEMICAL ABSTRACTS.

**Nitrogen Distribution in the Hydroxyproteic Acid Fraction of Urine.** L. BRINGS (*Biochem. Z.*, 1924, 154, 35—42).—A large part of the nitrogen of these acids is polypeptide in character, whilst another portion can be obtained as ammonia by hydrolysis with barium hydroxide and acids (cf. A., 1922, i, 692; 1923, i, 511, 617, etc.).

P. W. C.

**Precipitin Reaction of Bence-Jones' Protein.** L. HEKTOEN and W. H. WELKER (*J. Infect. Dis.*, 1924, 34, 440—446).—Bence-Jones' protein was prepared from the urine of a myeloma patient by precipitation with ammonium sulphate, followed by crystallisation by Hofmeister's method. Precipitin tests indicate that the protein is distinct from normal blood protein, and immunological varieties may depend on recognisable chemical differences (cf. Krauss, *Deut. Arch. klin. Med.*, 1921, 137, 257).

CHEMICAL ABSTRACTS.

**Detection of Nitroaminophenols in Urine.** L. DESVERGNES (*J. Pharm. Chim.*, 1925, [viii], 1, 56—59).—Since iodides and iodised peptones mask the colour produced by traces of nitroaminophenols in the ether layer in the Derrien azo reaction, it is necessary to remove them by preliminary treatment with chloroform.

D. G. H.

**Urochromogen.** W. O. MOOR (*Biochem. Z.*, 1924, 154, 486).—The tungstic acid and Prussian blue reactions given by urine (*ibid.*, 1924, 153, 19) are not due solely, nor even to a large extent, to uric acid.

H. D. K.

**Fluorescent Oxidation Products of Bilirubin and their Importance as Sources of Error in the Routine Detection of Urobilin.** A. ADLER (*Biochem. Z.*, 1924, 154, 125—126).—Reply to Barrenscheen and Weltmann (this vol., i, 187).

**Lactic Acid in Arthritis and Rheumatoid Conditions.** F. A. CAJORI, C. Y. CROUTER, and R. PEMBERTON (*Arch. Intern. Med.*, 1924, 34, 566—572).—Concentrations of lactic acid were: blood, 11—30 mg. per 100 c.c.; urine, 8—31 mg.; perspiration, 104—458 mg. These are normal values.

CHEMICAL ABSTRACTS.

**Biochemistry of Cancer Formation.** R. BIERICH and A. ROSENBOHM (*Biochem. Z.*, 1924, 152, 193—202).—A study of the chemical mechanism underlying the spread of cancer, induced in epithelial tissue by tar, into the underlying connective-tissue. The general conclusions are that the cancer cells in the epithelium, by degradation of carbohydrates, produce lactic acid which diffuses into the connective-tissue below, where it alters the protein of the collagen fibres into a gelatin-like substance which promotes the further growth of the cancer cells.

J. P.

**Mineral Metabolism in Diabetics. II. Disturbances in Intermediate Calcium and Chloride Metabolism.** R. MEYER-BISCH and F. GÜNTHER (*Biochem. Z.*, 1924, 152, 286—301).—Oral administration of 100 g. of lævulose to fifteen cases of diabetes



produced a temporary increase in blood calcium in nine cases, a fall in four cases, whilst two cases showed no alteration. In similar experiments, dextrose produced no alterations. The former results are independent of the degree of acidosis, whilst in normal subjects neither lævulose nor dextrose produced any change in the blood calcium. A diminution in the chlorides of blood and urine and a decrease in the water content of the former is observed in moderately severe cases of diabetes before there is any likelihood of coma. J. P.

**Echinococcal Fluid. II.** O. FLÖSSNER (*Z. Biol.*, 1924, **82**, 297—301).—The fluid from echinococcal cysts of swine and cattle contains sodium, potassium, ammonium, calcium, and magnesium as chlorides, carbonates, sulphates, and phosphates. Glycogen is the only carbohydrate found and creatinine is not a constant constituent, whilst there is no protein nor polypeptide. Succinic, *n*-valeric, propionic, and acetic acids are present. Glucosamine was isolated from the walls of the cysts. O. O.

**Occurrence of Iodine in Nature. II. Determination of Minute Quantities of Iodine.** T. VON FELLEBERG (*Biochem. Z.*, 1924, **152**, 116—127).—The method already described (*ibid.*, 1923, **139**, 391) has been improved and its application to water, sodium chloride containing traces of iodine, earths, minerals, plant and animal matter including the thyroid gland and urine is described (cf. also McClendon, A., 1924, ii, 624). J. P.

**Occurrence of Iodine in Nature. VI. Relation between the Incidence of Goitre and the Iodine Content of the Environment.** T. VON FELLEBERG (*Biochem. Z.*, 1924, **152**, 141—152).—From a comparison of the iodine content of the air, water, mineral matter, foodstuffs, etc., of the surroundings of villages with variable incidences of goitre, it is found that the latter is highest where iodine is lowest and *vice versa*. J. P.

**Determination of Phenolsulphonephthalein in the Urine of Jaundice.** H. A. ABRAMSON (*Arch. Intern. Med.*, 1924, **34**, 714—720).—Excess of saturated barium hydroxide solution is added to one half of the sample and, after dilution, the colour is compared with a standard. If the result is low, the determination is repeated on the remainder after the addition of a known quantity. In this way, the proportion absorbed is determined, and a suitable correction applied to the first result. CHEMICAL ABSTRACTS.

**Analyses of Gases in Cystic Intestinal Pneumatosis.** J. PASCUAL (*Anal. Fis. Quím.*, 1924, **22**, 506—508).—Analyses of the gases in the cysts gave the following figures: carbon dioxide 0.6—5.6%; oxygen 0.0—10.4%; nitrogen 78.9—89.0%. In one case, 14.6% of hydrogen was found. G. W. R.

**Influence of Polyneuritis on the Creatine Content of the Muscle.** A. KUDRJAWZEWA (*Z. physiol. Chem.*, 1924, **141**, 105—109).—The creatine content of the breast muscle of pigeons increases during polyneuritis, thus indicating a disturbance in the

creatine metabolism. The normal creatine content of the muscle varies between 0.441 and 0.464%. E. S.

**Fluctuations of the Iron in the Blood during the course of Experimental Scurvy.** G. MOURIGNAND, A. LEULIER, and P. MICHEL (*Compt. rend.*, 1925, **180**, 86—88).—With the object of investigating the cause of the anæmia which accompanies scurvy, analyses of the blood of some 50 animals (in three series) subjected to a *régime* producing scurvy, have been made. One kg. of the blood of the control animals contained water 819 g., ash 8.12 g., iron 0.53 g. Analyses (water and ash) of the blood of the scorbutic animals gave results so similar that no conclusions could be drawn. The amount of iron showed no change up to the 24th day, after which it began to fall. In series I, the amount on the 31st day was 0.27 and 0.21; series II, 27th day, 0.39, 33rd day, 0.31; series III, 25th day, 0.44 g. In the last two series, ceasing to impose the scurvy *régime* on the survivors led to the iron content becoming normal after 5—7 days. The amount of iron was observed to rise and fall with the hæmatological curve. A. C.

**Biochemistry of Experimental Scurvy. I.** A. PALLADIN. **II.** A. PALLADIN and A. KUDRJOWZEFF (*Wratschebnoje Djelo*, 1923, **6**, 24—26, 63—68; from *Chem. Zentr.*, 1924, ii, 1223).—I. Experimental scurvy in guinea-pigs is accompanied by disturbances in carbohydrate metabolism. An initial hyperglycæmia is succeeded by hypoglycæmia. The glycogen content of the liver falls throughout.

II. Scurvy induced in guinea-pigs by exclusion of vitamin-C from the diet is accompanied by disturbance of the nitrogen metabolism generally and of the creatine metabolism in particular. The creatine in the muscle increases from 0.369 to 0.508%. It also appears in the urine in increasing amounts and the excretion of ammonia also rises. G. W. R.

**Etiology of Tetany in Children.** G. H. ANDERSON and S. GRAHAM (*Quart. J. Med.*, 1924, **18**, 92—96).—Although active tetany is accompanied by a decreased amount of calcium in the serum, there is no proportionality. Acidosis leads to disappearance of the signs of tetany, irrespective of a rise in the calcium content of the serum. CHEMICAL ABSTRACTS.

**Tuberculosis and Calcification of Prostate.** D. W. MACKENZIE and M. I. SENG [with A. B. MACALLUM] (*Can. Med. Assoc. J.*, 1924, **14**, 912—914).—The calculus contained 30.39%  $\text{Ca}_3(\text{PO}_4)_2$ , 20.48%  $\text{Mg}_3(\text{PO}_4)_2$ , 2.10%  $\text{Na}_3\text{PO}_4$ , 0.35%  $\text{K}_3\text{PO}_4$ , and 46.69% (central part) of protein, nucleoprotein, and phospholipoids. CHEMICAL ABSTRACTS.

**Synthesis of Salicyluric Acid in Diseased Conditions.** A. BALDONI (*Biochem. therap. experim.*, 1923, **10**, 335—349; from *Chem. Zentr.*, 1924, ii, 493).—Salicylic acid and salicylates are excreted by man partly unaltered and partly as salicyluric acid. In grave diseases of the liver, the synthesis of the latter compound

is decreased, whilst in kidney diseases it is unaltered or even increased in amount.

G. W. R.

**Extraction of Proteins.** G. PINES, H. MILLER, and G. A. ALLES (*J. Amer. Med. Assoc.*, 1924, 83, 608—611).—In an investigation of methods of extracting substances responsible for allergic skin reactions, sodium chloride solution (up to 10%) was the best extractive for natural proteins without denaturation, and also for skin-reacting substances. Alcohol (95%) is a solvent for the latter, but not for the former. Neither the total nitrogen content nor the "protein nitrogen content by difference" is an indication of the activity of a solution.

CHEMICAL ABSTRACTS.

**Physiology of the Glands.** L. ASHER. LXX. **Experimental Hypoglycæmia and the Carbohydrate Metabolism of the Brain.** K. TAKAHASHI (*Biochem. Z.*, 1924, 154, 444—475).—Animals were made hypoglycæmic or brought into a condition of carbohydrate shortage by various means, viz., feeding with peptone, feeding with thyroid extract, injection of phloridzin, injection of insulin. Using a modification of Meyerhof's technique, "glycogen" and "residual" carbohydrate were determined in muscle, liver, and brain-tissue in experimental and in control animals.

Brain-tissue contains a small but definite quantity of both glycogen and other carbohydrate. Under the experimental conditions mentioned, the brain retains a much greater proportion of its original glycogen and "residual" carbohydrate than either muscle or liver. Insulin may even cause an increase in the glycogen and also in the total carbohydrate present in the brain, whilst in rabbits, only when violent convulsions occur does the total carbohydrate content of the brain diminish. The total carbohydrate in the heart rises after insulin has been administered to rabbits. Picrotoxin, which in rabbits produces convulsions similar to those following insulin injection, leads to a marked diminution in the total carbohydrate content of the brain, particularly in the amount of glycogen present. There is again an increase in the carbohydrate of the heart. There seems to be evidence of autonomous control of carbohydrate metabolism in the brain.

H. D. K.

**Effect of Carbohydrate Metabolism on the Synthesis of Hippuric Acid.** E. WIDMARK and K. JENSEN-CARLEN (*Compt. rend. Soc. Biol.*, 1924, 90, 1185—1186; from *Chem. Zentr.*, 1924, ii, 493).—Exclusion of carbohydrates from the food of men results in decreased excretion of hippuric acid. Under the same conditions ingested benzoic acid is excreted for the most part unaltered. The urine of diabetics on diets poor in carbohydrate is, similarly, rich in benzoic acid.

G. W. R.

**Metabolism of Mineral Salts in the Animal Body. I. Effect of Alkali Metals on the Growth of Animals.** R. SASAKI (*J. Sci. Agric. Soc. Japan*, 1924, No. 256, 133—150).—Young albino rats were fed with (a) a "perfect" food containing 0.354% of sodium and 0.545% of potassium, (b) a food containing 0.126% of sodium

and 0.841% of potassium, the amounts given in each case being 1 g. of Na + K per kg. body-weight. Sodium and potassium are absolutely necessary for growth but neither alone is sufficient. Satisfactory growth resulted with food (a) but not with (b) or with foods in which the Na:K ratio was intermediate. K. K.

#### **Behaviour of Tribromoethyl Alcohol in the Animal Body.**

C. ENDOH (*Biochem. Z.*, 1924, 152, 276—280).—On administering tribromoethyl alcohol to rabbits and dogs *per os*, *tribromoethylglycuronic acid*,  $C_8H_{11}O_7Br_3$ , hygroscopic, snow-white needles, m. p. 145.5°,  $[\alpha]_D^{23} - 79.09^\circ$  (in water), is recovered from the urine.

J. P.

#### **Biological Oxygen Transport by Sulphydryl Groups.**

R. E. MARK (*Biochem. Z.*, 1924, 154, 43—48).—The claim of Szent-Györgyi (A., 1924, i, 708) that thioglycollic acid unites with oxygen giving an active peroxide which can oxidise lactic acid cannot be maintained. This view has been independently adopted by the original author (A., 1924, i, 1284).

P. W. C.

#### **Specific Dynamic Action of Foodstuffs. III. Relation between Accessory Food Factors and Specific Dynamic Action of Flesh.**

K. MIYAZAKI and J. ABELIN (*Biochem. Z.*, 1924, 152, 29—50).—Flesh freed from vitamins by extraction with water, alcohol, and ether has a lesser specific dynamic action than normal raw flesh of like nitrogen content. Extraction with water alone does not impair the specific dynamic action.

J. P.

#### **Specific Dynamic Action of Foodstuffs. IV. Mechanism of Specific Dynamic Action.**

J. ABELIN (*Biochem. Z.*, 1924, 154, 52—66).—Experiments on rats indicate that the sodium salts of nucleic acid have no specific dynamic action. This is in agreement with the work of Ringer and Rapport (A., 1924, i, 450).

P. W. C.

#### **Animal Calorimetry. V. Specific Dynamic Action of**

**Fat.** J. MELLY and A. VON RÖTH (*Biochem. Z.*, 1924, 154, 127—140).—The effect of emulsions of olive oil and lard on the metabolism of starved curarised animals is investigated by means of respiratory data (cf. *ibid.*, 1924, 153, 285), the general method of Tangl (A., 1911, ii, 748) being followed. To account for the various results it is suggested that in the fats administered are two principles, the one leading to diminution, the other to increase of energy exchanges; the former is independent of the quantity of fat ingested and has an immediate effect, whilst the latter increases in action with increased fat absorption and its effect lasts for a long time.

P. W. C.

#### **Effect of Amino-acids in Producing an Increase in the Action of Adrenaline.**

E. ABDERHALDEN and E. GELLHORN (*Pflüger's Archiv*, 1924, 203, 42—56; from *Chem. Zentr.*, 1924, ii, 497).—The effect of adrenaline on striped cardiac muscle and on the smooth musculature of the œsophagus and stomach of frogs is increased by the presence of *d*- and *l*-alanine, *d*- and *l*-leucine, *d*- and

*l*-tyrosine and the corresponding 3:5-di-iodotyrosine compounds, *l*-histidine,  $\beta$ -alanine, and *l*-cystine. No difference in effect is observed between optical isomerides. Amino-acids as such exert no effect on the automatic contraction of these muscles. The lowering of temperature in mice consequent on intraperitoneal injection of adrenaline is increased by addition of amino-acids. The optical isomerides which occur naturally are particularly effective in this respect.

G. W. R.

**Influence of Magnesium on Intraocular Pressure.** T. KANEKO (*Biochem. Z.*, 1924, 154, 67—76).—The pressure-lowering effect of magnesium in the anterior chamber of the eye is confirmed but cannot be due to any increase in alkalinity since the latter increases the pressure. Injection of magnesium chloride into the eye does not cause a lowering of pressure. The normal magnesium content of the dog's aqueous humour is 2 mg./100 c.c. If the magnesium content of the posterior chamber be raised to 3—4 mg./100 c.c. by placing magnesium in the anterior chamber or by subcutaneous injection of magnesium chloride, pressure lowering takes place. A manometer for measuring intraocular pressure is described.

P. W. C.

**Pharmacological Action of Ethylene Oxide.** R. L. STEHLE, W. BOURNE, and E. LOZINSKY (*Arch. exp. Path. Pharm.*, 1924, 104, 82—86).—The toxic properties of ethylene oxide (lethal dose for dogs, 0.5 c.c. of a 20% solution per kg.) render this substance unsuitable as an anæsthetic.

E. S.

**Correlation of some Aromatic Types with Physiological Action.** Local Anæsthetics containing the Furan, Thiophen, and Pyrrole Nuclei. H. GILMAN and R. M. PICKENS (*J. Amer. Chem. Soc.*, 1925, 47, 245—255).—Diethylaminoethyl esters and benzyl esters of several heterocyclic carboxylic acids were prepared and the anæsthetic action, relative to cocaine=10, was determined. The values obtained were "procaine," 6; diethylaminoethyl benzoate, 4; diethylaminoethyl furan-2-acrylate, 3; diethylaminoethyl pyrrole-2-carboxylate, 2; diethylaminoethyl thiophen-2-carboxylate, 1; diethylaminoethyl furan-2-carboxylate, slight action; and diethylaminoethyl acetate, 0. Diethylaminoethyl phenylpropionate has a marked irritant action.

G. S. W.

**Trypanocidal Action and Chemical Constitution.** I. Arylamides of *p*-Aminophenylarsinic Acid. H. KING and W. O. MURCH.—(See i, 319.)

**Action of Potassium Cyanide and Copper on the Isolated Frog's Heart.** Y. FUJIMAKI (*Arch. exp. Path. Pharm.*, 1924, 104, 73—81).—Large variations have been found in the sensitivity of individual hearts towards potassium cyanide. In minute concentrations, potassium cyanide diminishes the activity of the heart by exciting the vagus end-plates; larger concentrations have an apparent stimulating action which is considered to be due to a removal of inhibitory effects, whilst high concentrations produce

paralysis. No evidence of the direct action of the cyanide on the heart muscle has been obtained.

Copper chloride paralyses all functions of the heart. Its action is not completely reversible, probably because the metal combines with the cell proteins. Adrenaline increases its action by increasing the permeability of the cell. E. S.

**Resorption of Bismuth in Relation to Bismuth Intoxication.**

G. FRITZ (*Orvosi Hetilap.*, 1923, 67, 333—335; from *Chem. Zentr.*, 1924, ii, 495—496).—Dipotassium bismuthotartrate in 5% solution (Richter's "bismoluol") injected intravenously (0.01 g. of bismuth per kg. body-weight) is fatal to rabbits (convulsions, dyspnoea, and cardiac paralysis). When this compound is administered intramuscularly, suspended in olive oil, resorption takes place rapidly, and in 8 to 10 days after administration of 0.05—0.1 g. of bismuth, the urine is free from bismuth. Resorption is slower and more irregular from a paraffin oil suspension. In its determination in urine, the bismuth, after oxidation with potassium chlorate and hydrochloric acid, is precipitated as sulphide, and, after solution of this in nitric acid, is precipitated and weighed as oxalate (dried to constant weight at 60°). G. W. R.

**Chlorohydrocarbons as Toxic Agents.** J. W. DOUGAL

(*Pharm. J.*, 1925, 114, 134—138).—The mechanism of the toxic action of the chlorohydrocarbons is discussed. The action of tetrachloroethane on the minnow (*Leuciscus phoxinus*) is given in detail. The penetration of the tissue by the toxic agent is a function of its physical properties; in the tissue, hydrochloric acid is produced and this may act in a variety of ways. O. O.

**Influence of Acids and Alkalis on the Action of some Convulsive Poisons.** A. FRÖHLICH and A. SOLÉ (*Arch. exp. Path. Pharm.*, 1924, 104, 32—55).

—The following drugs were examined: strychnine, thebaine, sodium perchlorate, sodium thiocyanate, picrotoxin, and curare. The increased reflex irritability which follows the administration of these substances is, in general, increased by the simultaneous or subsequent administration of alkali and diminished by the similar administration of lactic acid; picrotoxin, the action of which is uninfluenced by alkali, forms an exception. The authors consider that these effects are due to the direct action of the alkali or acid on the nerve-cells or fibres, and reject the explanation that they result from the liberation of free base from its salt, or its removal owing to salt formation, under the influence of alkali and acid respectively. Acids are known to exert a narcotic action; the action of the alkali is probably due to the neutralisation of acid produced locally in the nervous tissue and hence to a removal of its narcotic effect. E. S.

**Determination of Free Phenol and Cresol in Small Amounts of Blood and its Prognostic Significance in Cases of Poisoning.**

G. HAAS and E. F. SCHLESINGER (*Arch. exp. Path. Pharm.*, 1924, 104, 56—72).—The defibrinated blood or serum, made faintly acid with acetic acid, is distilled before and after addition of sulphuric

acid in amount necessary to bring the final concentration to 2%. The two fractions are collected separately and contain, respectively, the free phenols and the phenols resulting from hydrolysis of conjugated phenols. The amount in each fraction is determined colorimetrically by means of Millon's reagent as modified by Weiss. Using this method, it is shown that the commencement of toxic symptoms, following the administration of phenol to dogs, coincides with the appearance of free phenol in the blood. With non-toxic doses, no free phenol can be detected in the blood. E. S.

**Effect of Hydrogen-ion Concentration on the Determination of Diastatic Power by the Polarimetric Method.** H. C. GORE (*J. Amer. Chem. Soc.*, 1925, 47, 281—283).—The diastatic power of malt, calculated from polarimetric measurements, was determined at different hydrogen-ion concentrations. The results give a smooth curve showing a range of optimum diastatic power between  $p_H$  4.5 and 5.5. G. S. W.

**Antilipolytic Effect of Iodine.** H. VOLLMER, W. SCHMIDT, and J. SEREBRIJSKI (*Biochem. Z.*, 1924, 154, 476—482).—An alcoholic solution of iodine, added in small quantities to reaction mixtures of tributyrin and serum, or tributyrin and tissue extracts, in presence of phosphate buffer, inhibits the activity of the lipase. The extent of this inhibition varies with the amount of iodine added in such a way as to indicate an adsorption of iodine by the enzyme. The effect is not due to the alcohol. Ionised iodine (potassium iodide) is inactive. H. D. K.

**Autolysis. IV.** R. RONA, E. MISLOWITZER, and S. SEIDENBERG (*Biochem. Z.*, 1924, 154, 290—309).—After autolysis of liver (guinea-pig's) for several days, the diminution in the quantity of higher fatty acid present is small, never being greater than 20% of the amount originally present, and in many cases there appears to be no change. There is no evidence of fat being synthesised from carbohydrate or protein during autolysis.

The effect is described of several substances of pharmacological importance on protein autolysis in the liver. Sodium salicylate facilitates autolysis; quinine hydrochloride, arsenic trioxide, and pentoxide assist autolysis in very low, but hinder it in higher concentrations. Atoxyl hinders autolysis in all concentrations. H. D. K.

**Proteolytic Enzymes of the Liver.** C. G. ZACHRISSON (*Uppsala läkareförenings förhandl.*, 1923, 28, 333—340; from *Chem. Zentr.*, 1924, ii, 478).—The aqueous autolysate from liver contains two proteolytic enzymes, one having its optimum action at  $p_H$  4—5, probably corresponding with the  $\beta$ -protease of the spleen, and the other with optimum at  $p_H$  7, probably corresponding with erepsin. No analogue to  $\alpha$ -protease occurs. G. W. R.

**Influence of some Quinine Preparations on the Fermentation Processes of the Organism. III. Effect of some Compounds of Quinine and Urea on  $\alpha$ -Proteases.** I. A. SMORDINCEV and (MLLE.) A. N. ADOVA (*J. Russ. Phys. Chem. Soc.*, 1924, 55, 19—38).—Quinine hydrochloride has a retarding action on the

proteolytic action of trypsin on casein, 0.009% being sufficient to arrest it completely. Urea hydrochloride in small amounts (1/160 to 1/2480*N*) has a retarding action, whilst at high concentrations (1/20 to 1/80*N*) it produces a marked acceleration; the sulphate and nitrate behave in the same way, whilst the free base is inert. The double hydrochloride of quinine and urea behaves like a mixture of the two components: it shows an accelerating effect in *N* to 1/20*N* solution, although less pronounced than urea hydrochloride, and a retarding action below 1/310*N*, a concentration of 0.011% being sufficient to arrest digestion. Quinine sulphate has the same effect as the hydrochloride, the anion being, apparently, inert; it is found, however, that the hydrochloride has a greater effect on Köhler's preparation of trypsin and the sulphate on Riedl's preparation.

G. A. R. K.

**Enzymic Hydrolysis of Gentiacaulin. Production of a Xyloglucose, Primeverose.** M. BRIDEL (*Compt. rend.*, 1924, 179, 780—782; cf. A., 1913, i, 1212; 1914, i, 1203).—Gentiacaulin is hydrolysed by an enzyme extracted from seeds of *Rhamnus utilis*, L. (cf. Charaux, A., 1924, i, 1272), and also by one from *Monotropa hypopitys*, L. The products, identical in both cases, are gentiacaulein and a sugar which gives similar reactions to and is considered to be identical with primeverose (Goris, Mascré, and Vischniac, A., 1913, i, 576).

H. J. E.

**Gentiobiase.** P. KARRER and M. STAUB (*Biochem. Z.*, 1924, 152, 207—210).—Extracts of germinating spinach seeds, oats, barley, and snails contain gentiobiase in amounts proportional to their content of cellobiase and lichenase. Gentiobiase is regarded as being a constituent enzyme of the lichenase system having cellulose as a substrate.

J. P.

**Behaviour of Urease towards Alcohol.** L. ROSENFELD (*Biochem. Z.*, 1924, 154, 141—142).—Equally buffered urease solutions containing urea and 60, 70, and 80% of alcohol, respectively, showed ammonia formation but in decreasing amount.

P. W. C.

**Combination of Auxoureases with the Enzyme.** L. ROSENFELD (*Biochem. Z.*, 1924, 154, 143—147).—The auxoureases, potassium cyanide and glycine, are precipitated by a cholesterol-urease complex (but not by cholesterol alone), time and temperature being the most important factors regulating the amount of auxo-body precipitated.

P. W. C.

**Yeast Enzymes.** C. NEUBERG (*Biochem. Z.*, 1924, 152, 203—206).—A convenient lecture demonstration method of showing the action of carboxylase of yeast on pyruvic acid is described. The loss by a dried yeast preparation of sugar-fermenting power with retention of carboxylase action is described. No evolution of heat was detected during the action of yeast (juice) carboxylase on pyruvic acid (cf. Neuberg and Rosenthal, A., 1914, i, 636). An invertase solution (from autolysed press yeast) retained its activity undiminished after 12 years from the date of its preparation.

J. P.



**Kinetics of Zymase Fermentation.** P. B. JENSEN (*Biochem. Z.*, 1924, 154, 235—262).—Experiments of earlier workers have been repeated and extended, and the influence of various factors on the time taken for the carbon dioxide output to reach a maximum ("activation time") and the kinetics of the decomposition of sugar in presence of varied concentrations of zymase, co-enzyme, sugar, phosphate, hexose-phosphate, and acetaldehyde have been especially studied. The following rules apply to these factors: (1) in presence of small quantities of any one factor the velocity of fermentation (carbon dioxide evolution) is roughly proportional to the concentration of that factor; (2) when the limiting factor is present in greater amounts the velocity of fermentation ceases to be proportional to the concentration of that factor; (3) the velocity of fermentation in presence of a definite quantity of all these factors is limited by the amount of the component or components present in relatively smallest quantity, two or more components being able to act simultaneously as limiting factors. H. D. K.

**Influence of Acidity on the Action of Yeast Extracts on Concentrated Solutions of Dextrose.** R. KUHN and G. E. VON GRUNDHERR.—(See i, 203.)

**Fermentation of Dihydroxyacetone.** C. NEUBERG and A. GOTTSCHALK (*Biochem. Z.*, 1924, 154, 487—491).—With the exception of one strain, a Rotterdam bottom yeast, no yeast will ferment dihydroxyacetone at a rate which even remotely approaches the rate of fermentation of a dextrose solution, either when the triose is alone or when it is accompanied by sugar. The presence of the triose does not, however, interfere with the fermentation of the hexose. H. D. K.

**Reduction of  $\alpha\alpha$ -Dichloroacetone by Yeast.** H. K. SEN (*J. Indian Chem. Soc.*, 1924, 1, 1—8).—Yeast reduces  $\alpha\alpha$ -dichloroacetone to *l*- $\alpha\alpha$ -dichloroisopropyl alcohol, b. p. 146—148°, *d* 1.33,  $[\alpha]_D$   $-9^\circ$  (urethane,  $\text{CHCl}_2\cdot\text{CHMe}\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 61—63°,  $\alpha_D$   $-2.226^\circ$  for *c*=16.7 in ethyl alcohol). The alcohol and its urethane both have marked soporific properties. Monochloroacetone is not easily reduced as it tends to inhibit fermentation. G. M. B.

**Fermentation of Oxalacetic Acid.** C. NEUBERG and G. GORR (*Biochem. Z.*, 1924, 154, 495—502).—The fermentation of oxalacetic acid by yeast has yielded acetoin (acetylmethylcarbinol) isolated as its *p*-nitrophenylhydrazone (m. p. 304°). Malic acid and  $\alpha\beta$ -butylene glycol were also isolated and identified from the products of fermentation. The yield of acetoin was 15%.

H. D. K.

**Esterification of Phosphoric Acid by Yeast.** A. GOTTSCHALK and C. NEUBERG (*Biochem. Z.*, 1924, 154, 492—494).—Acetone yeast prepared from top yeast, which normally, in presence of dextrose and phosphate, does not produce any appreciable esterification, can be made to do so to the extent of 100%, if co-enzyme from bottom yeast be added. Addition of co-enzyme prepared from rabbit muscle causes a 50 to 60% esterification. H. D. K.



**Action of Distilled Water and Physiological Salt Solution on the Vitality of Bacteria.** L. PANISSET, J. VERGE, and V. CARNEIRO (*Ann. Inst. Pasteur*, 1925, **39**, 80—85).—Experiments on the period of survival of bacteria inoculated into distilled water or physiological (0.8%) salt solution confirm, in general, the conclusions of previous investigators that these substances have a toxic action towards the organisms. The intensity of the action varies with each species of organism; it is generally less marked with distilled water than with salt solution; organisms reinoculated into a nutrient medium after passage through salt solution show a delay in resumption of normal growth which may be as much as 72 hours. C. R. H.

**Chemical Mechanism of Bacterial Behaviour. I. Factors Controlling the Gram Reaction. II. Theory of the Gram Reaction. III. Bacteriostasis.** E. W. STEARN and A. E. STEARN (*J. Bact.*, 1924, **9**, 463—477, 479—489, 491—509).—I. Reversal of normal behaviour towards the Gram stain may be effected by increasing acidity or alkalinity.

II. The mordant in the Gram stain slightly increases the hydrogen-ion concentration by slight oxidation of the phosphatides; mild oxidation increases the affinity for basic dyes.

III. Bacteriostats probably act by formation of a loose compound between constituents of the media which are not easily hydrolysed by the bacteria.

CHEMICAL ABSTRACTS.

**Diphtheria Anatoxin and Anatoxins in General.** G. RAMON (*Ann. Inst. Pasteur*, 1925, **39**, 1—21).—Diphtheria toxin treated with formaldehyde by the author's method (A., 1924, i, 463) has been used with success for the hyperimmunisation of horses, to which it can be safely administered in large doses resulting in a correspondingly high yield of antitoxin. Administration of the anatoxin to human beings (especially small children) confers an immunity as indicated by the previously positive Shick reactions becoming negative. The anatoxin is stable for long periods at temperatures not exceeding 20° and will resist heating for 1 hour at 65—70°. The formaldehyde treatment has been applied also to the toxins of tetanus, botulism, and gas-gangrene, to toxic vegetable proteins, and to cobra-venom; in all cases products ("anatoxins") were obtained which were strongly antigenic but no longer toxic.

C. R. H.

**Occurrence of Iodine in Nature. IX. Iodine Liberation and Accumulation by Micro-organisms.** T. VON FELLEBERG and H. GEILINGER (*Biochem. Z.*, 1924, **152**, 185—190).—Neutral dilute alkali iodide solution exposed to air does not liberate molecular iodine; a little is set free in alkaline solutions, and still more in acid solutions. In the presence of bacteria or moulds less free iodine is found, since it is in part fixed by the organisms, although the part played by the latter is passive, the same result being obtained in the presence of egg-albumin. *Aspergillus niger* does not absorb iodine from a neutral iodide solution. J. P.

**Bio-reduction.** M. R. FERRO (*Revista Chim. pur. appl.*, 1920, 5, 30—49; from *Chem. Zentr.*, 1924, ii, 1215).—An alkaline solution containing 0.137% of bismuth was added to 10 times the volume of cultures of *Bacillus coli*, diphtheria, and typhus bacilli, *Micrococcus melitensis*, *Staphylococci*, and *B. anthracis*. In all cases, reduction, as shown by the production of a black precipitate of metallic bismuth, took place. Similar experiments, using ammonium molybdate and including *B. prodigiosus* in the series, also resulted in reduction, which took place more quickly when 1% of dextrose was added. The sensitiveness of inorganic substances to bio-reduction is correlated inversely with their atomic weights. The most convenient reagents are the alkali salts of selenium and tellurium, which may be used for testing the sterility of pharmaceutical preparations.

G. W. R.

**Oxidation and Reduction by *Pneumococcus*. VI. Oxidation of Enzymes in Sterile Extracts of *Pneumococcus*. VII. Enzyme Activity of Sterile Filtrates of Aërobic and Anaërobic Cultures of *Pneumococcus*.** J. M. NEILL and O. T. AVERY (*J. Exp. Med.*, 1924, 40, 405—422, 423—427; cf. A., 1924, i, 1015).—VI. Oxidising agents formed by the exposure to air of sterile extracts destroy certain enzymes of *Pneumococcus*, particularly invertase, raffinase, inulase, and amylase, but not lipase or peptonase.

VII. Sterile filtrates of autolysed anaërobic cultures contain much higher concentrations of active endocellular enzymes than do the filtrates of autolysed aërobic cultures. CHEMICAL ABSTRACTS.

**Transformation of Aromatic Compounds by *Bacillus pyocyaneus*.** J. SUPNIEWSKI (*Compt. rend. Soc. Biol.*, 1924, 90, 1111—1112; from *Chem. Zentr.*, 1924, ii, 483; cf. A., 1924, i, 914).—Most aromatic compounds, such as benzoic, phthalic, and salicylic acids, cannot serve as sources of carbon for *Bacillus pyocyaneus*. Mandelic and phenylacetic acids are assimilated with difficulty with partial formation of benzoic acid. Salicin is decomposed, the dextrose being oxidised to carbon dioxide, and the saligenin to salicylic acid; the optimum reaction is  $p_H$  6.6. Amines such as aniline, *o*-phenylenediamine, and sulphanilic acid cannot serve as sources of either carbon or nitrogen. Tyrosine, *l*-tryptophan, indole, *o*-aminobenzoic acid, and *o*-aminocinnamic acid are decomposed, whilst *m*- and *p*-aminobenzoic acids and *trans*-*o*- and *m*-aminocinnamic acids are unattacked.

G. W. R.

**Formation of Acraldehyde from Glycerol by *Bacillus welchii*.** F. B. HUMPHREYS (*J. Infectious Dis.*, 1924, 35, 282—290).—*Bacillus welchii* produces acraldehyde in glycerol broth in 18—24 hours in quantity sufficient to kill the organism; the reaction is believed to be characteristic for the group. The assumption that acraldehyde is an intermediate product in the *B. welchii* metabolism of glycerol explains the exception in the case of glycerol to the hypothesis (Kendall, Day, and Walker, *Physiol. Rev.*, 1923, 3, 438) that this micro-organism cannot directly ferment carbohydrates which do not contain an aldehyde radical.

CHEMICAL ABSTRACTS.

**Transformation of Pigments in Putrefying Flesh.** O. SCHUMM (*Z. physiol. Chem.*, 1924, **141**, 153—157).—A preliminary account of the spectroscopic examination of extracts from putrefying horse flesh (cf. Fischer and Schneller, A., 1924, i, 894). Horse flesh which has undergone putrefaction at the ordinary temperature appears to contain a hæmochromogen differing from hæmochromogen derived from hæmoglobin but identical with that from coproporphyrin and Nencki's hæmatoporphyrin; there is also present a chloroform-soluble porphyrin which is spectroscopically identical with Kammerer's porphyrin. When putrefaction takes place at 35—38°, there is, in addition, a large quantity of coproporphyrin. These and other results support the view of Günther (*Virchow's Arch.*, 1921, **230**, 146) that the muscle pigment (myohæmoglobin) differs from the blood pigment. E. S.

**Production of Gluconic and Citric Acids from Sucrose by Moulds.** W. BUTKEWITSCH (*Biochem. Z.*, 1924, **154**, 177—190).—Gluconic acid is produced during the fermentation of sucrose solutions by *Aspergillus niger* in culture media poor in nitrogen. Citric and oxalic acids are also formed, but although gluconic acid may be an intermediate stage in the production of oxalic acid, it does not appear to be such in the formation of citric acid. A low acidity of the medium favours the production of gluconic, a high acidity that of citric acid. The amount of alcohol formed during the fermentation of sucrose by *Aspergillus niger* is small. H. D. K.

**Utilisation of Mineral Nitrogen by the *Microsiphonæ* of the Soil.** G. GUITTONNEAU (*Compt. rend.*, 1924, **179**, 788—790; cf. this vol., i, 106).—Cultures of seven species of *Microsiphonæ* in different organic media containing ammonium carbonate or sulphate, potassium nitrite or nitrate, show that all three types of fixed nitrogen can be assimilated, although ammoniacal nitrogen appears to be most readily utilised under the experimental conditions. H. J. E.

**Silicon Metabolism of Diatoms.** F. BRIEGER (*Ber. deut. bot. Ges.*, 1924, **42**, 347—355).—Silica is necessary for the growth of diatoms. Increased development occurs in the neighbourhood of small pieces of calcium disilicate. In the case of potassium silicate there is an optimum concentration for growth which varies with different species of diatoms, *Fragilaria elliptica* requiring 0.063%, *Navicula* sp., 0.031%, and *Nitzschia palea*, 0.031%, respectively. Most diatoms require silica in soluble form, *Fragilaria* being the only one capable of utilising colloidal silica. The silica absorbed by diatoms is deposited in the walls, in which there is also an organic compound. It is not known whether the silica is actually combined with this organic substance, nor whether it is present in solid form or in colloidal solution. W. F. F. R.

**Determination of Adrenaline in Suprarenal Powders.** O. BAILLY.—(See ii, 248.)

**Isolation from Autolysed Yeast of a Crystalline Substance Melting at 223°, having the Properties of a Bios.** W. H. EDDY, R. W. KERR, and R. R. WILLIAMS (*J. Amer. Chem. Soc.*, 1924, **46**, 2846—2855).—By a process involving precipitation of colloidal impurities with ethyl alcohol, removal of vitamin-*B* with fuller's earth, precipitation with colloidal ferric hydroxide (Nelson and Kerr, A., 1924, i, 800) first at  $p_H$  4·7 and then at  $p_H$  5·3, and treatment of the latter precipitate, on which the bios is adsorbed, with sulphuric acid and barium hydroxide, the authors have obtained from autolysed yeast a solution of crude "bios" from which by evaporation a complex soluble in 50% alcohol is obtained. The alcohol is evaporated, the residual solution concentrated to a syrup, and the complex precipitated with absolute alcohol. On warming with 95% alcohol, this slowly separates into a viscous fraction, which settles, and a "bios" fraction, which separates from the solvent on cooling as "spherulites" or orthorhombic crystals,  $C_5H_{11}O_3N$ , m. p. 223°,  $n_D$  1·52—1·53. The crystals are nearly insoluble in cold 95% alcohol but soluble in alcohol weaker than 80%. On heating in a vacuum a sublimate, m. p. 223°, is formed which still shows "bios" activity. Heating with lime gives a *distillate*, b. p. 96°, and benzylsulphonyl chloride yields an additive *compound*, m. p. 119°, which shows liquid crystals at 91°. These results and a positive red pine-shaving test indicate a heterocyclic nitrogen-carbon ring, carrying a carboxyl group. Tests of its physiological activity by Funk and Dubin's procedure (A., 1921, ii, 72) indicate that in minute doses (0·005 mg. per c.c. of culture medium) it stimulates the growth of yeast; the effect varies with the type of yeast used, being greatest with bottom yeasts and least with the top yeasts. The substance has no anti-neuritic power and its difference from vitamin-*B* is thereby definitely demonstrated, but the tests have not determined whether the substance can affect mammalian growth if polyneuritis is prevented. R. B.

**Effect of Insulin and Other Substances on Lactic Acid Metabolism.** J. A. COLLAZO and J. SUPNIEWSKI (*Biochem. Z.*, 1924, **154**, 423—443).—Determinations of reducing substance (McLean) and lactic acid (Fürth and Charnas) in the blood of rabbits before and at intervals after the administration of different preparations of insulin, of insulin + glucose, of sodium lactate, and of a number of other substances have led to the following conclusions: (1) the effect of insulin on the lactic acid content of the blood depends on the kind of insulin used—either a rise or a fall (usually the latter with the purer insulin) may be produced; (2) administration of dextrose leads to a definite rise in blood lactic acid; (3) acetoacetic acid or adrenaline produces a fall; (4) pituitrin causes a very marked fall in lactic acid, and seems to produce changes in blood lactic acid similar to those of the blood-sugar under the action of insulin; (5) blood-sugar and blood lactic acid often change independently. Possibly lactic acid may have an important metabolism of its own, apart from its function as an intermediate metabolic product. H. D. K.

**Insulin. II.** J. A. COLLAZO, M. HÄNDEL, and P. RUBINO (*Deut. med. Woch.*, 1924, 50, 747—748; from *Chem. Zentr.*, 1924, ii, 1227; cf. *Klin. Woch.*, 1924, 3, 323).—The glycogen content of the liver and muscle of guinea-pigs to which 3 g. of dextrose and then insulin have been administered, and which show hypoglycæmia without convulsions, is 50—70% above normal. Insulin *in vitro* does not cause a synthesis of glycogen. In minced muscle (guinea-pig, dog, and rabbit), in the presence of sodium hydrogen carbonate at 35°, an appreciable increase in the production of lactic acid is observed within 2 hours, accompanied by an increase in inorganic phosphorus. The decomposition of lactacidogen is thus promoted by insulin. The seat of the action of insulin is held to be in the muscles. G. W. R.

**Dihydroxyacetone in Metabolism. Theory of the Action of Insulin.** S. ISAAC and E. ADLER (*Klin. Woch.*, 1924, 3, 1208—1210; from *Chem. Zentr.*, 1924, ii, 1228).—No increase in blood-sugar occurs after administration of dihydroxyacetone to normal men in amounts up to 150 g. and it is utilised for the formation of glycogen. A dose of 60 g. of dihydroxyacetone results in a threefold increase in the lactic acid of the blood and also in the appearance of lactic acid in the urine. With diabetic subjects, dihydroxyacetone is utilised better than dextrose, but an increase in the blood-sugar can occur. The increases in lactic acid are smaller than in the case of normal individuals, but become pronounced after administration of insulin. Dihydroxyacetone is thus suitable as a form in which to administer carbohydrate since it economises dextrose through being capable of transformation into glycogen. G. W. R.

**Insulin and its Action. IV. Influence of Insulin on the Lactic Acid Content and Hydrogen-ion Concentration of the Blood.** R. KUHN and H. BAUR [with R. HECKSCHER] (*Z. physiol. Chem.*, 1924, 141, 68—99).—It has been shown previously (*Münch. med. Woch.*, 1924, 187, 169, 541) that the lactic acid content of the muscles of animals which have died as a result of the administration of insulin is extremely small, and further that there is practically no post-mortem increase. The present paper deals with the variations in the lactic acid and sugar content and the hydrogen-ion concentration of the blood of goats following the administration of insulin. With fasting animals, no uniform changes were observed during the first half hour; in most cases, the lactic acid decreased considerably (50%) whilst the sugar remained constant or increased slightly. The hypoglycæmia which followed this period was accompanied by a large increase in the lactic acid, which reached a maximum in 3 to 4 hours and then decreased to or below the original value, where it remained constant until the death of the animal. The hydrogen-ion concentration of the blood ran parallel to the lactic acid content during the whole period. With animals receiving food, there was no initial decrease in lactic acid. It is pointed out that the acidosis and subsequent alkalosis which occur in the insulin animal may falsify conclusions based on measurements of the respiratory quotient. E. S.

**Symbiosis of Seeds and Bacteria.** G. J. FOWLER and (Miss) R. K. CHRISTIE (*J. Indian Inst. Sci.*, 1924, 7, 253—272).—Specific bacteria have been found on, or in, various seeds. In the case of indigo-seeds, they are aërobic, Gram-positive and do not ferment carbohydrates. The bacteria from poppy-seeds are strictly aërobic and are without effect on cellulose. These bacteria are not essential to the germination of the seed, but are helpful to growth of the seedling. This they effect by breaking down seed-proteins to simpler substances assimilable by the plants. Every seed examined contains a specific extractive which is of a basic or glucosidic nature. In a concentrated form, the extractives have a definite inhibitory effect, whilst in dilute solution they stimulate the bacteria, which in turn break down protein and thus assist the growth of the plant. O. O.

**Cause of the Varying Urea Content of Fungi.** N. N. IVANOV (*Biochem. Z.*, 1924, 154, 391—398).—The production and accumulation of urea in fungi is a result either of their development on a medium rich in nitrogen or one poor in carbohydrate. Fungi with a high total nitrogen content have usually also a high urea nitrogen, but with a low total nitrogen there may be little or no urea present. Pure cultures of the mushroom grown on gelatin + malt extract contain large quantities of urea; when grown on agar + malt extract no trace of urea is produced. H. D. K.

**Urea in the Lower Plants an Analogue of Asparagine.** N. N. IVANOV (*Biochem. Z.*, 1924, 154, 376—390).—Evidence is adduced to show that urea in certain fungi (*Lycoperdon*, *Psalliota*, and *Tricholoma*) plays a similar part to asparagine and glutamine in the higher plants. In absence of carbohydrate, urea in these fungi behaves as a waste product, but in presence of dextrose it serves as a source of nitrogen for the building up of more complicated nitrogenous substances. Simultaneously with the diminution in the amount of urea in the pileus, there is, in presence of dextrose, an increase in the nitrogen of the fungus precipitable by lead acetate. In absence of dextrose urea accumulates in the pileus. H. D. K.

**Relation of Low Temperatures to Respiration and Carbohydrate Changes in Potato Tubers.** E. F. HOPKINS (*Botan. Gaz.*, 1924, 78, 311—325).—The curve of respiration for temperatures from  $-0.83^{\circ}$  to  $11.5^{\circ}$  shows a minimum at  $3^{\circ}$ . As the temperature decreases respiration increases at  $0^{\circ}$  and again declines. The sugar accumulation at  $0^{\circ}$  is slow at first, then increases rapidly and finally decreases. At  $4.5^{\circ}$ , the sugar content is nearly constant; at  $1.17^{\circ}$ , it increases fairly rapidly from the start, whilst at  $-0.83^{\circ}$  there is a gradual increase in total sugars but a decrease in reducing sugars.

CHEMICAL ABSTRACTS.

**Influence of the End-products of Metabolism on Plants.**  
**IV. Influence of Nitrogen-free End-products of Plant Metabolism (Resins, Colouring Matters) on the Germination of Seeds.** W. SIGMUND (*Biochem. Z.*, 1924, 154, 399—422).—Of the series of resins and balsams tested, either by direct contact



or as vapour, all are more or less detrimental to the germination of the seeds of the vetch, of wheat, of mustard, and of rape and many are definitely toxic. Some naturally-occurring dyes have also been experimented with, and harmful effects of varying intensity are recorded, both on the process of germination and on the development of roots in the seedling.

H. D. K.

**Physiology of Apples. I. Change in the Acid Content of Stored Apples and its Physiological Significance.** D. HAYNES (*Ann. Bot.*, 1925, 39, 77—96).—During storage at low temperatures the rate of loss of acidity, as determined by titration, decreases, and the fluctuations in the acid content are increased under such conditions. The rate of loss follows the law:  $\log C = b - at$ , where  $C$  is the acid content of the apples,  $t$  is the time, and  $a$  and  $b$  are constants which depend on the kind of apples. The loss of acid is largely determined by the rate at which sugar is oxidised, and the variations cannot all be due to the reduction in respiration. Departures from the law are usually associated with internal breakdown.

O. O.

**Physiology of Apples. II. Nitrogen Content of Stored Apples.** H. K. ARCHBOLD (*Ann. Bot.*, 1925, 39, 97—107).—The total nitrogen in stored apples varies between 0.02% and 0.08% of the fresh weight, according to the variety under consideration. A high nitrogen content is accompanied by a high respiration and a low acidity. The nitrogen appears to be wholly protein in nature. During storage the total nitrogen decreases, and since no protein degradation products could be found in the juice it is suggested that the change is due to a process of protein oxidation.

O. O.

**Physiology of Apples. III. Determination of Dry Weight and the Amount of Cell-wall Material in Apples.** H. K. ARCHBOLD (*Ann. Bot.*, 1925, 39, 109—122).—In Bramley's Seedling the percentage of dry weight referred to fresh weight remains practically constant during storage at 1°. During storage at 3° the percentage decreases. The variation in the amount of cell-wall material follows approximately that of the dry weight.

O. O.

**Substances contained in the Leaves of Apple Trees and in Apple Skins.** G. RIVIÈRE and G. PICHARD (*Compt. rend.*, 1924, 179, 775—777).—On extraction of apple skins with alcohol, triacontane and heptacosanol were obtained together with a substance,  $C_{30}H_{48}O_3$ , m. p. 285°, which appears to be identical with malol (cf. Sando, A., 1923, i, 990). Malol is a hydroxy-acid and may be titrated in alcoholic solution with phenolphthalein as indicator; its *potassium* and *barium* salts were prepared. The name *maloloic acid* is suggested and the derivatives obtained by Sando (*loc. cit.*) are classified accordingly. Other substances obtained included saturated hydrocarbons from the skins of the fruit, and phloridzin, phloretin, fatty substances, and also maloloic acid from the fresh leaves.

H. J. E.

**Physiological Function of Tannins. Their Importance in the Ripening of Vine-shoots.** F. PICARD (*Compt. rend.*, 1924, 179, 778—780).—The proportion of dry matter in vine-shoots increases with ripening but in no definite ratio. The proportion of starch also increases, but there appears to be no relation between percentage of tannin and degree of ripeness. There seems to be no chemical method of testing the degree of ripeness, although the ratio of starch to tannin is greatest in moderately ripened shoots.

H. J. E.

**Bio-genesis of Mahua Oil.** G. J. FOWLER and T. DINANATH (*J. Indian Inst. Sci.*, 1924, 7, 273—284).—The weekly variation in the various constituents of the seed, husk, stalk, and stem of *Bassia longifolia* for the period June 21 to August 23, are given. Development of fat takes place in three distinct periods, the middle one showing a much larger increase than the other two. The seeds appear to contain no starch, but hemi-, pseudo-, or reserve-celluloses may occur freely. The amounts of carbohydrate and tannins in the seed vary together and conversely with the amount of oil. Thus carbohydrates (and possibly tannins) are probably changed to fats in the seed. In the husk, the sugars diminish as the starch content increases. The protein content of the seeds shows but little variation; in the husk there is an increase in the first stage of the development of the fruit. Later there is a steady decrease in protein, except at a stage, not fully understood, where all constituents appear to change abruptly. The fatty acids decrease gradually throughout.

O. O.

**Water-soluble Proteins of *Fagopyrum esculentum*, Moench.** S. SAWAMURA and R. SASAKI (*J. Sci. Agric. Soc. Japan*, No. 258, 261—266).—The aqueous extract of powdered *Fagopyrum esculentum*, Moench (17.7% husk and 82.3% seed), yielded a globulin-like protein on precipitation by acetic acid, and from the concentrated filtrate another protein having the properties of an albumin was precipitated by alcohol.

K. K.

**Protein and Oil Content of Soya Beans and the Iodine Number of Soya Bean Oil.** ANON. (*J. Amer. Soc. Agron.*, 1924, 16, 636—645).—Applications of lime, organic matter, and rock phosphate increased the percentage of protein and decreased the oil content of soya beans. Potassium applied in addition to phosphorus, lime, and residues decreased the protein content and increased that of oil. Production of oil was increased by applications of organic matter and limestone, whilst phosphorus and potassium had little effect. No consistent relation exists between the iodine number of the oil and the location or soil treatment. CHEMICAL ABSTRACTS.

**Sterol of *Boletus granulatus*.** H. R. MARSTON (*Austral. J. Exp. Biol. Med. Sci.*, 1924, 1, 53—55).—An acetone extract of the dried fruit of *Boletus granulatus* yields a crystalline sterol, m. p. 161°, apparently identical with that isolated by Ikeguchi (A., 1920, i, 160), and giving a violet colour in solution in arsenic trichloride.

CHEMICAL ABSTRACTS.

**Presence of Monotropitin in Fresh Roots of Three Species of Spiræa:** *S. ulmaria*, *S. filipendula*, and *S. gigantea* (var. *rosea*). M. BRIDEL (*J. Pharm. Chim.*, 1924, [vii], 30, 400—403).—The fresh roots of the above species are digested with alcohol, the extract is filtered and evaporated, by stages, to dryness. The crystalline product, after purification, is identical with the monotropitin obtained from *Monotropa hypopitys* and *Betula lenta*, and appears to be the parent glucoside of the methyl salicylate commonly found in plants. The yields of glucoside per kg. of roots are 0.297 g. from *Spiræa filipendula*, 0.180 g. from *S. gigantea*, and 0.058 g. from *S. ulmaria*.  
W. T. K. B.

**Alkaloids of Lobelia inflata.** H. STENZL (*Pharm. Zentr.*, 1924, 65, 730—731).—*Lobelia inflata* contains  $\alpha$ -lobeline (cf. Wieland, A., 1921, i, 802), which is non-toxic when pure and has a powerful action in stimulating respiration, together with other toxic alkaloids. Hence  $\alpha$ -lobeline alone, and not the whole plant, should be used in respiratory disorders.  
W. T. K. B.

**Bitter Principles in Hops and Beers.** L. KLEIN.—(See ii, 248.)

**Occurrence of Iodine in Nature. III. Iodine Determinations on Foodstuffs, Manures, and Swiss Mineral Waters.** T. VON FELLEBERG (*Biochem. Z.*, 1924, 152, 128—131).—Determinations of iodine in cereals, fruits, nuts, fungi, oils, cocoa, chocolate, coffee, tea, artificial manures, and Swiss mineral waters are tabulated.  
J. P.

**Urea Oxalates and their Determination as Secondary Oxalate in Fertilisers.** T. SABALITSCHKA and G. KUBISCH (*Z. Pflanz. Düng.*, 1924, A, 3, 406—407).—The method depends on the extraction of urea from the dried material with anhydrous amyl alcohol and its precipitation as oxalate by the addition of anhydrous oxalic acid in amyl alcohol solution. The precipitate is filtered, washed with ether, dried, and weighed.  
A. G. P.

**Relation of Concentration of the Soil Solution to Nitric Nitrogen in Soils containing Large Quantities of Available Nitrogen, and Effect on Plant Growth.** ANON. (*New Mexico Agr. Expt. Sta., Ann. Rep.*, 1923, 20 pp.).—There was but little difference in the nitrate content of the soil to which no nitrogen had been applied and where 220 and 1100 kg. per acre of sodium nitrate were applied. There was a marked accumulation where 2200 and 4400 kg. were applied.  
CHEMICAL ABSTRACTS.

**Accumulation of Nitrates in Soil following the Growth of Clover or Lucerne.** T. L. LYON, J. A. BIZZELL, and B. D. WILSON (*J. Amer. Soc. Agron.*, 1924, 16, 396—405).—The rapid and large accumulation of nitrates in soil previously planted to clover or lucerne, as compared with soil previously in timothy, appears to be connected with the higher nitrogen content of the former. It is not necessarily associated with a larger total quantity of nitrogen in the legume soil, but rather with its smaller quantity of non-nitrogenous organic matter.  
CHEMICAL ABSTRACTS.

**Soil Analysis.** W. T. MCGEORGE (*Louisiana Planter*, 1924, 72, 312—313).—A definite relation exists between the phosphate extracted by 1% citric acid solution and the response to growth of sugar cane. Soils showing less than 0.003%  $P_2O_5$  responded to phosphate fertilisation. For potassium determinations, 1% citric acid solution is best. Larger amounts of soluble silica are present where phosphates are more available. CHEMICAL ABSTRACTS.

**Carbon Dioxide Production in Soils.** O. LEMMERMANN and H. WIESSMANN (*Z. Pflanz. Düng.*, 1924, A, 3, 387—395).—Comparison was made of the rates of carbon dioxide production in soil treated with straw, lupin residues, and farmyard manure. Carbon dioxide was produced most rapidly and in greatest amounts from straw, and from the other materials in the order named. Graphical representation of the rate of production gives curves of a parabolic nature, from which only the initial (15-day) points deviated appreciably in a period of nearly 3 years. A. G. P.

**Heat of Wetting as a New Means of Determining the Colloidal Material in Soils.** G. J. BOUYOUKOS (*Science*, 1924, 60, 320).—The disadvantages incident to known methods of determining the colloidal material in soils are indicated. By the use of a method based on the observation that the heat of wetting of soils with water is due mainly, if not entirely, to their colloids, the colloidal content of soils has been found to range from 0 to 80% by weight. The reactivity of material depends not only on the size of the particles, but also on the state of activation; possibly the latter consideration is the more important. A. A. E.

**Universal Indicator for the Colorimetric Determination of  $p_H$  Values in Soil Experiments.** H. NIKLAS and A. HOCK (*Z. Pflanz. Düng.*, 1924, A, 3, 402—405).—The indicator consists of a mixture of alcoholic solutions of 0.04% bromophenol-blue (4 vols.), 0.04% bromocresol-purple (1 vol.), 0.02% methyl-red (6 vols.), and 0.04% bromothymol-blue (4 vols.). The effective range of the indicator is  $p_H$  3.5—7.6 and results agree fairly closely with those obtained by the Clarke and Michaelis methods. A. G. P.

**Effect of Drying on the Acidity of Soil Samples.** C. O. ROST and E. A. FIEGER (*Science*, 1924, 60, 297).—On drying in air, acid soils generally exhibit increased hydrogen-ion concentration. A group of glacial soils, partly acid and partly alkaline, became more acid; the alkaline soils showed the greater change, and a group of more acid loessial soils showed less change. Drying in an oven caused a greater increase in the hydrogen-ion concentration than drying in air. Samples moistened after drying in air became more acid than the original moist samples and usually more acid than the air-dried samples. In the majority of cases, moist samples become more acid when kept in sealed glass containers. Air-dried samples gave a more acid reaction by the potassium thiocyanate method than fresh, moist samples. A. A. E.

## Organic Chemistry.

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### Fifty Years of Stereochemical Theory and Investigation.

P. WALDEN (*Ber.*, 1925, **58**, [B], 237—265).—A lecture delivered before the German Chemical Society.

H. W.

### Syntheses in the Undecane Series. K. HESS and R. BAPPERT

(*Annalen*, 1925, **441**, 151—156).—*n*-Undecane, prepared by reduction of dipentyl ketone by Clemmensen's method, has b. p. 79—80°/16 mm.,  $n_D^{19.4}$  1.41862; from methyl nonyl ketone it has b. p. 79°/16 mm. or 194—195°/752 mm.,  $d_4^{19.8}$  0.7418,  $n_D^{19.5}$  1.41862. *n*-Undecan- $\zeta$ -ol, m. p. 16°, b. p. 235°/754 mm. (corr.),  $d_4^{21.8}$  0.8272,  $n_D^{19}$  1.43700, is obtained by reducing dipentyl ketone with sodium and alcohol. Treatment of ethyl *n*-butylacetoacetate with butyl bromide and sodium methoxide gives *ethyl di-n-butylacetoacetate*, b. p. 135.5°/15 mm.,  $d_4^{20}$  0.9320,  $n_D^{20}$  1.44042. Under different conditions, the product is ethyl  $\alpha$ -butylhexoate, b. p. 104°/18 mm.,  $d_4^{20}$  0.8636,  $n_D^{21}$  1.42223. "Ketonic hydrolysis" of the acetoacetate yields *methyl  $\epsilon$ -nonyl ketone*, b. p. 96—97°/16 mm.,  $d_4^{18.4}$  0.8299,  $n_D^{18.4}$  1.42795, together with methyl amyl ketone, b. p. 58°/16 mm. (from ethyl butylacetoacetate) and  $\alpha$ -butylhexoic acid, b. p. 139—140°/16 mm.,  $d_4^{18.4}$  0.8978,  $n_D^{17.4}$  1.43448. The ketone is easily reduced by sodium and alcohol to methyl- $\epsilon$ -nonylcarbinol, b. p. 108—109°/16 mm.,  $d_4^{17.9}$  0.8392,  $n_D^{18.2}$  1.44042. It is reduced by Clemmensen's method to  $\epsilon$ -ethylnonane, b. p. 71°/16 mm.,  $d_4^{19.2}$  0.7513,  $n_D^{19.5}$  1.42092.

C. H.

### Formation of Fatty Acids from "Protoparaffin." J.

MARCUSON (*Chem.-Ztg.*, 1925, **49**, 166).—Ceresin (refined ozokerite), m. p. 62—71°, was treated with oxygen at 125° in the presence of manganese dioxide on fuller's earth. The reaction was slower than with the lower paraffins, the acid value only reaching 21 after 35 hours. By increasing the temperature to 150°, an acid value of 39 was reached after a total of 90 hours. The originally hard ceresin had become soft, and it was then separated according to the method of Hönig and Spitz into saponifiable and unsaponifiable portions. The latter consisted of saturated and unsaturated hydrocarbons, ketones, and alcohols. The acids were separated into solid and liquid fractions by repeated application of Varrentrapp's lead salt method. The liquid acids contained some hydroxy-acids insoluble in light petroleum, but consisted chiefly of a soluble thick oil, acid value 115, iodine value 11,  $d < 1$ , which was a mixture of polymerised unsaturated fatty acids. The solid acids had m. p. 60—62°, acid value 146, corresponding with a molecular weight 384. In spite of this high molecular weight, the acid was soluble in alcohol, light petroleum, etc., this being consistent with the presence of branched carbon chains. The oxidation indicates the presence of isoparaffins in protoparaffin (e.g., ceresin).

P. M.

**Relative Rates of Catalytic Hydrogenation of Different Types of Unsaturated Compounds. I. Aliphatic Ethylenic Derivatives.** S. V. LEBEDEV, G. G. KOBLIANSKY, and A. O. YAKUBCHIK (*J. Chem. Soc.*, 1925, **127**, 418—440).—The rate of absorption of hydrogen by unsaturated ethylenic compounds in presence of platinum black is, in general, a linear function of the time. The highest rate of absorption is exhibited by mono-substituted compounds, and as the number of substituents increases the rate declines. Mono-, tri-, and tetra-substituted derivatives absorb hydrogen at a uniform rate throughout the greater period of the action, but disubstituted compounds do so only during a shorter period of the action. In certain cases where more than one ethylenic linking is present, there are two well-defined rates of absorption. Negative substituents cause an abnormally slow velocity of absorption, whilst conjugation with an alicyclic or carbonyl residue tends to increase the rate.

In a mixture of two similarly substituted ethylenic compounds the components are hydrogenated concurrently, but when dissimilarly substituted, the components are hydrogenated consecutively. When the two substances are substituted to different degrees they are attacked successively. In binary mixtures containing a monosubstituted compound, this maintains its characteristic, and more rapid, rate of absorption, and when a tetra-substituted derivative is present this also preserves its own rate of absorption. Di- and tri-substituted compounds in admixture exhibit either a lower or a higher rate of absorption than when hydrogenated alone, so that the two rates tend to approach one another.

These results may be utilised to determine the degree of substitution of an ethylenic compound by comparison of its rate of hydrogenation in the pure state and when in admixture with a typical substituted unsaturated compound, such as allyl alcohol etc. C. J. S.

**Electrolytic Preparation of Hexabromoethane.** M. DUSSOL (*Bull. Soc. chim.*, 1925, [iv], **37**, 161—167).—Electrolysis of aqueous potassium bromide solution between platinum electrodes in presence of acetylene affords a mixture of hexabromoethane (90%) and *s*-tetrabromoethane (10%), dibromoacetylene and tetrabromoethylene not being formed. The formation of hexabromoethane probably takes place by addition of bromine to the radical  $\cdot\text{C}\equiv\text{C}\cdot$ , derived from the acetylene by oxidation by hypobromite. *s*-Tetrabromoethane is not further brominated when agitated with potassium bromide which is being electrolysed. Addition of bromine to the electrolyte favours the formation of *s*-tetrabromoethane. The yield of hexabromoethane is depressed in presence of potassium hydroxide or of sodium hydrogen carbonate and carbon dioxide, whilst potassium dichromate is without influence.

F. G. W.

**Electrochemical Preparation of Di-iodoacetylene and "Di-iodoform" [Tetraiodoethylene].** M. DUSSOL (*Bull. Soc. chim.*, 1924, [iv], **35**, 1618—1629).—When acetylene is passed into a

solution of sodium hydroxide containing an excess of iodine, tetraiodoethylene is formed:  $C_2H_2 + NaOI + I_2 = C_2I_2 + NaI + H_2O$ ;  $C_2I_2 + I_2 = C_2I_4$ , the second reaction taking place when acid is added (cf. Maquenne, A., 1893, i, 449). The preparation is carried out readily and cheaply if acetylene be passed into a solution of potassium iodide, which need not be pure, undergoing electrolysis. When an excess of iodine is present at the start, almost pure tetraiodoethylene is obtained directly, but when no iodine is added, diiodoacetylene is produced. As, however, potassium iodate is simultaneously formed, simple acidification of the suspension suffices to set iodine free, and so effect the complete conversion. The product, after one recrystallisation, is almost pure; it has m. p. 191—192°. Under suitable conditions, the yield is 80—85% of that calculated on the current consumed. Addition of potassium hydroxide or of potassium carbonate (these variations were suggested by known improvements of the electrochemical method of making iodoform) depresses the yield, and passage of carbon dioxide, or addition of potassium iodate or of potassium chromate, has no beneficial effect. Moreover, the solution cannot be used continuously by adding further supplies of iodide, because it becomes more and more alkaline.

W. A. S.

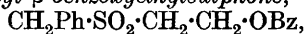
**$\alpha\beta$ -Dihydroxy- $\Delta\gamma$ -butinene.** R. LESPIEAU (*Compt. rend.*, 1925, 180, 442—444).—In ethereal solution dry potassium hydroxide converts  $\alpha$ -chloro- $\beta$ -hydroxy- $\Delta\gamma$ -butinene (cf. this vol., i, 225) into the corresponding *ethylene oxide*, b. p. 86—87°/760 mm.,  $d_{23}^{23}$  0.945,  $n_D$  1.427. By the action of water in a sealed tube at 100°, this gives  $\alpha\beta$ -dihydroxy- $\Delta\gamma$ -butinene (90% yield), m. p. 39.5—40.5°. Its constitution is proved by the preparation of its *diphenylurethane*, m. p. 134—134.5°, and also by the readiness with which it gives an additive *dibromo* derivative, m. p. 47—48°. The failure of the glycol to give a precipitate with ammoniacal cuprous chloride is attributed to the supposed solubility in water of its copper derivative, a property which this compound, in virtue of its hydroxyl groups, is likely to possess.

W. E. E.

**Oxonium Perbromides.** F. KEHRMANN and E. FALKE (*Helv. Chim. Acta*, 1924, 7, 992—995).—A number of compounds with bromine, hitherto supposed to be additive in nature, are now shown to be oxonium perbromides. Thus, Schützenberger's compound of ethyl ether and bromine, obtained (A., 1873, 487) by cooling a mixture of ether and bromine in a freezing mixture, has the composition  $Et_2O \cdot HBr \cdot Br_2$ , the analytical results for total bromine and "elementary" bromine—i.e., that reacting with potassium iodide—being in good agreement with this formula, that of a *diethyloxonium perbromide*. The compound formed by passing hydrogen bromide into a mixture of acetic acid and bromine is similarly constituted (cf. Baeyer and Villiger, A., 1901, i, 658). The product obtained from ethylene oxide and bromine by Würtz (*Ann. Chim.*, 1863, iii, 69, 321), actually, as he showed, derived from diethylene dioxide, is the perbromide,  $O:(CH_2 \cdot CH_2)_2:O \cdot HBr \cdot Br_2$ ,

and Wallach and Brass' cineole derivative (A., 1885, 171) has the composition  $C_{10}H_{18}O, HBr, Br_2$ .  
W. A. S.

**Derivatives of Monothioethylene Glycol.** E. FROMM and H. JÖRG (*Ber.*, 1925, 58, [B], 304—309).—Monothioethylene glycol,  $SH \cdot CH_2 \cdot CH_2 \cdot OH$ , b. p.  $61^\circ/18$  mm. (cf. Bennett, T., 1921, 119, 418—425), is most conveniently prepared by the reduction of  $\beta\beta'$ -hydroxydiethyl disulphide by zinc dust and sulphuric acid or by sodium and alcohol; it yields a *dibenzoyl* compound, m. p.  $39^\circ$ , and a *benzylidene* derivative,  $CHPh(S \cdot CH_2 \cdot CH_2 \cdot OH)_2$ , m. p.  $58^\circ$ . It is converted by benzyl chloride into *benzyl  $\beta$ -hydroxyethyl sulphide*, b. p.  $169^\circ/18$  mm., which can also be prepared from sodium benzyl sulphide and ethylene chlorohydrin or from benzyl mercaptan and ethylene oxide. If the hydroxyl group is protected by benzoylation, the *benzoate*,  $CH_2Ph \cdot S \cdot CH_2 \cdot CH_2 \cdot OBz$ , can be oxidised by permanganate to *benzyl- $\beta$ -benzoxyethylsulphone*,

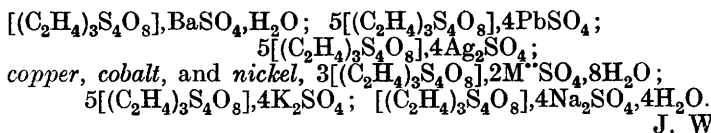


m. p.  $114^\circ$ , which is converted by alcoholic sodium ethoxide into *benzyl- $\beta$ -ethoxyethylsulphone*, m. p.  $53^\circ$ , and by aqueous sodium hydroxide into *benzyl- $\beta$ -hydroxyethylsulphone*, m. p.  $97^\circ$ .  $\beta\beta'$ -Dihydroxydiethyl disulphide yields a non-crystalline *dibenzoate*. It is converted by boiling concentrated hydrochloric acid into  $\beta\beta'$ -dichlorodiethyl disulphide, which with benzyl mercaptan gives *di- $\beta\beta'$ -benzylthioldiethyl disulphide*,  $(S \cdot CH_2 \cdot CH_2 \cdot S \cdot CH_2Ph)_2$ , m. p.  $70^\circ$ .  $\beta\beta'$ -Dichlorodiethyl disulphide is converted by sodium sulphide in the presence of anhydrous alcohol into the cyclic *tri-sulphide*,  $S < \begin{smallmatrix} CH_2 \cdot CH_2 \cdot S \\ CH_2 \cdot CH_2 \cdot S \end{smallmatrix}$ , m. p.  $74$ — $75^\circ$ , which can also be prepared

from  $\beta\beta'$ -dichlorodiethyl sulphide and sodium disulphide; reduction followed by treatment of the product with benzyl chloride converts it into *di- $\beta\beta'$ -benzylthioldiethyl sulphide*,  $S(CH_2 \cdot CH_2 \cdot S \cdot CH_2Ph)_2$ , m. p.  $53^\circ$ , which is oxidised to di- $\beta\beta'$ -benzylsulphonyldiethylsulphone, m. p. above  $300^\circ$ , identical with the product described by Fromm and Ungar (A., 1924, i, 69). The trisulphone is hydrolysed by alkali hydroxide to benzylsulphinic acid,  $\beta$ -hydroxyethylsulphinic acid, and benzyl- $\beta$ -hydroxyethylsulphone. Distillation of dihydroxydiethyl disulphide with zinc chloride, potassium hydrogen sulphate, or syrupy phosphoric acid gives diethylene disulphide,  $S(CH_2 \cdot CH_2)_2S$ , m. p.  $111^\circ$ , and carbonised products. H. W.

**Oxidation of Triethylene Tetrasulphide by means of Potassium Permanganate.** P. C. RÂY (*J. Indian Chem. Soc.*, 1925, 1, 207—212; cf. T., 1923, 123, 2176).—The oxidation of triethylene tetrasulphide with potassium permanganate in alkaline solution yields ethylenedisulphonic acid, whilst in dilute sulphuric acid solution the tetrasulphone is produced, but immediately combines with the manganese sulphate formed to produce a stable double compound,  $3[(C_2H_4)_3S_4O_8] \cdot 2MnSO_4 \cdot 12H_2O$ , sparingly soluble in cold but readily soluble in hot water; by the addition of various metallic salt solutions to this solution the following compounds are obtained,  $5[(C_2H_4)_3S_4O_8] \cdot 4CaSO_4$ ;  $5[(C_2H_4)_3S_4O_8] \cdot 4SrSO_4$ ;





J. W. B.

**Direct Combination of Ethylenic Hydrocarbons with Hydrogen Sulphites.** I. KOLKER and A. LAPWORTH (*J. Chem. Soc.*, 1925, 127, 307—315).—Under appropriate experimental conditions, hydrogen sulphites combine directly with ethylenic hydrocarbons, yielding as primary products saturated sulphonates, which are accompanied by varying proportions of other salts, possibly alkyl hydrogen sulphites. The general course of the reaction is represented thus:— $CR^I R^{II} \cdot CR^{III} R^{IV} + NaHSO_3 \rightarrow CHR^I R^{II} \cdot CR^{III} R^{IV} \cdot SO_3 Na$  or  $CHR^I R^{II} \cdot CR^{III} R^{IV} \cdot O \cdot SO_2 Na$ .

The yield of sulphonic acid increases with the dilution of the hydrogen sulphite up to at least  $M/4$ , and is considerably favoured by the presence of kieselguhr.

*cyclo*Hexene and ammonium hydrogen sulphite gave as main product barium *cyclo*hexanesulphonate. Other derivatives of *cyclo*hexanesulphonic acid which were prepared are: *sodium* salt,  $C_6H_{11} \cdot SO_3 Na, H_2O$ ; *ammonium* salt, *magnesium* salt; *copper* salt,  $(C_6H_{11} \cdot SO_3)_2 Cu, 4H_2O$ ; *sulphonyl chloride*, m. p.  $106^\circ$ , *sulphonamide*, m. p.  $93-94^\circ$ .

Ethylene yielded barium ethanesulphonate, from which ethane-sulphonamide, m. p.  $59-60^\circ$ , was obtained. Technical amylene and ammonium hydrogen sulphite, without kieselguhr, gave 86% of crude barium salts consisting only of true sulphonic derivatives. From dipentene there was obtained *barium menthanedisulphonate*,  $C_{10}H_{18}(SO_3)_2 Ba, H_2O$ .

C. J. S.

**Sudden Pyrogenic Decomposition of Methyl Formate and the Principle of Minimum Molecular Deformation.** J. A. MULLER and E. PEYTRAL (*Compt. rend.*, 1924, 179, 831—832; cf. Peytral, A., 1918, i, 1; 1920, i, 217; 1921, i, 156, 166; 1922, i, 219, 222; 1924, i, 1158, 1161; also Muller, A., 1919, ii, 500).—The vapour of methyl formate, on being heated at  $1150^\circ$ , decomposes into formaldehyde, carbon monoxide, and hydrogen. The two last-named substances are formed as the result of decomposition of the formaldehyde, which is the only primary product. This is regarded as a further example as regards pyrogenic decompositions of the successive changes of a series taking place with the least possible change in the atomic linkings concerned, *i.e.*, the "principle of minimum molecular deformation."

H. J. E.

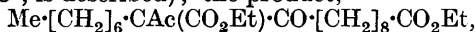
**Fatty Acid Constituents of some Natural Fats. I. Oils from the Coconut.** E. F. ARMSTRONG, J. ALLAN, and C. W. MOORE (*J. Soc. Chem. Ind.*, 1924, 44, 63—68t).—The value of fractional distillation of the fatty acid esters as a means of determining the composition of a mixture of these has been criticised, but the objections are not well founded. Homogeneous fractions can be obtained by the methods now described. A suitable quantity of the oil is saponified, the fatty acids are isolated, and their

saponification equivalent and iodine value determined. If the iodine value is below 20, the acids are converted into their ethyl esters, which are fractionally distilled. If the iodine value is 20—45, the fatty acids are separated by recrystallisation from 70% alcohol into the solid acids, iodine value below 3, and the liquid acids. The latter contain some solid acids which are separated by the Gusserow-Varrentrapp method. The solid and liquid acids are esterified separately and the esters are distilled in modified Ladenburg flasks at 3—5 mm. at the rate of 20 small drops per minute. In the case of soft fats the mixture of fatty acids is submitted to the Gusserow-Varrentrapp process and the solid and liquid acids are treated as before.

The acids from coconut kernel oil comprise octoic (2%), decoic (2%), lauric (28%), myristic (22%), palmitic (12%), stearic (?1%), oleic (23%), and linoleic (10%), whereas those from the parings oil consist of octoic (9.5%), decoic (4.5%), lauric (51%), myristic (18.5%), palmitic (7.5%), stearic (13.0%), oleic (5.0%), linoleic (1%). Hexoic acid may be present in coconut oil. F. B.

**Synthesis of Arachidic Acid and some Long-chain Compounds.** N. K. ADAM and J. W. W. DYER (*J. Chem. Soc.*, 1925, 127, 70—73).—By a modification of Bouveault and Blanc's method, ethyl stearate is reduced to octadecyl alcohol and ethyl arachidate to eicosyl alcohol, m. p. 65—65.5°, from which eicosyl acetate is prepared. Octadecyl iodide with sodium and ethyl malonate gives ethyl mono-octadecylmalonate, from which mono-octadecylmalonic acid is obtained by hydrolysis with potassium hydroxide; the ester reacts with octadecyl iodide and sodium, forming ethyl dioctadecylmalonate: *dioctadecylmalonic acid*, m. p. 93.5—94°. By heating the acid at 160°, it gives *dioctadecylacetic acid*, m. p. 81—82°, whilst mono-octadecylmalonic acid gives arachidic acid; methyl arachidate, m. p. 46—47°; ethyl arachidate, m. p. 41.5—42.5°; the anomalous m. p. in the literature are thus incorrect. The nitrile prepared from arachidamide is reduced by sodium in alcohol and *eicosylamine hydrochloride* is isolated; by evaporating with potassium cyanate, it yields *eicosylcarbamide*, m. p. 111.5°. The identity of these C<sub>20</sub> compounds is confirmed by examining uni-molecular films. Octadecylamine hydrochloride is distilled with lime, when the distillate with acetic anhydride yields *aceto-octadecylamide*, m. p. 79.5—80°; *acetoheptadecylamide* is prepared similarly. F. M. H.

**Synthesis of certain Higher Aliphatic Compounds. I. Synthesis of Lactarinic Acid and of Oleic Acid.** G. M. ROBINSON and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 175—180).—A method of preparing acids of the type  $R \cdot [CH_2]_m \cdot CO \cdot [CH_2]_n \cdot CO_2H$  is described. Ethyl sodio-*n*-heptylmalonate and  $\theta$ -carbethoxynonyl chloride in ether give a product which is converted by 1% oxalic acid into  $\iota$ -ketostearic acid; it is better to condense ethyl sodio-acetylnonoate with  $\theta$ -carbethoxynonyl chloride ( $\theta$ -carbethoxynonyl-anilide, m. p. 63°, is described); the product,



is hydrolysed first with cold dilute sodium hydroxide, then with boiling dilute sulphuric acid, and finally with boiling dilute sodium hydroxide, forming  $\iota$ -ketostearic acid, m. p.  $83^\circ$  ( $\theta$ -ketostearic acid also formed?). It is identical with the product of the action of sulphuric acid and water on stearolic acid. Its sodium salt, m. p.  $212^\circ$ , is reduced by sodium in alcohol to  $\iota$ -hydroxystearic acid, m. p.  $84.5^\circ$ , which with phosphorus tri-iodide and water gives  $\iota$ -iodostearic acid; the preparation of oleic acid from this (Arnaud and Posternak, A., 1910, i, 459) proves that the double bond is in the position  $\Delta^6$  or  $\Delta^7$ . Stearolic acid may be reduced by zinc and hydrogen chloride in presence of titanous chloride and acetic acid to *cis*-oleic acid, m. p.  $12.5$ – $13^\circ$ , which is oxidised by potassium permanganate to dihydroxystearic acid, m. p.  $132^\circ$ .

Ethyl sodioacetoacetate and *n*-undecyl iodide yield ethyl  $\alpha$ -acetyl-*n*-tridecoate, b. p.  $185^\circ/17$  mm. This with  $\delta$ -carbomethoxyvaleryl chloride forms  $\text{CH}_3\cdot[\text{CH}_2]_{10}\cdot\text{CAc}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot[\text{CH}_2]_4\cdot\text{CO}_2\text{Et}$ , from which by graduated hydrolysis is isolated  $\epsilon$ -ketostearic acid, m. p.  $87^\circ$ , and this is identical with lactarinic acid (cf. Bougault and Charaux, A., 1911, i, 835, 949).

Ethyl sodio- $\alpha$ -acetyl-*n*-tridecoate and  $\beta$ -carbomethoxypropionyl chloride, b. p.  $93^\circ/18$  mm. (*carbomethoxypropionanilide*, m. p.  $97$ – $99^\circ$ ), give  $\text{CH}_3\cdot[\text{CH}_2]_{10}\cdot\text{CAc}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{Me}$ , which by graduated hydrolysis yields  $\gamma$ -ketopalmitic acid, m. p.  $91$ – $92^\circ$ , *oxime*, m. p.  $54^\circ$ .  
F. M. H.

**Constitution of Natural Unsaturated Fatty Acids. I. New Method of Ascertaining the Position of the Ethylenic Linking in Acids of the Oleic Series.** E. F. ARMSTRONG and T. P. HILDITCH (*J. Soc. Chem. Ind.*, 1924, **44**, 43–47T).—The methods employed hitherto for locating the double bond in the higher unsaturated fatty acids are either too complicated and involve the possibility of a migration of the ethylenic linking, or they yield a variety of products from which it is difficult to deduce a structural formula. Oxidation of the methyl or ethyl esters of oleic acid in acetone or glacial acetic solution with potassium permanganate is not open to the former objection and there is a conversion of 50 to 80% of the ester into either nonoic acid or the half ester of azelaic acid. Esters of the saturated fatty acids were not oxidised when treated with permanganate in acetone or acetic acid solution.  
F. B.

**Preparation and Properties of Purified Oleic Acid and some of its Salts.** A. LAPWORTH, L. K. PEARSON, and E. N. MOTTRAM (*Biochem. J.*, 1925, **19**, 7–18).—Olive oil is hydrolysed with alcoholic sodium hydroxide and the resulting mixture is nearly neutralised with acetic acid. It is then treated with aqueous lead acetate and the lead precipitate dissolved in toluene. The solution is further treated with dehydrated lead acetate. After filtering, the toluene solution is decomposed with hydrochloric acid, filtered, and the solvent removed by distillation. The resulting fatty acids are then fractionally distilled and the barium salt is prepared from the middle fraction. After several recrystallisations from a mixture

of toluene and amyl alcohol, the salt is decomposed. The oleic acid thus obtained contains 2% of palmitic acid and small quantities of impurities. The latter can, however, be removed by draining on a porous plate in a vacuum. The properties of this pure preparation are given. S. S. Z.

**Additive Power of Iodine with Regard to Ethylenic Compounds.** E. ANDRÉ and (MLLE.) T. FRANÇOIS (*Bull. Soc. chim.*, 1925, [iv], **37**, 167—176; cf. A., 1924, i, 254).—The presence of cupric iodide (equivalent to 0.1% CuO) increases the rate of absorption of iodine, as well as the total amount of iodine absorbed, by ethylenic compounds (vegetable and fish oils) from solutions of iodine (2.1%) in glacial acetic acid. In the cases of acetic acid and olive or almond oil, the proportion of iodine absorbed is equal to the Hanus iodine value. Cupric iodide also renders the total absorption of iodine more regular under varying conditions of temperature. The absorption of iodine from glacial acetic acid solution by sperm oil is rapid at first, ceases temporarily after 3 hours, and then recommences, subsequent absorption being much more rapid in presence of cupric iodide. The absorption of iodine under similar conditions by linseed oil, in absence of cupric iodide, attains a maximum in 24 hours, thereafter undergoing apparent reversal, whereas in presence of the catalyst the absorption increases continuously to equilibrium. F. G. W.

**Polymerisation of Fatty Oils. III.** J. MARCUSSEN (*Z. angew. Chem.*, 1925, **38**, 148—149; cf. *ibid.*, 1922, **35**, 543).—Salway's theory (*J. Soc. Chem. Ind.*, 1920, **39**, 324) is criticised; it is not supported by Ubbelohde's results ("Analyse und Technologie der Öle und Fette," 1920, II, 351), or by the observation that when tung oil is heated under carbon dioxide at 280° and the unchanged oil afterwards removed by washing with acetone, benzene, and alcohol, a gelatinous mass remains. This is hydrolysed by hot alcoholic potassium hydroxide; the mixture of acids so obtained has a molecular weight (calculated from cryoscopic measurements in camphor or glacial acetic acid solution) of about 500. Polymerised linseed oil, isolated in a similar way, is a viscous mass, yielding fatty acids the mean molecular weight of which is again about 500. "True polymerisation" has therefore taken place. These polymerised oils contain no mono- or di-glycerides. W. A. S.

**Autoxidation of Fats, Resins, Terpenes, and Tannins.** A. TSCHIRCH (*Chem. Umschau*, 1925, **32**, 29—31).—Autoxidations occurring without the presence of a catalyst may be divided into reversible and irreversible. The oxidation of certain tannins in air with formation of phlobaphens is an example of the former, as reversal takes place with zinc dust in alcoholic solution. Irreversible oxidations take place when the original structure of the molecule is destroyed, generally by rupture at the double bond, as is the case in the development of rancidity in fats, and the resinification of turpentine oil. The first reaction is probably the formation

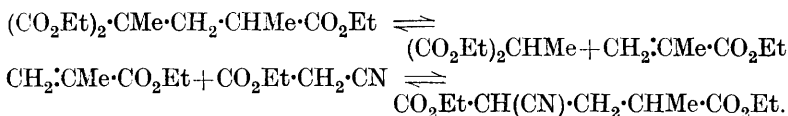
of a peroxide, which decomposes, forming an oxide, together with ozone and hydrogen peroxide, an ozonide then being formed which again breaks up into aldehydes and acids. This explanation is applied to the autoxidation of turpentine and of resin acids. A viscous, 30-year old sample of oil of turpentine yielded an aqueous extract of astringent acid taste giving the reactions of hydrogen peroxide and furnishing a resinous residue on distillation. The views of Fierz on the rancidity of fats are criticised as the conditions postulated by him are not likely to occur in practice.

P. M.

**Isomeric Hydrazones of Glyoxylic Acid. II. Remarkable, Different Behaviour of Stereoisomerides.** M. BUSCH and R. VON BEUST.—(See i, 400.)

**Aniline Hydrogen Salts of Acids of the Oxalic Series.** O. RAMBECH.—(See i, 385.)

**Correlation of Additive Reactions with Tautomeric Change. IV. Effect of Polar Conditions on Reversibility.** (MRS.) E. H. INGOLD (USHERWOOD) (*J. Chem. Soc.*, 1925, 127, 469—475).—Besides the normal addition, as indicated by the "positive-negative" rule, that occurs during Michael's reaction, addition in the opposite direction may take place. This abnormal addition might be due to recombination, in the reverse direction, of two esters formed by decomposition of the normal product. The reversibility of the normal reaction has been shown in the case of ethyl  $\alpha\alpha'$ -dimethyl- $\alpha$ -carboxyglutarate. The ester was heated in presence of ethyl sodiocyanoacetate, which combined with the  $\alpha$ -methylacrylic ester to form ethyl  $\alpha'$ -methyl- $\alpha$ -cyanoglutarate:



The reverse action, resulting in the formation of the abnormal type of product, does not take place under the conditions of the original condensation, but at a higher temperature it does occur to some extent. From ethyl *as*-dimethylecyanosuccinate by the action of concentrated alkali there was obtained *as*-dimethylcarboxysuccinic acid, m. p. 166—167° (decomp.). Ethyl *as*-dimethylcarboxysuccinate, b. p. 158—165°/22 mm., yielded only *as*-dimethylsuccinic acid on hydrolysis with hydrochloric acid. When the triethyl ester was treated with alcoholic sodium ethoxide at 78°, *as*-dimethylsuccinic acid, unaccompanied by  $\alpha$ -methylglutaric acid, was obtained, but when the reaction was conducted at 100°, the latter acid could be detected amongst the products.

C. J. S.

**Formation of Unsaturated and Cyclic Compounds from Halogen Open-chain Derivatives. VI. Products Derived from Halogenated  $\alpha$ -Methylglutaric Acids.** C. K. INGOLD (*J. Chem. Soc.*, 1925, 127, 387—398).—To substantiate the validity

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of the hypothesis that the angle between any two valencies of a carbon atom is determined by the molecular volumes of the four attached groups, the effect of branching of the  $-\text{CH}_2\cdot\text{CO}_2\text{H}$  groups in glutaric acids has been studied. According to theory, branching should cause a divergence of these groups and a lessening of the tendency to form cyclopropane derivatives. Experiment supports this view.

When the monobromination product of glutaric acid is treated with concentrated alkalis under standard conditions, cyclopropane ring formation takes place to a considerable extent. Thus ethyl monobromoglutarate gave 47% of the ring-acid and smaller amounts of hydroxyglutaric acid and glutaconic acid. Derivatives of  $\alpha$ -methylglutaric acid show a greatly decreased tendency to form compounds of the cyclopropane series when treated with dilute alkalis. By brominating  $\alpha$ -methylglutaric acid and pouring the crude product into methyl alcohol, there was produced methyl  $\gamma$ -bromo- $\alpha$ -methylglutarate, b. p.  $139-144^\circ/14-15$  mm., which contained as an impurity a small amount of the isomeric methyl  $\alpha$ -bromo- $\alpha$ -methylglutarate. The ester when treated with aqueous sodium carbonate gave rise to the lactones of  $\alpha$ -hydroxy- $\alpha$ -methylglutaric acid, m. p.  $71^\circ$ , and of  $\gamma$ -hydroxy- $\alpha$ -methylglutaric acid, b. p.  $185-187^\circ/14$  mm. The ethyl ester of the  $\gamma$ -lactone has b. p.  $170-172^\circ/14-15$  mm. The acids corresponding with the lactones are not stable in the free state, but their barium and silver salts were prepared. Other halogen derivatives described are: methyl  $\gamma$ -chloro- $\alpha$ -methylglutarate, b. p.  $120-124^\circ/15-16$  mm.; ethyl  $\gamma$ -chloro- $\alpha$ -methylglutarate, b. p.  $128-130^\circ/14-16$  mm.; methyl  $\alpha$ -iodo- $\alpha$ -methylglutarate, b. p.  $174-176^\circ/12-13$  mm.; ethyl ester, b. p.  $194-197^\circ/12-13$  mm. In each case the ester contains a small proportion of the isomeric  $\alpha$ -halogeno- $\alpha$ -methylglutaric ester.

The action of concentrated alkali on the monobromo ester gave rise to the formation of a considerable proportion of trans-1-methylcyclopropane-1 : 2-dicarboxylic acid, m. p.  $168^\circ$  (di-*p*-toluidide, m. p.  $255-260^\circ$ ), and a smaller quantity of the corresponding cis-1-methylcyclopropane-1 : 2-dicarboxylic acid, m. p.  $142^\circ$ . The cis-acid when heated above its melting point or boiled with acetyl chloride, passes into the anhydride, b. p.  $154-157^\circ/19-20$  mm., which can also be obtained by heating the trans-acid at  $180^\circ$  with acetyl chloride. In addition to the cis- and trans-acids, small quantities of  $\alpha$ -methylglutaconic and  $\alpha$ -methyleneglutaric acids, and compounds formed by fission of the cyclopropane ring, e.g., methylparaconic acid (from which the barium salt of methylitamic acid was prepared), are produced. C. J. S.

**$\beta$ -Dihydroxyadipic Acid.** K. PANKOKE (*Annalen*, 1925, 441, 188-191).—Ethyl sodiomalonate (2 mols.) condenses with oxalyl chloride (1 mol.) in ether to give a 22% yield of ethyl oxalyl-dimalonate, which does not crystallise and cannot be distilled even in a vacuum. It is completely decomposed by hydrolysis with alkali. Ethyl ketipate [diketoadipate] (Wislicenus, A., 1888, 1178; Fittig and Daimler, A., 1887, 362) is reduced by aluminium and

moist ether to ethyl  $\beta\gamma$ -dihydroxyadipate, from which by the action of phosphorus pentabromide ethyl  $\beta\gamma$ -dibromoadipate, m. p.  $64^\circ$ , is obtained. The latter, treated with alcoholic potassium hydroxide, gives muconic acid, m. p.  $157^\circ$ , in 82% yield, but Behrend and Koolman's synthesis (A., 1913, i, 8) is simpler and more convenient. C. H.

**$\alpha\gamma$ -Dialdehydopropane- $\beta\beta$ -dicarboxylic Acid and  $\alpha\gamma$ -Dialdehydopropane- $\beta$ -carboxylic Acid.** W. H. PERKIN, jun., and H. S. PINK (*J. Chem. Soc.*, 1925, 127, 191—194; cf. T., 1899, 75, 11).—The potassium derivative of ethyl acetal malonate is condensed with bromoacetal, by heating a toluene solution in an autoclave at  $200^\circ$ , to yield *ethyl diacetal malonate*, b. p.  $192$ — $196^\circ/18$  mm.,  $d_{25}^{25}$  1.031 (together with an oil, b. p.  $200$ — $250^\circ/20$  mm.). The ester with barium hydroxide in methyl-alcoholic solution yields *diacetal malonic acid*, a syrup, and with cold, concentrated hydrochloric acid gives  $\alpha\gamma$ -dialdehydopropane- $\beta\beta$ -dicarboxylic acid, m. p.  $122^\circ$  (decomp.) (*di-p-nitrophenylhydrazone*, m. p.  $156^\circ$ ), whilst with *N*-hydrogen chloride *ethyl  $\alpha\gamma$ -dialdehydopropane- $\beta\beta$ -dicarboxylate*, b. p.  $174$ — $178^\circ/18$  mm. (*di-p-nitrophenylhydrazone*, m. p.  $170^\circ$ ), is produced. The constitution of the above acid is established by its reduction with sodium amalgam to bis- $\gamma$ -butyrolactone- $\alpha\alpha$ -spiran and its oxidation, with potassium dichromate and sulphuric acid, to propane- $\alpha\beta\gamma$ -tetracarboxylic acid, converted by heat into tricarballic acid; by heating with water in a sealed tube at  $180^\circ$  carbon dioxide is eliminated, giving  $\alpha\gamma$ -dialdehydopropane- $\beta$ -carboxylic acid as a syrup; *di-p-nitrophenylhydrazone*, m. p.  $198^\circ$  (decomp.). F. M. H.

**Preparation of [Citric] Esters.** F. HEFTI and W. SCHILT.—(See i, 394.)

**Resolution of Chlorosulphoacetic Acid into its Optically Active Components.** H. J. BACKER and W. G. BURGERS (*J. Chem. Soc.*, 1925, 127, 233—237).—Chloroacetic acid and sulphur trioxide at  $0^\circ$  yield the mixed anhydride of sulphuric and chloroacetic acids, which is converted by sulphuric acid into chlorosulphoacetic acid; after purification through its barium salt, being freed from barium chloromethanedisulphonate, it is obtained as a very hygroscopic substance ( $+1H_2O$ ), m. p.  $83^\circ$  (yield 80%). Its sodium salt is treated with a soluble alkaloidal salt in the cold; the precipitated alkaloidal salt of chlorosulphoacetic acid is decomposed with ammonia, and the same method of "cold crystallisation" is repeated. The following salts were examined: normal quinine salt ( $+4H_2O$ ), normal *d*-cinchonine salt ( $+1H_2O$ ) by means of which the *l*-acid is obtained, normal *l*-strychnine salt ( $+3H_2O$ ) by means of which, or of the yohimbine salt, the *d*-acid is obtained. For chlorosulphoacetic acid in aqueous solution are found  $[M]_D^{25} \pm 39^\circ$ ,  $[M]_{533}^{25} \pm 50^\circ$ ,  $[M]_{494}^{25} \pm 62^\circ$ , and for its normal ammonium salt  $[M]_D^{25} \pm 20^\circ$ ,  $[M]_{533}^{25} \pm 26^\circ$ ,  $[M]_{494}^{25} \pm 34^\circ$ . The acids and salts gradually racemise, especially in the presence of bases. F. M. H.

**Condensation of Furfuraldehyde with Aliphatic Aldehydes.**  
D. IVANOV.—(See i, 421.)

**Mixed Dismutation of Aldehydes. II.** R. NAKAI (*Biochem. Z.*, 1924, 152, 258—275).—By the condensation in the presence of magnesium methoxide or aluminium ethoxide of the following pairs of aldehydes: acetaldehyde and furfuraldehyde, furfuraldehyde and isobutaldehyde, and bromal and acetaldehyde, there were obtained, respectively, the following mixed esters: *isoamyl pyromucate*, b. p. 111—111.5°/11 mm.,  $d_4^{20}$  1.0367; *furyl isobutyrate*, b. p. 85—86°/15 mm.,  $d_4^{20}$  1.0313, and the two esters *tribromoethyl acetate*, b. p. 109—109.3°/17 mm.,  $d_4^{20}$  2.2577, and *tribromoethyl tribromoacetate*, m. p. 69°, b. p. 206—207°/15.5 mm. The interaction of these pairs of aldehydes together with that of chloral and acetaldehyde is considered from the theoretical point of view of the Cannizzaro reaction, e.g.  $R\cdot CH(OH)_2 + R\cdot CHO \rightarrow R\cdot CO_2H + R\cdot CH_2OH \rightarrow R\cdot CO_2\cdot CH_2R$ , in which the aldehyde itself acts as an acceptor of hydrogen from the hydrated form. A method is described for the preparation of tribromoethyl alcohol from acetaldehyde and bromal, using magnesium methoxide as a condensing agent. Trichloroethyl alcohol can be prepared in a similar way. J. P.

**Highly Polymerised Substances. III. Constitution of the Polyoxymethylenes.** H. STAUDINGER and M. LÜTHY (*Helv. Chim. Acta*, 1925, 8, 41—64; cf. A., 1920, i, 517; 1924, i, 274).—Previous work on the polyoxymethylenes is critically reviewed. The authors' suggestion previously put forward that these substances contain chains of the type  $\cdots CH_2\cdot O\cdot [CH_2\cdot O]_n\cdot CH_2\cdot O\cdots$  is supported by the production from them, by the action of acetic anhydride, acyl chlorides, and acids, of derivatives of moderate molecular weight which undoubtedly contain this type of grouping. Although it is uncertain whether these products are produced through unimolecular formaldehyde or not, it is more probable that they are formed directly from larger fragments of the whole polymeric molecules.

The interaction of varying molecular proportions of acetic anhydride and polyoxymethylene is described, 24—100 hours' heating at 130—170° being required to complete the reaction. The results are in the main the same whether commercial paraformaldehyde is used or  $\alpha$ -,  $\beta$ -,  $\gamma$ -, or  $\delta$ -polyoxymethylene, except that the  $\gamma$ - and  $\delta$ -forms are much less reactive. The substances produced are polyoxymethylene diacetates,  $AcO\cdot [CH_2O]_n\cdot Ac$ .

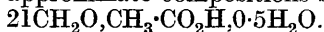
When the molecular ratio used is  $Ac_2O : CH_2O = 1 : 1$  or  $1 : 2$  the values of  $n$  in the products are 1, 2, 3, and 4. With higher molecular ratios, the products include (a) solid substances insoluble in ethyl acetate having values of  $n$  of 20 or more, (b) crystalline solids separated from ethyl acetate and petroleum ( $n=8-17$ ), and (c) liquids separated by distillation in a high vacuum. Their formulæ are established by determinations of  $CH_2O$  and  $Ac_2O$ , as ultimate analysis does not differentiate them sharply.



*Trioxymethylene diacetate*, b. p. 113—115°/2 mm.; *tetraoxymethylene diacetate*, b. p. 132—134°/2 mm.; *pentaoxymethylene diacetate*, b. p. 160—165°/0.4 mm., solidifying in a freezing mixture; *heptaoxymethylene diacetate*, b. p. 180—190°/0.3 mm., m. p. about 15°; *octaoxymethylene diacetate*, m. p. 27.5—28.5°; *nonaoxymethylene diacetates*, m. p. 50—51° and 46—48°; *undecaoxymethylene diacetate*, m. p. 64—65°; *dodecaoxymethylene diacetate*, m. p. 66—67°; *heptadecaoxymethylene diacetates*, m. p. 103—107° and 105—107°; *polyoxymethylene diacetates*, m. p. 120° and 125—128°, having  $n$  about 21 and 24, respectively.

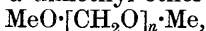
The action of acetyl chloride or bromide on polyoxymethylene produces chloro- or bromo-methyl acetate and in the latter case a mixture of other substances which could not be separated. Benzoyl chloride produced chloromethyl benzoate, methylene dibenzoate, the compound,  $\text{CH}_2\text{Cl}\cdot\text{O}\cdot\text{CH}_2\cdot\text{OBz}$ , m. p. 32°, which could not be obtained by heating chloromethyl benzoate with polyoxymethylene, and, lastly, *dioxymethylene dibenzoate*, m. p. 46°, converted by warming with zinc chloride into methylene dibenzoate.

Distillation of a solution of polyoxymethylene in acetic acid yields white solids, m. p. 147—148° (decomp.), and m. p. 107—110°, which separate from the cooled distillate and are polyoxymethylene acetate hydrates of approximate compositions such as



Pure substances are not obtainable in this case, or by use of formic or propionic acid.

$\gamma$ -Polyoxymethylene is a dimethyl ether of the type



the methyl alcohol present in its preparation acting, not catalytically, as has been assumed, but as a component of the reaction. The presence of methyl alcohol in the decomposition products of the  $\gamma$ -substance has been proved by the isolation of methyl *p*-nitrobenzoate.  $\delta$ -Polyoxymethylene also contains traces of methyl alcohol, and may also be a polyoxymethylene ether. This conception is supported by the isolation from a sodium sulphite extract of crude  $\beta$ - and  $\gamma$ -polyoxymethylenes of a small quantity of precipitate containing ethers of the above general formula: *substances*, m. p. 51—52° ( $n=5$  or 6); m. p. 72° ( $n=8-10$ ); m. p. 87—88° ( $n=14-15$ ), and *dimethyldodecaoxymethylene ether*, m. p. 78—80°, which crystallises from hot water and has the required molecular weight.

G. M. B.

**Highly Polymerised Substances. IV. Tri- and Tetraoxymethylenes.** H. STAUDINGER and M. LÜTHY (*Helv. Chim. Acta*, 1925, 8, 65—67; cf. preceding abstract).—Trioxymethylene is only obtainable from the polyoxymethylenes in the presence of moisture. Its direct formation from the polymeride does not seem possible, unimolecular formaldehyde being a necessary intermediate stage. By heating the insoluble polyoxymethylene diacetates of high molecular weight in a vacuum, a new *tetraoxymethylene* is obtained, m. p. 112°, subliming unchanged and having

the correct vapour density at 200°. It is readily soluble in water and in organic solvents, and as it gives no aldehyde reactions in the cold it is regarded as an eight-ring compound,  $O \begin{matrix} \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \end{matrix} O$ .

Tetraoxymethylene was not obtained when the soluble polyoxymethylene diacetates or the hydrated acetates were treated in a similar way. The substance reacts more rapidly than trioxymethylene with *p*-nitrophenylhydrazine, in accordance with a lower stability of the ring.

G. M. B.

**Highly Polymerised Compounds. V. Constitution of the Polyoxymethylenes and Other Highly Polymerised Substances.** H. STAUDINGER (*Helv. Chim. Acta*, 1925, 8, 67—70).—The polyoxymethylenes are regarded as the highest members of the homologous series of substances of various kinds obtainable from them (cf. preceding abstracts) which evidently approach more and more closely to the composition  $(\text{CH}_2\text{O})_n$  as their molecular weight increases. They must be regarded as having a true molecular weight even when this cannot be determined, and the high molecular weight may not necessarily preclude a crystalline form. The case is compared with those of amorphous sulphur, grey arsenic, and red phosphorus. Other highly polymerised organic substances such as polymeric *cyclopentadiene*, cellulose, caoutchouc, starches, polymerised dimethylketen, etc., must have macromolecules in a similar manner.

G. M. B.

**Autoxidation and Anti-oxygenic Action. XIII. Deactivation of Acraldehyde by Quinol. Experiments with Light. Deactivation brought about by Quinol does not explain the Anti-oxygenic Action.** C. MOUREU and C. DUFRAISSE (*Bull. Soc. chim.*, 1924, [iv], 35, 1564—1572; cf. A., 1923, i, 91, 267; this vol., i, 117).—Acraldehyde alone remains unchanged in the dark; no disacryl is formed even in a year. A small proportion is converted into a gelatinous substance, but even this is not produced if a little phthalic acid is added to counteract the alkalinity of the glass. When, however, the tube containing the acraldehyde is illuminated, disacryl is rapidly formed. Addition of quinol inhibits this formation of disacryl; thus, the presence of 1% causes the aldehyde to remain stable for 25 days when exposed to light such that disacryl is formed in 12 minutes from acraldehyde alone. By comparing the data obtained with those furnished by earlier work, the authors arrive at the conclusion that the antioxygenic action of quinol is not solely due to deactivation of the acraldehyde.

W. A. S.

**Autoxidation and Anti-oxygenic Action. XIV. Activation of Acraldehyde by Light.** C. MOUREU, C. DUFRAISSE, and M. BADOCHÉ (*Bull. Soc. chim.*, 1924, [iv], 35, 1572—1591; cf. preceding abstract).—Light has a feeble, but quite definite, accelerating effect on the autoxidation of acraldehyde. The acceleration of this action, however, is to that of the formation of disacryl as 4 : 100,000. Hence it is doubtful whether light activates acraldehyde at all.

In accelerating the complete change (the product of which is acrylic acid), the blue and violet rays are the most active; it is to be noted that it is these rays that are absorbed by acraldehyde (cf. Henri, A., 1924, ii, 513).  
W. A. S.

**Autoxidation and Anti-oxygenic Action. XV. Activation of Acraldehyde by Oxygen and by Light and Deactivation by Quinol, particularly in connexion with the Condensation to Disacryl.** C. MOUREU, C. DUFRAISSE, and M. BADOCHÉ (*Bull. Soc. chim.*, 1924, [iv], 35, 1591—1607; cf. preceding abstracts).—Oxygen has a similar effect to light on the condensation of acraldehyde, but may cause the formation of a different product. Even very small proportions of oxygen (1 : 1,000,000) are effective. The condensation, not the preliminary activation, of the acraldehyde is the stage at which the acceleration proceeds. When light and oxygen act together, they do not help one another, but rather appear to inhibit each other's effect.  
W. A. S.

**Claisen Condensation.** G. T. MORGAN, H. D. K. DREW, and C. R. PORTER (*Ber.*, 1925, 58, [B], 333—341).—A number of examples are cited in which the Claisen condensation between esters and ketones occurs normally at a low temperature, whereas alcoholysis takes place when the temperature is raised with consequent decomposition of the  $\alpha\gamma$ -diketone. Thus diethyl ketone is converted by ethyl acetate in the presence of sodium at the atmospheric temperature into  $\gamma$ -methylhexa- $\beta\delta$ -dione, whereas if the mixture is warmed towards the end of the reaction hexa- $\beta\delta$ -dione is produced, probably as a result of the secondary condensation of the excess of ethyl acetate with methyl ethyl ketone produced according to the scheme:  $[\text{COMe}\cdot\text{CMe}\cdot\text{COEt}]\text{Na} + 2\text{EtOH} = \text{NaOEt} + \text{CH}_3\cdot\text{CO}_2\text{Et} + \text{C}_2\text{H}_5\cdot\text{CO}\cdot\text{C}_2\text{H}_5$  or  $\text{CH}_3\cdot\text{CO}\cdot\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\cdot\text{CO}_2\text{Et}$ . Similarly, diethyl ketone and ethyl propionate at 0° yield  $\delta$ -methylhepta- $\gamma\epsilon$ -dione, whereas ethyl propionate, propionic acid, and autocondensation products of diethyl ketone are obtained from the heated mixture. Ethyl *n*-propyl ketone reacts very slowly with cold ethyl acetate and the primary products of the change were not isolated; the heated mixture yields hexa- $\beta\delta$ -dione and hepta- $\beta\delta$ -dione, together with ethyl acetate, propionate, and *n*-butyrate. Di-*n*-propyl ketone and ethyl acetate at 0° give  $\gamma$ -ethylhepta- $\beta\delta$ -dione, whereas hepta- $\beta\delta$ -dione and ethyl *n*-butyrate result from the heated mixture. Propiophenone and ethyl acetate yield primarily  $\beta$ -hexa- $\beta\delta$ -diones and  $\alpha$ -phenyl- $\beta$ -methylbuta- $\alpha\gamma$ -dione; ethyl benzoate, hexa- $\beta\delta$ -dione, and  $\alpha$ -phenylpenta- $\alpha\gamma$ -dione (prepared also from methyl ethyl ketone, ethyl benzoate, and sodium, and characterised as the copper salt, m. p. 153—154°) are obtained from the heated mixture. Phenyl benzyl ketone does not condense with ethyl acetate under the experimental conditions used; sodium dissolves in the ketone with evolution of hydrogen. Benzyl ethyl ketone, b. p. 223—225° (semicarbazone, m. p. 154—155°, whereas Senderens [A., 1911, i, 302] gives m. p. 135·5°), and cold ethyl acetate yield  $\gamma$ -phenylhexa- $\beta\delta$ -dione, m. p. 24—26°, b. p. 136—137°/15 mm. (copper salt, m. p. 162—163°), which is hydrolysed by aqueous potassium hydroxide

solution to benzyl methyl ketone and benzyl ethyl ketone; condensation in warm solution gives  $\gamma$ -phenylhexa- $\beta\delta$ -dione mixed with  $\alpha$ -phenylpenta- $\beta\delta$ -dione and  $\alpha\epsilon$ -diphenylpenta- $\beta\gamma$ -dione.  $\alpha$ -Phenylhexa- $\beta\delta$ -dione, prepared from methyl ethyl ketone, ethyl phenylacetate, and sodium at  $0^\circ$ , has b. p.  $153\text{--}154^\circ/13$  mm. (copper salt, m. p.  $185^\circ$ ). Benzyl methyl ketone and ethyl acetate condense in cold solution to  $\gamma$ -phenylpenta- $\beta\delta$ -dione, m. p.  $58\text{--}60^\circ$ , b. p.  $127\text{--}128^\circ/15$  mm. (copper salt, decomp.  $222\text{--}224^\circ$  after softening at  $210^\circ$ ), and  $\alpha$ -phenylpenta- $\beta\delta$ -dione; when the mixture is warmed, the condensation proceeds further, causing a diminution in the yield of the former product and an increase in that of the latter.

H. W.

**Action of Phosphorus Pentachloride on certain Aldehydes and Ketones.** M. BOURGUEL (*Bull. Soc. chim.*, 1924, [iv], 35, 1629—1638).—A detailed account of an investigation already described (*A.*, 1924, i, 701). Methyl *n*-propyl ketone yields, besides  $\beta$ -chloro- $\Delta^2$ -pentene, b. p.  $86\text{--}89^\circ$ ,  $45^\circ/130$  mm.,  $d_4^{24}$  0.903,  $n_D^{24}$  1.421,  $\gamma$ -chloro- $\Delta^2$ -pentene, b. p.  $91\text{--}92^\circ$ ,  $d_4^{20}$  0.904,  $n_D^{20}$  1.423, and a mixture of  $\beta\beta$ -dichloropentane with some  $\beta\gamma$ -derivative; when it is treated with zinc dust and alcohol,  $\Delta^2$ -pentene is produced, together with some  $\beta$ -chloro- $\Delta^2$ -pentene. The latter is formed presumably by removal of hydrogen chloride from the  $\beta\beta$ -dichloropentane, the zinc and alcohol acting as zinc ethoxide. Diethyl ketone yields, besides the acetylenic hydrocarbon (*loc. cit.*),  $\gamma$ -chloro- $\Delta^2$ -pentene, and the above dichloro derivatives in slightly different proportions. Dipropyl ketone affords (together with the other products) an analogous mixture (b. p.  $86^\circ/27$  mm.,  $d_4^{17}$  1.008,  $n_D^{17}$  1.448), composed chiefly of  $\delta\delta$ -dichloroheptane, but also containing the  $\gamma\delta$ -derivative, since when it is treated with zinc and alcohol  $\Delta^7$ -heptinene, b. p.  $97\text{--}98^\circ$ ,  $d_4^{17}$  0.690,  $n_D^{17}$  1.393, is produced. The products of the other reactions already discussed (*loc. cit.*) are briefly described.

W. A. S.

**Synthesis of  $\alpha$ -Hydroxyketones.** I. E. SCHMIDT and A. ASCHERL (*Ber.*, 1925, 58, [B], 356—358).—Catalytic reduction transforms the group  $-\text{CCl}(\text{NO}_2)-$  into  $-\text{CO}-$  according to the scheme:  $>\text{CCl}\cdot\text{NO}_2 + 6\text{H} = \text{CO} + \text{NH}_4\text{Cl} + \text{H}_2\text{O}$ . Thus,  $\gamma$ -chloro- $\gamma$ -nitropentane- $\beta\delta$ -diol is converted by hydrogen in aqueous solution in the presence of palladised barium sulphate into pentan- $\beta$ -ol- $\gamma$ -one, b. p.  $45\text{--}48^\circ/11$  mm.,  $d_4^{20}$  0.9692,  $n_D^{20}$  1.4218 (*phenylosazone*, m. p.  $167^\circ$ ). Similarly,  $\beta$ -chloro- $\beta$ -nitrobutane- $\alpha\gamma$ -diol yields butan- $\beta$ -ol- $\beta$ -one, b. p.  $43\text{--}45^\circ/11$  mm.,  $d_4^{20}$  1.0272,  $n_D^{20}$  1.4189, which appears to exist in the cyclic form,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}_2$ .  $\beta$ -Chloro- $\beta$ -nitropentane- $\alpha\gamma$ -diol gives pentan- $\alpha$ -ol- $\beta$ -one, b. p.  $54\text{--}56^\circ/11$  mm.,  $d_4^{24}$  0.9860,  $n_D^{20}$  1.4234 (*phenylosazone*, m. p.  $110\text{--}111^\circ$ ). H. W.

**Constitution of the Normal Monosaccharides.** II. **Arabinose.** E. L. HIRST and G. J. ROBERTSON (*J. Chem. Soc.*, 1925, 127, 358—364).—Normal stable derivatives of *l*-arabinose are shown to belong to the amylenoxide type, whereas (see

following abstract) derivatives of the  $\gamma$ -series are of the butylene-oxide form. Methylation of *l*-arabinose with methyl sulphate yields *trimethyl  $\beta$ -methylarabinoside*, m. p. 46—48°,  $[\alpha]_D +24^\circ$  in methyl alcohol,  $[\alpha]_D +46.2^\circ$  in water. Polarimetric observations indicate that this compound and the isomeric *trimethyl  $\alpha$ -methylarabinoside* are interconvertible forms and contain the same type of oxide linking. As in the case of galactose (this vol., i, 117), the presence of isomerides possessing a different ring structure is also indicated. Oxidation of *trimethyl  $\alpha$ -methylarabinoside* with nitric acid, followed by treatment with methyl-alcoholic hydrogen chloride, yielded *methyl trimethoxyglutarate*, b. p. 143°/18 mm.,  $n_D^{21} 1.4355$ ,  $[\alpha]_D +47.3^\circ$  in methyl alcohol,  $[\alpha]_D +45^\circ$  in water; the corresponding *diamide* has m. p. 232—233°,  $[\alpha]_D +50^\circ$  in water. Methylation of arabotrihydroxyglutaric acid gave rise to the same ester.

C. J. S.

**Synthesis of Derivatives of  $\gamma$ -Arabinose.** S. BAKER and W. N. HAWORTH (*J. Chem. Soc.*, 1925, 127, 365—369).—A series of levorotatory derivatives of *l*-arabinose has been isolated belonging to the  $\gamma$ -type of sugars and having an oxide ring linking differing from those hitherto prepared. Condensation of *l*-arabinose with methyl-alcoholic hydrogen chloride has been conducted at a lower temperature (18°) than that previously employed, and gave rise to the formation of  *$\gamma$ -methylarabinoside*, b. p. 173—175°/0.15 mm.,  $n_D 1.4880$ ,  $[\alpha]_D -71.3^\circ$  in methyl alcohol,  $-46.8^\circ$  in water. This differs from Fischer's compound in its extreme instability towards permanganate, and its ready hydrolysis with very dilute acids. When methylated, it gave  $\alpha$ - and  $\beta$ -forms of *trimethyl  $\gamma$ -methylarabinoside*, b. p. 85—87°/0.3 mm.,  $n_D 1.4355$ ,  $[\alpha]_D -55.8^\circ$  in water. The  $\beta$ -variety is hydrolysed by *N*/100-hydrochloric acid, whereas the  $\alpha$ -compound is scarcely affected at this concentration; both forms undergo hydrolysis with *N*/15-acid to yield *trimethyl  $\gamma$ -arabinose*, b. p. 97—99°/0.18 mm.,  $n_D 1.4503$ ,  $[\alpha]_D -39.5^\circ$  in water, which instantaneously reduces Fehling's solution and neutral permanganate. Oxidation of *trimethyl  $\gamma$ -arabinose* with nitric acid forms trimethoxyhydroxyvalerolactone and the more highly oxidised compound, dimethoxyhydroxyglutaric acid. It is concluded that the  $\gamma$ -sugars of the pentose series belong to the butylene-oxide type (cf. preceding abstract).

C. J. S.

**Constitutional Studies in the Monocarboxylic Acids Derived from Sugars. III. Isomeric Tetramethyl Galactonolactones and Trimethyl Arabonolactones.** J. PRYDE, E. L. HIRST, and R. W. HUMPHREYS (*J. Chem. Soc.*, 1925, 127, 348—357).—Tetramethyl *d*-galactonolactone, having a specific rotation  $+106.7^\circ$  in water, was obtained in an earlier investigation (T., 1923, 123, 1808) and to this the amylenoxide structure was ascribed. This substance is now regarded as a mixture of isomeric amylenoxide and butylene-oxide forms, since a product has now been obtained, from tetramethylgalactose as initial material, having  $[\alpha]_D^{17} +160.7^\circ$  in water, this value dropping to  $+47.6^\circ$  after 20 hours. Direct methylation of galactose with methyl sulphate

gave tetramethylgalactose,  $[\alpha]_D +83.3^\circ$  in water, from which a crystalline tetramethyl galactonamide, m. p.  $121^\circ$ , was obtained. What is presumably the butylene-oxide form of tetramethyl galactonolactone was prepared by the methylation of *d*-galactonolactone, and has  $[\alpha]_D +29^\circ$  in water (initially).

Experiments with *l*-arabinose gave similar results. From trimethyl  $\alpha$ -methyl *l*-arabinoside there has been obtained  $\alpha$ -trimethyl *l*-arabonolactone having an initial value of  $[\alpha]_D +138^\circ$  in water, this value falling to  $+22.4^\circ$  after 24 hours, the lactone being converted into the corresponding trimethylarabonic acid. The amylene-oxide linking is presumed from the evidence of the presence of this form of oxygen bridge in the normal fully methylated arabinose.  $\alpha$ -Trimethyl *l*-arabonolactone forms a crystalline amide, m. p.  $95-100^\circ$ .

Oxidation of mixed trimethyl methylarabinosides with nitric acid resulted in the formation of a mixture of dimethyl trimethoxyglutarate and what is regarded as the butylene-oxide form of trimethyl arabonolactone.

C. J. S.

**Occurrence of a Rhamnosan.** E. O. VON LIPPMANN (*Ber.*, 1925, 58, [B], 425).—A rhamnosan,  $[\alpha]_D^{20}$  about  $-135^\circ$ , has been obtained as a clear, transparent gum from the blossoms of a water-lily which, in consequence of a sinking of the water, was resting on the bottom of a pond. It was hydrolysed by the expressed sap of the plant to rhamnose.

H. W.

**[Nomenclature of Steric Series].** A. WOHL and K. FREUDENBERG (*Ber.*, 1925, 58, [B], 451; cf. A., 1923, i, 182).—A correction. *l*(-)-Galactose and *l*(-)-mannose should replace *d*(-)-galactose and *d*(-)-mannose respectively.

H. W.

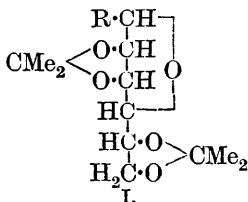
**Formation of Sorbose by Condensation of Formaldehyde.** W. KÜSTER and F. SCHODER (*Z. physiol. Chem.*, 1924, 141, 110—131).—The presence of *dl*-fructose ( $\alpha$ -acrose) and a ketopentose in the mixture of sugars (formose) which results from the polymerisation of formaldehyde under the influence of certain alkaline condensing agents has been confirmed. In addition, sorbose has been isolated from the reaction product and identified as such by comparison of its phenylhydrazone with that obtained from sorbose (prepared from mountain-ash berries) and also by oxidation with nitric acid to trihydroxyglutaric acid and trihydroxybutyric acid. Disodium hydrogen phosphate, magnesium peroxide, and sodium perborate do not promote the condensation of formaldehyde to formose; the presence of phosphates inhibits the condensing action of lead hydroxide but not of calcium carbonate.

E. S.

**Acetone Sugars. V. Synthesis of Aminohexoses from Galactose.** K. FREUDENBERG and A. DOSER (*Ber.*, 1925, 58, [B], 294—300; cf. A., 1923, i, 652, 1179).—The *p*-toluenesulphonyl derivative of galactose diisopropylidene ether is transformed by liquid ammonia at the atmospheric pressure or, preferably, by methyl-alcoholic ammonia at  $100^\circ$  into a mixture of diisopropylidene-galactosylamine and di-diisopropylidenegalactosylamine in which the

precise position of the amino group has not been located. The primary amine has b. p.  $122\text{--}126^\circ/0.5\text{--}1\text{ mm.}$ ,  $[\alpha]_{578}^{19} -63.09^\circ$ ; it yields an unstable *hydrochloride*, decomp.  $229^\circ$ , a *picrolonate*, m. p.  $223^\circ$  (decomp.), and (?) a *monobromo* derivative. The *benzoyl* derivative has m. p.  $132.5^\circ$ ,  $[\alpha]_{578}^{18} -26.74^\circ$  in acetone. The *isopropylidene* groups can be removed from the amine by dilute sulphuric acid, but the *galactosylamine* could not be caused to crystallise or transformed into crystalline salts. Deamination results in a mixture of sugars which is transformed by nitric acid into oxalic acid and only half the quantity of mucic acid which would be yielded by pure galactose. The deaminised mixture yields two *phenylhydrazones* which could not be isolated in the homogeneous condition. Galactose does not appear to be present, since the characteristic *o*-tolylhydrazone could not be isolated. Deamination of *diisopropylidenegalactosylamine* yields *diisopropylidenegalactose* smoothly, showing that transformations have not occurred within the molecule. Oxidation of the free amino-sugar with mercuric oxide yields *galactosamic acid*,  $\text{C}_6\text{H}_{13}\text{O}_6\text{N}$ ,  $[\alpha]_{578}^{16} +9.23^\circ (\pm 1)$  in *N*/5-sodium hydroxide solution; the corresponding *phenylhydrazide* was prepared. When *diisopropylidenegalactosylamine* is *benzoyl*-ated and the *isopropylidene* groups are removed, amorphous *benzoylgalactosylamine* is produced, which is characterised as the crystalline *phenylhydrazone*, m. p.  $201^\circ$ . *Di-diisopropylidenegalactosylamine* forms crystals, m. p.  $108^\circ$  from aqueous-methyl alcohol, m. p.  $125\text{--}126^\circ$  from light petroleum,  $[\alpha]_{578}^{18} -84.35^\circ$  in acetone. It yields a *benzoyl* derivative, m. p.  $129^\circ$ ,  $[\alpha]_{578}^{18} -53.9^\circ$  in acetone, and a *nitroso* compound, m. p.  $181\text{--}182^\circ$ ,  $[\alpha]_{578}^{19} -7.9^\circ$  in acetone, which can also be prepared by the action of nitrous acid on *as*-*di-diisopropylidenegalactosylhydrazine* (A., 1923, i, 1179), proving thus that the *isopropylidene* groups do not suffer displacement during these changes. *Digalactosylamine* is a pale yellow syrup which yields a *bisphenylhydrazone*, decomp.  $192^\circ$ . H. W.

**Acetone Sugars. VI. Constitution of Diacetone-mannose [Mannose Diisopropylidene Ether].** K. FREUDENBERG and A. WOLF (*Ber.*, 1925, 58, [B], 300—303).—*Diisopropylidenemannose*, m. p.  $123^\circ$  [Freudenberg and Hixon (A., 1923, i, 1179) record m. p.  $118^\circ$ ], is converted by a solution of ammonia in methyl alcohol at  $95\text{--}98^\circ$  into *diisopropylidenemannosylamine* (I,  $\text{R}=\text{NH}_2$ ), b. p.  $128\text{--}129^\circ/1\text{ mm.}$ ,  $[\alpha]_{578}^{17} +9.4^\circ$  in ethyl alcohol, which is tolerably stable towards alkalis but extremely sensitive to acids, which immediately regenerate *diisopropylidenemannose*. The corresponding *benzoyl* derivative has m. p.  $178^\circ$ . The primary amine is readily converted by heat into the secondary amine,  $(\text{C}_{12}\text{H}_{19}\text{O}_5)_2\text{NH}$ , m. p.  $160^\circ$ ,  $[\alpha]_{578}^{17} +26^\circ$  in *s*-tetrachloroethane, which yields *diisopropylidenemannose* with acids. The existence



of the secondary amine renders it very improbable that the primary compound contains the basic group in an  $\alpha\delta$ -bridge, and this

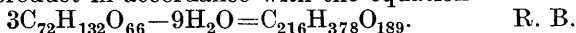
possibility is excluded by the observation that dimethylamine behaves in the same manner as ammonia towards diisopropylidenemannose, yielding *diisopropylidenemannosyldimethylamine* (I,  $R = NMe_2$ ), m. p.  $76^\circ$ ;  $[\alpha]_{D}^{25} +42.5^\circ$  in ethyl alcohol. The observations necessitate a revision of the constitution ascribed by Freudenberg and Hixon (*loc. cit.*) to diisopropylidenemannose, to which the formula I ( $R = OH$ ) is now allotted, whereby the production of mannose from diisopropylidenemethylmannose ( $R = OMe$ ) is readily explained. The inability of diisopropylidenemannose to reduce Fehling's solution in spite of the presence of a free hydroxyl group is ascribed to the non-production or extremely short duration of the oxo stage in the mutual conversion of the  $\alpha$ - and  $\beta$ -forms. In contrast to diisopropylidenedextrose, diisopropylidenemannose exhibits only a very slow mutarotation, which is catalytically accelerated by alkali hydroxide. It yields a sodium compound when treated with concentrated sodium hydroxide solution, but the analytical data do not establish whether the substance is a derivative (I,  $R = ONa$ ) or an additive compound of sodium hydroxide and diisopropylidenemannose.

H. W.

**Non-Reducing "Limit Dextrin I."** V. SYNIEWSKI (*Annalen*, 1925, **441**, 285—297).—The constitution previously proposed for starch (A., 1903, i, 69) is now supported by the isolation of the non-reducing "limit dextrin I" predicted as arising from starch by exclusive  $\alpha$ -carbonyl hydrolysis, through the discovery of a nearly pure  $\alpha$ -carbonyl hydrolytic agent in the diastatic enzyme of unmalted barley. When an amylopectin solution, prepared from potato starch, is treated with barley extract at the ordinary temperature, the amylopectin rapidly undergoes hydrolysis until in about 75 minutes, as shown by treating samples of the solution with Fehling's solution, 64% of the amylopectin has been converted into maltose, after which very little further change takes place. The solution contains, besides maltose, a dextrin which does not reduce Fehling's solution and gives a blue colour with iodine, thereby sharply distinguishing the product from that resulting in the action of a malt diastase on amylopectin. To isolate the new dextrin, the solution is poured into boiling water to destroy the diastase and the filtered solution poured into alcohol. The precipitated dextrin is further purified by successive solution in water and precipitation with alcohol. "Limit dextrin I"  $C_{72}H_{132}O_{66}$ , is a white substance,  $[\alpha]_{D}^{20} +194.92^\circ$ , mol. wt. 6002 in aqueous solution, with a reducing power of about 1% in terms of maltose. This slight reducing power is probably due to decomposition of the dextrin through heating in strongly alkaline solution produced by Fehling's reagent. By the action of malt extract at  $75^\circ$ , the new dextrin rapidly undergoes  $\beta$ -hydrolysis, yielding in 50 to 60 mins. a solution which gives no colour with iodine and has a reducing power in terms of maltose of 13.6%, and contains the previously described reducing "limit dextrin I," identical with Lintner's achroodextrin. Acetylation of the dextrin yields an *acetyl* derivative containing 50% of acetyl. This result indicates that the non-reducing "limit dextrin I" con-



tains 48 acetylisable hydroxyl groups, and from the formula previously developed for amylopectin (*loc. cit.*) it is deduced that the remaining oxygen atoms are present, 6 in  $\alpha$ -carbinol linkings and 12 in  $\beta$ -carbonyl linkings. The action of  $\alpha$ -diastase on the amylopectin is thus represented by the equation,  $C_{216}H_{372}O_{186} + 12H_2O = 12C_{12}H_{22}O_{11} + C_{72}H_{132}O_{66}$ . The high molecular weight of the "limit dextrin" in aqueous solution is attributed to the formation of a reversion product in accordance with the equation



**Oxidation of Amylopectin.** V. SYNIEWSKI (*Annalen*, 1925, **441**, 277—285; cf. A., 1903, i, 69).—On oxidation with bromine at 40—50° in the presence of barium carbonate, amylopectin yields *amylopectinic acid*,  $C_{216}H_{348}O_{198}$ ,  $[\alpha]_D^{20} + 191.1^\circ$ . The new acid, which was obtained pure by repeated solution in water and precipitation with alcohol, readily reduces Fehling's solution at the ordinary temperature, the reducing power being equivalent to 23.24% of maltose, and gives a silver mirror with alkaline silver solutions. Phenylhydrazine hydrochloride in the presence of sodium acetate gives a brick-red *hydrazide*,  $C_{288}H_{420}O_{186}N_{24}$ , m. p. 153° on rapid heating; on slowly heating, this begins to melt at 142°. A quantitative study of the oxidation shows that about 48 atoms of bromine are used in the oxidation of 1 mol. of amylopectin. Analyses of the neutral and basic *barium* salts and of the basic *lead* salt indicate that the acid has a basicity of twelve. These results lead to the development of the following formula,  $[(C_{18})\{ > (C_6) - O - CH \cdot [CH \cdot OH]_2 \cdot CH \cdot CH(OH) \cdot CO_2H \}_3]_4$ , for

amylopectinic acid from that previously proposed for amylopectin (*loc. cit.*), the presence of glycuronic acid residues in the molecule being further indicated by the formation of about 5% of furfuraldehyde on distillation of the amylopectinic acid with hydrochloric acid, an amount which corresponds with the 34.57% of glycuronic acid anhydride theoretically present. It is suggested that in the animal body glycuronic acid is produced by hydrolysis of an oxidation product of glycogen analogous to amylopectinic acid, and not by the oxidation of the primary alcohol group of dextrose (cf. Fischer, A., 1891, 677). These results lead to the further suggestion that oxycellulose contains glycuronic acid residues as well as dextrose residues.

R. B.

**Action of Strong Bases on Cotton Cellulose.** I. II. F. DEHNERT and W. KÖNIG (*Cellulosechem.*, 1924, **5**, 107—112; 1925, **6**, 1—10).—The compound  $(C_6H_{10}O_5)_2 \cdot NaOH$  is formed in aqueous sodium hydroxide solutions at concentrations between 4*N* and 6*N*; possibly another compound,  $(C_6H_{10}O_5)_2 \cdot NaOH$ , exists at concentrations of 10—12*N*. The compound  $(C_6H_{10}O_5)_2 \cdot KOH$  is formed at 4.5*N* concentration and there is no evidence of further combination;  $(C_6H_{10}O_5)_2 \cdot LiOH$  exists at concentrations of 0.6—2.0*N*. The strong organic bases also show the phenomena of mercerisation. Trimethyl-sulphonium hydroxide and -guanidonium hydroxide combine with 2 mols. of cellulose to 1 mol. of base in a manner

exactly similar to the inorganic alkali hydroxides. Tetramethylammonium hydroxide combines in the ratio of 3 or 4 mols. of cellulose to 1 mol. of base. Phenyltrimethylammonium hydroxide forms two compounds in which 4 mols. of cellulose are combined respectively with 1 mol. and 3 mols. of the base. Mercerisation is regarded as a chemical process typical of the action of cold aqueous solutions of strongly basic substances on cellulose. The product is permanently modified and is termed "mercellulose." The appearance of the phenomena at different molar concentrations of the different bases is attributed to viscosity differences influencing the ease of hydrolysis of the various alkali-celluloses. Mercellulose, no matter by what alkali it has been produced, shows the same increased absorptive capacity in dilute solutions of sodium hydroxide, which is as 3 : 2 compared with ordinary cotton. The degree of dissociation of alkali-cellulose in 0.5*N*-sodium hydroxide is calculated at about 75%. Repeated mercerisation with the same or different alkalis produces no modification of the properties of "mercellulose."

J. F. B.

**Alkali-Cellulose.** E. KNECHT and J. H. PLATT (*J. Soc. Dyers and Col.*, 1925, **41**, 53—55).—Measurement of the preferential absorption of sodium hydroxide by cotton yarn when placed in solutions of sodium hydroxide shows that the amount of sodium hydroxide absorbed by cotton increases with increasing concentration of the alkali hydroxide, but remains constant at about 12.28% in solutions of density 1.20—1.47, and indicates that a compound  $2C_6H_{10}O_5 \cdot NaOH$  is formed. Similar measurements support less conclusively the formation of a compound,  $2C_6H_{10}O_5 \cdot KOH$ , when cotton is treated with potassium hydroxide solution (*d* 1.35—1.48).

A. J. H.

**Action of Heat on Cotton Cellulose.** E. KNECHT and E. F. MULLER (*J. Soc. Dyers and Col.*, 1925, **41**, 43—47).—Air-dry, bleached cotton is affected by prolonged heating (1866 hrs.) at 90°, its copper number being increased from 0.4 to 1.0—2.0 and its tensile strength considerably reduced. Heating in a vacuum causes much less deterioration than heating in an open tube. Discoloration of cotton by heat is not commensurate with its deterioration. Cotton mercerised by means of sodium hydroxide or nitric acid is more susceptible to the action of heat than unmercerised cotton. During the prolonged heating of cotton at 90° an empyreumatic odour and a volatile acid are produced and the cellulose is partly converted into a soluble carbohydrate. Lignin obtained from wood was less discoloured than the accompanying cellulose after being heated at 90° in a sealed tube for 2276 hrs. [Cf. *B.*, 1925, 200.]

A. J. H.

**Degradation of Cellulose by Formic Acid.** E. HEUSER and W. SCHOTT (*Cellulosechem.*, 1925, **6**, 10—11).—When viscose cellulose was heated with 5% formic acid at 160°, the formation of dextrose was 17% after  $\frac{1}{2}$  hr. and 50% after 1 hr. At 180°, more than 50%

of dextrose was produced in  $\frac{1}{2}$  hr. The amount of dextrose was much smaller when the liquid was heated rapidly to the maximum temperature than when it was heated slowly. Hydroxymethylfurfuraldehyde is a secondary product of the action of the acid; 4% of this aldehyde was found after heating at  $160^\circ$  for 1 hour. The residue is hydrocellulose either partly or completely soluble in 8% sodium hydroxide solution. No gaseous decomposition of the formic acid was observed, practically the whole of the acid being recovered after the hydrolysis. J. F. B.

**Ethers of Polysaccharides and Hydroxy-Acids.** R. O. HERZOG (*Biochem. Z.*, 1924, **152**, 257).—A reply to Weltzien (this vol., i, 12) on behalf of Chowdhury (*A.*, 1924, i, 1029). J. P.

**Stability of Cellulose Esters.** A. CAILLE (*Chim. et Ind.*, 1925, **13**, 11—13).—Cellulose hydrogen sulphate, prepared by the action of a mixture of 100% sulphuric acid and glacial acetic acid on cotton, cannot be washed neutral by distilled water owing to the continuous hydrolysis of the ester; neutral washings can, however, be obtained by use of alcohol or calcareous water. In the latter case, the acid function of the cellulose sulphuric ester is neutralised by the mineral bases of the water. Sulphuric ester groups thus neutralised are regarded as substantially stable, and a series of partly neutralised cellulose acetates prepared in 1918 was found to be more or less decomposed in proportion as their sulphuric acid groups were unneutralised or neutralised in the process of manufacture. The unneutralised sulphuric acid ester groups of these cellulose acetates had been completely hydrolysed to free sulphuric acid during the prolonged storage, and profound hydrolysis of the acetic ester had been induced. The neutralised portion of the sulphuric ester group in cellulose acetate is stable, and resists hydrolysis on heating with water at  $120^\circ$ , whereas the unneutralised portion is rapidly converted into free sulphuric acid. J. F. B.

**Röntgen Spectrographic Comparison of Tunicin and Lichenin with Cellulose.** R. O. HERZOG and H. W. GONELL (*Z. physiol. Chem.*, 1924, **141**, 63—67).—The Röntgen diagrams obtained from tunicin and cellulose (ramie fibres) were completely identical and entirely different from that given by lichenin. The two former carbohydrates are thus chemically identical, whilst the crystalline constituents of the latter evidently differ from those of the former. E. S.

**Constitution of Pine Lignin. IV.** P. KLASON (*Ber.*, 1925, **58**, [B], 375—380; cf. *A.*, 1920, i, 822; 1922, i, 324; 1923, i, 187).—The action of sulphite solutions on pine lignin gives a mixture of the dibasic and monobasic sulphonic acids,  $2C_{20}H_{20}O_6 \cdot 2H_2SO_3$  and  $2C_{20}H_{20}O_6 \cdot H_2SO_3$ , the latter being obtained when the process is effected at as low a temperature as possible. The lignosulphonic acid isolated by Dorée and Hall (*A.*, 1924, i, 1049) appears to be a mixture of these two acids. The formula,  $C_{20}H_{20}O_6$ , used previously

for lignin for the sake of simplicity requires to be doubled (cf. Klason, A., 1920, i, 149).

Proof is afforded that the  $\beta$ -naphthylamine salt of  $\alpha$ -lignosulphonic acid is transformed by an excess of aqueous sodium hydroxide solution partly into  $\alpha$ -lignosulphonic acid and partly into the acid  $R \cdot CH_2 \cdot CH(SO_3H) \cdot CH:N \cdot C_{10}H_7$ .

Experimental evidence is quoted against the view of Willstätter and Kalb (A., 1922, i, 989) that aromatic substances are not formed in appreciable amount by the degradation of lignin. H. W.

**Chemistry of Lignin. II. Comparison of Lignins Derived from Various Woods.** W. J. POWELL and H. WHITTAKER (*J. Chem. Soc.*, 1925, 127, 132—137; cf. *ibid.*, 1924, 125, 357).—On acetylation of lignin derived from poplar, birch, ash, spruce, larch, and pine, or of flax lignin, the total number of acetyl + methoxyl groups (calculated from the formula  $C_{45}H_{48}O_{16}$ ) is 9, whilst methylation followed by acetylation again yields a similar product in each instance; it is concluded that the natural lignins are derivatives of the same polyhydroxy compound (8—10 OH groups), differing only in the number of methoxyl groups (3—5). The absence of carboxyl groups may be inferred from the insolubility of the acetyl compounds in cold alkali. The six dodecabromolignins, their acetyl derivatives, and two dodecachlorolignins are similar to the corresponding derivatives of flax lignin; so also with the six nitrolignins, in which three nitro groups are present, and the existence of an aromatic nucleus is indicated; in addition to nitration, oxidation occurs, and the solubility of acetylnitrolignin in alkali may be due to a carboxyl group. Whilst flax lignin gives a monophenylhydrazone, under different conditions methyl-lignin reacts with 3 mols. of phenylhydrazine, whence the presence of two keto groups in addition to the aldehydo group is deduced. To the parent hydroxy compound is given the name lignol and the formula  $C_{38}H_{30}O_4(CO)_2(CHO)(OH)_9$ . On purification of the six wood lignins, the pentosan (<1%) disappears. F. M. H.

**Constitution of the Natural Humic Acids.** O. BURIAN (*Brennstoff-Chem.*, 1925, 6, 52—54).—Humic acids prepared by heating cellulose under pressure with water in the absence of air and those extracted from Kassel lignite yield furfuraldehyde when distilled with lime; its presence is shown by the green coloration of a pine-wood shaving moistened with hydrochloric acid and by its red coloration with aniline acetate. This supports the view that cellulose is the source of the furfuraldehyde, although the presence of the furan ring in the humic acid itself as suggested by Marcusson is doubted. Comparison is made with the decomposition of lignin from pine wood yielding dextrose and coniferyl alcohol, and it is suggested that the dextrose is subsequently converted into humic acids. A. C. M.

**Constitution of Natural Humic Acids.** W. ELLER (*Brennstoff-Chem.*, 1925, 6, 55).—The experiments of Burian (*vide supra*) as to the cellulose origin of the humic acids are criticised. The

colour reactions used by Burian for the identification of furfuraldehyde in the distillates from humic acids are considered unsatisfactory. Although externally similar, the humic acids from cellulose are not identical with natural humic acids (cf. Eller, A., 1923, i, 543).  
A. C. M.

**Fusain and its Oxidation. Composition of Coal.** F. V. TIDESWELL and R. V. WHEELER (*J. Chem. Soc.*, 1925, 127, 125—132).—From the rate of absorption of oxygen at 30° and at 100°, it is concluded that the oxidisability of fusain increases less rapidly with temperature than does that of the associated coal. A certain amount of "reactive" material is present with "true fusain," and the difference in the degree of oxidisability of fusains from different sources is attributed to the varying proportions of these constituents.  
F. M. H.

**Banded Bituminous Coal. Composition of Coal.** F. V. TIDESWELL and R. V. WHEELER (*J. Chem. Soc.*, 1925, 127, 110—112; cf. T., 1919, 115, 619; 1922, 121, 2345).—Ulmification is the main chemical process during the decay of plants; with ageing of peat, the amount of material soluble in alkali increases, but in coals the ulmins are converted into insoluble cementing material. The "reactive" matter of vitrain, clarain, and durain is assessed at 100%, 90%, and 70%, respectively.  
F. M. H.

**Oxidation of Banded Bituminous Coal at Low Temperatures. Composition of Coal.** W. FRANCIS and R. V. WHEELER (*J. Chem. Soc.*, 1925, 127, 112—125).—By means of regulated oxidation by moist air, or by hydrogen peroxide, it is possible to obtain similar alkali-soluble ulmins from vitrain, durain, and fusain; for vitrain, which is the most readily attacked, this oxidation by air is complete at 150°, and is accompanied by destruction of the compounds which are soluble in both pyridine and chloroform. It is considered that the alkali-soluble ulmins, which have disappeared during natural carbonisation, are thus regenerated by oxidation; the "reactive" group of compounds is specified as those which can be thus oxidised.  
F. M. H.

**$\alpha\beta\gamma$ -Triaminopropane and its Complex Metallic Compounds.** F. G. MANN and W. J. POPE (*Proc. Roy. Soc.*, 1925, A, 107, 80—92).—A detailed account of work, in part abstracted previously (A., 1924, i, 1049). The following additional compounds are described:  $\alpha\beta\gamma$ -triaminopropane hydrochloride and the corresponding hydrobromide ( $+H_2O$ ), m. p. (anhydrous), 307—310° (decomp.);  $\alpha\beta\gamma$ -triacetamidopropane, m. p. 200—202° (corr.), and the corresponding benzoyl derivative, m. p. 217—218° (corr.); cobaltditriaminopropane iodide  $[Co\ ptn_2]I_3$  and the chloroplatinate,  $[Co\ ptn_2, 3PtCl_6, 6H_2O]$ , m. p. (anhydrous), 270° (decomp.) after darkening at 255°; rhodiditriaminopropane tri-iodide and the corresponding chloroplatinate ( $+4H_2O$ ), m. p. (anhydrous) 328° (decomp.) after darkening at 295°; diaminoacetoxime dihydrochloride; diacet-

*amidoacetonephenylhydrazone*, m. p. 115—118°; *acetamidomethylglyoxalosazone*,  $\text{NHAc}\cdot\text{CH}_2\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$ , m. p. 186°.  
M. S. B.

**Permanence of Choline Solutions in Ampoules.** J. W. LE HEUX (*Arch. Pharm.*, 1924, 262, 570—575).—Solutions of choline hydrochloride will keep good, both chemically and physiologically, for at least three years in brown (Jena-Violax) glass if made up with 0.001*N*-hydrochloric acid. In common glass, or when the solution is made up with water alone, decomposition takes place in less than a year, and if the solution be made up with water and then be sealed up in common glass, it will not keep for six months unchanged. Choline solutions may be sterilised without damage.

W. A. S.

**Preparation of Derivatives of Basic Hydroxyalkyl Ethers.** FARBENFABRIKEN VORM. F. BAYER & CO., and J. CALLSEN (D.R.-P. 398010; from *Chem. Zentr.*, 1924, ii, 1399—1400).—Derivatives of basic hydroxyalkyl ethers are obtained by the action of alkylene-glycols, alkylenechlorohydrins, or alkylene oxides on aliphatic amines or their halogen salts, and treatment of the resulting dialkyl-aminoalkyl hydroxyalkyl ether with alkylating agents; or alternatively by the conversion of an alkylamine into a quaternary compound, converting this into its hydroxyalkyl ether, or treating the halogenated hydroxyalkyl ether with tertiary amines. The compounds obtained from choline or its *N*- and *C*-homologues by replacement of the hydroxylic hydrogen by hydroxyalkyl groups are comparatively less toxic, with a pronounced action like that of arecoline, and are valuable substitutes for this alkaloid. Dimethyl-aminoethyl alcohol with xylene, sodium, and ethylenechlorohydrin at high temperatures, or with ethylene oxide at 140° under pressure, or the action of dimethylaminoethyl chloride on the monosodium compound of ethylene glycol, yields *dimethylaminoethoxyethyl alcohol*,  $\text{NMe}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 88—98°/40 mm., which with methyl-alcoholic methyl iodide yields the corresponding quaternary *iodide*, m. p. 116—117°. The same compound is obtained by the action of trimethylamine on iodoethoxyethyl alcohol, or of ethylene oxide on choline iodide. The *bromide*, m. p. 83—86°, and *nitrate* are described. The monosodium derivative of ethylene glycol and diethylaminoethyl chloride in benzene yield diethyl-aminoethoxyethyl alcohol, similarly converted into the corresponding *methiodide*, m. p. 117—120°. Similarly, diethylaminoethyl alcohol in xylene on treatment with sodium and dichlorohydrin yields the *glyceryl ether* of the diethylamino compound,  $(\text{NEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2)_2\text{CH}\cdot\text{OH}$ ; the corresponding *methiodide* is described.

R. B.

[**Mechanism of Oxidation Processes.**] O. WARBURG (*Biochem. Z.*, 1924, 152, 191—192).—A reply to Wieland and Bergel (*A.*, 1924, i, 1172).

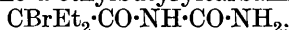
J. P.

**Preparation of  $\beta$ -Keto-Bases.** C. MANNICH (D.R.-P. 393633; from *Chem. Zentr.*, 1924, ii, 1025).—Acetoacetic acid and its mono-

substitution products condense with formaldehyde and primary or secondary amines thus: (i)  $\text{COMe} \cdot \text{CHR} \cdot \text{CO}_2\text{H} + \text{CH}_2\text{O} + \text{NHR}^1_2 = \text{COMe} \cdot \text{CHR} \cdot \text{CH}_2 \cdot \text{NR}^1_2 + \text{H}_2\text{O} + \text{CO}_2$ ; (ii)  $2\text{COMe} \cdot \text{CHR} \cdot \text{CO}_2\text{H} + 2\text{CH}_2\text{O} + \text{NH}_2\text{R}^2 = [\text{COMe} \cdot \text{CHR} \cdot \text{CH}_2]_2\text{NR}^2 + 2\text{H}_2\text{O} + 2\text{CO}_2$  (where R and  $\text{R}^1 = \text{H}$  or a univalent radical,  $\text{R}^2 =$  a univalent radical). It is sufficient to hydrolyse the acetoacetic esters, neutralise the solution, and treat the latter with the equivalent amount of amine hydrochloride; formaldehyde is then added to the well-cooled solution and left for an hour; concentrated hydrochloric acid is added during the condensation to maintain the acidity of the mixture. The resulting  $\beta$ -keto-bases are precipitated by adding potassium hydroxide and purified by distillation in a vacuum; they are of value in the manufacture of drugs. Ethyl ethylacetoacetate, formaldehyde, and dimethylamine afford  $\alpha$ -dimethylamino- $\beta$ -ethylbutan- $\gamma$ -one, b. p. 62—64°/14 mm., hydrochloride, m. p. 131°; ethyl ethylacetoacetate, piperidine, and formaldehyde afford  $\alpha$ -piperidino- $\beta$ -ethylbutan- $\gamma$ -one, b. p. 108—110°/15 mm., hydrochloride, m. p. 136°; ethyl benzylacetoacetate, piperidine, and formaldehyde afford  $\alpha$ -piperidino- $\beta$ -benzylbutan- $\gamma$ -one, b. p. 180—183°/14 mm., hydrochloride, m. p. 144°. Ethyl acetoacetate, formaldehyde, and dimethylamine afford a mixture of  $\alpha$ -dimethylaminobutan- $\gamma$ -one, b. p. 51—52°/12 mm., and  $\alpha$ -dimethylamino- $\beta$ -dimethylaminomethylbutan- $\gamma$ -one, b. p. 85—90°/12 mm., picrate, m. p. 136.5°. F. A. M.

**Mechanism of Reactions in the Carbamide Series.** T. L. DAVIS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 68—73).—Evidence is cited in favour of the view that the mechanism of many reactions in the carbamide series is the reversible combination of molecules, and all the carbamide derivatives studied “dearrange” or break down, often in more than one manner, but always in a predictable fashion analogous to that in which carbamide “dearranges” into ammonia and cyanic acid. The ease with which the various substituted carbamides undergo “dearrangement” is governed by the nature and position of the substituent groups. By applying the end-products as reagents it has been found possible to simplify a number of syntheses. J. S. C.

**Action of Alkali Hydroxide on  $\alpha$ -Bromo- $\alpha$ -ethylbutyrylcarbamide.** G. NEWBERRY (*J. Chem. Soc.*, 1925, **127**, 295—307).—Interaction of  $\alpha$ -bromo- $\alpha$ -ethylbutyrylcarbamide,

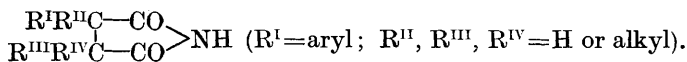


and 2*N*-sodium hydroxide (cf. Rosenmund and Hermann, A., 1912, i, 244) yields: (a)  $\alpha$ -ethylcrotonylcarbamide, m. p. 198°, (b) a small amount of the isomeride, m. p. 158°, probably formed directly by elimination of hydrogen bromide, (c)  $\alpha$ -ethylcrotonamide, m. p. 104°, (d) two  $\alpha$ -ethylcrotonic acids, (e) diethyl ketone, and (f) its equivalent of cyanide, perhaps due to intermediate formation of  $\alpha$ -bromo- $\alpha$ -ethylbutyramide (cf. Mannich and Zernik, A., 1908, i, 399), (g) carbamide, and (h) *s*-bisdiethylglycollylcarbamide, b. p. 283—286°/760 mm., m. p. 29° (cf. Clemmensen and Heitman, A., 1908, i, 771); its silver salt with ethyl iodide gives *bis*- $\alpha$ -ethoxy-

$\alpha$ -ethylbutyrylcarbamide, b. p.  $240^\circ$ , hydrolysed to  $\alpha$ -ethoxy- $\alpha$ -ethylbutyramide, m. p.  $36^\circ$ .  $\alpha$ -Bromo- $\alpha$ -ethylbutyrylcarbamide or  $\alpha$ -ethylcrotonylcarbamide is hydrolysed to  $\alpha$ -ethylcrotonic acid by alkali, which under similar conditions does not appreciably affect the corresponding amides.

Labile  $\alpha$ -ethylcrotonylcarbamide, m. p.  $198^\circ$ , is converted by hydrogen bromide into the stable isomeride, m. p.  $158^\circ$ , whilst either, with hydrogen bromide, yields a small amount of  $\beta$ -bromo- $\alpha$ -ethylbutyrylcarbamide, m. p.  $179^\circ$ . By hydrogen bromide, heat, or concentrated alkali, labile  $\alpha$ -ethylcrotonamide, m. p.  $104^\circ$ , is converted into the stable isomeride, m. p.  $118^\circ$ . The stable forms of carbamide or amide on treatment with concentrated alkali give stable  $\alpha$ -ethylcrotonic acid, whereas the labile isomerides give a mixture of the two acids. From the acid chloride, only stable forms of carbamide, amide, and acid are obtained. On reduction the carbamides yield  $\alpha$ -ethylbutyrylcarbamide, which is hydrolysed to  $\alpha$ -ethylbutyramide, also obtained by reduction of the  $\alpha$ -ethylcrotonamides. The amides are more readily attacked by bromine than are the carbamides, that of m. p.  $104^\circ$  giving  $\alpha\beta$ -dibromo- $\alpha$ -ethylbutyramide, m. p.  $128^\circ$ , whilst that of m. p.  $118^\circ$  gives the isomeride, m. p.  $79^\circ$ ; the carbamide, m. p.  $198^\circ$ , forms  $\alpha\beta$ -dibromo- $\alpha$ -ethylbutyrylcarbamide, m. p.  $143^\circ$ , whilst that of m. p.  $158^\circ$  forms the isomeride, m. p.  $112^\circ$ .  
F. M. H.

**Preparation of CC-Substituted Succinimides.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRUNING, M. BOCKMÜHL, and A. SCHWARZ (D.R.-P. 389948; from *Chem. Zentr.*, 1924, ii, 889—890).—CC-Substituted succinimides are prepared from succinic acids containing at least one aryl group, and alkyl groups, and from their derivatives (such as anhydrides, ester-acids, di-esters, ester-nitriles, nitriles, ester-amides, or diamides) by the methods generally used for preparing succinimide. The imides have the general formula



Thus,  $\alpha$ -phenylbutyronitrile is treated with sodamide in ether, and the resultant sodium compound heated with ethyl bromoacetate; the resultant nitrile,  $\text{CPhEt}(\text{CN})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p.  $155\text{--}170^\circ/11$  mm., is added to strong sulphuric acid, affording ethyl  $\alpha$ -phenyl- $\alpha$ -ethylsuccinamate, m. p.  $105^\circ$ , which is converted by dilute alkali into  $\alpha$ -phenyl- $\alpha$ -ethylsuccinimide, m. p.  $99^\circ$ , which is also obtained by heating the ester-amide at  $200^\circ$ , or by heating the ester-nitrile with alcoholic ammonia at  $190\text{--}195^\circ$ . In a similar manner,  $\alpha$ -phenyl- $\alpha$ -isopropylsuccinimide, m. p.  $107^\circ$ , is prepared from ethyl  $\alpha$ -phenylisopropylsuccinamate, m. p.  $107^\circ$ , and  $\alpha$ -phenyl- $\alpha$ -allylsuccinimide, m. p.  $89^\circ$ , from ethyl  $\alpha$ -phenyl- $\alpha$ -allylsuccinamate, m. p.  $98^\circ$ . The ester-amides are obtained by hydrolysis of corresponding nitriles, b. p.  $175\text{--}178^\circ/14$  mm.,  $170\text{--}173^\circ/12$  mm., respectively, with strong sulphuric acid, the ester-nitriles themselves being formed from ethyl bromoacetate and the sodium compounds of  $\alpha$ -phenyl- $\beta$ -methylbutyronitrile, b. p.  $123\text{--}124^\circ/15$  mm., or  $\alpha$ -phenyl- $\Delta^2$ -



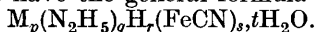
pentenenitrile, b. p. 131—133°/15 mm., respectively, the nitriles being obtained by alkylation of phenylacetonitrile.

$\alpha$ -Bromo- $\alpha$ -ethylbutyronitrile (obtained by distilling the corresponding amide with phosphoric oxide) condenses with sodio-phenylmalononitrile to give  $\alpha$ -cyano- $\alpha$ -phenyl- $\alpha'$ -diethylsuccinonitrile,  $(\text{CN})_2\text{CPh}\cdot\text{CET}_2\cdot\text{CN}$ , b. p. 100°/10 mm., m. p. 74°, which eliminates ammonia and carbon dioxide on heating with aqueous alkali to give  $\alpha$ -phenyl- $\alpha'$ -diethylsuccinimide, m. p. 110°.

The sodium compound of  $\alpha$ -phenylbutyronitrile condenses with ethyl  $\alpha$ -bromobutyrate to give the nitrile,  $\text{CET}_2(\text{CN})\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$ , b. p. 180°/19 mm., which is hydrolysed by strong sulphuric acid to the ester-amide, which yields  $\alpha$ -phenyl- $\alpha'$ -diethylsuccinimide, m. p. 119°, on heating with ammonia at 120°. The products have a powerful soporific and sedative effect, and are free from deleterious action on the stomach and general condition. F. A. M.

**Preparation of Tetramethylguanidines.** M. SCHENCK and F. VON GRAEVENITZ (*Z. physiol. Chem.*, 1924, **141**, 132—145).—The yield of  $\alpha\alpha\beta\gamma$ -tetramethylguanidine (Schenck, A., 1912, i, 425) is considerably improved when Lecher and Graf's (A., 1923, i, 761) modification of the method is employed.  $\alpha\alpha\beta\beta$ -Tetramethylguanidine (cf. Schenck, *loc. cit.*) may be obtained under the same conditions from *NNS*-trimethyl- $\psi$ -thiocarbamide and dimethylamine. It is also formed when cyanogen iodide is heated on a water-bath with excess of anhydrous dimethylamine for half an hour. *as*-Dimethylthiocarbamide has m. p. 164°, which is somewhat higher than the value given in the literature. E. S.

**Double Ferrocyanides of Hydrazine and Metallic Elements.** P. R. RAY and P. N. D. GUPTA (*Z. anorg. Chem.*, 1924, **140**, 81—92).—Potassium ferrocyanide solution is treated with concentrated hydrochloric acid until it becomes turbid and the solution is then cleared by the careful addition of water. Excess of ether then precipitates ether-ferrocyanide, which is dissolved in alcohol and re-precipitated with ether. On solution in water hydroferrocyanic acid is formed, which is neutralised with hydrazine hydrate and the salt precipitated with excess of alcohol, first as an oil which later turned to a horny, bright yellow mass. This is soluble in water and yields amorphous compounds, insoluble in dilute mineral acids, on precipitation with salts of copper, nickel, cobalt, iron, and zinc. The composition varies with the manner of precipitation, but the precipitates have the general formula



No regularity in the values for different metals with the same procedure was found. All the compounds are unstable in air and are decomposed by sodium hydroxide giving the metallic hydroxide, and all but the iron salts are acid. L. J. H.

**Preparation of Pure Calcium Cyanamide.** K. YASUDA (*Tech. Rep. Tôhoku*, 1924, **4**, 153—158).—Crude calcium cyanamide (1 part) is shaken during 3 hours with water (4 parts), and the calcium precipitated from the solution by addition of aluminium

sulphate. Evaporation of the filtrate, after addition of ammonia, gives a 60% yield of dicyanodiamide. Calcium cyanamide (purity 99.71%) is obtained by heating dicyanodiamide (70 parts) and calcium oxide (30 parts) in an atmosphere of nitrogen at 900–920° for 15–20 minutes and allowing the product to cool out of contact with air.

C. S.

**Fluorides of Organo-metallic Compounds. III. Thallium Alkyl and Aryl Fluorides.** E. KRAUSE and A. VON GROSSE (*Ber.*, 1925, 58, [B], 272–275).—*Thallium dimethyl fluoride*,  $\text{TlMe}_2\text{F}$ , decomp. above 230° when slowly heated, is prepared by the action of silver fluoride on a warm aqueous solution of thallium dimethyl bromide; the corresponding *dodecahydrate* is described. *Thallium diethyl fluoride*, decomp. above 170° when slowly heated, and its (?) *dodecahydrate* are obtained similarly. *Thallium diphenyl fluoride* has m. p. 305–310° (decomp.) when cautiously heated. The thallium diphenyl ion is characterised by its ability to form a very sparingly soluble nitrate. In contrast to the corresponding chlorides, bromides, and iodides, the fluorides described above are freely soluble in water, the series thus resembling the simple thallous and silver halides.

H. W.

**Residual Affinity and Co-ordination. XXIII. Interactions of Trimethylstibine and Platinic and Palladous Chlorides.** G. T. MORGAN and V. E. YARSLEY (*J. Chem. Soc.*, 1925, 127, 184–190).—Trimethylstibine reduces chloroplatinic acid and, in alcoholic solution, gives (I) an orange, insoluble compound and (II) *bis(trimethylstibine)dichloroplatinum*,  $[\text{2Me}_3\text{Sb}, \text{PtCl}_2]$ , which is yellow and soluble; in aqueous solution, only (I) is formed, which by heating at 60° is converted into (II). Either (I) or (II) with excess of trimethylstibine yields (III) *tetrakis(trimethylstibine)platinous chloride*,  $[\text{Pt}, 4\text{Me}_3\text{Sb}]\text{Cl}_2$  (characterised by its *chloroplatinate*), and this with potassium chloroplatinate gives (I), which is therefore *tetrakis(trimethylstibine)platinous chloroplatinate*,  $[\text{Pt}, 4\text{Me}_3\text{Sb}]\text{PtCl}_4$ . (III) with chloroplatinic acid gives *tetrakis(trimethylstibine)platinous chloroplatinate*,  $[\text{Pt}, 4\text{Me}_3\text{Sb}]\text{PtCl}_6$ , which is hydrolysed by excess to (I) and (II); (III) is converted by palladous chloride into *tetrakis(trimethylstibine)platinous chloropalladite*.

Trimethylstibine and palladous chloride give *bis(trimethylstibine)dichloropalladium*,  $[\text{2Me}_3\text{Sb}, \text{PdCl}_2]$ , (yellow), which is converted by excess of trimethylstibine into *tetrakis(trimethylstibine)palladous chloride*,  $[\text{Pd}, 4\text{Me}_3\text{Sb}]\text{Cl}_2$ , (orange); this is converted by dilute hydrochloric acid into *trimethylstibinedichloropalladium hydrochloride*,  $[\text{Me}_3\text{Sb}, \text{PdCl}_2]\text{H}$ , which is comparatively stable.

F. M. H.

**Direct Combination of Ethylenic Hydrocarbons with Hydrogen Sulphites.** I. KOLKER and A. LAPWORTH.—(See i, 353.)

**Migratory Tendencies of Organic Radicals. I. M. TIFFENEAU and A. ORÉKHOV** (*Bull. Soc. chim.*, 1924, [iv], 35, 1639–1653).—A review of published information on the migration

of radicals in such changes as the pinacolinic transposition, various other reactions being discussed. The comparative migratory tendencies bear no simple relation to the comparative affinities (cf. A., 1923, i, 333; 1924, i, 283, 729).  
W. A. S.

**Benzene Ring Problem.** E. SCHROER (*Z. Elektrochem.*, 1925, **31**, 53—54).—An electronic model of the benzene ring based on the theory of Kossel is described. It is shown to afford a satisfactory explanation of certain chemical properties of benzene and its derivatives.  
N. H. H.

**Mechanism of Substitution Reactions in the Aromatic Nucleus.** H. J. PRINS (*Rec. trav. chim.*, 1925, **44**, 166—172; cf. A., 1919, i, 71; this vol., i, 18; Barnett, A., 1924, i, 1292; Barnett and Matthews, this vol., i, 18).—It is claimed that the author's theory of substitution in the aromatic nucleus, involving the equilibrium between atom-energy and bond-energy, receives experimental confirmation from various sources. It is considered that for analogous reactions, the velocity is determined by the amount of atom-energy. By applying the electronic theory of valency, it appears that "electrophilic" atoms (atoms showing a pronounced tendency to take up electrons), if directly attached to the nucleus, are *op*-directing, but if attached indirectly by a less electrophilic atom are *m*-directing, which agrees with the deductions from the original theory. The bond between the nucleus and a *m*-directing group is non-polar and the bond-energy small, whilst between the nucleus and *op*-directing groups it is more polar, with considerable bond-energy. When there is more than one substituent, the dominating group is probably the one with the more polar character.  
F. M. H.

**Syntheses by Means of Organic Peroxides. I. Action of Benzoyl Peroxide and some of its Derivatives on Boiling Benzene.** H. GELISSEN and P. H. HERMANS (*Ber.*, 1925, **58**, [B], 285—294).—The decomposition of benzoyl peroxide dissolved in boiling benzene results in the formation of carbon dioxide, benzoic acid (partly in the form of unidentified esters), diphenyl, phenyl benzoate, bisdiphenyl, and a resinous material from which 1 : 4-diphenylbenzene can be extracted in small amount. Reaction occurs mainly according to the schemes:  $\text{Ph}\cdot\text{CO}\cdot\text{O}\cdot\text{O}\cdot\text{CO}\cdot\text{Ph} + \text{C}_6\text{H}_6 \rightarrow \text{Ph}\cdot\text{CO}_2\text{H} + \text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_5 + \text{CO}_2$  and  $\text{Ph}\cdot\text{CO}_2\text{Ph} + \text{C}_6\text{H}_6 + \text{CO}_2$ . 1 : 4-Diphenylbenzene and bisdiphenyl are produced by the action of the peroxide on diphenyl and 1 : 4-diphenylbenzene, respectively, whereby also benzoic acid, carbon dioxide, and complex esters of benzoic acid are formed; these substances are also produced by the action of benzoyl peroxide on diphenyl at 110°. The participation of benzene in the reaction, contrary to the statement of Lippmann, is established by the weights of the products and by the observation that *p*-chlorobenzoyl peroxide, m. p. 137—138° (decomp.) (prepared by the action of sodium hydroxide and hydrogen peroxide on *p*-chlorobenzoyl chloride in the presence of acetone), is transformed by boiling benzene into carbon dioxide, *p*-chlorobenzoic

acid, and 4-chlorodiphenyl, whereas, according to Lippmann, 4:4'-dichlorodiphenyl should be produced:  $(C_6H_4Cl \cdot CO \cdot O)_2 \rightarrow C_6H_4Cl \cdot C_6H_4Cl + 2CO_2$ . Further, *m*-nitrobenzoyl peroxide and benzene yield carbon dioxide, *m*-nitrobenzoic acid, and *m*-nitrodiphenyl.

The thermal decomposition of benzoyl peroxide results in the evolution of approximately 1 mol. of carbon dioxide from each molecule of peroxide; diphenyl is also produced in small amount. In the presence of certain catalysts (which will be described subsequently), decomposition proceeds very uniformly with evolution of nearly 2 mols. of carbon dioxide and formation of diphenyl in excellent yield.

H. W.

**Condensation Reactions with Nitrosyl Chloride.** A. SCHAARSCHMIDT and M. RAECK (*Ber.*, 1925, 58, [B], 348—352).—In continuation of the investigation of the action of nitrogen peroxide on benzene and halogenated benzenes in the presence of aluminium chloride (Schaarschmidt, this vol., i, 123), it is shown that reaction only occurs to a very slight extent when nitrosyl chloride is brought into contact with aromatic hydrocarbons in the presence of aluminium chloride at the atmospheric temperature owing to the stability of the additive compound of aluminium chloride and nitrosyl chloride. The authors' theory that the hydrocarbon and not the acid chloride is activated by aluminium chloride in the Friedel-Crafts reaction appears thus to receive further confirmation. If the mixture is warmed hydrogen chloride is evolved and the residue yields *p*-aminodiphenyl in addition to resinous, brown condensation products and a little phenol and bases with an odour of pyridine. The yield of condensation products increases with increasing proportion of aluminium chloride and the amount of amorphous products increases with rise of temperature.

H. W.

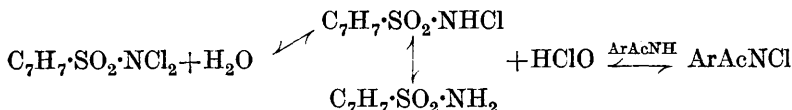
**Separation of *o*- from *p*-Nitrotoluene and *o*- from *p*-Nitrochlorobenzene by Rectification in a Vacuum.** V. MOLINARI (*Atti Congr. Naz. Chim. Ind.*, 1924, 402—406).—Rectification of mixtures of *o*- with *p*-nitrotoluene or *o*- with *p*-nitrochlorobenzene at a pressure of about 20 mm. by means of a column containing Lessing or Prym rings and capped with an automatic dephlegmating device yields the components in almost pure condition.

T. H. P.

**Alkali Salts of Aromatic N-Halogenosulphonamides.** CHEMISCHE FABRIK VON HEYDEN A.-G. (D.R.-P. 390658; from *Chem. Zentr.*, 1924, ii, 888).—Alkali salts of aromatic N-halogenosulphonamides are prepared by treating the sulphonamides or their salts with calcium hypohalogenites and alkali salts. Thus, the calcium salt of *p*-toluenesulphonamide is added to an aqueous suspension of calcium hypochlorite, stirred for several hours, and sodium *p*-toluenesulphonchloroamide precipitated from the filtered solution by adding sodium chloride or acetate; sodium *p*-toluenesulphonbromoamide and benzenesulphonchloroamide are prepared analogously. The products, free from calcium salts, serve as disinfecting or bleaching agents.

F. A. M.

**Hydrolysis of Acylchloroamines in Water.** F. G. SOPER (*J. Chem. Soc.*, 1925, 127, 98—102).—Owing to the slight extent of the reversible hydrolysis of chloroamines in water,  $\text{NCl} + \text{H}_2\text{O} \rightleftharpoons \text{NH} + \text{HClO}$ , the hydrolysis has been studied in the presence of another amine the conditions of equilibrium of which are known. *p*-Toluenesulphondichloroamide was selected for reasons previously given (A., 1924, i, 1176). The method employed depends on the following considerations. *p*-Toluenesulphondichloroamide dissolves in solutions of anilides with the formation of the corresponding chloroamines :

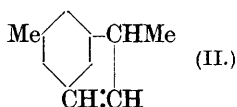
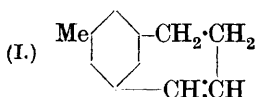


From the increase in the solubility of the sulphondichloroamide, as measured by the thiosulphate titre of the saturated solution, the concentrations of the chloroamines formed in solution can be calculated. The determination of the solubility of *p*-toluenesulphondichloroamide in solutions of anilides was carried out in the same way as that in aqueous solutions of *p*-toluenesulphonamide (cf. Soper, *loc. cit.*). The hydrolysis constant is given by the expression  $[\text{HClO}][\text{anilide}]/[\text{chloroamine}] = [\text{HClO}]x/(d-x)$ . The following values for  $k_h \times 10^7$  have been determined : *N*-chloroacetanilide, 7.27; *N*-chloroformanilide, 2.4; *N*-chloroaceto-*o*-toluidide, 3.3; *N*-chloroaceto-*p*-toluidide, 22.0; *No*-dichloroacetanilide, 6.9; *Np*-dichloroacetanilide, 15.0. A comparison of these values with those of the ionisation constants of similarly substituted compounds and with the equilibrium constants of the hydrolysis of anilides into amine and acid (cf. McBain and Davies, A., 1912, ii, 33) is given, and shows that the relative effects of the *o*- and *p*-methyl groups on the hydrolysis of the chloroamines and the ionisation of the amines are almost identical, as are also those of the *o*- and *p*-chlorine atoms on the chloroamines and the phenols. A. C.

**Electrochemical Oxidation of Homologues of Benzene. I. *m*-Xylene.** F. FICHTER and J. MEYER (*Helv. Chim. Acta*, 1925, 8, 74—83; cf. A., 1924, i, 629).—The electrochemical oxidation of *m*-xylene in an emulsion with aqueous sulphuric acid yields small quantities of *m*-tolualdehyde and *isophthalic* acid. When the oxidation is conducted in sulphuric acid-acetone solution, the same products are observed together with the intermediate *m*-toluic acid, whilst a second type of oxidation gives rise to 1 : 3 : 4-xylenol, toluquinone, dixylenol,  $[3 : 5 : 2\text{-C}_6\text{H}_2\text{Me}_2(\text{OH})_2]$ , m. p. 137.5° (*diacetyl* derivative, m. p. 109.5°, *monomethyl ether*, m. p. 88°), and *p*-xyloquinone. The production of the quinone of the para series from specially purified *m*-xylene was confirmed and found to be due to the intermediate formation of dimethyl- $\psi$ -quinol hydrate, converted into the *p*-xyloquinone by acids (Bamberger and Brady, A., 1901, i, 142). This constitutes a new method for preparing  $\psi$ -quinols. G. M. B.

### Ring Closures in the Meta Position in the Benzene Series.

III. J. VON BRAUN and O. ENGEL (*Ber.*, 1925, **58**, [B], 281—285; cf. A., 1920, i, 87, 251).—*ωω'*-Dibromomesitylene is most advantageously prepared by the action of bromine vapour (1 mol.) on boiling mesitylene and treatment of the product with an additional molecule of halogen at 130°. It is converted rapidly by potassium cyanide into 5-methylphenylene-1:3-diacetonitrile, b. p. 224—225°/14 mm., m. p. 73°, the homogeneity of which is established by its hydrolysis to 5-methylphenylene-1:3-diacetic acid, m. p. 173°, and smooth oxidation of the latter to trimesic acid. When reduced with sodium and alcohol, the nitrile gives the corresponding diamine in amount too small for extended investigation and, mainly, the secondary amine,  $C_{11}H_{14}NH$ , b. p. 110—111°/13 mm., which yields a non-crystalline nitroso derivative and benzenesulphonyl compound and a quaternary methiodide,  $C_{13}H_{20}NI$ , m. p. 253° (corresponding chloroplatinate,  $C_{26}H_{40}N_2Cl_6Pt$ , m. p. 233°). The methiodide is converted by treatment with silver oxide followed by distillation of the ammonium base in a vacuum into water, dimethylamine, and a hydrocarbon (I or II), b. p. 71—72°/14 mm.,  $d_4^{20}$  0.9012,  $n_D^{20}$  1.5371, which yields a dibromide, m. p. 90°. The

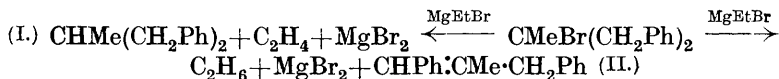


smooth oxidation of the hydrocarbon to trimesic acid and the presence of only one double bond proves that the  $C_4H_6$  complex must be united in the form of a ring to two meta carbon atoms of the benzene nucleus.

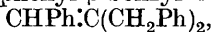
H. W.

**Preparation of Quaternary Hydrocarbons.** E. R. TROTMAN (*J. Chem. Soc.*, 1925, **127**, 88—95).—Attempts are described to prepare quaternary hydrocarbons of the type  $(CH_2Ph)_2CR'R''$ .  $\beta$ -Bromo- $\alpha$ -phenyl- $\beta$ -methylbutane,  $CH_2Ph \cdot CMeEtBr$ , an oil with mint odour and irritating action on the eyes, decomposing on distillation under 11 mm., is obtained in almost theoretical yield by the action of hydrogen bromide on benzylmethylethylcarbinol (cf. Konovalov, A., 1904, i, 496). Magnesium ethyl bromide reacts with  $\beta$ -bromo- $\alpha$ -phenyl- $\beta$ -methylbutane with evolution of ethane and ethylene and formation of an oil, b. p. 195—205°, which appears to contain  $\alpha$ -phenyl- $\beta$ -methyl- $\Delta^a$ -butene and probably  $\alpha$ -phenyl- $\beta$ -methylbutane, b. p. 203—204°. The presence of any quaternary hydrocarbon could not be proved. An attempt to convert the bromide into a Grignard compound and react on it with ethyl bromide resulted in the same products. *Dibenzylmethylethylcarbinol*, a sweet-smelling liquid, b. p. 195—200°/14 mm. (slight decomp.), prepared from magnesium benzyl chloride and ethyl acetate, was converted into  $\beta$ -bromo- $\alpha$ -phenyl- $\beta$ -benzylpropane,  $(CH_2Ph)_2CMeBr$ , prisms, m. p. 78.5°, which loses hydrogen bromide on heating, even under 0.2 mm. It reacted with magnesium ethyl bromide, giving off a mixture of gases consisting of 42% of ethane and 58% of

ethylene, and formed a yellow oil from which a small amount of  $\alpha\delta$ -diphenyl- $\beta\gamma$ -dibenzyl- $\beta\gamma$ -dimethylbutane, m. p.  $171^\circ$  (cf. Späth, A., 1914, i, 1), was isolated. The main product was a mixture of  $\alpha\gamma$ -diphenyl- $\beta$ -methylpropane (I), b. p.  $290$ — $294^\circ$ , and an olefine (II),



$\text{C}_{16}\text{H}_{16}$ , b. p.  $294$ — $296^\circ$ , believed to be  $\alpha\gamma$ -diphenyl- $\beta$ -methyl- $\Delta^a$ -propene. The quaternary hydrocarbon expected,  $\alpha$ -phenyl- $\beta$ -benzyl- $\beta$ -methylbutane, was not present in the reaction products.  $\beta$ -Bromo- $\alpha$ -phenyl- $\beta$ -benzylpropane reacted with magnesium benzyl chloride at  $100^\circ$  to form an oil which gave a small quantity of  $\alpha$ -phenyl- $\beta\beta$ -dibenzylpropane, m. p.  $113^\circ$ ; the main product contained the olefine (II), and probably (I). Tribenzylmethyl bromide treated with magnesium ethyl bromide gave a small yield of hexabenzylethane, m. p.  $82$ — $83^\circ$  (cf. Schmerda, A., 1909, i, 563); the main product was  $\alpha\gamma$ -diphenyl- $\beta$ -benzyl- $\Delta^a$ -propene,



m. p.  $42$ — $43^\circ$ , which Orékov and Grinberg (A., 1917, i, 450) described as a viscous oil. Tribenzylmethyl bromide reacts with magnesium benzyl bromide to form  $\alpha\gamma$ -diphenyl- $\beta$ -benzyl- $\Delta^a$ -propene (see above) as chief product, but about 5% of the yield consisted of tetrabenzylmethane,  $\text{C}(\text{CH}_2\text{Ph})_4$  ( $\alpha\gamma$ -diphenyl- $\beta\beta$ -dibenzylpropane), cubic crystals, m. p.  $164^\circ$ . As there seemed to be indications that the halogen atom of tertiary halides is more readily displaced by a benzyl than by an ethyl group,  $\beta$ -bromo- $\alpha$ -phenyl- $\beta$ -methylpropane, a liquid which does not distil unchanged under 11 mm., was treated with magnesium benzyl bromide.  $\alpha$ -Phenyl- $\beta$ -benzyl- $\beta$ -methylpropane,  $(\text{CH}_2\text{Ph})_2\text{CMe}_2$ , b. p.  $293$ — $294^\circ$ , was isolated, but about 50% of the product consisted of  $\alpha$ -phenyl- $\beta$ -methyl- $\Delta^a$ -propene, b. p.  $181^\circ$  (cf. Klages, A., 1904, i, 497). It is concluded that the reaction between Grignard reagents and tertiary halogen derivatives does not follow the normal course. Späth's (*loc. cit.*) view of the mechanism of the reaction is criticised. In an attempt to prepare diketones of the type  $\text{COPh}\cdot\text{CR}(\text{CH}_2\text{Ph})\cdot\text{CO}\cdot\text{Me}$ , benzylbenzoylacetone,  $\text{C}_{17}\text{H}_{16}\text{O}_2$ , m. p.  $60$ — $61^\circ$ , yield 50%, was prepared from the sodium derivative of benzoylacetone and benzyl chloride; on treatment with sodium ethoxide and ethyl bromide, it lost an acetyl group, giving phenyl  $\beta$ -phenylethyl ketone instead of the quaternary hydrocarbon hoped for. A. C.

**Perylene and its Derivatives.** VII. A. ZINKE, F. LINNER, and O. WOLFBauer (*Ber.*, 1925, 58, [B], 323—329).—3 : 9-Dibenzoylperylene (cf. Scholl, Seer, and Weitzenböck, A., 1910, i, 616) loses hydrogen chloride when heated with aluminium chloride at  $180^\circ$  and yields isoviolanthrone. Bromination of dry perylene or of the hydrocarbon dissolved in sulphuric acid, nitrobenzene, glacial acetic acid, carbon tetrachloride, or carbon disulphide gives a mixture of 3 : 10-dibromoperylene, m. p. about  $190^\circ$  (the constitution of which is established by its oxidation by sulphuric acid

to 3 : 10-perylenequinone; cf. Zinke and Unterkreuter, A., 1920, i, 541), and 3 : 9-dibromoperylene, m. p. 289·5—291°, which is oxidised by concentrated sulphuric acid to a new perylenequinone. The constitution of the latter bromo compound follows from its conversion by benzoyl chloride and aluminium chloride in the presence of carbon disulphide into 3 : 9-dibromo-4 : 10-dibenzoylperylene, m. p. about 355° (decomp.) after darkening at 340°, and the conversion of this substance by aluminium chloride at 170° into isoviolanthrone.

H. W.

**Perylene and its Derivatives. VIII.** A. ZINKE, A. PONGRATZ, and K. FUNKE (*Ber.*, 1925, 58, [B], 330—332).—A convenient method for the chlorination of perylene consists in the gradual addition of regulated amounts of hydrogen peroxide and hydrochloric acid, each diluted with glacial acetic acid, to a solution of perylene in nitrobenzene. The following substances are obtained in this manner : 3 : 9-dichloroperylene, m. p. 280—281°, the constitution of which is established by its conversion successively into 3 : 9-dichloro-4 : 10-dibenzoylperylene, which does not melt below 360°, and isoviolanthrone (cf. preceding abstract); (?) 3 : 10-dichloroperylene; tetrachloroperylene, m. p. 350°, in which the chlorine atoms probably occupy the 3 : 4 : 9 : 10-positions and from which a halogenated isoviolanthrone cannot be produced; hexachloroperylene, m. p. 356—357°.

H. W.

**Closure of the Fluorene Ring in the Di- $\alpha$ -naphthylmethane Series.** O. I. MAGIDSON (*Ber.*, 1925, 58, [B], 433—442; cf. Schmidlin and Massini, A., 1909, i, 561; Tschitschibabin and Magidson, A., 1915, i, 239).—The action of crystalline phosphoric acid on di- $\alpha$ -naphthylcarbinol proceeds in accordance with the scheme  $2(\text{C}_{10}\text{H}_7)_2\text{CH}\cdot\text{OH} \rightarrow [(\text{C}_{10}\text{H}_7)_2\text{CH}]_2\text{O} \rightarrow (\text{C}_{10}\text{H}_7)_2\text{C}:\text{C}(\text{C}_{10}\text{H}_7)_2 \rightarrow 2(<\text{C}_{10}\text{H}_6)_2\text{CH}_2$ , in which the velocities of the individual phases are of a closely similar order of magnitude. The product contains about 65% of di- $\alpha$ -naphthafluorene, 10% of tetra- $\alpha$ -naphthylethylene, and 25% of a difficultly separable mixture of the hydrocarbons. By conducting operations under diminished pressure, it is possible to make tetra- $\alpha$ -naphthylethylene the main product of the change. The correctness of the assumed course of the action is confirmed by the observation that di- $\alpha$ -naphthafluorene is formed from tetra- $\alpha$ -naphthylethylene when the latter is boiled with zinc dust and glacial acetic acid in the presence of hydrogen chloride. The action of phosphoric acid on tetra- $\alpha$ -naphthylethylene is more complicated and leads to the production of di- $\alpha$ -naphthylmethane and bisdi- $\alpha$ -naphthafluorenyl,  $\text{C}_{42}\text{H}_{26}$ , m. p. 345—350°, which is synthesised from di- $\alpha$ -naphthylfluorenyl bromide and copper powder and from magnesium di- $\alpha$ -naphthylfluorenyl bromide and iodine. The tendency of derivatives of di- $\alpha$ -naphthylmethane to form the fluorene ring is illustrated by the conversion of di- $\alpha$ -naphthyl ketone by phosphorus pentachloride into di- $\alpha$ -naphthafluorenone chloride, m. p. 256—258°, which is quantitatively transformed by boiling amyl alcohol in the presence of sulphuric acid into di- $\alpha$ -naphthafluorenone. Benz-



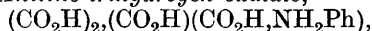
hydrol is converted by phosphoric acid at 200° into tetraphenylethylene, diphenylmethane, and benzophenone, whereas xanthydrol yields a mixture of xanthone and xanthene.

Tetra- $\alpha$ -naphthylethylene differs from tetraphenylethylene in that it does not add halogen. Further, the latter hydrocarbon is smoothly converted by phosphorus pentachloride into benzophenone chloride, whereas tetra- $\alpha$ -naphthylethylene gives *di- $\alpha$ -naphthafluorenyl chloride*, m. p. 220—222°, the identity of which is established by its production from di- $\alpha$ -naphthafluorenol and hydrogen chloride in glacial acetic acid solution at 100°.

The action of copper powder in the absence of air and moisture on di- $\alpha$ -naphthafluorenone chloride in the presence of benzene yields *bisdi- $\alpha$ -naphthafluorenylene*,  $C_{42}H_{24}$ , m. p. 308—310°, which can be reduced to bisdi- $\alpha$ -naphthafluorenyl and, like tetra- $\alpha$ -naphthylethylene, does not add bromine, but forms a *dibromo* derivative,  $C_{42}H_{22}Br_2$ , decomp. 380° after darkening at 325°. Attempts to cause magnesium di- $\alpha$ -naphthafluorenyl bromide to react with xanthone resulted in the production of bisdi- $\alpha$ -naphthafluorenyl.

H. W.

**Aniline Hydrogen Salts of Acids of the Oxalic Series.** O. RAMBECH (*J. Pharm. Chim.*, 1925, [viii], 1, 150—154).—Succinic, malic, and tartaric acids form no ammonium salts. Glutaric and adipic acids and, contrary to the account in the literature, sebacic acid form no aniline salts. By mixing aqueous or alcoholic solutions of the calculated quantities of the constituents, the following salts were prepared: *Aniline trihydrogen oxalate*,



m. p. 155° (decomp.); *aniline trihydrogen malonate*, m. p. 87—89°; *aniline trihydrogen succinate*, m. p. 127°; *aniline trihydrogen malate*, m. p. 138—139°,  $[\alpha]_D^{18}$  4.1° in water; *aniline trihydrogen tartrate*, m. p. 177°,  $[\alpha]_D^{18}$  15.9° in water. In no case except in that of oxalic acid could the corresponding normal or monohydrogen salt be obtained.

W. E. E.

**Mechanism of the Formation of Thiocarbanilide.** S. J. C. SNEDKER (*J. Soc. Chem. Ind.*, 1925, 44, 74—76T).—A nearly quantitative yield of thiocarbanilide was obtained when equimolecular quantities of aniline and carbon disulphide were heated, whereas the yield was 62% when 2 mols. of aniline and 1 mol. of carbon disulphide were used. These facts do not accord with the view that the reaction occurs according to the equation  $CS_2 + 2NH_2Ph = CS(NHPh)_2 + H_2S$ , nor with the view of Losanitsch (A., 1892, 55) that thiocarbanilide is a secondary product derived from phenylthiocarbimide and aniline. The intermediate product is phenyldithiocarbamic acid,  $NHPh-CS-SH$ , and thiocarbanilide is formed from this by the condensation of 2 mols. with the removal of hydrogen sulphide and carbon disulphide:  $2NHPh-CS-SH \rightarrow NHPh-CS-NPh-CS-SH \rightarrow (NHPh)_2CS$ . When methylaniline is heated with carbon disulphide no thiocarbamide is formed because phenylmethylcarbamic acid has no hydrogen attached to the nitrogen atom. Pure thiocarbanilide was obtained by adding slowly sulphur

dichloride (1 mol.) to a stirred mixture of aniline (4 mols.) and excess of carbon disulphide maintained at 6°. The precipitated aniline hydrochloride was removed and thiocarbamilide separated out in quantitative yield:  $4\text{NH}_2\text{Ph} + \text{CS}_2 + \text{SCL}_2 = 2\text{NH}_2\text{Ph.HCl} + \text{CS}(\text{NHPh})_2 + 2\text{S}$ . The thiocarbamides corresponding with *o*-, *m*-, and *p*-toluidine, *m*- and *p*-chloroaniline, *o*- and *p*-phenetidine, and  $\alpha$ - and  $\beta$ -naphthylamine were prepared. *o*- and *p*-Nitroaniline failed to react.

F. B.

**Nitration by Means of Nitrates.** J. B. MENKE (*Rec. trav. chim.*, 1925, 44, 141—149).—Nitration is effected by means of acetic anhydride (cf. Bamberger, A., 1895, i, 261, 273; Orton, T., 1902, 81, 806) together with an inorganic nitrate, such as ferric, cupric, nickel, cobalt, aluminium, cerium, or uranyl nitrate. The reactions, which may be regulated by choice of a suitable nitrate and temperature, and by diluting the acetic anhydride with acetic acid, yield products free from tar, whilst one nitro compound may be obtained, although other methods may yield a mixture of isomerides. When aniline is treated with crystalline cupric (or ferric) nitrate and acetic anhydride below 30° and then at 30—36°, water precipitates *o*-nitroacetanilide; no oxidation occurs, whereas if a benzene solution of aniline is boiled with cupric nitrate, aniline-black is produced. Similarly, ethyl acetoacetate is nitrated with cupric nitrate and acetic anhydride at 50° and the nitroacetic ester formed is isolated as its potassium salt. Phenol is converted by ferric nitrate and acetic anhydride at 70—85° into picric acid, benzene at 80° into nitrobenzene, chlorobenzene at 40—45° into *p*-chloro-nitrobenzene, and toluene at 40° into *o*-nitrotoluene.

By the use of cupric nitrate and acetyl chloride at —14°, phenol is simultaneously nitrated and chlorinated, yielding 4 : 6-dichloro-2-nitrophenol. The reagent may be modified by dilution with acetic acid, or by using a mixture of acetic acid and a phosphorus halide.

Potassium hydrogen sulphate, aluminium sulphate, and cerium sulphate influence the hydration velocity of acetic anhydride, and a mixture of sulphate with acetic anhydride may therefore be expected to exert a sulphonating action.

F. M. H.

**Relation between Resin-forming Capacity and Chemical Constitution.** W. HERZOG (*Chem.-Ztg.*, 1925, 49, 119—120; cf. A., 1923, i, 1107).—The diarylthiocarbamides,  $\text{CS}(\text{NHR})_2$ , which lose hydrogen sulphide on heating with formation of diarylcarbodi-imides,  $\text{C}(\text{NR})_2$ , form an important group of resin-forming substances, one of which, diphenylcarbodi-imide,  $\text{C}(\text{NPh})_2$ , is a commercial article resembling colophony in its properties. A second group consists of the diarylolefine ketones, such as distyryl ketone, which without exception undergo polymerisation, forming lac resins when heated above their melting points, whilst by continued heating at a higher temperature they are converted into insoluble resins. The addition of further unsaturated groupings to the molecule containing these "resinophore" groups frequently causes the resinification to proceed so rapidly as to become explosive when the required temperature is reached.

P. M.

**Condensation of Phenylethylamine with *s*-Dichlorodimethyl Ether.** W. F. SHORT (*J. Chem. Soc.*, 1925, 127, 269—271).— $\beta$ -Phenylethylamine (2 mols.), prepared by Wohl and Berthold's method (A., 1910, i, 619), was mixed with *s*-dichlorodimethyl ether (1.25 mols.) (cf. Stephen, Short, and Gladding, T., 1920, 117, 513) in dry ether at the ordinary temperature in the presence of zinc chloride, and the mixture heated at 100°. The product, a brown syrup, consisted of tetrahydroisoquinoline (59% yield) (Becker and Decker, A., 1912, i, 844, obtained  $\beta$ -phenylethyldimethylamine) and *di*( $\beta$ -phenylethylamino)methane, m. p. 153° (*diacetyl* derivative, m. p. 191°), corresponding with about 10% of the  $\beta$ -phenylethylamine. A. C.

**Preparation of Primary, Secondary, and Tertiary Amines.** K. KINDLER (D.R.-P. 396453; from *Chem. Zentr.*, 1924, ii, 1404).—Primary, secondary, and tertiary amines are obtained in excellent yield by the electrolytic reduction of acid amides, or of mono- or di-alkyl-substituted acid amides, at 40—50° in the presence of metals, such as arsenic, antimony, bismuth, tin, and lead, which form hydrogen compounds. The reduction is effected in acid solution in an organic solvent miscible with water, and the metal may be present in an electrode or as a salt. Thus benzamide in alcoholic hydrochloric or sulphuric acid in the presence of antimony, with a current density of 0.2—0.3 amp./cm.<sup>2</sup> with a lead cathode is converted quantitatively into benzylamine. Similarly, *N*-methylphenylacetamide yields  $\beta$ -phenylethylmethylamine, b. p. 203°. *N*-Dimethyl-*p*-nitrophenylacetamide gives *p*-aminophenylethyldimethylamine, m. p. 41—42°, b. p. 150°/18 mm., the diazo compound of which on boiling is converted into hordenine, the reaction establishing the constitution of this alkaloid as *p*-hydroxyphenylethyldimethylamine. R. B.

**Reactions of Diphenylamine. Preparation of Diphenylbenzidine. Action of Acids on Diphenylnitrosoamine in Aqueous-Alcoholic Solution.** M. MARQUEYROL and H. MURAOUR (*Mém. Poudres*, 1924, 21, 259—271, 272—276).—These are reprints of papers already abstracted (cf. A., 1914, i, 577, 829). W. A. S.

**Iodine as a Catalyst in Reactions Involving Elimination of Hydrogen Halides.** R. D. DESAI (*J. Indian Inst. Sci.*, 1924, 7, 235—251).—Iodine in small amount catalyses the reaction between some organic halides and primary, secondary, or tertiary amines; in some cases the reaction is assisted by the presence of sodium acetate. With tertiary amines, the replacement of methyl and ethyl by the benzyl radical was effected.

Thus prepared, diphenylbenzylamine has m. p. 88—88.5°. Benzylmethylaniline has b. p. 161—162°/8 mm.,  $d_{20}^{25}$  1.0422,  $n_D^{29.5}$  1.6008, and its picrate m. p. 128—128.5°. The following new substances are described. *Diphenylbenzylamine hydrochloride* and *chloroplatinate*; *p*-nitrodiphenylbenzylamine, m. p. 163°; *diphenyl-p*-nitrobenzylamine, m. p. 93.5°; *diphenyl-p*-aminobenzylamine, a viscid oil, forming a double zinc chloride, an *acetyl* derivative, m. p.

165—166°, and a *benzoyl* derivative, m. p. 136—137°; *as-phenyl-benzyl-p-phenylenediamine*,  $\text{CH}_2\text{Ph}\cdot\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , m. p. 100—101°, its *zinc double chloride*, m. p. 215—220°, *acetyl* derivative, m. p. 201°, and *benzoyl* derivative, m. p. 245—246°; 6-*benzyl-phenthiazine*, m. p. 90.5—91°, and the corresponding *sulphone*, m. p. 211—212°. B. F.

**Action of Hydrohalogen Acids (and Sulphuric Acid) on Arylhydroxylamines.** E. BAMBERGER (*Annalen*, 1925, 441, 297—318).—The experimental basis of results the theoretical significance of which has been previously discussed (A., 1921, i, 723). R. B.

**Nitro Derivatives of *o*-Cresol.** G. P. GIBSON (*J. Chem. Soc.*, 1925, 127, 42—48; cf. A., 1906, i, 837; 1907, i, 1030; 1921, i, 779).—*o*-Cresol has been nitrated at  $-15^\circ$  by Hofmann and Millar's method (A., 1881, 592). That part of the product volatile in steam, m. p. 55—65°, is mainly 3-nitro-*o*-cresol, m. p. 70°, b. p. 102—103°/9 mm., with a small amount of the 3 : 5-dinitro compound. The residue from the steam distillation separated by means of 50% alcohol gives 3 : 5-dinitro-*o*-cresol and 5-nitro-*o*-cresol. The 5-nitro compound is dimorphous and is deposited from hot benzene in yellow needles (unstable form), which on being kept in the mother-liquor changes to the stable variety, large, colourless plates, m. p. 96°; the m. p. of the needles depends on the rapidity of the heating and may be as low as 75°. From aqueous alcohol or acetone, the monohydrate, m. p. 30—40° (cf. Neville and Winther, *Ber.*, 1882, 15, 2978), is deposited. Using a greater proportion of nitric acid (at 0°), the chief nitration product is 3 : 5-dinitro-*o*-cresol with small quantities of the 3- and 5-mononitro compounds. Pure 3 : 5-dinitro-*o*-cresol is obtained free from 5-nitro-*o*-cresol by formation of its sodium salt. *Sodium 3 : 5-dinitro-*o*-tolylloxide* forms yellow, hydrated needles which change to a brick-red powder at 100°. *Sodium 3-nitro-*o*-tolylloxide* (sinters at 100°), *sodium 5-nitro-*o*-tolylloxide*, and *pyridine 3 : 5-dinitro-*o*-tolylloxide*,  $\text{C}_{12}\text{H}_{11}\text{O}_5\text{N}_3$ , m. p. 96°, are described. Derivatives of 5-nitro-*o*-cresol are obtained in good yields by ordinary methods, but probably owing to the proximity of two groups ortho to the reacting hydroxyl group, poor results are obtained for the 3-nitro- and 3 : 5-dinitro-*o*-cresols. 5-Nitro-*o*-tolyl acetate has m. p. 88°; 3-nitro-*o*-tolyl acetate, m. p. 42°; 3 : 5-dinitro-*o*-tolyl acetate, m. p. 96°. Of the *benzoates*, the 5-nitro- has m. p. 128°; the 3-nitro-, m. p. 42°, b. p. 218—220°/9 mm.; the 3 : 5-dinitro- has m. p. 132°. 5-Nitro-*o*-tolyl toluene-*p*-sulphonate has m. p. 107°, the corresponding 3-nitro-, m. p. 66°, b. p. 205—210°/0.5 mm., 257°/11 mm. (decomp.). Very small quantities of 3-nitro-*o*-chlorotoluene and 3 : 5-dinitro-*o*-chlorotoluene (m. p. 63°) are formed at the same time when benzoyl or toluene-*p*-sulphonyl chloride acts on the sodium compounds of the corresponding cresols (cf. Ullmann and Sané, A., 1912, i, 104).

5-Nitro-*o*-tolyl methyl ether has m. p. 64°; Cain and Simonsen (T., 1914, 105, 2390) give 62°. From sodium 3-nitro-*o*-tolylloxide

and methyl sulphate a nearly theoretical yield of the methyl ether, b. p. 121—122°/10 mm., m. p. 30°, is obtained, but if methyl hydrogen sulphate is present the yield is greatly reduced by the formation of sulphonic derivatives. Quantitative methylation takes place with sodium 3:5-dinitro-*o*-tolylxide and methyl sulphate, the occupation of the 5-position hindering the formation of sulphonic derivatives. Good yields of the methyl and ethyl ethers of 3-nitro- and 3:5-dinitro-*o*-cresols are obtained on heating the corresponding anhydrous sodium salts with methyl or ethyl toluene-*p*-sulphonates.

A. C.

### Diazotisation and Nitration of 3:5-Dibromo-*o*-anisidine.

L. ELION and C. JANSSEN, jun. (*Rec. trav. chim.*, 1925, **44**, 192—195; cf. Fuchs, A., 1915, i, 520).—3:5-Dibromo-*o*-anisidine is obtained as a colourless substance, m. p. 27° (Fuchs describes it as a yellow oil), by hydrolysing *aceto*-3:5-dibromo-*o*-anisidide m. p. 185—186°; the *hydrochloride* has m. p. about 200° (decomp.). The hydrobromide, or, better, the base, is mixed with potassium pyrosulphate and diazotised by adding to nitric acid at 0°. Water precipitates a by-product, and the filtrate is reduced, by heating with alcohol in presence of copper sulphate, to 5-bromo-3-nitro-anisole, m. p. 86°, whilst only a very small quantity of 3:5-dibromo-anisole is formed.

F. M. H.

### Mechanism of the Transformation of Phenyl Allyl Ethers.

L. CLAISEN and E. TIETZE (*Ber.*, 1925, **58**, [B], 275—281; cf. A., 1912, i, 965; 1913, i, 1175; 1919, i, 266).—Cinnamyl bromide, m. p. 28.2°, b. p. 130—131°/15 mm., prepared in 80—85% yield by stirring cinnamyl alcohol with hydrobromic acid (48%) at the atmospheric temperature, is converted by methyl-alcoholic sodium phenoxide solution into phenyl cinnamyl ether, m. p. 66—66.5°, b. p. 189—191°/13 mm., the constitution of which is established by its hydrogenation to phenyl  $\gamma$ -phenylpropyl ether. The unsaturated ether is transformed in boiling diethylaniline into *o*- $\alpha$ -phenylallyl-phenol, b. p. 183—185°/12 mm. (*phenylcarbamate*, m. p. 91—91.5°), which is converted by glacial acetic and hydrobromic acids into 3-phenyl-2-methylcoumaran, b. p. 167—168°/13 mm., 306°/760 mm. The presence of the phenyl group in the  $\alpha$ -position in the side-chain of the phenol follows from the non-identity of the compound and its derivatives with *o*- $\gamma$ -phenylallylphenol and its derivatives (obtained by the action of cinnamyl bromide on sodium phenoxide in the presence of benzene). In a similar manner, *p*-tolyl cinnamyl ether is transformed into 3- $\alpha$ -phenylallyl-*p*-cresol, b. p. 191°/12.5 mm. (*phenylcarbamate*, m. p. 113.5—114.5°). It is thus established that in certain (and probably all) cases of indirect transformation the side-chain becomes attached to the benzene nucleus at the terminal carbon atom instead of at that which was previously attached to the oxygen atom. Union cannot, however, occur previous to the disruption of the molecule, since this would yield chromanes which are very stable and not convertible into allyl-phenols.

H. W.

*p*\*

**Sulphur Phenyl Chloride [Chlorothiolbenzene]. II.** H. LECHER [with F. HOLSCHNEIDER, K. KÖBERLE, W. SPEER, and P. STÖCKLIN] (*Ber.*, 1925, **58**, [B], 409—416; cf. A., 1924, i, 728).—Chlorothiolbenzene may be prepared by the action of chlorine on diphenyl disulphide dissolved in carbon tetrachloride, but the process is less advantageous than the preparation from thiophenol. *p*-Thioltoluene and chlorine yield *p*-chlorothioltoluene, b. p. 77·5—78·5°(corr.)/2·5 mm., but a similar method cannot be applied to 2-thiolnaphthalene, which, under these conditions, gives 1-chloro-2-chlorothiolenaphthalene (cf. Zincke and Eismayer, A., 1918, i, 385). Bromothiolbenzene is prepared in small yield by the action of bromine on thiophenol dissolved in carbon tetrachloride, but the product is too unstable to be isolated, and its formation is established by its conversion into benzenesulphendiethylamide. Chlorothiolbenzene is converted by dilute sodium hydroxide solution into diphenyl disulphide and benzenesulphinic acid (benzenesulphenic acid is doubtless produced primarily) and by methylalcoholic sodium methoxide solution into diphenyl disulphide and methyl benzenesulphenate,  $C_6H_5 \cdot S \cdot OMe$ , b. p. 88—89°(corr.)/4 mm. By a complicated change phenol and chlorothiolbenzene give diphenyl disulphide and *p*-hydroxydiphenyl sulphide, which is isolated as its methyl ether. With silver benzenesulphinate, chlorothiolbenzene gives diphenyl disulphoxide, m. p. 43·5—45°. Magnesium phenyl bromide converts chlorothiolbenzene and chlorothiol-*p*-toluene into diphenyl sulphide and phenyl *p*-tolyl sulphide, respectively. Ethylene is readily absorbed by a solution of chlorothiolbenzene in carbon tetrachloride at the atmospheric temperature with production of phenyl  $\beta$ -chloroethyl sulphide, b. p. 122°/13 mm.; *p*-tolyl  $\beta$ -chloroethyl sulphide, prepared similarly, has b. p. 139·5—140·5°(corr.)/17 mm., whereas *o*-nitrophenyl  $\beta$ -chloroethyl sulphide, prepared in ethylene bromide solution at 100°, has m. p. 50—52°. The physiological properties of the chloro compounds resemble those of di- $\beta$ -chloroethyl sulphide. Benzenesulphendimethylamide,  $C_6H_5 \cdot S \cdot NMe_2$ , b. p. 63·5—64°(corr.)/3 mm., is prepared by the interaction of chlorothiolbenzene and dimethylamine in anhydrous ether. Benzenesulphenanilide, m. p. 53—55°, and *p*-toluenesulphenanilide, m. p. 80—81°, are obtained in ethereal solution; nitrous acid converts *p*-toluenesulphenanilide into *pp'*-ditolyl disulphoxide, m. p. 75·5—77°. The action of ammonia on chlorothiolbenzene in the presence of ether leads mainly to the production of benzenesulphenimide,  $(Ph \cdot S)_2NH$ , m. p. 126·5—128°(corr.) after softening at 120°; the amide could not be isolated. *p*-Toluenesulphenimide, m. p. 103° (decomp.), was not obtained in the homogeneous condition.

H. W.

**Valency Problem of Sulphur. VIII.** H. LECHER (*Ber.*, 1925, **58**, [B], 417—422).—Attempts to apply to compounds of sulphur those methods (such as replacement of the group R in the compounds  $RX \cdot XR$  by the group  $RX \cdot$ ) which have been shown to promote dissociation into radicals in the cases of compounds of nitrogen and carbon (cf. Goldschmidt, A., 1920, i, 257; Schlenk

and Mark, A., 1922, i, 1002), have failed to give any evidence of the existence of radicals with univalent sulphur. It appears that atoms and groups of atoms which readily give anions by union with electrons and therefore have a marked affinity for electrons are incapable of existence as free atoms or radicals.

[With F. HOLSCHNEIDER.]—Diphenyl trisulphide, prepared by the action of thiophenol on sulphur dichloride, is obtained in an approximately homogeneous form by repeatedly freezing out the crude product from ether; it has m. p. about  $-5^{\circ}$ . Attempts to prepare the compound from sulphonylbisdiethylamide, thiophenol, and hydrogen chloride or by the action of hydrogen sulphide on thiocyanothiolbenzene or chlorothiolbenzene were less successful. It is decomposed by mercury at the atmospheric temperature into mercury sulphide and diphenyl disulphide. Diphenyl tetrasulphide can be obtained in the crystalline condition, m. p.  $34-35^{\circ}$ , by the interaction of highly purified thiophenol and sulphur chloride in anhydrous ether. It is an unstable substance which is decomposed by mercury at the atmospheric temperature into diphenyl disulphide and sulphur. The molecular weight in freezing benzene is normal and cannot be determined at higher temperatures owing to decomposition. Colour and thermochromism are such as would be expected from diphenyl tetrasulphide; there is no indication of a pronounced colour change suggesting the formation of radicals.

H. W.

**Valency Problem of Sulphur. IX. New Class of Organic Radicals.** H. LECHER, K. KÖBERLE, and P. STÖCKLIN (*Ber.*, 1925, **58**, [B], 423—424).—If a solution of benzenesulphenimide,  $(\text{PhS})_2\text{NH}$ , in anhydrous ether or benzene is shaken with lead peroxide and potassium carbonate an intensely violet solution is formed which does not obey Beer's law. On evaporation of the solutions, colourless crystals are obtained which give violet solutions in indifferent media. The crystals doubtless contain the hydrazine  $(\text{PhS})_2\text{N}\cdot\text{N}(\text{SPh})_2$  which is extensively dissociated in solution into radicals with bivalent nitrogen. The isolation of the hydrazine has not been effected, since the imide is oxidised only slowly by lead peroxide to which the radical itself is not indifferent. Silver oxide dehydrogenates the imide slowly and decomposes the radical instantaneously. *o*-Nitrobenzenesulphenimide under similar conditions gives a reddish-violet solution which is decolorized by nitric oxide and triphenylmethyl, and doubtless contains the corresponding radical. *p*-Toluenesulphenanilide gives a red solution when shaken with lead peroxide in the presence of benzene or ether.

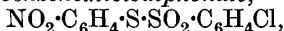
H. W.

**Constitution of Disulphoxides. II.** C. J. MILLER and S. SMILES (*J. Chem. Soc.*, 1925, **127**, 224—233; cf. A., 1924, i, 275).—Formula (I) has usually been adopted for the disulphoxides, although much evidence has been brought forward in favour of (II) (cf. Gibson and Smiles, *loc. cit.*; Zincke, A., 1912, i, 763).

(I)  $\text{Ar}\cdot\text{S}\cdot\text{S}\cdot\text{Ar}$ , (II)  $\text{Ar}\cdot\text{SO}_2\cdot\text{S}\cdot\text{Ar}$ , (III)  $\text{Ar}\cdot\text{S}\cdot\text{O}\cdot\text{S}\cdot\text{Ar}$ . Conclusive



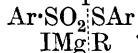
evidence for (II) is now given. The following disulphoxides were prepared, those with dissimilar groups by the reaction of a silver sulphinate with the appropriate sulphur chloride: *o*-nitrophenyl *p*-toluenethiolsulphonate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4\text{Me}$ , m. p.  $97^\circ$ ; alcoholic solution becomes blue with aqueous sodium hydroxide; *o*-nitrophenyl *p*-chlorobenzenethiolsulphonate,



m. p.  $123^\circ$ ; *o*-nitrophenyl 2:5-dichlorobenzenethiolsulphonate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_3\text{Cl}_2$ , m. p.  $142^\circ$ ; 2:5-dichlorophenyl *o*-nitrobenzenethiolsulphonate,  $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{S} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , m. p.  $129^\circ$ ; 2:5-dichlorophenyl 2:5-dibromobenzenethiolsulphonate,



m. p.  $119^\circ$ ; 2:5-dibromophenyl 2:5-dichlorobenzenethiolsulphonate,  $\text{C}_6\text{H}_3\text{Br}_2 \cdot \text{S} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_3\text{Cl}_2$ , m. p.  $125^\circ$ . Sulphur 2:5-dichlorophenyl chloride,  $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{S} \cdot \text{Cl}$ , golden-yellow needles, m. p.  $32-33^\circ$ , is prepared by saturating a solution of the corresponding disulphide in carbon tetrachloride with chlorine; sulphur 2:5-dibromophenyl bromide was obtained similarly as yellow crystals, but was too unstable for analysis, losing bromine with formation of disulphide. The disulphoxides react readily with Grignard reagents and high yields (63–90%) of the sulphinic acids have been obtained in every case examined, fission of the disulphoxide taking place apparently according to the scheme

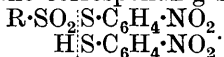


the symmetrical formula,  $\begin{array}{c} \text{ArSO} \cdot \text{SO} \cdot \text{Ar} \\ \text{IMg} \cdot \text{R} \end{array}$ , fission of the molecule

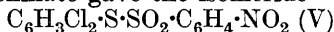
should result in a sulfoxide, and this has not been observed. The fate of the thioaryl group of the disulphoxide depends on the magnesium compound used; with magnesium methyl iodide the aryl methyl sulphide,  $\text{Ar} \cdot \text{S} \cdot \text{Me}$ , was usually obtained, but with magnesium phenyl iodide the disulphide and diphenyl were also observed. The substances were identified by comparison with authentic samples and by conversion into the methylsulphones. *p*-Chlorophenylmethylsulphone,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{SO}_2\text{Me}$ , has m. p.  $96^\circ$ ; 2:5-dichlorophenylmethylsulphone,  $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{SO}_2\text{Me}$ , m. p.  $88^\circ$ . The argument that since the disulphoxides on reduction give disulphides the structure should be represented by (I) (cf. Hinsberg, A., 1908, i, 875; 1909, i, 6, 374; Fries, *ibid.*, 1914, i, 676) is shown to be insufficient, and accords equally with the thiosulphonate (II) structure. Experiments are described which show that fission of the molecule takes place during reduction with hydrogen iodide (cf. Hinsberg); for example, when *o*-nitrophenyl *p*-toluenethiolsulphonate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{SO}_2 \cdot \text{C}_7\text{H}_7$ , and *o*-nitrophenyl *p*-chlorobenzenethiolsulphonate,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4\text{Cl}$ , are reduced, a good yield of *o*-nitrophenyl disulphide is obtained in both cases and in the case of the chloro derivative *p*-chlorophenyl disulphide is also formed. This does not favour the symmetrical and exclude the unsymmetrical structure. Using milder conditions of reduction, it is found that nitrophenyl toluenethiolsulphonate yields *p*-toluenesulphinic acid and *o*-nitrophenyl disulphide,  $2\text{C}_7\text{H}_7 \cdot \text{SO}_2 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \rightarrow 2\text{C}_7\text{H}_7 \cdot \text{SO}_2\text{H} + (\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S})_2$ , whilst nitrophenyl chlorobenzene-



thiolsulphonate gives *p*-chlorobenzenesulphinic acid and the nitro-disulphide; this is in accordance with (II), but from the symmetric structure (I) two sulphinic acids would be expected. A number of examples of these reductions is given, only one sulphinic acid being obtained in each case. The action of mercaptans with these disulphoxides is closely analogous (cf. Smiles and Gibson, A., 1924, i, 275). *o*-Nitrophenyl mercaptan yields in both cases the *o*-nitrophenyl disulphide and the corresponding sulphinic acid:



Other disulphoxides are shown to act similarly, the yields of the products being of the order of 80% of theory. To establish more firmly the unsymmetrical constitution, disulphoxides each containing different aromatic groups have been synthesised by alternate methods. Sulphur *o*-nitrophenyl chloride and silver 2 : 5-dichlorobenzenesulphinate gave the compound  $\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{SO}_2\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$  (IV), (m. p. 142°), whilst sulphur 2 : 5-dichlorobenzene chloride and silver *o*-nitrobenzenesulphinate gave the isomeride



(m. p. 129°). On treatment with *o*-nitrophenyl mercaptan, (IV) gave a dichlorosulphinic acid whilst (V) gave a nitrosulphinic acid. Summarising the results of these and other experiments it is claimed that an asymmetric structure must be assigned to the disulphoxides, and that whilst (II) agrees with all the facts discovered there is good reason for discarding (III) (cf. Fries, *loc. cit.*). A. C.

**Preparation of Benzylresorcinol.** H. HIRZEL (Brit. Pat. 222136).—By reduction of benzoylresorcinol, m. p. 143—144°, with zinc amalgam and a mineral acid, *benzylresorcinol*, m. p. 78—79°, b. p. 220—222°/10 mm., is formed. [Cf. B., 1925, 265.]

B. W. A.

**Preparation of Polyalkylhydroxyarylamino propanes or their N-Monoalkyl Derivatives.** E. MERCK, O. WOLFES, and A. DÜTZMANN (D.R.-P. 398011; from *Chem. Zentr.*, 1924, ii, 1403).—An extension of the procedure of D.R.-P. 274350 (A., 1915, i, 11) to allylpolyphenols containing two or more alkoxy groups in the nucleus. Thus elemicine (3 : 4 : 5-trimethoxy-1-allylbenzene) with hydrobromic acid at 0° yields 3 : 4 : 5-trimethoxy-1- $\gamma$ -bromopropylbenzene, a viscous, heavy oil, which with alcoholic methylamine under pressure at 100° yields 3 : 4 : 5-trimethoxy-1- $\gamma$ -methylaminopropylbenzene, m. p. 61—62°, b. p. 171—173°/15 mm. Alcoholic ammonia at 100—120° converts this into 3 : 4 : 5-trimethoxy-1- $\gamma$ -aminopropylbenzene, a viscous, highly refracting oil, b. p. 174°/15 mm., which resembles mezcaline. R. B.

**Action of X-Rays on Cholesterol.** A. F. ROFFO (*Compt. rend.*, 1924, 180, 228—229).—When cholesterol, dissolved in chloroform or benzene, is exposed to X-rays it is decomposed. Solid cholesterol is unaffected. Soft, unfiltered rays are the most active. Ozone or nascent oxygen has no effect on cholesterol under similar con-

ditions. The product of the action of the X-rays is a dark green, oleaginous mass, having an aromatic odour. W. A. S.

**Sitosterol.** A. WINDAUS and J. BRUNKEN (*Z. physiol. Chem.*, 1924, **140**, 52—56).—Products corresponding with those obtained from cholesterol (A., 1919, i, 203) have been prepared from sitosterol (A., 1918, i, 388) by submitting this substance to the same treatment. This confirms the view that the portions of the molecules of the two sterols which are susceptible to chemical attack are structurally identical. The side-chains also appear to be identical; sitosterol, like cholesterol, yields acetone and probably also methyl isohexyl ketone on energetic oxidation.

Sitosteryl chloride (Burian, A., 1898, i, 72), after repeated recrystallisation, melts at 92—94°, but the m. p. does not remain constant, probably owing to the formation of two stereoisomerides. Both evidently yield the same sitostene, since this substance melts sharply at 76—77°. Nitration of the latter in acetic acid suspension with fuming nitric acid (*d* 1.50) yields *nitrositostene*,  $C_{27}H_{45}O_2N$ , m. p. 89—89.5°, which is reduced by zinc dust in boiling 90% acetic acid to *heterositostanone*,  $C_{27}H_{46}O$ , m. p. 105—106° (*oxime*, m. p. 191—192°). Oxidation of heterositostanone with a mixture of fuming nitric (*d* 1.50) and acetic acids gives a *dicarboxylic acid*,  $C_{27}H_{46}O_4$ , m. p. 278° (decomp.) after sintering at 268°, which is converted by Blanc's method into an *anhydride*,  $C_{27}H_{44}O_3$ , m. p. 154—154.5°. The acid is regenerated from the anhydride by warming with potassium hydroxide and acidifying. E. S.

**Stigmasterol.** A. WINDAUS and J. BRUNKEN (*Z. physiol. Chem.*, 1924, **140**, 47—51).—Stigmasteryl acetate (A., 1907, i, 129), on reduction with hydrogen in the presence of platinum black, takes up four atoms of hydrogen with the formation of *tetrahydrostigmasteryl acetate*, m. p. 128°. Hydrolysis of this yields *tetrahydrostigmasterol* (*stigmastanol*),  $C_{30}H_{54}O$ , m. p. 134—134.5°. The latter is oxidised by chromic acid to *stigmastanone*,  $C_{30}H_{52}O$ , m. p. 155—155.5°, which forms an *oxime*,  $C_{30}H_{53}ON$ , m. p. 215—216°, and to a *dicarboxylic acid*,  $C_{30}H_{52}O_4$ , m. p. 229—230°. When distilled at 2 mm., the latter loses carbon dioxide and water and yields a *ketone*,  $C_{29}H_{50}O$ , m. p. 110—111° (*oxime*,  $C_{29}H_{51}ON$ , m. p. 208.5—210.5°). *Stigmastane*,  $C_{30}H_{54}$ , m. p. 84—84.5°, is formed by the reduction of stigmastanone with zinc amalgam and hydrochloric acid in boiling acetic acid solution.

Stigmasterol thus resembles sitosterol and cholesterol in containing a secondary alcohol group which is present in a six-membered ring. It is also evident from the formula of stigmastane that this substance, like cholestane and sitostane, contains four reduced rings. E. S.

**Preparation of [Citric] Esters.** F. HEFTI and W. SCHILT (Brit. Pat. 227232).—Citric acid or a salt thereof, heated, under suitable conditions, with a benzylating agent, yields benzyl esters, chiefly *tribenzyl citrate*, m. p. 51°. *Dibenzylcitric acid*, obtained from the mother-liquor, forms sparingly soluble calcium, ferric, and silver salts. B. W. A.

**Grignard's Reaction in Presence of Water.** H. SCHMALFUSS and M. WETZEL (*J. pr. Chem.*, 1925, [ii], 109, 158—160).—In the preparation of diphenylmethylcarbinol from benzophenone, the authors obtained a yield of 98%, using moist ether. In the same way, from magnesium methyl chloride and ethyl benzoate yields of 37% and 38% of phenyldimethylcarbinol, using dry and moist ether, respectively, were obtained. With moist ethyl bromide, a 64% yield of phenyldiethylcarbinol was obtained, against 53% in the absence of moisture. Using a sufficient excess of Grignard reagent to allow for its decomposition by the water in the ether, moist ether can accordingly be used in the Grignard reaction.

R. B.

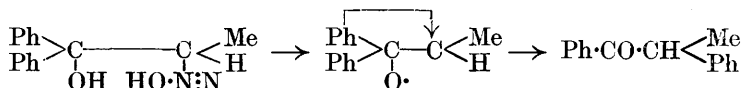
**Polyarylated Vinylcarbinols and their Derivatives. V. Anomalous Etherification in the Triphenylallyl Series.** K. ZIEGLER (*Ber.*, 1925, 58, [B], 359—361; cf. Ziegler and Ochs, A., 1922, i, 1047).—Crude diphenylstyrylcarbinol, obtained by the action of magnesium  $\beta$ -styryl bromide on benzophenone in ethereal solution (cf. Ziegler, A., 1922, i, 151; Meyer and Schuster, A., 1922, i, 540), is readily converted by sulphuric acid and methyl alcohol into a methyl ether, m. p. 97—98°, which is identical with Meyer and Schuster's "diphenylstyrylcarbinol" and with the product of the methylation of  $\alpha\gamma$ -triphenylallyl alcohol (Ziegler, Grabbe, and Ulrich, this vol., i, 131). In one of the cases, therefore, etherification must be accompanied by migration of the double bond. The substance obtained by the action of hydrogen chloride on the methyl ether from  $\alpha\gamma$ -triphenylallyl alcohol appears beyond doubt to be  $\alpha\gamma$ -triphenylallyl chloride.

H. W.

### Conversion of Amino-acids into Tertiary Amino-alcohols.

A. MCKENZIE and G. O. WILLS (*J. Chem. Soc.*, 1925, 127, 283—295; cf. McKenzie and Richardson, T., 1923, 123, 79; McKenzie and Roger, A., 1924, i, 650; McKenzie and Dennler, this vol., i, 26).—The product of the action of nitrous acid on  $\beta$ -amino- $\alpha\alpha$ -diphenylethyl alcohol, thought to be *as*-diphenylethylene oxide by Paal and Weidenkaff (A., 1905, i, 436) and shown to be deoxybenzoin by Bettzieche (this vol., i, 251), is probably formed by semipinacolinic deamination (cf. McKenzie and Richardson, *loc. cit.*) on the lines of the scheme given below.

$\beta$ -Amino- $\alpha\alpha$ -diphenyl-*n*-propyl alcohol,  $C_{15}H_{17}ON$ , m. p. 101.5—102.5°, was prepared from ethyl *r*-alanine hydrochloride and magnesium phenyl bromide. On deamination by means of nitrous acid it was converted into methyldeoxybenzoin, m. p. 50—51°,



identical with that prepared by McKenzie and Roger (*loc. cit.*) by the dehydration of methylhydrobenzoin with concentrated sulphuric acid. On further treatment with magnesium phenyl bromide, it formed  $\alpha\alpha\beta$ -triphenylpropyl alcohol, m. p. 86.5—87.5°

(Levy, A., 1921, i, 860). The optically active  $\beta$ -amino- $\alpha\alpha\beta$ -triphenylethyl alcohols have now been prepared from the corresponding ethyl *d*- and *l*-phenylaminoacetates. The resolution of the *r*-phenylaminoacetic acid into its optically active components was carried out by means of Reychler's *d*-camphor- $\beta$ -sulphonic acid by the method of Betti and Mayer (A., 1908, i, 639) as modified by Ingersoll and Adams (A., 1923, i, 200). *l*-Camphorsulphonic acid combines with *l*-phenylaminoacetic acid to form a salt having  $[\alpha]_D -71.7^\circ$ . The diastereoisomeric salt from *d*-camphorsulphonic acid and *l*-phenylaminoacetic acid has  $[\alpha]_D -44.07^\circ$  in water. Ethyl *l*-phenylaminoacetate hydrochloride is described by Fischer and Weichhold (A., 1908, i, 419) as dextrorotatory,  $[\alpha]_D^{20} +88.95^\circ$  in water, probably a typographical error, as it is now found to have  $[\alpha]_D -89.3^\circ$  and Marvel and Noyes (A., 1921, i, 15) give  $[\alpha]_D -84.6^\circ$ . Ethyl *d*-phenylaminoacetate hydrochloride has  $[\alpha]_D +90.7^\circ$ .

*d*- $\beta$ -Amino- $\alpha\alpha\beta$ -triphenylethyl alcohol,  $C_{20}H_{19}ON$ , has m. p. 129.5—130°,  $[\alpha]_D^{15} -243^\circ$  in chloroform,  $[\alpha]_D^{17.5} -233^\circ$  in benzene, the sign of rotation being opposite to that of the ester hydrochloride from which it was made by the action of magnesium phenyl bromide. There is no configurative change here, since there is no substitution of a group directly attached to the asymmetric carbon atom. The *l*-ester hydrochloride of phenylaminoacetic acid gave *l*- $\beta$ -amino- $\alpha\alpha\beta$ -triphenylethyl alcohol, m. p. 129.5—130°,  $[\alpha]_D^{15.5} +243^\circ$  in chloroform,  $[\alpha]_D^{15} +234^\circ$  in benzene. The action of nitrous acid on the *d*-amino-alcohol gives the optically inactive (owing to semipinacolinic deamination) phenyldeoxybenzoin, m. p. 134—135°. The following isomeric camphorsulphonates of the *d*- and *l*-amino-alcohols are described: *l*- $\beta$ -Amino- $\alpha\alpha\beta$ -triphenylethanol *d*-camphorsulphonate,  $C_{10}H_{16}O_4S$ , m. p. 200—201°,  $[\alpha]_D^{17} +121^\circ$  in ethyl alcohol; *d*- $\beta$ -amino- $\alpha\alpha\beta$ -triphenylethanol *l*-camphorsulphonate, m. p. 200—201° (decomp.)  $[\alpha]_D^{15} -119^\circ$  in ethyl alcohol; *l*- $\beta$ -amino- $\alpha\alpha\beta$ -triphenylethanol *l*-camphorsulphonate, m. p. 213.5—214.5° (decomp.),  $[\alpha]_D^{16.5} +76^\circ$ ; *d*- $\beta$ -amino- $\alpha\alpha\beta$ -triphenylethanol *d*-camphorsulphonate, m. p. 213.5—214.5°,  $[\alpha]_D^{15} -76^\circ$ . The concentrations employed in the determination of specific rotatory power were necessarily low, so that the values have little significance. The resolution of the *r*-alcohol by *d*-camphor- $\beta$ -sulphonic acid was too slow and imperfect to be used for the preparation of the *d*- and *l*-amino-alcohols.  $\beta$ -Amino- $\alpha\alpha\beta$ -triphenylpropyl alcohol,  $C_{21}H_{21}ON$ , m. p. 113—114°, is obtained by the action of magnesium phenyl bromide on  $\alpha$ -aminohydratropic acid. *r*- $\beta$ -Amino- $\alpha\alpha$ -diphenyl- $\beta$ -benzylethyl alcohol (cf. McKenzie and Richardson, *loc. cit.*) was prepared in a similar way from *r*-phenylalanine. By the action of magnesium phenyl bromide,  $\alpha$ -phenylalanine was converted into *d*- $\beta$ -amino- $\alpha\alpha$ -diphenyl- $\beta$ -benzylethyl alcohol, m. p. 143—144°,  $[\alpha]_D^{16.5} +85^\circ$  in chloroform,  $[\alpha]_D^{19} +105.3^\circ$  in benzene.

Ethyl *l*-phenylaminoacetate hydrochloride after hydrolysis with ethyl-alcoholic potassium hydroxide had  $[\alpha]_D -12.4^\circ$ , whereas the pure *l*-acid has  $[\alpha]_D -157.8^\circ$ . The racemisation is attributed to the attachment of a phenyl and migrational hydrogen atom to the

same asymmetric carbon atom. Sodium nitrite allowed to act on an acid solution of *l*-phenylaminoacetic acid for 23 hours in the cold did not cause any appreciable racemisation.

Ethyl *l*-phenylaminoacetate when deaminated by the method of Fischer and Weichhold gave ethyl mandelate having  $[\alpha]_D +9^\circ$  (approx.); this is in agreement with the results of these workers (A., 1908, *loc. cit.*) and at variance with those of Marvel and Noyes (A., 1921, i, 15), who obtained a levorotatory product. A repetition of the experiment by the method of Marvel and Noyes also resulted in a levorotatory product (which, however, was contaminated with a nitrogen compound, probably a diazo compound), due to a too rapid isolation of the ethyl mandelate. Fischer and Weichhold's conclusion  $d\text{-CHPh(NH}_2\text{)}\cdot\text{CO}_2\text{Et} \rightarrow l\text{-CHPh(OH)}\cdot\text{CO}_2\text{Et}$  is therefore correct (cf. McKenzie and Clough, T., 1909, 95, 777). A. C.

**Preparation of Condensation Products of the Indophenol Type.** L. CASSELLA & Co., G. M. B. H., and B. HELMERT (D.R.-P. 397814; from *Chem. Zentr.*, 1924, ii, 1407—1408).—Phenyl alkyl ethers or phenylalkylamines, including alkylcarbazoles, which contain a free para position and are substituted in the alkyl side-chain, are condensed with *p*-nitrosophenol in the presence of sulphuric acid, *d* 1.71, or hydrochloric acid to form indophenols which can be used for the preparation of sulphur dyes. The indophenols obtained from *p*-nitrosophenol and phenyl hydroxyethyl ether, phenyl  $\beta$ -bromoethyl ether, hydroxyethylaniline, *m*-tolyl hydroxyethyl ether, ethyl carbazole-9-acetate, *o*-chlorophenyl hydroxyethyl ether, from 6-nitroso-*m*-cresol and phenyl hydroxyethyl ether, and from 2-chloro-4-nitrosophenol and hydroxyethylaniline are described. *m*-Tolyl hydroxyethyl ether, from sodium *m*-tolyl oxide and ethylene dichloride, has b. p. 250—255°.

R. B.

### Halochromism of Triphenylmethane and Azo Compounds.

**X. Thiophenols and the Bathochromic Effect of the Alkylmercapto Group.** K. BRAND, O. STALLMANN, W. GROEBE, and H. STEIN (*J. pr. Chem.*, 1925, [ii], 109, 1—40).—A comparison of the auxochromic effect of the methylthiol group with that of the methoxyl and of the dimethylamino group in halochromic solutions of azoanisoles, azophenyl methyl sulphides, methoxy-, methylthiol-, and dimethylamino-triphenylcarbinols, using a König-Martens spectrometer, confirms the greater bathochromic effect of the methylthiol group. *o*- and *p*-Nitroanisole in acetic acid, and *o*- and *p*-nitrophenyl methyl sulphide, all show halochromism on addition of sulphuric or hydrochloric acid, probably through the addition of acid to the oxygen of the nitro group, *e.g.*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\ldots\text{HX}$  and  $\text{SMe}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\ldots\text{HX}$  (cf. Cherbuliez, A., 1923, i, 452), since the *o*-nitrophenyldimethylsulphonium halides are colourless. The absorption curves of azoxyanisole and azoxyphenyl methyl sulphide also confirm the greater auxochromic power of the methylthiol group, but halochromism could not be established with these compounds, owing to their conversion by acid into the corresponding azo compounds. *oo'*-Azoanisole shows a

maximum absorption at  $\lambda$  490, *pp'*-azoanisole at  $\lambda$  500; in the corresponding *oo'*- and *pp'*-azophenyl methyl sulphides these maxima are shifted to  $\lambda$  620 and  $\lambda$  577, but probably on account of hydrolysis, the molecular extinction at the maximum of *oo'*-azophenyl methyl sulphide is smaller than that of *oo'*-azoanisole. *o*-Methoxytriphenylcarbonium chloride in a mixture of acetic and sulphuric acids has a band at  $\lambda$  550; the *oo'*-dimethoxy compound shows maxima at  $\lambda$  577 and 495, and the *oo'o''*-trimethoxy compound shows only one large band between the positions of the bands of the *oo'*-dimethoxy compound. The corresponding *o*-methylthioltriphenylcarbonium chlorides all show similar absorption curves with minima in the visible spectrum at about  $\lambda$  510, but show no maxima in the visible spectrum. With the para-substituted derivatives of triphenylcarbinol in acetic-hydrochloric acid solution, the introduction of the first methoxyl group produces a maximum at  $\lambda$  470; with a second methoxyl group the band is moved to  $\lambda$  550, whilst with a third methoxyl group the maximum retreats to  $\lambda$  480, and the molecular extinction decreases. Similarly, the first methylthiol group produces a maximum at  $\lambda$  546, which is moved to  $\lambda$  600 by the introduction of a second methylthiol group, whilst a fresh maximum appears at  $\lambda$  470. A third methylthiol group decreases the molecular extinction and the curve shows only one maximum, at  $\lambda$  577. In the same way, whilst *p*-dimethylaminotriphenylcarbonium chloride shows no maximum in the visible spectrum, the introduction of a second dimethylamino group (giving malachite-green) produces a maximum at  $\lambda$  620, which with a third dimethylamino group (giving crystal-violet) retreats to  $\lambda$  590. The absorption curves of these two typical triphenylmethane dyes thus show absorption bands corresponding very closely in position, breadth, and height with those observed for the *pp'*- and *pp'p''*-trimethylthioltriphenylcarbonium chlorides. The second, less pronounced, band observed in the curve for *pp'*-dimethylthioltriphenylcarbonium chloride is probably analogous to that reported by Hantzsch (A., 1919, ii, 255) in the curve for malachite-green on the ultra-violet limits of the visible spectrum.

The apparent hypsochromic effect of the third dimethylamino group in crystal-violet is due to the band at  $\lambda$  620 being pushed into the infra-red region whilst the band observed by Hantzsch advances from the limits of the ultra-violet to  $\lambda$  590. The third dimethylamino group thus acts consistently with the first two as a bathochrome, and a similar interpretation is placed on the successive replacement of the hydrogen atoms by *p*-methoxyl, *p*-methylthiol, and *o*-methoxyl groups. In view of these regular changes in the optical properties of the triphenylcarbonium chlorides through the introduction of auxochromic groups, the authors regard the basic triphenylmethane dyes as possessing a constitution fundamentally the same as the other triphenylcarbonium salts (cf. Kaufmann, A., 1912, i, 397) and the general formula  $[\text{Ar}_3\text{C}]\text{X}$  is taken to represent the structure of all members of the group, from triphenylcarbonium chloride to crystal-violet. The structure of the inner complex  $\text{Ar}_3\text{C}$  is regarded as undetermined.

These views are confirmed by results by Baeyer and Villiger's method (A., 1902, i, 769) on the stability of the *o*-methylthiol-, *o*-methoxy-, *o*-ethylthiol-, and 5-chloro-2-methylthiol-triphenylcarbonium salts towards hydrolysis. The absolute values for the stability vary with the nature of the anion, but the order of relative stability is independent of the anion and rises in the order ethylthiol-, methylthiol-, and methoxy-triphenyl carbonium salts. In these three cases, the stability increases with the number of substituent groups; with 5-chloro-2-methylthioltriphenylcarbonium salts, the stability decreases with the number of chlorine atoms present, and the stability values are less than those for the unsubstituted triphenylcarbonium salts. This is in accordance with the decrease in colour intensity with the number of chlorine atoms previously observed and indicates that the *m*-chlorine atom exercises a stronger influence on both optical properties and stability than the *o*-methylthiol group. In the *p*-methoxy and *p*-methylthiol series the stability increases regularly with the number of substituent groups, but not in accordance with Baeyer's power law: the following numerical relations obtain: *p*-methylthiol,  $(1+n)$ ; *pp'*-dimethylthiol,  $(1+n)^2$ ; *pp'p''*-trimethylthiol,  $(1+n)^2$ ; *p*-methoxy,  $(1+n)$ ; *pp'*-dimethoxy,  $(1+n)^5$ ; *ppp'*-trimethoxy,  $(1+n)^5$ . These results indicate that all three aryl groups in the salts possess similar constitutions. The *p*-methylthioltriphenylcarbonium salts are less stable to hydrolysis than the *p*-methoxytriphenylcarbonium salts and do not approach the *p*-dimethylaminotriphenylcarbonium salts in stability. There is thus no direct connexion between optical properties and stability towards hydrolysis in these triphenylcarbonium salts, although within most of the series the colour changes with substitution are parallel with the stability towards hydrolysis (cf. Stobbe and Haertel, A., 1910, i, 43).

The absorption curve of *pp'*-azoanisole shows some resemblance to that of *pp'p''*-trimethoxytriphenylcarbonium chloride, and that of *pp'*-azophenyl methyl sulphide in hydrochloric acid resembles the curve for *pp'p''*-trimethylthioltriphenylcarbonium chloride; on these grounds the authors support formulæ  $\left[ \begin{array}{c} \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \\ \text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \end{array} \right] \text{Cl}$  and  $\left[ \begin{array}{c} \text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \\ \text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \end{array} \right] \text{Cl}$  similar to those advanced by Hantzsch (*loc. cit.*).

R. B.

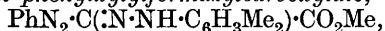
**Di-*sec*.-butylaminoalkyl Esters of Aromatic Acids.** R. ADAMS, E. H. VOLWILER, and R. L. JENKINS (U.S. Pat. 1513730).—Condensation of ethylene chlorohydrin with di-*sec*.-butylamine yields  $\beta$ -di-*sec*.-butylaminoethyl alcohol, b. p. 225–226°/750 mm. (*p*-aminobenzoate hydrochloride, m. p. 185–187°; benzoate hydrochloride, an oil).  $\gamma$ -Di-*sec*.-butylaminopropyl *p*-aminobenzoate hydrochloride has m. p. 164–165°.

CHEMICAL ABSTRACTS.

**Ethyl Ester of  $\alpha$ -Phenyl-*p*-nitrocinnamic Acid.** F. RANFALDI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 38–42).—This ester forms crystals which belong to the prismatic class of the mono-

clinic system,  $a : b : c = 1.82871 : 1 : 0.91775$ ,  $\beta = 69^\circ 29'$ , and differ appreciably from those of the corresponding methyl ester, m. p.  $141-142^\circ$  (cf. Scacchi, A., 1895, i, 533). T. H. P.

**Isomeric Hydrazones of Glyoxylic Acid. II. Remarkable, Different Behaviour of Stereoisomerides.** M. BUSCH and R. VON BEUST (*Ber.*, 1925, 58, [B], 442-447; cf. Busch, Achterfeldt, and Seufert, A., 1917, i, 228).—Either form of glyoxylic acid phenylhydrazone is converted by benzenediazonium chloride into formazylcarboxylic acid or the corresponding hydrocarbon formed therefrom by loss of carbon dioxide. A difference in behaviour is, however, observed with stereoisomeric hydrazones of glyoxylic esters with diazonium chlorides, since the  $\alpha$ -forms react normally, whereas the  $\beta$ -varieties pass with evolution of nitrogen into the hydrazones of arylglyoxylic esters. Thus methyl glyoxylate  $\alpha$ -phenylhydrazone and benzenediazonium chloride give methyl formazylcarboxylate,  $\text{PhN}_2\cdot\text{C}(\text{N}\cdot\text{NHPh})\cdot\text{CO}_2\text{Me}$ , m. p.  $134-135^\circ$ , whilst with *p*-nitrobenzenediazonium chloride the corresponding nitro compound, m. p.  $182-183^\circ$ , is produced. Benzenediazonium chloride and glyoxylic acid  $\beta$ -*as-m*-xylylhydrazone yield the compound,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{N}\cdot\text{NPh}$ , m. p.  $162-163^\circ$ . Benzene-diazonium chloride converts methyl glyoxylate  $\alpha$ -*as-m*-xylylhydrazone into methyl phenylxylylformazylcarboxylate,



m. p.  $138^\circ$ , whereas the corresponding  $\beta$ -derivative is transformed into the xylylhydrazone of methyl benzoylformate, m. p.  $111-112^\circ$ , which is hydrolysed to benzoylformic acid xylylhydrazone, m. p.  $161-162^\circ$ , the identity of which is established by its formation from benzoylformic acid. Analogously *p*-nitrobenzenediazonium chloride gives methyl *p*-nitrophenylxylylformazylcarboxylate, m. p.  $208^\circ$ , with the  $\alpha$ -variety and methyl *p*-nitrophenylglyoxylate xylylhydrazone, orange-yellow needles or reddish-brown prisms, m. p.  $152^\circ$ , with the  $\beta$ -form. Methyl *p*-bromophenylxylylformazylcarboxylate, m. p.  $177^\circ$ , and methyl *p*-bromophenylglyoxylate xylylhydrazone, m. p.  $176^\circ$  [xylylhydrazone of *p*-bromophenylglyoxylic acid, m. p.  $177^\circ$  (decomp.) after softening at  $170^\circ$ ] are similarly obtained by the use of *p*-bromobenzenediazonium chloride. H. W.

**Preparation of Derivatives of Hydroxyanthranilic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING, and M. LANGE (D.R.-P. 397750; from *Chem. Zentr.*, 1924, ii, 1404).—*N*-Monoacyl derivatives of hydroxyanthranilic acid are readily obtained by acylation of the acid in the presence of the salt of an organic acid or of hydroxyanthranilic acid itself. 2-Acetamido-4-hydroxybenzoic acid has m. p.  $246^\circ$  (decomp.); 2-acetamido-5-hydroxybenzoic acid, m. p.  $232^\circ$  (decomp.); and 2-benzamido-4-hydroxybenzoic acid, m. p.  $265^\circ$  (decomp.). R. B.

**Transformation of Mandelonitrile to Mandeloisonitrile.** C. E. WOOD and H. S. LILLEY (*J. Chem. Soc.*, 1925, 127, 95-98).—Mandeloisonitrile ( $\alpha$ -hydroxybenzylcarbylamine), m. p.  $196^\circ$ , is



obtained in nearly theoretical yield spontaneously from mandelonitrile, its rate of formation depending on the purity of the potassium cyanide used in preparing the nitrile. Its constitution is established by (a) its reduction to  $\alpha$ -hydroxybenzylmethylamine, m. p.  $180^\circ$  [nitrosoamine, and picrate, m. p.  $238^\circ$  (decomp.) prepared], and (b) oxidation with mercuric oxide, when ammonia produces  $\alpha$ -hydroxybenzylcarbamide, m. p.  $76^\circ$ , of which the nitrate, chloromercurate, and picrate are described; the carbylamine differs from the product of interaction of the nitrile and hydrogen chloride (cf. Minovici, A., 1899, i, 890). During hydrolysis, the carbylamine partly reverts to the normal form. Hexahydromandelonitrile isomerises similarly on keeping.

F. M. H.

### Reactions of Displacement in the Tropic Acid Group. I.

A. McKENZIE and R. C. STRATHERN (*J. Chem. Soc.*, 1925, 127, 82—88).—*r*- $\beta$ -Aminohydratropic acid prepared by a modification of Possner's method (A., 1912, i, 453) had m. p.  $222$ — $224^\circ$  (Possner gives  $233^\circ$ ). It was accompanied by an equal quantity of phenylacetaldoxime, m. p.  $103$ — $104^\circ$ . The action of nitrous acid on *r*- $\beta$ -aminohydratropic acid is irregular, only a very small yield of the expected *r*-tropic acid, m. p.  $116$ — $117^\circ$ , being obtained. The main product is an oil which is neither *r*-tropic nor *r*-isotropic acid. *r*- $\beta$ -Chlorohydratropic acid prepared from atropic acid (cf. McKenzie and Wood, T., 1919, 115, 828) has been resolved by means of morphine in methyl alcohol solution. The morphine compound of the *l*-variety separates as glassy prisms; 56 g. of crude material yielded 6 g. of pure morphine *l*-salt, from which 2.1 g. of *l*- $\beta$ -chlorohydratropic acid, m. p.  $62.5$ — $63.5^\circ$ ,  $[\alpha]_D^{25} -122.6^\circ$  in benzene, were obtained. Hydrolysis of the acid gave *l*-tropic acid having  $[\alpha]_D^{25} -58.1^\circ$  in ethyl alcohol, some racemisation apparently taking place.

The action of ammonia on *l*- $\beta$ -chlorohydratropic acid converts it into *l*-tropamide, m. p.  $195$ — $199^\circ$ ;  $\alpha_D^{25} -0.38^\circ$  in ethyl alcohol ( $l=2$ ,  $c=0.3472$ ). It is concluded that a  $\beta$ -lactone is produced as an intermediate phase,  $l\text{-CHPh} \begin{smallmatrix} \text{CH}_2\text{Cl} \\ \text{CO}_2\text{H} \end{smallmatrix} \rightarrow l\text{-CHPh} \begin{smallmatrix} \text{CH}_2\text{Cl} \\ \text{CO}_2\text{NH}_4 \end{smallmatrix} \rightarrow l\text{-CHPh} \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} \text{O} \rightarrow l\text{-CHPh} \begin{smallmatrix} \text{CH}_2\cdot\text{OH} \\ \text{CO}\cdot\text{NH}_2 \end{smallmatrix}$ , and that some racemisation accompanies the change (cf. Holmberg, A., 1918, i, 523; McKenzie and Smith, T., 1922, 121, 1348). The amide prepared from *l*-tropic acid by acting on the ethyl ester with ammonia had m. p.  $195$ — $197.5^\circ$ ,  $\alpha_D -0.24^\circ$  in ethyl alcohol ( $l=1$ ,  $c=0.377$ ). The  $\beta$ -aminohydratropic acid, m. p.  $169$ — $170^\circ$ , of Merling (A., 1881, 1143) has been shown to be the isomeride *r*-tropamide, as suggested by Possner (A., 1905, i, 577). On adding sodium ethoxide to a solution of *l*-tropamide, the laevorotation gradually fell to zero, and *r*-tropamide, m. p.  $170$ — $171^\circ$  (identical with Merling's  $\beta$ -aminohydratropic acid), was isolated from the solution. The *r*-tropamide prepared by the action of ammonia on *r*-tropic acid and on *r*- $\beta$ -chlorohydratropic acid was found to be identical with that from methyl *dl*-tropate.

A. C.

**Preparation of 4-Allyloxyphenylmalonic Acid and its Esters.** AKT.-GES. FÜR ANILIN FABRIKATION and M. BACHSTETZ (D.R.-P. 389405; from *Chem. Zentr.*, 1924, ii, 888; addition to D.R.-P. 371692; A., 1923, i, 995).—4-Amino-1-allyloxybenzene is treated with ethyl diethylmalonate as described in D.R.-P. 371692, giving 4-allyloxyphenylmalonic acid, m. p. 136°; ethyl ester, m. p. 105—107°. The products have a more pronounced action on the nervous system than the corresponding ethoxy compounds.

F. A. M.

**Transformation of Stereoisomeric Acids and their Esters.** W. HÜCKEL and E. GOTH (*Ber.*, 1925, 58, [B], 447—450).—The conversion of labile hydroaromatic carboxylic acids into the stable form, generally effected by the action of concentrated hydrochloric acid at 180—210°, has been considered by Aschan (A., 1912, i, 599) and Mohr (A., 1912, i, 362) to proceed through an intermediate enolic form. It must therefore be confined to acids which contain at least one carboxyl group attached to a secondary ring carbon atom. The sole recorded exception to this generalisation appears to be afforded by cyclohexane-1-acetic-2-propionic acid, the *cis*-form, m. p. 116°, of which, according to Eisenlohr (A., 1924, i, 1291), is converted into the *trans*-variety, m. p. 145°. Attempts to effect this change with the *cis*-acid, m. p. 109°, were unsuccessful (cf. Hückel, A., 1924, i, 31). The *trans*-acid has therefore been prepared by the condensation of ethyl oxalate with a mixture of *cis*- and *trans*-2-ketodecahydronaphthalene, isolation of ethyl *trans*-2-ketodecahydronaphthalene-3-carboxylate (or its desmotropic form), m. p. 46—47°, and fission of the latter by a solution of sodium in cyclohexanol. cycloHexane-1-acetic-2-propionic acid, thus prepared, has m. p. 115—116° (corresponding dianilide, m. p. 210°). Its melting point is greatly depressed by admixture with the acid of m. p. 109°. Its *trans*-configuration is further established by its conversion into ethyl *trans*- $\beta$ -decalonecarboxylate and *trans*- $\beta$ -decalone. Eisenlohr's acid is therefore *trans*-cyclohexane-1-acetic-2-propionic acid; the nature of the acid of m. p. 145° is unexplained.

The esters of stereoisomeric acids suffer inter-conversion more readily than the parent acids, the change occurring through an intermediate enolic form. Thus, the potassium derivative of ethyl *cis*-hexahydrophthalate is decomposed by sulphuric acid with production of the ethyl ester of the *trans*-acid. The *cis*-ester, when hydrolysed by an excess of sodium ethoxide, gives the pure *trans*-acid and when warmed for a short time with a trace of sodium ethoxide the *trans*-ester.

H. W.

**Formation and Spectrochemical Behaviour of Hydrogenated Naphthalene Derivatives.** K. VON AUWERS and K. MÖLLER (*J. pr. Chem.*, 1925, [ii], 109, 124—152).—Bougault's method for the synthesis of indene derivatives has now been applied to the synthesis of naphthalene derivatives by substituting ethyl  $\gamma$ -phenylbutyrate for ethyl hydrocinnamate. Ethyl  $\alpha$ -ox-

allyl- $\gamma$ -phenylbutyrate,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , ethyl  $\gamma$ -phenyl- $\alpha$ -hydroxymethylenebutyrate,  
 $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{OH}$ ,  
 and ethyl  $\beta$ -phenylethylacetoacetate,  
 $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{C}(\text{OMe})=\text{CH}_2$ ,

in all of which the ketonic form predominates, readily undergo ring closure when treated with sulphuric acid, yielding dihydronaphthalene derivatives. On the other hand, the analogous ethyl  $\alpha$ -oxalyl- $\gamma$ -phenyl- $\Delta^2$ -butenoate,  $\text{CHPh}\cdot\text{CH}=\text{CH}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , consists practically of the pure keto form and shows no tendency towards enolisation, and could not be converted into a naphthalene derivative. It is suggested that the double bond in the side-chain may restrict its mobility and that the molecule may have a *trans*-

structure, such as  $\text{HC}(\text{CO}_2\text{R})=\text{CH}\cdot\text{CH}(\text{Ph})\cdot\text{CO}\cdot\text{CO}_2\text{R}$ , in which ring closure is not readily possible. Similarly, ethyl  $\gamma$ -phenyl- $\alpha$ -hydroxymethylene- $\Delta^2$ -butenoate,  $\text{CHPh}\cdot\text{CH}=\text{C}(\text{CO}_2\text{Et})\cdot\text{CH}\cdot\text{OH}$ , which definitely shows enolic properties, ethyl  $\alpha$ -benzoyl- $\gamma$ -phenylbutyrate,

$\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})\cdot\text{C}(\text{OPh})=\text{CH}_2$ ,  
 and  $\gamma$ -[ $\beta$ -phenylethyl]acetylacetone,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}(\text{C}(\text{OMe})=\text{CH}_2)_2$ , are not converted by sulphuric acid into naphthalene derivatives, although the last-named readily forms a pyrazole derivative with semicarbazide. This method of ring closure is thus not generally applicable, and it is not possible to predict beforehand in what cases it is suitable and when failure is probable.

The optical refractions and dispersions of the ethyl  $\Delta^1$ - and  $\Delta^2$ -dihydro- $\alpha$ -naphthoates and of the three dihydro- $\beta$ -naphthoates show the exaltations to be expected from their accepted constitutions. A comparison of the values obtained for 3:4-dihydro-1-methylnaphthalene-2-carboxylic acid and the corresponding 1-methyl-2-naphthoic acid with corresponding dihydronaphthalene compounds shows that the methyl group tends to reduce the exaltation in refraction and dispersion, this influence being less pronounced in the true naphthalene series than in the hydroaromatic; in the indene series, its influence approximates to that exerted in the naphthalene series.

$\gamma$ -Phenylbutyl alcohol,  $d_4^{20}$  1.001,  $n_{\text{He}}^{20}$  1.5269, is converted into ethyl  $\gamma$ -phenylbutyrate, b. p. 135—136°/12 mm.,  $d_4^{20}$  1.001,  $n_{\text{He}}^{20}$  1.4937,  $n_a^{19.45}$  1.49028,  $n_b^{19.45}$  1.503117, which condenses with ethyl oxalate in the presence of potassium ethoxide to give, in 85.90% yield, ethyl  $\alpha$ -oxalyl- $\gamma$ -phenylbutyrate,  $d_4^{20}$  1.112;  $n_{\text{He}}^{15.75}$  1.49526, which gives a strong enol reaction with ferric chloride, although the spectroscopic constants prove it to be ketonic. It is converted by concentrated sulphuric acid at -15° into ethyl 3:4-dihydronaphthalene-1:2-dicarboxylate, m. p. 73°; the  $\alpha$ -monoethyl ester has m. p. 117—118°. At the ordinary temperature, sulphuric acid converts the ethyl  $\alpha$ -oxalyl- $\gamma$ -phenylbutyrate into the anhydride of 3:4-dihydronaphthalene-1:2-dicarboxylic acid, needles, m. p. 125—126°, readily attacked by potassium permanganate. The free

*acid*, m. p. 134—135° (silver salt, colourless, *methyl ester*, m. p. 55—56°) is only slowly attacked by potassium permanganate and not at all by alkaline potassium ferricyanide. Bromine in acetic acid at 100° converts the anhydride into naphthalene-1:2-dicarboxylic acid anhydride, whilst on reduction with sodium amalgam the free acid is converted into 1:2:3:4-tetrahydronaphthalene-1:2-dicarboxylic acid, m. p. 193° (rapid heating), 173° (slow heating); *anhydride*, m. p. 66—67°. The anhydride is readily reconverted into the acid, which is accordingly regarded as having the *cis*-configuration. Attempts to obtain the *trans*-isomeride were unsuccessful.

*Ethyl Δ<sup>2</sup>-dihydro-α-naphthoate*, b. p. 166—167°/17 mm., has  $d_4^{20}$  1.089,  $n_{\text{He}}^{19.6}$  1.53486; *ethyl Δ<sup>1</sup>-dihydro-α-naphthoate*, b. p. 185—186°/17 mm.,  $d_4^{20}$  1.102,  $n_{\text{He}}^{20.2}$  1.55896; *ethyl Δ<sup>3</sup>-dihydro-β-naphthoate*, b. p. 152—153°/12 mm.,  $d_4^{20}$  1.085,  $n_{\text{He}}^{18.2}$  1.55133; *ethyl Δ<sup>2</sup>-dihydro-β-naphthoate*, b. p. 163°/12 mm.,  $d_4^{20}$  1.202,  $n_{\text{He}}^{16.2}$  1.55396, and *ethyl Δ<sup>1</sup>-dihydro-β-naphthoate*, b. p. 159—160°/12 mm.,  $d_4^{20}$  1.093,  $n_{\text{He}}^{18}$  1.57919, are also described. The last-named ester was obtained by condensing ethyl γ-phenylbutyrate with amyl formate in the presence of sodium ethoxide, to *ethyl γ-phenyl-α-hydroxymethylenebutyrate*, which with cold concentrated sulphuric acid yields Δ<sup>1</sup>-dihydro-β-naphthoic acid.

Ethyl acetoacetate and β-phenylethyl bromide in the presence of sodium ethoxide condense to *ethyl β-phenylethylacetoacetate*, b. p. 175°/11 mm.,  $d_4^{20}$  1.048,  $n_{\text{He}}^{24.75}$  1.49636, which is converted by sulphuric acid at —15° into Δ<sup>1</sup>-α-methyl-β-naphthoic acid, m. p. 129—130°. The *ethyl ester* has b. p. 173°/13 mm.,  $d_4^{20}$  1.087,  $n_{\text{He}}^{15.8}$  1.57438. Bromine in carbon disulphide converts the acid into α-methyl-β-naphthoic acid, m. p. 177—178° (*ethyl ester*, b. p. 184°/13 mm.,  $d_4^{20}$  1.113,  $n_{\text{He}}^{22.1}$  1.59408), whilst with sodium amalgam, 1:2:3:4-tetrahydro-1-methyl-2-naphthoic acid, m. p. 83—84°, is obtained. Ethyl γ-phenylisocrotonate (Vorländer, A., 1906, i, 362) and ethyl γ-phenyl-Δ<sup>β</sup>-butenoate condense in the presence of potassium ethoxide to give *ethyl α-oxalyl-γ-phenyl-Δ<sup>β</sup>-butenoate*, m. p. 77—78°; with ethyl formate, *ethyl γ-phenyl-α-hydroxymethylene-Δ<sup>β</sup>-butenoate*, a brown oil, is produced. Ethyl benzoylacetate and β-phenylethyl bromide in the presence of sodium ethoxide yield *ethyl α-benzoyl-γ-phenylpropionate*, a yellow oil, b. p. 225—230°/11 mm., hydrolysed by alcoholic sodium hydroxide to *phenyl γ-phenylpropyl ketone*, m. p. 53—55° (*semicarbazone*, m. p. 125—126°). γ-(β-Phenylethyl)acetylacetone, pale yellow oil, b. p. 172—175°/19 mm., was obtained by the action of β-phenylethyl bromide on the potassium salt of acetylacetone in acetone at 100°. With semicarbazide it yields 1-carbamido-3:5-dimethyl-4-β-phenylethylpyrazole, m. p. 139—140°.

R. B.

**New Synthesis of the Meconines.** G. A. EDWARDS, W. H. PERKIN, jun., and F. W. STOYLE (*J. Chem. Soc.*, 1925, **127**, 195—199).—Boiling the veratric acids with formaldehyde and concentrated hydrochloric acid causes the introduction of a  $-\text{CH}_2\cdot\text{OH}$  group in the *ortho*-position to the carboxyl group, and the product by losing water becomes a meconine,  $\text{C}_8\text{H}_3(\text{MeO})_2\cdot\text{CO}_2\text{H} + \text{CH}_2\text{O}$

$\rightarrow \text{C}_6\text{H}_2(\text{MeO})_2 \begin{smallmatrix} \text{CO}_2\text{H} \\ \text{CH}_2\text{OH} \end{smallmatrix} \rightarrow \text{C}_6\text{H}_2(\text{MeO})_2 \begin{smallmatrix} \text{CO}^- \\ \text{CH}_2 \end{smallmatrix} \text{O}.$  *o*-Veratric acid, m. p. 120—122°, prepared by oxidising *o*-veratraldehyde with potassium permanganate, gave a 25—30% yield of meconine, m. p. 102°, under the above conditions. The meconine so obtained, on oxidation with sulphuric acid and manganese dioxide, gave opianic acid, m. p. 146°, identical with that obtained from narcotine. The opianic acid was oxidised by means of lead dioxide and sulphuric acid at 100° to hemipinic acid, m. p. 177°; the latter, on heating with excess of acetyl chloride, yields hemipinic anhydride, m. p. 168°, leading to an indirect synthesis of  $\psi$ -meconine (cf. Salamon, A., 1887, 585). It was not found possible to prepare  $\psi$ -opianic acid by oxidation of the  $\psi$ -meconine. Veratric acid (preparation given) was obtained in a semi-gelatinous state, m. p. 179°. It was converted by formaldehyde into *m*-meconine, m. p. 155—157°, identical with that of Perkin (T., 1916, 109, 815). The lactone ring of *m*-meconine opens up on treatment with hot aqueous sodium hydroxide and gives 4:5-dimethoxy-2-carboxybenzyl alcohol, m. p. 146—149° (indefinite); strong mineral acids cause re-formation of the lactone. Oxidation of *m*-meconine with manganese dioxide and sulphuric acid gave only a small yield of *m*-opianic acid, identified by its phenylhydrazone, m. p. 228° (cf. Perkin and Fargher, T., 1921, 119, 1743), but with alkaline permanganate *m*-hemipinic acid, yellow crystals, m. p. 203° (decomp.), was obtained in good yield. Attempts to obtain the methylene ether of 4:5-dihydroxyphthalide from piperonylic acid and formaldehyde were not successful.

A. C.

**Chenodeoxycholic Acid.** A. WINDAUS, A. BOHNE, and E. SCHWARZKOPF (*Z. physiol. Chem.*, 1924, 140, 177—185).—From the product of the hydrolysis of goose bile with potassium hydroxide a bile acid, "chenodeoxycholic acid,"  $\text{C}_{24}\text{H}_{40}\text{O}_4$ , m. p. 140°, isomeric with deoxycholic acid, has been isolated. This acid, which is identical with the acid obtained by Wieland and Reverey (this vol., i, 181) from human bile, constitutes the major proportion of the acids present in goose bile, although other bile acids are present in small amount. Chenodeoxycholic acid contains the same carbon skeleton as cholanic acid, and of the two hydroxyl groups contained in the molecule, one is attached to carbon 2 or 3 (probably the latter; for numbering see Wieland, Honold, and Pascual Vila, A., 1923, i, 1206), whilst the second is probably in position 13. Chenodeoxycholic acid forms crystalline *sodium* and *barium* salts and when carefully oxidised with chromic acid yields *chenodehydrodeoxycholic acid*,  $\text{C}_{24}\text{H}_{36}\text{O}_4$ , m. p. 153° (after sintering) (*methyl* ester, m. p. 161—162° after sintering at 155°; *ethyl* ester, m. p. 133°), which is converted into cholanic acid on reduction by Clemmensen's method. Cholanic acid is also formed when chenocholadienecarboxylic acid (obtained by distillation of chenodeoxycholic acid) is reduced catalytically. On oxidation with either chromic acid or potassium permanganate, the diketo-acid (chenodehydrodeoxycholic acid) gives a small yield of *chenodeoxybilanic*

acid,  $C_{24}H_{36}O_7$ , m. p.  $230^\circ$  (trimethyl ester, m. p.  $92^\circ$ ; trimethyl isodeoxybilianate has m. p.  $136-137^\circ$ ), which is reduced by Clemmensen's method to lithobilianic acid, the identity of which was confirmed by conversion into its trimethyl ester and into pyro-lithobilianic acid (methyl ester, m. p.  $96-97^\circ$ ). E. S.

**Preparation of apoCholic Acid.** J. D. RIEDEL AKT.-GES. (D.R.-P. 397312; from *Chem. Zentr.*, 1924, ii, 1409—1410; cf. A., 1922, i, 553).—Cholic acid and glycocholic acid on heating with dehydrating agents are converted into neutral compounds from which the apocholeic acid is isolated, after treatment with alkali, as the additive compound previously described. The resinous product obtained by boiling cholic acid with 20% hydrochloric acid for 1 hr. is washed with dilute ammonia and then with water, and boiled with 8% potassium hydroxide, and on acidification with aqueous hydrochloric acid the apocholeic acid is precipitated as a nearly colourless powder which, after drying and solution in acetic acid, separates as the acetic acid additive compound. The process has the advantage over that previously described that the intermediate neutral compound is readily separated from unchanged material. R. B.

**Preparation of Perylenetetracarboxylic Acid and its Derivatives.** KALLE & Co. A.-G., W. NEUGEBAUER, and M. P. SCHMIDT (D.R.-P. 394794; Fr. Pat. 567181; Swiss Pat. 103431; from *Chem. Zentr.*, 1924, ii, 1276).—Perylenetetracarboxydi-imide (obtained by the alkaline fusion of 1 : 8-naphthalimide, cf. D.R.-P. 276357, and Brit. Pat. 26690/1913) is heated at  $200^\circ$  with concentrated sulphuric acid, or *NN'*-di-(*p*-chlorophenyl)perylene-tetracarboxydi-imide (obtained from perylenetetracarboxylic acid and *p*-chloroaniline) is heated with sulphuric acid at  $210-220^\circ$ , the bluish-red solution turning violet-red and dark needles separating. On pouring on to ice brownish-red needles of perylenetetracarboxylic anhydride separate. The alkali salts of the acid are sparingly soluble; the calcium salt affords perylene on dry distillation; with amines the acid yields vat-dyes. Tetrachloroperylene-tetracarboxydi-imide (obtained by chlorinating perylenetetracarboxylic acid in fuming sulphuric acid under pressure, or dissolved in chloro-sulphonic acid), on heating with concentrated or fuming sulphuric acid at  $230-235^\circ$ , affords the corresponding anhydride, brownish-red leaflets; it dissolves in alkalis to yellow solutions with green fluorescence, from which acids precipitate the acid as a yellow substance which is reconverted on heating into the anhydride. When the di-imides are heated for a shorter time with sulphuric acid at  $180-190^\circ$ , the monoimides are formed; thus the unsubstituted di-imide affords a mixture of the tetracarboxylic acid and perylenetetracarboxylic acid monoimide, a brownish-red powder, forming deep red alkali salts. F. A. M.

[Oxidation of Eugenol, Methylheptenone, and Citral with Ozone.] Reply to V. Grignard. A. VERLEY (*Bull. Soc. chim.*, 1924, [iv], 35, 1653—1655).—Controversial (cf. Verley, A., 1924, i, 865; Grignard, *Bull. Soc. chim.*, 1924, [iv], 35, 932).—When

eugenol is oxidised by ozone (details of the large-scale operation are given), the product contains almost as much vanillin as homovanillin. The former must therefore be derived from eugenol itself, and not from the small proportion of *isoeugenol* that may be present. This indicates that some change takes place in the ozonide before or during its decomposition. For this and other reasons, the author disagrees with the conclusions of Grignard and his collaborators (*loc. cit.*), viz., that citral and methylheptenone occur naturally in the  $\beta$ -form. He failed again to obtain acetone by oxidising methylheptenone with ozone, and suggests that this is because his sample of methylheptenone was not from the same natural source as that studied by Grignard.

W. A. S.

**Preparation of 1-Alkylcyclohexan-3-ones.** F. SEIFERT D.R.-P. 389851; from *Chem. Zentr.*, 1924, ii, 889).—1-Alkylcyclohexan-3-ones are prepared by reducing alkylidihydroresorcinols with hydrogen in presence of catalysts. Thus *isopropyl*dihydroresorcinol dissolved in acetone or alcohol is treated with hydrogen in presence of palladium-coated charcoal until the theoretical quantity is absorbed; the resultant 1-*isopropyl*cyclohexan-3-one has b. p. about  $94^{\circ}/15$  mm.; *semicarbazone*, m. p.  $187^{\circ}$ . The products have therapeutic value.

F. A. M.

**Preparation of Cyclic Ketones.** J. D. RIEDEL AKT.-GES. (D.R.-P. 397150; from *Chem. Zentr.*, 1924, ii, 1404—1405; addition to D.R.-P. 346948, Schroeter, A., 1922, i, 1036).—Substitution derivatives of tetrahydronaphthalene or analogous polycyclic hydrogenated compounds can be oxidised to  $\alpha$ -ketones by chromic acid. Polycyclic hydrogenated compounds such as *s*-octahydrophenanthrene behave similarly, the product in this case being 1-*keto-s*-octahydrophenanthrene, m. p.  $81-82^{\circ}$ , b. p.  $206-208^{\circ}/12$  mm. (*semicarbazone*, m. p.  $254-256^{\circ}$ ; *oxime*, m. p.  $185-186^{\circ}$ ), identical with the product obtained by heating  $\gamma$ -*ar*-tetrahydro- $\alpha$ -naphthylbutyryl chloride through loss of hydrogen chloride and ring-closure.

*ar*-Tetrahydro- $\beta$ -naphthyl methyl ether in acetic acid with chromic acid yields *ar*-7-methoxy-4-ketotetrahydronaphthalene, m. p.  $80^{\circ}$ , b. p.  $171^{\circ}/11$  mm. (*semicarbazone*, m. p.  $233^{\circ}$ , *oxime*, m. p.  $133^{\circ}$ ). The position of the methoxyl with respect to the ketonic group is proved by the independent synthesis of the 1:7-isomeride.  $\beta$ -Anisoylpropionic acid is reduced to  $\gamma$ -*anisyl*butyric acid,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ , m. p.  $62-63^{\circ}$ , which with aluminium chloride yields *ar*-7-methoxy-1-ketotetrahydronaphthalene, m. p.  $63-64^{\circ}$  (*semicarbazone*, m. p.  $222^{\circ}$ ). Similarly, 1- and 2-*ar*-nitrotetrahydronaphthalene yield *ar*-1-nitro-5(?8)-ketotetrahydronaphthalene, m. p.  $102^{\circ}$  (*semicarbazone*, m. p.  $231^{\circ}$ ), and *ar*-2-nitro-5(?8)-ketotetrahydronaphthalene, m. p.  $118^{\circ}$  (*semicarbazone*, m. p.  $235^{\circ}$ ), respectively.

R. B.

**Claisen Condensation.** G. T. MORGAN, H. D. K. DREW, and C. R. PORTER.—(See i, 363.)

**Reaction of Ketones with Alcohols under the Influence of Light.** J. BÖESEKEN, W. D. COHEN, and S. L. LANGEDIJK. I. **Absorption Spectra of some Ketones.** S. L. LANGEDIJK (*Rec. trav. chim.*, 1925, **44**, 173—191).—For the visible and ultra-violet regions, the absorption spectra of molten benzophenone, and of its alcoholic solutions, and of alcoholic and light-petroleum solutions of fluorenone and of terephthalophenone, have been examined. The ketones give characteristic curves, indicating an absorption maximum in the ultra-violet, but not in the chemically active part of the spectrum. F. M. H.

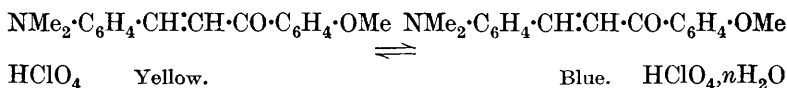
**Isomeric Chalkones [Phenyl Styryl Ketones].** W. DILTHEY and W. RADMACHER (*Ber.*, 1925, **58**, [B], 361—362; cf. Weygand, A., 1924, i, 521).—Acetylation of phenyl 3-aminostyryl ketone yields phenyl 3-acetamidostyryl ketone, m. p. 104° (cf. Rupe and Porai-Koschitz, A., 1906, i, 754), when the operation is effected with boiling glacial acetic acid in a sterile atmosphere. In the case of an unsuccessful pyrylium salt condensation with phenyl 3-aminostyryl ketone, an isomeric phenyl 3-acetamidostyryl ketone, m. p. 119—120°, was isolated which appears to be identical with a compound obtained by Kauffmann and Burckhardt (A., 1914, i, 55). The compound passes into the isomeride of lower m. p. when preserved for a few weeks in a closed tube. A similar instance of isomerism is encountered with *p*-tolyl *o*-hydroxystyryl ketone, which usually crystallises in colourless leaflets, m. p. 147—148° (cf. Zwayer and von Kostanecki, A., 1908, i, 443), but was obtained on one occasion as yellow needles, m. p. 134—135°. H. W.

**Preparation of Oxidoketones.** E. WEITZ (D.R.-P. 395435; from *Chem. Zentr.*, 1924, ii, 1403—1404).—Oxidoketones are obtained by the oxidation of  $\alpha\beta$ -unsaturated ketones, with the exception of diphenylindenone and its nearest analogues, with hydrogen peroxide or peroxides in alkaline solution, the carbonyl group being unattacked. Styryl methyl ketone with alkaline hydrogen peroxide at temperatures up to 50° yields *styryl methyl ketone oxide*,  $\begin{array}{c} \text{---O---} \\ | \\ \text{CHPh}\cdot\text{CH}\cdot\text{COMe} \end{array}$ , partly as an oil, partly as crystals, m. p. 53°, which appear to be, respectively, the *cis*- and *trans*-forms of the oxide. Phenyl styryl ketone similarly yields an *oxide*, m. p. 90°. Mesityl oxide with hydrogen peroxide and sodium hydroxide in methyl alcohol yields the *oxide*,  $\begin{array}{c} \text{---O---} \\ | \\ \text{CMe}_2\cdot\text{CH}\cdot\text{COMe} \end{array}$ , b. p. 44—48°/15 mm. The hydrogen peroxide can be replaced by percarbonates, perborates, Caro's acid, or loose additive products of hydrogen peroxide, such as the carbamide derivatives. R. B.

**Halochromism of Aromatic Aminoketones.** P. PFEIFFER [with O. ANGERN, P. BACKES, W. FITZ, E. PRAHL, H. RHEINBOLDT, and W. STOLL] (*Annalen*, 1925, **441**, 228—265).—To obtain confirmation of the oxonium salt structure,  $\text{R}_2\text{C}^+\text{O} \dots \text{HClO}_4$ , proposed for the perchlorates of aromatic ketones (A., 1917, i, 205), the behaviour of a series of aromatic aminoketones and polyketones



with this acid has been examined. Aminoketones of the chalkone, distyryl, phenyl cinnamylidenemethyl ketone, and dibenzylidenecyclohexanone series readily yield well-crystallised perchlorates, stable in the absence of moisture, in which the number of mols. of perchloric acid is generally equal to, but never exceeds, the sum of the amino and carbonyl groups present, but is not related to the number of ethylene linkings. Perchlorates of the "maximal" or highest type are generally regarded as possessing an oxonium structure, and the amino, alkylamino, and methoxyl groups exert their usual auxochromic effect, except where it is diminished by salt formation on the amine-nitrogen atom. Similarly, the deeply coloured aminoketones of the lower type, in which monoaminoketones are combined with 1 mol. and the diaminoketones are combined with 2 mols. of perchloric acid, are regarded as oxonium salts and the bathochromic influence of the *p*-methoxyl and *p*-dialkylamino groups is well marked. The less deeply coloured perchlorates of the chalkone series are regarded as ammonium salts, and probably those of di-*p*-dimethylaminobenzylidenecyclohexanone and di-*p*-dimethylaminostyryl ketone belong to the same class. The determining influence appears to be the relative basicity of the amino and carbonyl groups in the aminoketone, and it is probable that in solutions of the lower type of perchlorates we have equilibrium mixtures of oxonium and ammonium salts. The equilibrium will vary with the temperature, which, together with solubility, will determine which of the two isomerides crystallises out. The conversion of the deep blue hydrated perchlorate of *p*-anisyl *p*-dimethylaminostyryl ketone into the yellow, anhydrous form, and the reversion of the latter in moist air into the blue form, is probably accompanied by the tautomeric change:

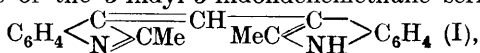


The formulæ proposed by Straus (A., 1922, i, 148) and Hantzsch (A., 1921, i, 556) are discussed and also the alternative quinonoid structure, *e.g.*,  $\text{ClO}_4 \cdot \text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} : \text{C}(\text{OH}) : \text{CH} : \text{CH} \cdot \text{Ph}$ . All three formulæ, however, are only approximation formulæ when the crystal structure of the salts is considered, and none of them represents correctly the valency distribution in the crystal space lattice. *p*-Nitro-*p*'-methoxydistyryl ketone has m. p. 185—186°; phenyl *o*-nitrocinnamylidenemethyl ketone, m. p. 142°; anisyl *o*-nitrocinnamylidenemethyl ketone, m. p. 128°, sintering from 126°; anisyl *p*-nitrocinnamylidenemethyl ketone, m. p. 163°; styryl *o*-nitrocinnamylidenemethyl ketone, m. p. 121°, sintering from 118°; *p*-methoxystyryl *o*-nitrocinnamylidenemethyl ketone, m. p. 126—127°, sintering from 124°; styryl *m*-nitrocinnamylidenemethyl ketone, m. p. 145—146°; *p*-methoxystyryl *p*-nitrocinnamylidenemethyl ketone, m. p. 197—198°; 2 : 6-di-*m*-nitrobenzylidenecyclohexanone, m. p. 194°, and 2 : 6-di-*p*-nitrobenzylidenecyclohexanone, m. p. 207°, were prepared from cyclohexanone and the nitrobenzaldehyde in yields amounting to 34 and 39% of theory, respectively. All the

above are yellow. *p*-Dimethylaminobenzophenone when dissolved in 70% perchloric acid or when treated with perchloric acid in acetic acid solution yields a colourless *monoperchlorate*,  $C_{15}H_{15}ON, HClO_4$ ; no stannic chloride compound was obtained. Phenyl *m*-aminostyryl ketone yields the yellow *monoperchlorate*,  $C_{15}H_{13}ON, HClO_4$ ; a solution in perchloric acid deposits a mixture of mono- and di-perchlorates. Phenyl *p*-aminostyryl ketone, m. p. 147—148°, obtained by condensation of *p*-benzamidobenzaldehyde, m. p. 146°, with acetophenone in alcoholic solution in the presence of sodium hydroxide, and hydrolysis of the phenyl *p*-benzamidostyryl ketone, m. p. 177—178° (cf. Kauffmann and Burckhardt, A., 1914, i, 56), gives a *monoperchlorate*, brown needles, and a mixture of mono- and di-perchlorates. The red hydrochloride described by Rupe and Porai-Koschitz (A., 1906, i, 754) could not be obtained; the flesh-coloured hydrochloride, obtained with 10% hydrochloric acid, has the composition  $C_{15}H_{13}ON, HCl$ . Phenyl *p*-dimethylaminostyryl ketone yields a nearly colourless *monoperchlorate*,  $C_{17}H_{17}ON, HClO_4$ ; the *monohydrochloride*, bright yellow, gives a reddish-violet solution in hydrochloric acid, which deposits colourless needles, changing in a desiccator to the yellow, anhydrous salt. From concentrated hydrochloric acid bright blue laminae are deposited. The *chlorostannate*,  $C_{17}H_{17}ON, SnCl_4$ , black powder, sensitive to light, was obtained by heating the aminoketone with stannic chloride in dry benzene. *p*-Anisyl *m*-aminostyryl ketone, m. p. 141°, obtained by condensing *m*-acetamidobenzaldehyde with *p*-methoxyacetophenone in alcoholic sodium hydroxide and hydrolysing the *p*-methoxyphenyl *m*-acetamidostyryl ketone, m. p. 144—145°, yields in acetic acid a bright yellow *monoperchlorate*, and with perchloric acid alone an orange *diperchlorate*,  $C_{16}H_{15}O_2N, 2HClO_4$ . Reduction of *p*-anisyl *p*-nitrostyryl ketone with stannous chloride in acetic acid saturated with hydrogen chloride yields *p*-anisyl *p*-aminostyryl ketone, brownish-yellow, m. p. 173—174° (benzoyl derivative, m. p. 199—201°), giving an orange-brown *diperchlorate*. *p*-Anisyl *p*-dimethylaminostyryl ketone, m. p. 127°, from *p*-dimethylaminobenzaldehyde and *p*-methoxyacetophenone, yields a blue *monoperchlorate*,  $C_{18}H_{19}O_2N, HClO_4 + 1.5H_2O$ , giving a yellow anhydrous salt. The *diperchlorate*,  $C_{18}H_{19}O_2N, 2HClO_4$ , is orange-yellow, the *chlorostannate*,  $C_{18}H_{19}O_2N, SnCl_4$ , nearly black. *m*-Aminodistyryl ketone, m. p. 138—139°, yields in acetic acid a pale orange-yellow *monoperchlorate*, and with perchloric acid alone an ochreous *diperchlorate*. *p*-Dimethylaminodistyryl ketone, similarly, yields a dark green *monoperchlorate* and an orange-brown *diperchlorate*, converted into the *monoperchlorate* on exposure to the air. The *chlorostannate*,  $C_{19}H_{19}ON, SnCl_4, C_6H_6$ , is nearly black. *m*-Aminostyryl *p*-methoxystyryl ketone yields a Bordeaux-red *diperchlorate* and a reddish-brown *monoperchlorate*. *p*-Aminostyryl *p*-methoxystyryl ketone, m. p. 158—160°, yields a *diperchlorate*, nearly black with blue iridescence. *p*-Dimethylaminostyryl *p*-methoxystyryl ketone, orange-yellow, m. p. 140°, gives a violet-black *diperchlorate* and a black *chlorostannate*,  $C_{22}H_{21}O_2N, SnCl_4$ , very sensitive to light. Di-*p*-

dimethylaminostyryl ketone, orange brown, m. p. 191°, yields a *triperchlorate*, bright yellow, which on treatment with water is converted into the nearly colourless *diperchlorate*, and then more slowly into a dark brown *monoperchlorate*,  $3\text{C}_{21}\text{H}_{24}\text{ON}_2 \cdot 4\text{HClO}_4$ , also obtained by adding perchloric acid to a solution of the base in acetic acid. The *monoacetate*,  $\text{C}_{21}\text{H}_{24}\text{ON}_2 \cdot \text{C}_2\text{H}_4\text{O}_2$ , is dark red. *cycloHexanone* and *p*-dimethylaminobenzaldehyde in alcoholic solution in the presence of sodium ethoxide yield 2-*p*-dimethylaminobenzylidenecyclohexanone, m. p. 127—128°, which condenses further with benzaldehyde in the presence of sodium ethoxide, yielding 2-*p*-dimethylaminobenzylidene-6-benzylidenecyclohexanone, m. p. 137—138°, yielding a green *monoperchlorate*, and a reddish-brown *diperchlorate*. 2-*p*-Dimethylaminobenzylidene-6-*p*-anisylidenecyclohexanone, m. p. 177—178°, gives in alcohol a deep-green *monoperchlorate*, and with perchloric acid alone, a dark, blood-red *diperchlorate*, with steel-blue lustre. 2:6-*Di-m-aminobenzylidenecyclohexanone*, m. p. 145° (*hydrochloride*,  $\text{C}_{23}\text{H}_{25}\text{ON}_2 \cdot 2\text{HCl}$ , bright yellow), is obtained by reducing the nitrobenzylidene derivative. The yellow *diacetyl* derivative, m. p. 249°, obtained by condensation of cyclohexanone with *m*-acetamidobenzaldehyde in the presence of alcoholic sodium hydroxide, is not readily hydrolysed to the amine. 2:6-*Di-p-aminobenzylidenecyclohexanone*, brown, m. p. 240—242° (bright yellow *dihydrochloride*), and its deep yellow *diacetyl* derivative, m. p. 296—297°, are analogously prepared. 2:6-*Di-p-dimethylaminobenzylidenecyclohexanone*, m. p. 248—249°, gives in acetic acid a bright yellow *diperchlorate*, and with perchloric acid alone, a bright yellow *triperchlorate*. R. B.

**Halochromic Compounds of Imines.** P. PFEIFFER, H. RHEINBOLDT, and J. WOLF (*Annalen*, 1925, 441, 265—276).—To determine how close a parallel there is between the halochromism of imines and that of ketones, the additive compounds of distyryl ketone, *p*-methoxydistyryl ketone, and *p*-dimethylaminodistyryl ketone with acids and metallic salts have been compared with those of the corresponding quinaldine bases, 2-styrylquinoline, 2-*p*-methoxystyrylquinoline, and 2-*p*-dimethylaminostyrylquinoline. In both series, coloured monoperchlorates are formed, in which the *p*-methoxyl group exerts a bathochromic influence, and this influence is manifested in the hydrochlorides, oxalates, and acid cadmium chlorides. The cadmium chloride compounds of the quinaldine series, in which 2 mols. of the metallic chloride are in combination with 1 mol. of the base, are analogous to the chlorostannates of the ketone series. *p*-Dimethylaminostyrylquinoline, like *p*-dimethylaminodistyryl ketone, gives a deep green monoperchlorate and only a yellow diperchlorate. In the monoperchlorate the acid is attached to the imine nitrogen atom, and in the diperchlorate also to the dimethylamino group, the bathochromic influence of the latter being thereby destroyed. The cyclic imines of the 3-indyl-3-indolidenemethane series,



investigated by König (A., 1911, i, 808) yield halochromic cadmium chloride compounds, and a further series of halochromic salts has been obtained from the analogous base,  $\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}$  (II) (Zincke, A., 1904, i, 921), which results when the pyridine rings are opened. In these salts, the acid is linked to the imine nitrogen as the deepened colour produced can only be explained on this assumption, addition to the auxochrome group producing salts which are less highly coloured than the free base. In view of these results and the series of halochrome salts obtained from Zincke's second base,  $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NH}\text{Et}$  (III), in which only one aromatic ring is present (A., 1905, i, 923), it is concluded that the amino and hydroxyl groups can exert their auxochromic influence when they are separated from a chromophore by a continuous chain of ethylenic linkings; whether such ethylenic linkings belong to an open chain or partly to the aromatic ring is immaterial.

The following compounds of benzyldienequinoline (2-styrylquinoline) are described: *hydrochloride*,  $\text{C}_{17}\text{H}_{13}\text{N}\cdot\text{HCl}$ , m. p. 112—113°; *perchlorate*,  $\text{C}_{17}\text{H}_{13}\text{N}\cdot\text{HClO}_4$ ; *oxalate*,  $\text{C}_{17}\text{H}_{13}\text{N}\cdot\text{H}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ , m. p. 176—177° (decomp.); *cadmium chloride* compounds,  $\text{C}_{17}\text{H}_{13}\text{N}\cdot 2\text{CdCl}_2$  and  $2\text{C}_{17}\text{H}_{13}\text{N}\cdot\text{H}_2\text{CdCl}_4$ . Similarly, 2-*p*-methoxystyrylquinoline yields an *oxalate*,  $\text{C}_{18}\text{H}_{15}\text{ON}\cdot\text{C}_2\text{H}_2\text{O}_4$ , m. p. 205° (decomp.), and *cadmium chloride* compounds,  $\text{C}_{18}\text{H}_{15}\text{ON}\cdot 2\text{CdCl}_2$  and  $3\text{C}_{18}\text{H}_{15}\text{ON}\cdot\text{H}_3\text{CdCl}_5$ ; all the above are yellow. 2-*p*-Dimethylaminostyrylquinoline yields a yellow *dihydrochloride*, a bright yellow *diperchlorate*, and a dark *monoperchlorate*, with a strong green lustre; an *oxalate*,  $\text{C}_{19}\text{H}_{18}\text{N}_2\cdot 2\text{C}_2\text{H}_2\text{O}_4$ , violet-black, m. p. 108—110°; a black *cadmium chloride* compound, possessing a green lustre; a silver-grey *cadmium chloride-hydrochloride*,  $\text{C}_{19}\text{H}_{18}\text{N}_2\cdot\text{H}_2\text{CdCl}_4$ , and a dark-coloured *cadmium chloride-hydrochloride*,  $2\text{C}_{19}\text{H}_{18}\text{N}_2\cdot\text{H}_2\text{CdCl}_4$ , with a green lustre. The  $\alpha$ -methylindyl- $\alpha$ -methylindolidenemethane of König (*loc. cit.*) yields a rust-brown *cadmium chloride* compound,  $\text{C}_{19}\text{H}_{17}\text{N}_2\cdot 2\text{CdCl}_2$ , and *zinc chloride-hydrochloride* compound,  $5\text{C}_{19}\text{H}_{17}\text{N}_2\cdot 5\text{HCl}\cdot 2\text{ZnCl}_2$ , dense reddish-brown crystals with brilliant blue lustre. Similarly, Zincke's anilinoanil base,  $\text{C}_{17}\text{H}_{16}\text{N}_2$ , yields a *monoperchlorate*, red needles; a *trichloroacetate*,  $\text{C}_{17}\text{H}_{16}\text{N}_2\cdot\text{CCl}_3\cdot\text{CO}_2\text{H}\cdot\text{MeOH}$ , red needles with a blue lustre, a *zinc chloride-hydrochloride* compound,  $5\text{C}_{17}\text{H}_{16}\text{N}_2\cdot 5\text{HCl}\cdot 2\text{ZnCl}_2$ , reddish-brown, with a green lustre, and a rust-brown *cadmium chloride* compound,  $\text{C}_{17}\text{H}_{16}\text{N}_2\cdot 2\text{CdCl}_2$ . The base III (above), obtained by the action of ethylamine on dinitrophenylpyridinium chloride, yields a yellowish-red *perchlorate*,  $\text{C}_{13}\text{H}_{14}\text{O}_4\text{N}_4\cdot\text{HClO}_4$ .

R. B.

**Reactions in Solutions of Quinone.** L. MEUNIER and M. QUEROIX (*J. Soc. Leather Trades Chem.*, 1925, 9, 26—31).—Aqueous solutions of quinone of different  $p_{\text{H}}$  values were kept in the dark for 6 days. Using a disodium phosphate-phosphoric acid buffer mixture, the conversion of quinone into quinol and oxidation products commenced at  $p_{\text{H}}$  6.5, and at  $p_{\text{H}}$  7.5 20% of the quinone had been transformed. The amount of quinol formed was practically half that of the quinone which had disappeared. In sodium

acetate-acetic acid and sodium acetate-sodium hydroxide buffer mixtures, the quinone was transformed more rapidly. The transformation curve shows a maximum at  $p_H$  5.0, a minimum about  $p_H$  6.5, after which the amount of transformation increases very rapidly with rising  $p_H$ . The amount of quinone transformed increases very much in presence of protein matter. [Cf. *B.*, 1925, 219.] D. W.

**New Derivatives of Naphthaquinone.** SOC. ANON. DES MATIÈRES COLORANTES ET PRODUITS CHIMIQUES DE SAINT-DENIS, A. R. WAHL, and R. LANTZ (Brit. Pat. 206150).—Various 1-arylamino- $\beta$ -naphthols (Brit. Pat. 182084), by the action of hypochlorites or of other oxidising agents on their alkaline solutions, yield 1-arylimino- $\beta$ -naphthaquinones (cf. Brit. Pat. 191064). Examples of these are: 1-*o*-methoxyphenylimino- $\beta$ -naphthaquinone, 1-tolylimino- $\beta$ -naphthaquinone and 1-naphthylimino- $\beta$ -naphthaquinone. They form unstable, dark green crystals, and are highly reactive, forming with alkali sulphites and hydrogen sulphites of 1-arylamino- $\beta$ -naphtholsulphonic acids. B. W. A.

**Oxidation in Light.** A. ECKERT (*Ber.*, 1925, 58, [B], 313—320; cf. Schaarschmidt and Kasai, A., 1924, i, 1327).—Autoxidation of 2-methylanthraquinone in glacial acetic acid solution under the influence of light leads to the production of anthraquinone-2-carboxylic acid and *s*-2-dianthraquinonylethane, m. p. 342°, the constitution of which is established by its oxidation to anthraquinone-2-carboxylic acid. 5:8-Dichloro-, 5:6:7:8-tetrachloro-, 1-methoxy-, and 1-hydroxy-2-methylanthraquinones are much less readily affected; the halogenated compounds yield acids in quantity too small for investigation. 4-Chloro-1-methylanthraquinone, under similar conditions, gives 4-chloroanthraquinone-1-carboxylic acid, m. p. 220—223°, and, apparently, *s*-di-4-chloroanthraquinonylethane, m. p. 290—300° (decomp.). Autoxidation of 2-methylanthraquinone occurs far less readily in the presence of toluene than of glacial acetic acid, whilst the solvent is itself oxidised. The same action is induced by anthraquinone, under the influence of which (presumably owing to the transient production of anthraquinol) toluene yields benzaldehyde, benzoic acid, dibenzyl, *isohydrobenzoin*, *hydrobenzoin*, and (?) benzil. Illumination of toluene in the presence of anthraquinone and acetic anhydride gives benzyl acetate. Dibenzyl, *hydrobenzoin*, benzil, and benzoin are transformed into benzoic acid by photo-oxidation in glacial acetic acid solution in the presence of anthraquinone. *p*-Benzoquinone, naphthaquinone, xanthone, acridone, and benzophenone stimulate the production of benzoic acid to a much smaller extent than anthraquinone. The nitrotoluenes give small quantities of acidic products when illuminated in the presence of anthraquinone; *o*-nitrobenzoic acid has been identified. *m*- and *p*-Xylenes are converted into the corresponding toluic acids. Naphthalene is not affected in glacial acetic acid solution, whereas quinol is very readily transformed into quinhydrone. An aqueous, alkaline solution of lead hydroxide is photo-oxidised to lead dioxide

in the presence of potassium anthraquinone-1-sulphonate. Chromium sulphate is converted similarly into chromic acid, whilst tervalent arsenic and antimony pass into the quinquivalent state. Illumination of sodium anthraquinone-2-sulphonate dissolved in dilute hydrochloric acid causes the liberation of chlorine and production of 2-chloroanthraquinone; the corresponding 1-sulphonate appears to suffer a similar change.

H. W.

### Preparation of Nitrogenous Anthraquinone Derivatives.

BADISCHE ANILIN- & SODA-FABRIK, M. A. KUNZ, and K. SAURWEIN (D.R.-P. 396509; from *Chem. Zentr.*, 1924, ii, 1408—1409).

—By the action of nitrosyl chloride on 1-amino-2-methylantraquinone in nitrobenzene or benzene suspension, a mixture of anthraquinone-1 : 2-isooxazole, a yellowish-brown substance containing nitrogen, m. p. 173—175°, and anthraquinone-1 : 2-indazole, is obtained, in proportions varying with the temperature and with amount and the rate of addition of the nitrosyl chloride. Similarly, 4-chloro-1-amino-2-methylantraquinone yields a substance, orange-yellow needles, giving an orange solution in sulphuric acid with evolution of nitrogen. The new products are used for the preparation of dyes.

R. B.

### Dyes of the Anthraquinone Series. J. BADDILEY, W. W.

TATUM, and THE BRITISH DYESTUFFS CORPORATION, LTD. (Brit. Pat. 227923).—By condensing 4 : 8-dichloroanthrarufin with 2 mols. of anthranilic acid in nitrobenzene solution in presence of sodium carbonate and copper powder, 4 : 8-diphenylaminoanthrarufin-o : o'-dicarboxylic acid is formed. In a similar way, by condensing 1 : 5-dichloro-4 : 8-dinitroanthraquinone with anthranilic acid and reducing the product with sodium sulphide, 1 : 5-diamino-4 : 8-diphenylaminoanthraquinone-o : o'-dicarboxylic acid is formed. The former dyes cellulose acetate greenish-blue, the latter green.

E. H. R.

**Dianthraquinonyl.** A. ECKERT (*Ber.*, 1925, 58, [B], 321—322).—1 : 1-Dianthraquinonyl is readily converted by molten potassium hydroxide at 200° into benzoic and diphenyl-3 : 3'-dicarboxylic acids; diphenic acid appears also to be produced, but, under the conditions of the reaction, to be transformed into fluorenone. Helianthrone (cf. Scholl, A., 1910, i, 494) is stable towards potassium hydroxide at 200°, but is converted at 290° into mesonaphthadanthrone.

H. W.

**Chlorination of Helianthrone.** A. ECKERT (*Ber.*, 1925, 58, [B], 322—323).—Helianthrone [*mesobenzdianthrone*] is converted by phosphorus pentachloride in the presence of boiling phosphoryl chloride into 4 : 5 : 8 : 4' : 5' : 8'-hexachloromesobenzdianthrone. The constitution of the product is deduced from the observation that it is converted by exposure to light in sulphuric acid solution into 4 : 5 : 4' : 5'-tetrachloromesonaphthadanthrone (cf. Eckert and Tomaschek, A., 1919, i, 163).

H. W.

**Condensation of Menthone with *p*-Tolualdehyde.** B. SAMDAHL (*J. Pharm. Chim.*, 1925, [viii], 1, 145—149).—A mixture of

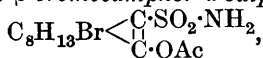
menthone and *p*-tolualdehyde saturated at 0° with dry hydrogen chloride gives (i) *p*-tolylidenementhone hydrochloride, m. p. 133°,  $[\alpha]_D^{24} -83.1^\circ$  in chloroform, from which water or alcohol easily removes hydrogen chloride, and (ii) an uncrystallisable oil. The product, b. p. about 180°/7 mm., obtained by decomposing the latter with alcoholic potassium hydroxide, yields *p*-tolylidenementhone,  $C_8H_{16} \begin{smallmatrix} < C:CH \cdot C_6H_4Me \\ & CO \end{smallmatrix}$ , m. p. 77°,  $[\alpha]_D^{20} -193.2^\circ$  in chloroform.

The mother-liquors from the crystallisations of this compound yield an oil, b. p. 183—184°/7 mm.,  $[\alpha]_D^{20} -56.5^\circ$  in chloroform,  $d_4^{17} 1.0077$ ,  $n_D^{20} 1.5412$ , which consists of one or more stereoisomeric modifications of the crystalline *p*-tolylidenementhone. With hydroxylamine, this oil gives an additive compound, m. p. 174°,  $[\alpha]_D^{23} -52.2^\circ$  in chloroform; it is reduced by sodium and ether saturated with water to *p*-methylbenzylmenthol, m. p. 150°,  $[\alpha]_D^{23} -30.9^\circ$  in chloroform.

W. E. E.

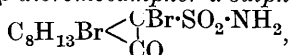
**Halogen Derivatives of Camphor. VI.  $\beta$ -Bromocamphor- $\alpha$ -sulphonic Acid. VII. Constitution of the Reychler Series of Camphorsulphonic Acids. Experiments on Chlorosulphoxides.** H. BURGESS and T. M. LOWRY (*J. Chem. Soc.*, 1925, 127, 271—283; cf. Armstrong and Lowry, T., 1902, 81, 1445).—VI.—After blocking the  $\beta$ -position by means of a bromine atom, the authors have succeeded in sulphonating camphor in the  $\alpha$ -position.  $\beta$ -Bromocamphor added to a mixture of acetic anhydride and concentrated sulphuric acid yielded a brown substance (15—20% of the bromocamphor undergoing sulphonation), from which, by treatment with calcium carbonate, calcium  $\beta$ -bromocamphor- $\alpha$ -sulphonate,  $(C_{10}H_{14}OBr \cdot SO_3)_2Ca \cdot 4H_2O$ , m. p. above 250°,  $[\alpha]_{5780} +50^\circ$ ,  $[\alpha]_{4385} +116.5^\circ$  in water (2 g. per 100 c.c.), was isolated. Potassium  $\beta$ -bromocamphor- $\alpha$ -sulphonate,  $C_{10}H_{14}OBr \cdot SO_3K$ , by treatment with phosphorus pentachloride, is converted into  $\beta$ -bromocamphor- $\alpha$ -sulphonyl chloride,  $C_8H_{13}Br \begin{smallmatrix} < CH \cdot SO_2Cl \\ & CO \end{smallmatrix}$ , m. p. 97°; the

corresponding sulphonamide has m. p. 100—102° (decomp.),  $[\alpha]_{5780} +39.3^\circ$ ,  $[\alpha]_{4358} +99^\circ$  (in alcohol); the crystals, which at first are tough and fibrous, become opaque and friable on keeping. Attempts to prepare an anhydramide (cf. Lowry, *loc. cit.*) gave a negative result with concentrated hydrochloric acid, but with acetic anhydride the product was acetyl- $\beta$ -bromocamphor- $\alpha$ -sulphonamide,



m. p. 217° (rapid decomp.).  $\beta$ -Bromocamphor- $\alpha$ -sulphonyl bromide is an oil; when it is refluxed in dry xylene, sulphur dioxide is evolved and some charring occurs. The product gave three successive crops of crystals from dilute alcohol, the first a mixture of  $\alpha\beta$ - and  $\alpha'\beta$ -dibromocamphors, the second  $\alpha'\beta$ -dibromocamphor, m. p. 133—135°,  $[\alpha]_{5461} -77^\circ$  (in acetone), the third,  $\alpha\beta$ -dibromocamphor, m. p. 113—114°. This suggested that the sulphonic acid occupied the  $\alpha$ -position, and confirmation was obtained when the sulphonamide on bromination lost the sulphonamide group and

gave the same  $\alpha\beta$ -dibromocamphor. Bromination of the acetyl derivative (above) resulted in the elimination of the acetyl group and formation of  $\alpha\beta$ -dibromocamphor- $\alpha$ -sulphonamide,



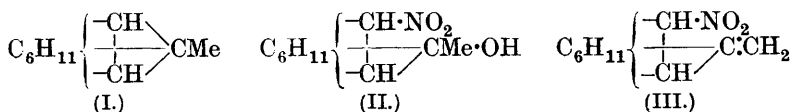
m. p.  $145^\circ$  (80% yield),  $[\alpha]_{5461} -29^\circ$  in benzene (2.64 g. per 100 c.c.). This loss of the acetyl group suggested an enolic acetate rather than the  $-\text{SO}_2 \cdot \text{NHAc}$  compound. The dibromosulphonamide when dissolved in alcohol undergoes spontaneous oxidation and the solution deposits  $\beta$ -bromocamphorquinone, bright yellow prisms, m. p.  $122^\circ$ , characteristic odour unlike that of camphorquinone. Oxidation of the dibromosulphonamide with hydrogen peroxide in aqueous alcoholic solution gave the intense colour of the quinone, but it could not be isolated, being further oxidised to  $\beta$ -bromocamphoric anhydride, m. p. about  $143^\circ$ . The views of Lipp and Lausberg (A., 1924, i, 655) that  $\beta$ -bromocamphor and the Reychler series of camphorsulphonic acids have the same orientation are thus confirmed.

VII.—The evidence put forward by Wedekind, Schenk, and Stüsser (A., 1923, i, 346) that the sulphonic radical in Reychler's camphorsulphonic acid (A., 1899, i, 447) has entered a methyl group is at variance with equally definite evidence indicating that it has entered a methylene group in the ring. An alternative mechanism to explain the formation of 10-ketopinic acid from a 6-derivative of camphor (cf. Wedekind, *loc. cit.*) which involves the wandering of the sulphonyl group is given. This change in orientation does not appear to take place, since the tricarboxylic acid and the anhydride formed on oxidising  $\alpha$ -bromocamphor- $\pi$ -chlorosulphoxide,  $\text{C}_9\text{H}_{12}\text{BrO} \cdot \text{CCl} \cdot \text{S} \cdot \text{O}$ , m. p.  $158-159^\circ$ ,  $[\alpha]_{5780} +31^\circ$  in benzene (prepared from ammonium  $\alpha$ -bromocamphor- $\pi$ -sulphonate by Wedekind's method), with nitric acid are identical and not isomeric with those obtained by Kipping and Pope by the oxidation of  $\pi$ -bromocamphor. It thus appears that the halogen in  $\beta$ -bromocamphor, as well as the sulphonic group in Reychler's acid, has entered a methyl group and occupies the 10-position of the camphor molecule. No reaction is known in which  $\beta$ -bromocamphor behaves as if it contains a  $-\text{CH}_2\text{Br}$  group. It is thought that there must be some link between the 6- and 10-positions which is not expressed in the conventional camphor formula (cf. Armstrong and Lowry, T., 1902, 81, 1469). A crystalline *by-product*, m. p. about  $202^\circ$  (decomp.),  $[\alpha]_{5461} +19.4^\circ$  in acetone, isolated from the benzene extract after oxidation of  $\alpha$ -bromocamphor- $\pi$ -chlorosulphoxide, was expected to be  $\pi$ -chlorodinitro- $\alpha$ -bromocamphor, but differed from the compound obtained by Wedekind under analogous conditions in being soluble in alkalis. An attempt to make toluene-*o*-chlorosulphoxide by heating *o*-toluenesulphonyl chloride with dry piperidine was unsuccessful. A. C.

**Secondary  $\alpha$ -Nitrocamphene.** S. NAMETKIN and A. ZABRODIN (*Annalen*, 1925, 441, 181-187).—The nitration of tricyclene (I), now made available by the method of Meerwein and van Emster



(A., 1920, i, 855), is found to proceed *via* the additive product (II), which loses water to give *sec.*- $\alpha$ -nitrocamphene (III), b. p. 119—119.5°/14 mm.,  $d_4^{20}$  1.0689,  $n_D^{20}$  1.4942. The isolation of isocamphoronic acid, the oxidation product of camphene, from the acid products of the reaction shows that nitration has preceded oxidation (cf. Kononov, A., 1904, i, 257). Nitrations generally may



be regarded as additive processes in the first instance. The  $\alpha$ -nitrocamphene forms a  $\psi$ -nitrole, m. p. 99°, and on reduction gives  $\alpha$ -aminocamphene, b. p. 197—198°/750 mm. C. H.

**Essential Oils.** SCHIMMEL & Co. (*Rep. Schimmel & Co.*, 1924, 1—236; from *Chem. Zentr.*, 1924, ii, 892—894).—Bay oil had a variable phenol content from 35% to 60%. Citronella oil: the statement of de Jong and van Harpen (*Ber. Afd. Handelsmuseum Kolonial Inst.*, 1923, No. 13) that the viscosity of the oil varies inversely with the citronellal content is not confirmed; the determining factor is probably the degree of resinification. Jaborandi leaf oil: the characteristic odour is probably due to a ketone; a sample of oil having  $d^{15}$  0.8694,  $\alpha_D +0^\circ 54'$ ,  $n_D^{20}$  1.45442, acid number 6.72, acetyl number 7.65, on extraction with sodium hydrogen sulphite yielded a *methyl nonyl ketone*, b. p. 231.5—232.5°/752;  $d^{15}$  0.8297;  $\alpha_D$  0,  $n_D^{20}$  1.42855, acetyl number 11.7; the lower-boiling fractions afforded a *hydrocarbon*, b. p. 162—166°,  $d^{15}$  0.8519,  $\alpha_D +17.4^\circ$ ,  $n_D^{20}$  1.46757, which absorbs hydrogen chloride to give a liquid *hydrochloride*, whilst the higher fractions afforded a hydrocarbon, m. p. 27—28°, previously described. Oil from *Monarda fistulosa*: on steam distillation the plant yielded 0.3% of a deep reddish-brown oil,  $d^{15}$  0.9219; 5% potassium hydroxide solution extracted about 30%, chiefly carvacrol, traces of thymol, and probably some thymoquinol. Oil from *Monodora myristica* obtained from West African seeds gave 5.06% of a pale yellow oil with an odour of phellandrene,  $d^{15}$  0.8511,  $\alpha_D 86^\circ 20'$ ,  $n_D^{20}$  1.47613, acid number 0.4, acetyl number 6.5; after fusion of the nitrite (102°), it gave  $\beta$ -phellandrene; it also seemed to contain some cineole. A vetiver oil from Java had a powerful odour and dark brown colour,  $d^{15}$  0.9926—1.0444,  $\alpha_D +20^\circ 50'$  to  $+41^\circ 40'$ ,  $n_D^{20}$  1.51889—1.53020, acid number 9.3 to 28, acetyl number 5.6—20.6, after acetylation 107.3—151.2; some "light oils" occasionally present had  $d^{15}$  0.9852—0.9944,  $\alpha_D 14^\circ 25'$  to  $24^\circ 10'$ ,  $n_D^{20}$  1.52430—1.52604, acid number 7.5 to 11.2, acetyl number 7.5—14.9, after acetylation 102.7 to 108.3. Specimens of (presumably synthetic) menthol had m. p. 32—36.5°,  $\alpha_D -39^\circ 55'$  to  $-41^\circ 30'$ , and are probably made from piperitone.

The details given by Reclaire (*Perf. Essent. Oil Rec.*, 1923, 14, 293) for the identification of esters of non-volatile acids in oils are confirmed, but acids slowly volatile in steam, such as lauric

acid, are likely to be overlooked. The qualitative tests of Bennett and Garratt (*ibid.*, 1924, 14, 359) are useful, but in negative tests the acid number should be determined. F. A. M.

**Essential Oil of the "Rimu" (*Dacrydium cupressinum*).** F. H. McDOWALL and H. J. FINLAY (*J. Soc. Chem. Ind.*, 1924, 44, 42T).—*Dacrydium cupressinum* grows abundantly in New Zealand, and its leaves, by treatment with supersaturated steam, yield 0.17% of an oil consisting of a saturated pentacyclic diterpene,  $C_{20}H_{32}$ , m. p. 55.5°, b. p. 320°,  $[\alpha]_D$  (in chloroform) 53.7°, another saturated diterpene, m. p. 92°, which is probably formed from the above during distillation; and a small quantity of a sesquiterpene, b. p. 152–157°/40 mm.,  $n_D^{20}$  1.5005,  $d_4^{20}$  0.9219,  $[\alpha]_D$  (in chloroform) 17.81°. The oil was free from aldehydes and ketones and contained only a very small quantity of phenols and acids. F. B.

**Essential Oil of *Meriandra benghalensis*, Benth.** F. C. PALAZZO and E. ALINARI (*Atti Congr. Naz. Chim. Ind.*, 1924, 245–250).—This oil, obtained by distillation of the leaves, contains about one-third of its weight of camphor, together with cineole, camphene, and another terpene. [Cf. *B.*, 1925, 264.]

T. H. P.

**Essential Oil of Calantas Wood.** W. L. BROOKE (*Philippine J. Sci.*, 1925, 26, 1–8).—The physical constants of the odoriferous essential oil of calantas wood (*Toona calantas*) are given and cadinene is shown to be one of the principal constituents. L. F. H.

**Relationships between Vegetable Aromatic Substances and their Origin.** L. RETI (*Atti Congr. Naz. Chim. Ind.*, 1924, 250–256).—Attention is directed to the occurrence of the coniferyl grouping in the molecules of large numbers of vegetable compounds, such as glucosides, the constituents of essential oils, resins, colouring matters, etc., and it is shown that the reactions of coniferylaldehyde are identical with those of Czapek's hadromal (A., 1899, i, 560). Further, the dihydroxycinnamic grouping, from which the coniferyl grouping is derived by simple methylation, is found in the molecules of numerous tannin substances, almost all the flavones, and many glucosides and colouring matters. In view of the relationships which such a large number of these so-called accessory substances of plants bear to coniferylaldehyde, which is closely allied to lignin (cf. Klason, A., 1920, i, 822; 1922, i, 324; 1923, i, 187), it seems likely that rational utilisation of lignin might lead to the isolation of many aromatic compounds, at present obtainable only by complicated and indirect methods. T. H. P.

**Polysaccharides. XXIX. Chitin (II) and the Configuration of Glucosamine.** P. KARRER, O. SCHNIDER, and A. P. SMIRNOV (*Helv. Chim. Acta*, 1924, 7, 1039–1045; cf. A., 1923, i, 122).—When chitin is distilled with zinc dust, the chief product is 2-methyl-1-*n*-hexylpyrrole (*loc. cit.*); if the chitin molecule consists only of two glucosamine residues, it should have the constitution of a reduced "fructosazine" (cf. Stolte, A., 1908, i, 833). It is now

indicated that this is not so; when fructosazine is distilled with zinc dust, an oily product sparingly soluble in dilute sulphuric acid is obtained, of which, after repeated fractional distillation, the main fraction has b. p. 150—156° (2.1 g. of b. p. 150—169° from 300 g. fructosazine). This is still a mixture, but consists chiefly of 2:5-dialkylpyrazines, since when it is oxidised with a hot dilute solution of potassium permanganate it affords pyrazine-2:5-dicarboxylic acid. That part of the original oily distillate dissolved by dilute sulphuric acid consists of similar pyrazine derivatives, together with substituted pyridines. This fraction affords a *picrate*, m. p. 145°. It thus appears that chitin is not formed simply by the union of two glucosamine residues.

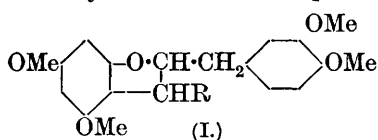
When chitosan is similarly distilled with zinc dust, the oil, obtained in most meagre yield, affords a pyrrole fraction (b. p. 190—220°), resembling that from chitin, and a pyridine fraction which yields the picrate mentioned above.

When glucoseanilide is treated with nitrous acid, diazoaminobenzene is obtained. This quantitative scission resembles that taking place in chitosan when it is treated with the same reagent (cf. Karrer and Smirnov, A., 1923, i, 122).

The configuration of glucosamine is discussed with copious citations from the literature, and the conclusion is reached that this compound is the amino derivative corresponding with mannose.

W. A. S.

**Tannins and Similar Substances. XVIII. Catechin.** K. FREUDENBERG, H. FIKENTSCHER, and M. HARDER (*Annalen*, 1925, 441, 157—180; cf. this vol., i, 51; A., 1924, i, 868).—It has been shown (*loc. cit.*) that *p*-toluenesulphonyl-*d*-catechin tetramethyl ether (I, R=MeC<sub>6</sub>H<sub>4</sub>·SO<sub>3</sub>) gives with hydrazine a little of the primary hydrazine (I, R=NH·NH<sub>2</sub>) but mainly phloroglucinol dimethyl ether and 3-*mp*-dimethoxyphenylpyrazoline, which is



further confirmation of the suggested *trans* configuration of the OH in *d*-catechin tetramethyl ether. It is now found that *l*-epicatechin tetramethyl ether (I, R=OH) behaves as the *cis*-isomeride.

The *p*-toluenesulphonyl derivative, m. p. 165—168°, reacts with hydrazine to form the unsaturated *anhydroepicatechin tetramethyl ether*, m. p. 119°, in 70% yield. This is optically inactive and probably has the structure of a tetramethoxybenzylcoumarone. It is reduced by hydrogen and platinum to *deoxyepicatechin tetramethyl ether* (I, R=H), m. p. 112°. The anhydro compound is different from and isomeric with (a) the product of the action of quinoline upon *p*-toluenesulphonylcatechin tetramethyl ether and (b) the substance obtained by Drumm (A., 1923, i, 1221) from the chloride and pyridine. The corresponding saturated compounds are also different and the isomerism is thus not merely geometric.

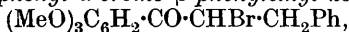
The formation of phloroglucinol trimethyl ether from catechin

tetramethyl ether is not inconsistent with the formula (I,  $R=OH$ ), for it is shown that the trimethyl ether is obtainable in about 10% yield by heating phloroglucinol dimethyl ether with barium hydroxide.

The *p*-nitrobenzoate of pentahydroxydiphenylpropane tetramethyl ether (A., 1923, i, 1219) is readily methylated to pentamethoxydiphenylpropane, m. p. 87–88°, identical with the synthetic product.

For the synthesis of tetramethoxybenzylcoumarone (cf. Dumont and Tambor, A., 1910, i, 579) phloroglucinol trimethyl ether is condensed by Hoesch's method with chloroacetonitrile to give trimethoxyphenacyl chloride, m. p. 95–96° (bromide prepared in the same way melts at 86°). These do not undergo ring closure with alcoholic potassium acetate, and Dumont and Tambor's product was probably partly demethylated. Demethylation with aluminium chloride or bromide gives 5-hydroxy-1:3-dimethoxyphenacyl chloride, m. p. 144–146°, or bromide, m. p. 130–131°, from which 3:5-dimethoxycoumarone, m. p. 137°, is easily obtained. The *mp*-dimethoxybenzylidene derivative of the latter is reduced best by hydrogen in the presence of nickel instead of platinum and gives 3:5:3':4'-tetramethoxy-1-benzylcoumarone, m. p. 136°, b. p. 210–220°/1.5 mm., isomeric with anhydroepicatechin tetramethyl ether. With phenylhydrazine, it gives a mixture, m. p. 176°, of the phenylhydrazone and the osazone. Reduction with zinc and sodium hydroxide converts it into the dihydrochalkone, m. p. 127°. *mp*-Dimethoxybenzylidenecoumarone, m. p. 150°, from coumarone and veratraldehyde, is reduced by hydrogen and nickel to dimethoxybenzylcoumarone, m. p. 78–79°, which reacts normally with phenylhydrazine to form a *phenylhydrazone*, m. p. 171°.

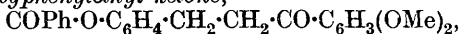
$\alpha$ -Bromo- $\beta$ -phenylpropionitrile, b. p. 130–135°/10 mm., prepared from the *amide*, m. p. 127°, and thionyl chloride, is condensed with phloroglucinol trimethyl ether by Hoesch's method and gives 2:4:6-trimethoxyphenyl  $\alpha$ -bromo- $\beta$ -phenylethyl ketone,



m. p. 101–102°.

1-Benzoylcoumarone (Stoermer, Chydenius, and Schinn, A., 1924, i, 409), m. p. 91°, is reduced by aluminium amalgam to coumaronylphenylcarbinol (*ibid.*), m. p. 76°.

Phenacylsaligenin,  $OH \cdot CH_2 \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CPh$ , m. p. 86–87°, prepared from phenacyl bromide, salicyl alcohol, and potassium carbonate, is converted by distillation in a vacuum into 1-benzoylcoumarone. The corresponding *o*-phenacyloxybenzyl bromide,  $CH_2Br \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CPh$ , melts at 93°. Phenacyl bromide condenses with resorcinol monomethyl ether to give *resorcinol phenacyl methyl ether*, m. p. 85–86°. A good yield of 4-bromoveratrole, m. p. 127–128°, is obtained by bromination of guaiacol in the presence of quinoline followed by methylation. The *benzoate* of 3:4-dimethoxyphenyl *o*-hydroxystyryl ketone, m. p. 127–128°, is reduced by hydrogen and platinum to the *benzoate* of the corresponding  $\beta$ -*o*-hydroxyphenylethyl ketone,



m. p. 100–101° (*oxime*, m. p. 150–151°; *oxime-acetate*, m. p.

120—121°). Phloroglucinaldehyde trimethyl ether condenses with acetoveratrone to give 3 : 4-dimethoxyphenyl 2 : 4 : 6-trimethoxystyryl ketone, m. p. 164—165°, which is reduced to 3 : 4-dimethoxyphenyl  $\beta$ -2 : 4 : 6-trimethoxyphenylethyl ketone, m. p. 111° (oxime, m. p. 140°). C. H.

**Condensation of Furfuraldehyde with Aliphatic Aldehydes.** D. IVANOV (*Bull. Soc. chim.*, 1924, [iv], 35, 1658—1665).—When furfuraldehyde is treated with an excess of an aliphatic aldehyde in presence of sodium hydroxide and ice, furfurylidene compounds are formed. At the low temperature, a superior yield to that hitherto recorded is obtained (cf. Schmidt, A., 1881, 247, 573, 889; Röhmer, A., 1898, i, 300).  $\alpha$ -Furfurylideneacetaldehyde (yield, 70%), has m. p. 51.5°, b. p. 97°/10 mm. It has an agreeable odour, readily yields a sodium hydrogen sulphite compound, and is easily reduced by hydrogen in presence of platinum black. The semicarbazone has m. p. 219.5° (on the Maquenne block; all these semicarbazones were tested in this way because in the sulphuric acid bath they decompose and a lower m. p. is indicated; cf. Röhmer, *loc. cit.*); the oxime has m. p. 110—111°; the phenylhydrazone forms yellow crystals, m. p. 125—126°.  $\alpha$ -Furfurylidenepropaldehyde (yield, 72%) is a yellow oil, b. p. 227—228°, 155°/110 mm., 100°/11 mm. (cf. Schmidt, *loc. cit.*),  $d_4^{15}$  1.1022,  $n_D^{15}$  1.613; semicarbazone, m. p. 250.5—251.5°; oxime, m. p. 108—109°; phenylhydrazone, m. p. 143—144°. A sodium hydrogen sulphite compound is readily produced.  $\alpha$ -Furfurylidenebutaldehyde is a yellow oil, b. p. 234—235° or 112—113°/14 mm.,  $d_4^{16}$  1.065,  $n_D^{16}$  1.595; semicarbazone, m. p. 220—221°; oxime, m. p. 67—68°; phenylhydrazone, m. p. 97—97.5°. No hydrogen sulphite compound is afforded by this substance, nor by either of its congeners described below.  $\alpha$ -Furfurylidenevaleraldehyde, an oil, b. p. 245—246°, or 120—121°/14 mm.,  $d_4^{23}$  1.0299,  $n_D^{23}$  1.5744, yields a semicarbazone, m. p. 176—177°, an oxime, m. p. 75.5—77°, a phenylhydrazone, m. p. 81—82° (decomp.), and a 2 : 4-dinitrophenylhydrazone, m. p. 147°.  $\alpha$ -Furfurylideneheptaldehyde (yield, 10%) has b. p. 275—276° or 135—136.5°/11 mm.,  $d_4^{14}$  0.9761,  $n_D^{14}$  1.534; semicarbazone, m. p. 134°; oxime, an oil; phenylhydrazone (unstable), m. p. 80—81.5°. The solubilities of the semicarbazones in alcohol at 22° are recorded. W. A. S.

**Manganous Salts of Comenic and Meconic Acids. Intramolecular Wandering of Metal Atoms.** P. E. VERKADE (*Rec. trav. chim.*, 1925, 44, 82—89).—By treating comenic acid or meconic acid with the appropriate quantity of potassium hydroxide, and adding manganous sulphate, the following salts are prepared: sec.-manganous comenate, yellow crystals, which lose water at 160°, turning orange; tert.-manganous meconate (+8H<sub>2</sub>O, losing 2H<sub>2</sub>O at 110°), and sec.-manganous meconate (+3½H<sub>2</sub>O). By the action of barium hydroxide on the acid, sec.-barium meconate (+4H<sub>2</sub>O) is prepared as a colourless salt which at 110—115° loses 3½H<sub>2</sub>O, becoming lemon-coloured (cf. Peratoner and Tamburello, A., 1904, i, 172); sec.-calcium meconate behaves similarly, but the potassium

salt remains colourless at 110°. When the hydrogen of the hydroxyl group in comenic or meconic acid is replaced by a metal (*sec.*-comenates and *tert.*-meconates), the salt is more or less abnormally coloured, but primary comenates and primary and secondary meconates are colourless. When secondary manganous meconate is dehydrated at 110°, the colour deepens, and this is attributed to wandering of the metal atom,

$$\text{Mn}'\text{O}_2\text{C}\overset{\text{CH}\cdot\text{CO}\cdot\text{CO}}{\underset{\text{CH}\cdot\text{CO}\cdot\text{C}\cdot\text{OMn}'}{\text{C}}}\text{O}\text{---}\text{CH}\cdot\text{CO}_2\text{Mn}' \rightarrow \text{Mn}'\text{O}_2\text{C}\overset{\text{CH}\cdot\text{CO}\cdot\text{C}\cdot\text{OMn}'}{\underset{\text{CH}\cdot\text{CO}_2\text{H}}{\text{C}}}\text{O}$$

This explanation is confirmed by the fact that at 160—165° carbon dioxide is lost and secondary manganous comenate produced.

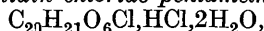
F. M. H.

### Synthesis of Pyrylium Salts of Anthocyanidin Type. V. Synthesis of Cyanidin Chloride and of Delphinidin Chloride.

D. D. PRATT and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 166—175; cf. T., 1923, 123, 750).—A new and better method for the preparation of  $\omega$ -methoxyacetoveratrone (*loc. cit.*) in an application of the syntheses of acetophenone from benzoyl chloride by way of ethyl benzoylacetate is described. Ethyl methoxyacetate, b. p. 131° (from ethyl chloroacetate and sodium methoxide), with sodium yields a sodium compound as a thick syrup, affording, on acidification, *ethyl  $\alpha$ -dimethoxyacetoacetate*, b. p. 130°/15 mm. The condensation product from ethyl sodio- $\alpha$ -dimethoxyacetoacetate and benzoyl chloride when hydrolysed with dilute sulphuric acid gave a substance from which phenylglyoxaldiphenylhydrazone, m. p. 152°, was obtained, but with aqueous sodium hydroxide gave a small yield of  $\omega$ -methoxyacetophenone (semicarbazone, m. p. 85°) (II, *loc. cit.*).

$$\text{OMe}\cdot\text{CBz}(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OMe} \rightarrow \text{OMe}\cdot\text{CH}_2\text{Bz} + \text{OMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{K}.$$

$\omega$ :4-Dimethoxyacetophenone, m. p. 40°, was derived in a similar manner from anisoyl chloride, and condensed in alcoholic potassium hydroxide solution with 6-aminopiperonal to form 3-methoxy-6:7-methylenedioxy-2-p-methoxyphenylquinoline, m. p. 152°. With veratroyl chloride, the product was  $\omega$ -methoxyacetoveratrone  $(\text{OMe})_2\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OMe}$ , m. p. 62°, which yields 3-methoxy-6:7-methylenedioxy-2-mp-dimethoxyphenylquinoline, m. p. 155°, when condensed with 6-aminopiperonal. Pure  $\omega$ -methoxyacetoveratrone gives only one semicarbazone, m. p. 178°, identical with the semicarbazone-*b* (II, *loc. cit.*), the m. p. of which rose to 178° on repeated crystallisation. The semicarbazone-*a*, m. p. 205°, is that of  $\alpha$ :3:4-trimethoxyphenylacetaldehyde. *Fisetinidin chloride trimethyl ether*,  $\text{C}_{18}\text{H}_{17}\text{O}_5\text{Cl}\cdot 2\text{H}_2\text{O}$ , darkening at 135°, decomp. 188—189°, reddish-violet by transmitted light, is formed by passing hydrogen chloride through a dry ethereal solution of  $\omega$ -methoxyacetoveratrone and  $\beta$ -resorcyraldehyde. A small amount of the ferrichloride, m. p. 156° (*loc. cit.*), was obtained from the mother-liquors. *Cyanidin chloride pentamethyl ether*,



red needles, m. p. 152°, is obtained in a similar way from 2-hydroxy-

4 : 6-dimethoxybenzaldehyde and  $\omega$ -methoxyacetoveratrone. From 7% aqueous hydrochloric acid, a *monochloride*,  $C_{20}H_{21}O_6Cl \cdot 3H_2O$ , separates in orange-brown needles. The *ferrichloride*, reddish-brown needles with bronze lustre, has m. p. 194—200° (decomp.). Demethylation takes place on boiling with methyl iodide and phenol, with formation of cyanidin iodide. This was converted into cyanidin chloride, reddish-brown prisms with green lustre, identical with the cyanidin chloride of natural origin (cf. Willstätter and Everest, A., 1913, i, 1371). Attempts to convert it into a flavonol colouring matter by oxidation with hydrogen peroxide (cf. Willstätter and Everest, *loc. cit.*) were not successful.  $\omega$  : 3 : 4 : 5-*Tetramethoxyacetophenone* (from trimethylgalloyl chloride) had b. p. 212°/15 mm., m. p. 54° (*semicarbazone*, m. p. 158°). 3-*Methoxy*-6 : 7-*methylenedioxy*-2-mm'p-*trimethoxyphenyl-quinoline*, m. p. 159°, violet fluorescence in alcohol, forms a yellow *hydrochloride*, and an orange-yellow *methosulphate*. Comparison with the intensely coloured delphinidin chloride hexamethyl ether shows that the quinolinium and benzopyrylium nuclei function quite differently as chromophores. *Delphinidin chloride hexamethyl ether* was prepared from  $\omega$  : 3 : 4 : 5-tetramethoxyacetophenone and 2-hydroxy-4 : 6-dimethoxybenzaldehyde, and was obtained as red needles with green lustre, m. p. 164° [*ferrichloride*, brownish-red needles, m. p. 169—170°; *sulphate*, m. p. 225° (decomp.)]. On demethylation as above, delphinidin chloride,  $C_{15}H_{11}O_7Cl \cdot 1.5H_2O$ , m. p. above 350°, brown crystals from 25% hydrochloric acid, was obtained. The hydrates containing 1, 2, and 4H<sub>2</sub>O (cf. Willstätter and Weil, A., 1917, i, 46) were prepared. The substance agreed in all its properties with natural delphinidin chloride (cf. Willstätter and Mieg, A., 1915, i, 284). A. C.

**Synthesis of Myricetin and of a Galangin Monomethyl Ether Occurring in Galanga Root.** J. KALFF and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 181—184).—The method of synthesising flavones described by Allan and Robinson (this vol., i, 148) has been extended.  $\omega$ -Methoxyphloroacetophenone (cf. Slater and Stephen, T., 1920, 117, 316), heated with sodium benzoate and benzoic anhydride, yielded a product the *diacetyl* derivative of which (boiling acetic anhydride) had m.p. 175—176°. This agrees with that of the diacetate of the galangin monomethyl ether from galanga root (cf. Testoni, A., 1901, i, 92). After hydrolysis with aqueous potassium hydroxide, the phenol was obtained in yellow plates, m. p. 299° (sodium salt, yellow needles). The properties of this substance agree with those given by Testoni (*loc. cit.*) for the natural 3-galangin monomethyl ether, which is therefore 5 : 7-dihydroxy-3-methoxyflavone. Demethylation resulted in the formation of galangin, m. p. 214—215°. 3 : 3' : 4' : 5'-*Tetramethylmyricetin diacetate*, m. p. 159° (corr.), was obtained on heating trimethyl gallic anhydride, m. p. 159° (cf. Fischer and Freudenberg, A., 1913, i, 479), with sodium trimethylgallate and  $\omega$ -methoxyphloroacetophenone at 175°, and boiling the crude product with acetic anhydride. Hydrolysis with boiling concentrated hydrochloric acid gave

myricetin 3 : 3' : 4' : 5'-tetramethyl ether. This substance is almost devoid of mordant dyeing properties; on demethylation by means of a boiling mixture of hydriodic acid and acetic anhydride, the red, crystalline myricetin hydriodide was obtained, which on decomposition by hot water gave myricetin, agreeing in all its properties with the natural product (cf. Perkin and collaborators, T., 1896, 69, 1287; 1902, 81, 204, etc.). The hexa-acetate had m. p. 214—216° (literature : 211—212°). A. C.

**Reaction between Diazodeoxybenzoin and Carbon Disulphide.** J. MEYER (*Helv. Chim. Acta*, 1925, 8, 38—41).—Phenylbenzoyldiazomethane reacts with carbon disulphide to give the  $\gamma$ -thiolactone of  $\beta$ -keto- $\gamma$ -thiol- $\alpha$ -benzoyl- $\alpha\gamma\gamma$ -triphenyldithiobutanoic acid,  $\text{CPhBz}\cdot\text{CO}\cdot\text{CPh}_2$ , m. p. 153—154°, decomposed by alcoholic potassium hydroxide with production of benzoic and phenylacetic acids together with an acid of m. p. 141—146°, probably identical with thiobenzilic acid. The first step in the above reaction is probably the formation of the  $\beta$ -lactone,  $\text{CPhBz}\cdot\text{CPh}\cdot\text{Bz}$ , which then undergoes benzilic acid transformation to give the  $\gamma$ -lactone.

G. M. B.

**Synthesis of "Psicaine."** R. WILLSTÄTTER (*Münch. Med. Woch.*, 1924, 71, 849—850; from *Chem. Zentr.*, 1924, ii, 1202).—In the various syntheses of cocaine (cf. Willstätter, Wolfes, and Mäder, A., 1924, i, 70), two racemic alkaloids are formed, one corresponding with ordinary *l*-cocaine. The other, *dl*- $\psi$ -cocaine, m. p. 81.5°, has been resolved into its optically active forms by removing the benzoic acid and converting the resulting ecgonine ester into the bromocamphorsulphonate, in ethyl acetate solution; m. p. 46—47°. According to Gottlieb (*Arch. exp. Path. Pharm.*, 1923, 97, 113), the *d*-form has the greatest effect on nervous tissue and relatively slight toxicity. In the form of its tartrate,  $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}\cdot\text{C}_4\text{H}_6\text{O}_6$ , it is termed "Psicaine," forming a micro-crystalline powder,  $[\alpha]_D^{20} + 43^\circ$  in 5% aqueous solution. The  $p_H$  of the aqueous solution is 3.4 to 3.7. The solutions have a bitter taste and produce prolonged insensitiveness. The substance remains unchanged in steam at 110°. F. A. M.

**Benzoylallylecgonine and Benzoylbenzylecgonine.** E. POULSON and G. WEIDEMANN.—(See i, 466.)

**Hygrine Alkaloids. V. Degradation of Cuskygrine to Undecane and Undecan-6-ol.** K. HESS and R. BAPPERT (*Annalen*, 1925, 441, 137—150).—Hess and Fink (A., 1920, i, 497) obtained by the action of nitric oxide on cuskygrine a base,  $\text{C}_{11}\text{H}_{22}\text{N}_2$ , to which was assigned the structure (I)  $\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2$ , in accord with (II),  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CHAc}\cdot\text{C}_5\text{H}_{10}\text{N}$ , for the alkaloid rather than Liebermann's formula (III),  $\text{C}_5\text{H}_{10}\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_5\text{H}_{10}\text{N}$  (A., 1895, i, 310). Hess and Anselm (A., 1921, i, 881) synthesised



the compound of structure (I) and found it not identical with Fink's base. Since this may be due to space isomerism (see below) further light on the constitution of cuskhygrine is sought.

Exhaustive methylation of cuskhygrine fails owing to complete resinification during distillation of the ammonium base, but after reduction of the carbonyl group satisfactory results are obtained. The reduction of cuskhygrine creates a new asymmetric centre and two stereoisomeric secondary alcohols result, both of which regenerate cuskhygrine on oxidation. Formula (II), like trihydroxyglutaric acid, implies two meso forms and one racemic form, whilst (III), like tartaric acid, has one meso and one racemic form. The formation of two dihydro compounds shows that cuskhygrine is either the meso form of (III) or the racemic form of (II), assuming that no isomerisation occurs during reduction. Exhaustive methylation of the two dihydrocuskhygrines leads to *n*-undecane and *n*-undecan- $\zeta$ -ol and is thus in accord with Liebermann's structure (III), since (II) would give  $\epsilon$ -ethylnonane and  $\gamma$ -*n*-butylheptan- $\beta$ -ol. Further work is necessary to decide between the structures (II) and (III).

Cuskhygrine [*methiodide*, m. p. 244°; *hydrobromide*, m. p. 234°; *nitrate*, m. p. 209° (decomp.)] is reduced by sodium and alcohol at 80° to an equimolecular mixture separable by fractional crystallisation of the picrates into  $\alpha$ -*dihydrocuskhygrine*, b. p. 156—157°/14 mm.,  $d_4^{20}$  0.9750,  $n_D^{16}$  1.48876 [*picrate*, m. p. 127°; *methiodide*, m. p. 261—262°; *nitrate*, m. p. 176—177°; *hydrobromide*, m. p. 210°; *hydrochloride*, m. p. 222° (decomp.); *benzoate*, m. p. 206°], and  $\beta$ -*dihydrocuskhygrine*, b. p. 160—161°/16 mm.,  $d_4^{15}$  0.9792,  $n_D^{16.5}$  1.48742 [*picrate*, m. p. 215°; *methiodide*, m. p. 266°; *nitrate*, m. p. 209° (decomp.); *hydrobromide*, m. p. 247°; *hydrochloride*, m. p. 230° (decomp.)]. By repeated alternate exhaustive methylations and catalytic reductions the mixture of dihydro compounds yields *n*-undecane, b. p. 73°/12 mm. or 194°/750 mm. (corr.),  $d_4^{16.3}$  0.7455,  $n_D^{20.2}$  1.41842, and *n*-undecan- $\zeta$ -ol, m. p. 16°, b. p. 111°/12 mm.,  $d_4^{20}$  0.8334,  $n_D^{20}$  1.4370.

Ethyl *N*-methyl- $\alpha$ -pyrrolidylacetate (Hess and Fink, A., 1920, i. 497) is not condensed by sodium ethoxide to the compound (III). C. H.

**Preparation of  $\alpha$ -Lobeline.** C. H. BOEHRINGER SOHN, CHEMISCHE FABRIK, and J. BAEUMER (D.R.-P. 389816; from *Chem. Zentr.*, 1924, ii, 892).— $\alpha$ -Lobeline is obtained by treating the crude alkaloids from *Herba lobelia* with a suitable solvent such as ether and allowing the solution to crystallise during several days after seeding with a crystal of  $\alpha$ -lobeline. After one recrystallisation from ether, the product melts at 127°.  $\beta$ - and  $\gamma$ -Lobelines may be recovered from the mother-liquors by conversion into the hydrochlorides and treatment with chloroform.  $\alpha$ -Lobeline is of value against asthma and similar diseases. F. A. M.

**Asymmetric Tervalent Nitrogen Atom. V. Conhydrine and Methylisopelletierine.** K. HESS and R. GRAU (*Annalen*, 1925, 441, 101—137; cf. A., 1920, i, 330).—The attempted conversion

of conhydrine (I),  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHEt}\cdot\text{OH} \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{NH} \end{array}$ , into *isopelletierine* and

*methylisopelletierine* (II, R = H or Me)  $\begin{array}{c} \text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{Et} \\ \text{CH}_2\cdot\text{CH}_2\cdot\text{NR} \end{array}$ ,

gives instead the isomerides *conhydrinone* and *methylconhydrinone*. The present experiments prove that these substances are respectively structurally identical and that the isomerism must be attributed to the configuration of the groups attached to the nitrogen atom. Several facts are adduced which indicate a closer relation of the N to the O in *conhydrinone* and *methylconhydrinone* than in *isopelletierine* and *methylisopelletierine*.

*d*-Methylconhydrine, prepared by methylation of conhydrine with formaldehyde and formic acid (Hess and Eichel, A., 1917, i, 350; Hess, A., 1919, i, 345), has b. p. 94—95°/11 mm.,  $d_4^{20}$  0.9400,  $n_D^{19}$  1.47076; it contains a trace of conhydrine, which is only detected on oxidation. Oxidation with chromic and acetic acids generally removes the methyl group and gives *d*-conhydrinone, but occasionally pure *d*-methylconhydrinone is obtained. The density of the product indicates whether one or both are formed. *d*-Conhydrinone has b. p. 84—85°/9—10 mm. and  $d_4^{20}$  0.9386. *d*-Methylconhydrinone boils at 80—81°/8 mm. and has  $d_4^{20}$  0.9343,  $n_D^{20}$  1.46105. The conditions for the preparation of one alone are not yet determined, but the secondary base is easily obtained from a mixture by means of ethyl azodicarboxylate. *d*-Methylconhydrinone forms a *picrate*, m. p. 86—87°, *hydrobromide*, m. p. 152—153°, *oxime*, b. p. 135°/10 mm. (*oxime picrate*, m. p. 152°), and a *methiodide*, m. p. 112°, identical with Hess and Eichel's preparation from *d*-conhydrinone and methyl iodide. The *methiodide* changes on long keeping, probably into methylpyrrolidylbutan-2-one, m. p. 212°. By repeated boiling with alcoholic hydrazine hydrate *d*-methylconhydrinone gives a *hydrazone*, b. p. 126—128°/12 mm., and in almost equal amount pure *methylconhydrine* (by reduction). *d*-Conhydrinone, obtained from the above oxidation product by means of ethyl azodicarboxylate, has the properties already described (Hess and Eichel, *loc. cit.*), except that the *picrate* has m. p. 107—108°, not 91—92°.

In order to prove structural identity with synthetic 1- $\alpha$ -*N*-methylpiperidylpropan-1-one, the *d*-methylconhydrinone must be racemised. Neither *d*-conhydrinone nor its methyl derivative is racemised by aqueous or alcoholic alkali. Acetic anhydride at 100° converts *d*-conhydrinone into an *enol-acetate*, b. p. 96—97°/10 mm., from which the base may be recovered unracemised. The *enol-acetate* of *d*-methylconhydrinone, b. p. 96—97°/9 mm., similarly regenerates unchanged base. Racemisation occurs, however, when the base or one of its salts (especially the *picrate*) is kept for some months. *dl*-Methylconhydrinone *picrate* melts at 107°, the *hydrobromide* at 152—153°, and mixed m. p. with the synthetic products confirm their identity. *dl*-Conhydrinone, obtained from a racemised oxidation mixture by means of ethyl azodicarboxylate, has b. p. 90—92°/11 mm.,  $d_4^{20}$  0.9380,  $n_D^{20}$  1.46065 (*picrate*, m. p. 107—108°;

hydrobromide, m. p. 151—152°; methiodide, m. p. 118—119°, agreeing in all respects with synthetic *dl*-conhydrinone prepared by demethylation of 1- $\alpha$ -*N*-methylpiperidylpropan-1-one with ethyl azodicarboxylate.

On passing conhydrine over platinised or palladiumised asbestos at 240—250°, dehydrogenation occurs, with formation of a mixture of 1- $\alpha$ -pyridylpropan-1-ol and tetrahydropyridyl ethyl ketone. The mixture is nitrosated and fractionated, giving a *nitroso* compound, b. p. 130—166°/10 mm.,  $[\alpha]_D +1.30^\circ$ , and a lower-boiling fraction, b. p. 86—110°/10 mm., from which the crystalline nitrate of 1- $\alpha$ -pyridylpropan-1-one, m. p. 105—106°, may be obtained. The base liberated from the nitrate has b. p. 91—92°/10 mm.,  $d_4^{20}$  1.0530,  $n_D^{20}$  1.52529 (picrate, m. p. 125°), agreeing in every respect with synthetic 1- $\alpha$ -pyridylpropan-1-one. Hydrazine hydrate reduces it to pyridylpropanol. The above nitroso compound is denitrosated by zinc and hydrochloric acid to a mixture of hydropyridines, b. p. 105—150°/11 mm., which on reduction with sodium and alcohol gives *dl*-conhydrine, m. p. 69—70°, identical with Hess'  $\beta$ -1- $\alpha$ -piperidylethylalkine (A., 1920, i, 329). Methylated *dl*-conhydrine is similarly identical with Hess'  $\beta$ -1-methylpiperidylpropan-1-ol. 1- $\alpha$ -Pyridylpropan-1-ol, obtained as picrate, m. p. 94—95°, from the mother-liquor after separation of the above nitrate, has b. p. 112—113°/13 mm.,  $d_4^{20}$  1.0501, agreeing with the constants for the secondary alcohol prepared by the reduction of 1- $\alpha$ -pyridylpropan-1-one. *dl*-Conhydrinone is not dehydrogenated under the above conditions.

Methylisopelletierine, b. p. 91.5°/10 mm.,  $d_4^{20}$  0.9488,  $n_D^{20}$  1.46632, extracted from pomegranate, is very slightly dextrorotatory. It is demethylated by Hess' method (A., 1919, i, 347) to isopelletierine, b. p. 95—97°/10 mm.,  $d_4^{20}$  0.9589,  $n_D^{20}$  1.46789. The latter is reduced by sodium amalgam to a mixture of two racemic *dihydroisopelletierines*, b. p. 110—115°/12 mm. and 115—124°/12 mm., which are not separated. The dehydrogenation of isopelletierine and of the mixed *dihydroisopelletierines* does not proceed smoothly, the side-chain being attacked as well as the nucleus, with formation of  $\alpha$ -picoline and conyrine ( $\alpha$ -propylpyridine). 1- $\alpha$ -Pyridyl ethyl ketone is identified amongst the products of dehydrogenation of isopelletierine with platinised asbestos at 240—250°. A table of m. p. or b. p. of nineteen conhydrine and isopelletierine derivatives and their salts is appended.

C. H.

**Preparation of Papaverine (Nitrite.** C. H. BOEHRINGER SOHN CHEMISCHE FABRIK (D.R.-P. 392456 and 392459; additions to D.R.-P. 391071; from *Chem. Zentr.*, 1924, ii. 892).—Residual unaltered papaverine is dissolved in excess of dilute acid at about 0° either during the reaction or after; the reaction between nitrites and salts of papaverine is effected in concentrated solution, and the addition of substances to remove free papaverine base may occasionally be dispensed with. Papaverine nitrite is practically unattacked by cold dilute acids, so that the free base may be removed by their aid with little risk of decomposing the nitrite or

of converting it into papaveralldoxime. Thus, a solution of papaverine sulphate at  $0^{\circ}$  is treated with 10% aqueous phosphoric acid and then with 30% sodium nitrite solution so long as a precipitate is formed; after a few hours, the resultant oil crystallises, or the product from sodium nitrite and papaverine salts is extracted with ice-cold 10% hydrochloric acid. By treating papaverine salts with sodium nitrite in as concentrated solution as possible the hydrolysis of the salts by the nitrite is so far suppressed that a special extraction of the free base is unnecessary; thus finely-powdered sodium nitrite is added to a well-stirred paste of papaverine sulphate; after a time the solidified oil may be washed free from sodium sulphate and nitrite.

F. A. M.

**Halogen-alkylated Aromatic Amines and a New Pyrrolidine Ring Closure.** P. WOLFF (*Ber.*, 1925, 58, [B], 404—406).—Ethylaniline, preferably diluted with diethylaniline, is converted by trimethylene dibromide and treatment of the crude product with concentrated hydrochloric acid (cf. von Braun and Kirschbaum, A., 1920, i, 29) into a mixture of *ethyl- $\gamma$ -chloropropylaniline*, b. p.  $146\text{--}150^{\circ}/13$  mm., and diphenyldiethyltrimethylenediamine,  $\text{NEtPh}[\text{CH}_2]_3\text{NEtPh}$  (cf. Fröhlich, A., 1907, i, 346). If the chlorinated base is heated with hydrobromic acid and the product is distilled, hydrogen bromide is evolved and 1-phenyl-2-methylpyrrolidine, b. p.  $126\text{--}128^{\circ}/13$  mm. [*methiodide*, m. p.  $159^{\circ}$  (decomp.)], is produced.

H. W.

**Hydrogenation of Indole to Perhydroindole [Octahydroindole] and to *o*-Ethylhexahydroaniline.** R. WILLSTÄTTER, F. SEITZ, and J. VON BRAUN (*Ber.*, 1925, 58, [B], 385—387).—Re-examination of the product of the complete hydrogenation of indole in the presence of nickel at  $225^{\circ}$  (cf. von Braun, Bayer, and Blessing, A., 1924, i, 545) shows it to be *o*-ethylhexahydroaniline and not octahydroindole as stated previously. The latter substance is prepared by hydrogenation of indole at the atmospheric temperature in presence of spongy platinum (cf. Willstätter and Jacquet, A., 1918, i, 392); it has  $d_4^{20}$  0.9472 instead of 0.9947 recorded previously.

H. W.

**Catalytic Hydrogenation of Indole Bases.** J. VON BRAUN and O. BAYER (*Ber.*, 1925, 58, [B], 387—393).—The observation that indole suffers ring fission with production of *o*-ethylcyclohexylamine when hydrogenated in the presence of nickel at  $225^{\circ}$  (cf. Willstätter, Seitz, and von Braun, preceding abstract) has necessitated a revision of previous work (von Braun, Bayer, and Blessing, A., 1924, i, 545), whereby it is established that the stability of the pyrrolidine ring in dicyclic perhydroindole bases is increased by the presence of alkyl substituents, particularly when they are in close proximity to the nitrogen atom. Thus, 2-methylindole is converted almost exclusively at  $200^{\circ}$  into 2-methyloctahydroindole (benzenesulphonyl derivative, m. p.  $120\text{--}121^{\circ}$ , instead of  $110\text{--}112^{\circ}$  recorded previously); at  $240\text{--}250^{\circ}$ , however, ring opening occurs with the production of *o*-propylcyclohexylamine, b. p.  $60^{\circ}/14$  mm.,  $d^{19}$  0.8752 (the hygroscopic hydrochloride, chloroplatinate, m. p.  $213^{\circ}$ ,

*benzenesulphonyl* derivative, m. p. 131—132°, and quaternary *methiodide*, m. p. 208—210°, are described). 3-Methylindole at 205° gives almost homogeneous 3-methyloctahydroindole, b. p. 75°/15 mm.,  $d_4^{17}$  0.9080 (*picrate*, m. p. 150°); at 250°, *o*-isopropylcyclohexylamine, b. p. 68°/15 mm.,  $d_4^{17}$  0.8790, is produced, and this base is also present in the mixture formed at 220°; the benzene-sulphonyl derivative, m. p. 132°, and the *picrate*, m. p. 194—195°, described previously as derived from 3-methyloctahydroindole, are compounds of *o*-isopropylcyclohexylamine. 1:2-Dimethylindole is converted at 240° mainly into 1:2-dimethyloctahydroindole with a small proportion of *o*-propylhexahydromethylaniline. 3-Ethylindole at 235° yields mainly *o*-isobutylcyclohexylamine, b. p. 92°/18 mm.,  $d_4^{17}$  0.8900 (*hydrochloride*, m. p. 212—214°; *chloroplatinate*, decomp. 217°; *benzoyl* derivative; *phenylthiocarbamide* compound; quaternary *methiodide*, m. p. 236—237°). 1-*n*-Butylindole, b. p. 145°,  $d_4^{18}$  1.002 (the *picrate* is described), is obtained by the action of *n*-butyl bromide on the potassium derivative of indole. When hydrogenated at 235°, it yields mainly 1-*n*-butyloctahydroindole, b. p. 102—103°/16 mm.,  $d_4^{16}$  0.8873 (the *picrate*, m. p. 135°, very hygroscopic *hydrochloride*, *chloroplatinate*, and non-crystalline *methiodide* are described); in addition, *o*-ethylcyclohexylamine is formed in small amount, doubtless owing to primary, reductive elimination of the butyl group followed by opening of the ring.

H. W.

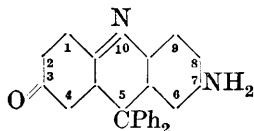
**Preparation of Acridine Derivatives.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING, L. MACK, and A. FEHLE (D.R.-P. 393411 and 395683 [additions to D.R.-P. 360421, A., 1923, i, 1130], and Brit. Pat. 199870 [addition to Brit. Pat. 176038, A., 1923, i, 1132]; from *Chem. Zentr.*, 1924, ii, 1025—1026).—The preparation is described of acridine derivatives by the method of D.R.-P. 360421, consisting (1) in heating 9-halogenacridines with salts of ammonia, amines, hydroxylamine, acid amides, etc., in presence or absence of solvents (in particular, phenol), after a preliminary treatment with alkali alkoxide or phenoxide, if desired; (2) in heating 9:9-diaryloxy- or 9:9-alkoxyaryloxy-9:10-dihydroacridines with ammonia or aliphatic amines or their salts, or with acid amides and subsequent removal of the acid radical (cf. D.R.-PP. 364031—364037, A., 1923, i, 1130); suitable acid amides are carbamide, dicyanodiamide, acetamide, benzamide, and toluene-*p*-sulphonamide. Thus 9-amino-2-ethoxyacridine is prepared from 9-chloro-2-ethoxyacridine and ammonium oxalate, ammonium sulphite, carbamide, or acetamide (9-acetamido-2-ethoxyacridine being formed intermediately) using phenol as a solvent; or from 9-phenoxy-2-ethoxyacridine, m. p. 85°, and ammonium carbonate or acetate in presence of phenol; or by heating 9-phenoxy-2:9-diethoxy-9:10-dihydroacridine with a solution of ammonia in phenol at 140°. 9-Phenoxy-2:9-diethoxy-9:10-dihydroacridine, yellow crystals, m. p. 77°, is formed by heating 2:9-diethoxyacridine (m. p. 83°, from 9-chloro-2-ethoxyacridine and sodium ethoxide) with phenol at 100°.

3 : 9-Diamino-7-ethoxyacridine is formed by treating 9-chloro-3-amino-7-ethoxyacridine with ammonium chloride or sulphate in phenol; by treating 3-amino-7 : 9-diethoxyacridine with carbamide in phenol or cresol, or by heating 3-amino-7-ethoxy-9 : 9-diphenoxy-9 : 10-dihydroacridine (orange crystals, m. p. 155°, hydrochloride, decomp. 278°) with aqueous or alcoholic ammonia, ammonium sulphate or carbonate, or carbamide. The 3-amino-9 : 9-diphenoxy-7-ethoxy-9 : 10-dihydroacridine hydrochloride was prepared by reducing 9-chloro-3-nitro-7-ethoxyacridine with stannous chloride at 65—70° to 9-chloro-3-amino-7-ethoxyacridine, yellow crystals, m. p. 192° (hydrochloride, red crystals); the base is heated at 100° with phenol, and on pouring into dilute sodium hydroxide the 9 : 9-diphenoxy compound is precipitated. 3-Amino-9-ethylamino-7-ethoxyacridine (m. p. 126°, decomp.) is formed on heating 9-chloro-3-amino-7-ethoxyacridine with ethylamine hydrochloride in phenol at 130°, or by heating 3-amino-7-ethoxy-9 : 9-diphenoxy-9 : 10-dihydroacridine with ethylamine hydrochloride in amyl alcohol at 160—190°.

3-Amino-7-ethoxy-9-hydroxyethylaminoacridine is formed by heating the corresponding 9 : 9-diphenoxy-9 : 10-dihydroacridine derivative with hydroxyethylamine in absolute alcohol at 170°; m. p. 166°, hydrochloride, yellow crystals. 3 : 9-Diaminoacridine is formed by heating 9-chloro-3-aminoacridine with carbamide, or hydroxylamine hydrochloride and sodium acetate, in phenol. 9 : 9-Diphenoxy-9 : 10-dihydroacridine hydrochloride, decomp. 200°, is formed from 9-chloroacridine and phenol. 9 : 9-Diphenoxy-7-ethoxy-9 : 10-dihydroacridine hydrochloride, decomp. 238°, is formed from 9-chloro-7-ethoxyacridine and phenol. 3-Nitro-9 : 9-diphenoxy-7-ethoxy-9 : 10-dihydroacridine, m. p. 121° (formed from 9-chloro-3-nitro-7-ethoxyacridine and phenol), and 3-amino-9 : 9-di-*p*-tolyl-7-ethoxy-9 : 10-dihydroacridine, m. p. 95° (formed from 9-chloro-3-amino-7-ethoxyacridine and *p*-cresol), when heated with ammonia, aliphatic amines or their salts, or with acid amides, are converted into the corresponding 9-aminoacridine derivatives. F. A. M.

#### Carbazones [5 : 5 - Diphenyldihydroacridones]. IV. Coloured Derivatives of Tetraphenylmethane. F. KEHRMANN

and J. TSCHUI (*Helv. Chim. Acta*, 1925, 8, 23—27; cf. A., 1921, i, 600).—Amino- and hydroxy-carbazones are obtained from diamino-carbazine derivatives in a manner exactly analogous to the preparation of aposafranone from aposafranine. 7-Amino-5 : 5-diphenyl-3-carbazone (7-amino-5 : 5-diphenyl-5 : 10-dihydro-3-acridone) (annexed formula), small, brassy needles giving a violet powder, m. p. 248—249°, is obtained by the action of alcoholic sodium hydroxide on 2-aminocarbazine. It has an intense colour and fluorescence which vary in a remarkable way with the solvent employed. Prolonged



action of the alkali converts it into 2-hydroxycarbazonone (7-hydroxy-5 : 5-diphenyl-5 : 10-dihydro-3-acridone), dark brown crystals with a green, metallic lustre, m. p. 233—233° (acetyl derivative, m. p. 208—

209°). 7 : 9-Diaminocarbazono (7 : 9-diaminodiphenyldihydroacridone), black plates with a green reflex, m. p. 277—278°, was obtained in the same way from the corresponding imino compound (acetyl derivative, m. p. 236—237°), the final product of the action of alkali being probably 1-amino-7-hydroxydiphenyldihydroacridine.

G. M. B.

**Diphenylmethylcarbazine [Diphenylmethyldihydroacridine] and some Nitro Derivatives. V. Coloured Derivatives of Tetraphenylmethane.** F. KEHRMANN and J. TSCHUI (*Helv. Chim. Acta*, 1925, 8, 27—31; cf. A., 1919, i, 551, 552).—The name "carbazine" is suggested instead of 5 : 10-dihydroacridine (cf. A., 1921, i, 600). Methylation of diphenyldihydroacridine by methyl iodide in methyl-alcoholic solution at 130° yields 5 : 5-diphenyl-10-methylcarbazine, colourless crystals, m. p. 162—163°. One to four nitro groups may be introduced into this substance by means of nitric acid and acetic acid under various conditions. 3-Nitro-5 : 5-diphenyl-10-methylcarbazine, lemon-yellow crystals, was reduced by tin and hydrochloric acid to a base which was demethylated when boiled with hydrobromic acid and was then oxidised by ferric chloride to the known diphenylcarbazine. 3 : 7-Dinitro-5 : 5-diphenyl-10-methylcarbazine, lemon-yellow prisms, m. p. 279°, was converted by reduction, demethylation, and subsequent oxidation into 2-aminodiphenylcarbazine. 1 : 3 : 7-Trinitro-5 : 5-diphenyl-10-methylcarbazine, lemon-yellow needles, m. p. 305° (decomp.), was converted as before into 2 : 5-diaminocarbazine. 1 : 3 : 7 : 9-Tetranitro-5 : 5-diphenyl-10-methylcarbazine, yellow, insoluble crystals (decomp.), was reduced to yield a base giving violet-red ethereal solutions and identical with 1 : 3 : 9-triaminocarbazine. The oxidation of the above-mentioned reduction products of the four nitro compounds without demethylation, gave rise to unstable, coloured substances which were not isolated.

G. M. B.

**Absorption Spectra of Pyrrole and its Derivatives. III. Influence of Amino and Ureido Groups on the Absorption Spectra of Pyrrole Derivatives.** G. KORSCHUN and (MME.) C. ROLL.—(See ii, 258.)

**Pyrrole and Melanins. Spectrophotometric Studies.** G. GALLERANI.—(See ii, 266.)

**Preparation of Alkyl Homologues of Pyridine.** CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING), M. DOHRN, and H. HORSTERS (D.R.-P. 390333; from *Chem. Zentr.*, 1924, ii, 891).—Alkyl homologues of pyridine are prepared by reducing pyridine or its homologues in acetic anhydride solution, leaving for 24 hours, adding water, and then excess of potassium carbonate. 4-Ethylpyridine is thus obtained from pyridine as a thick, yellow oil, b. p. 165—167°, which is oxidised to isonicotinic acid by permanganate. In a similar way  $\alpha$ -picoline affords 2-methyl-4-ethylpyridine, b. p. 169—174°

F. A. M.

**cis-trans-Isomerism in the Stilbazole Series.** C. RÄTH and E. LEHMANN (*Ber.*, 1925, 58, [B], 342—346).—2-Methylpyridine is converted by *o*-nitrobenzaldehyde at 220—225° into 2'-nitro-2-stilbazole, m. p. 101° [Feist (*A.*, 1901, i, 290) gives m. p. 95—96°]; the hydrochloride, m. p. 216° (decomp.) (Feist gives m. p. 206—212°), and the *picrate*, m. p. 211—212°, are described. If the substances are allowed to react at temperatures below 150° in the presence of water, 2'-nitro-2-stilbazolealkine (2- $\beta$ -hydroxy- $\beta$ -*o*-nitrophenylethylpyridine) is exclusively produced (cf. Roth, *A.*, 1901, i, 165). The alkyne is converted by zinc chloride in the presence of alcohol at 110° into a mixture of *trans*- and *cis*-2'-nitro-2-stilbazole, m. p. 95°, the isomerism of which is established by the conversion of each into the same dibromide, m. p. 182° [Feist (*loc. cit.*) gives m. p. 167—168°]. *trans*-2'-Nitro-2-stilbazole is reduced by zinc dust in strongly acid solution to *trans*-2'-amino-2-stilbazole, m. p. 98—99°, b. p. 197—200°/12 mm. (*hydrochloride*, m. p. 250°; *picrate*, m. p. 158—159°). In a similar manner, 2'-nitro-2-stilbazolealkine is reduced to 2'-amino-2-stilbazolealkine, m. p. 109°, which gives a very hygroscopic *hydrochloride*. The alkyne is converted by zinc chloride at 155—160° into a mixture of *trans*-2'-amino-2-stilbazole and *cis*-2'-amino-2-stilbazole. Treatment of 2'-nitro-2-stilbazolealkine with a solution of hydrogen bromide in glacial acetic acid at 125° gives minimal quantities of 2- $\beta$ -bromo- $\beta$ -*o*-nitrophenylethylpyridine *hydrobromide*; the main product is a mixture of *trans*- and *cis*-2'-nitro-2-stilbazoles, the formation of which is due to the transformation of the primary bromo derivative into the hydrobromide of 2'-nitro-2-stilbazole. H. W.

**Condensation of Hydroxy- and Methoxy-quinaldines, and 2-Hydroxylepidine with Aromatic Aldehydes.** J. TRÖGER and E. DUNKER (*J. pr. Chem.*, 1925, [ii], 109, 88—123; cf. *A.*, 1912, i, 895).—Further investigations on the condensation products of 2-, 3-, and 4-methoxyquinaldines with aromatic aldehydes have shown that when the methoxyl group occupies the 2- and 3-position in the pyridine ring the condensation products obtained do not form crystalline salts (cf. Tröger and others, *A.*, 1912, i, 895; 1913, i, 748) and hence the third methoxyl group must occupy either the 4-position or a position in the benzene ring (cf. Späth and Eberstaller, *A.*, 1924, i, 1335). Attempts to obtain similar condensation products from 2-methoxylepidine lead to demethylation of the base, and the condensation products of 2-hydroxylepidine are obtained. These do not yield crystalline salts or double salts. The use of unmethylated hydroxyquinaldines or hydroxyaldehydes generally hinders the condensation or prevents it altogether. Thus if 4-hydroxy-2-methylquinoline is substituted for 4-methoxy-2-methylquinoline in Späth and Brunner's synthesis of cusparine (*A.*, 1924, i, 1226), no condensation takes place, whilst no crystalline bases or derivatives are obtained when salicylaldehyde is used. Preliminary experiments on the reduction of these condensation products indicate that the sodium and alcohol method is not generally applicable and that palladised charcoal and hydrogen



give the best results, although the catalyst tends to be poisoned fairly rapidly. Tin and hydrochloric acid tend to reduce the pyridine ring as well as the double linking, yielding tetrahydroquinoline derivatives.

2-Methoxy-4-methylquinoline, on heating at 160–170° with anisaldehyde, with or without zinc chloride, yields 2-hydroxy-4-methylquinoline, although on heating alone at this temperature no demethylation takes place.

2-Hydroxy-4-methylquinoline (obtained by heating acetoacetanilide with concentrated sulphuric acid at 120°), condenses with benzaldehyde, in presence of zinc chloride, to give 2-*hydroxy-4-β-styrylquinoline*, brown powder, m. p. 130°. Salicylaldehyde similarly affords 2-*hydroxy-4-β-o-hydroxystyrylquinoline*, yellow powder, m. p. above 360°; anisaldehyde, 2-*hydroxy-4-β-p-hydroxystyrylquinoline*, brown, amorphous substance, m. p. above 360°, and vanillin, 2-*hydroxy-4-β-p-hydroxy-m-methoxystyrylquinoline*, chocolate-brown. These condensation products are weakly basic and do not yield crystalline salts. With protocatechualdehyde extensive decomposition takes place.

3-Hydroxy-2-methylquinoline, obtained by Königs and Stockhausen's method (A., 1902, i, 693), forms a *methiodide*, pale yellow needles, m. p. 235–240°; the methohydroxide could not be isolated, but from its solution the *chloroplatinate*, long, yellow needles (+3H<sub>2</sub>O), is obtainable. Methyl iodide and alcoholic potassium hydroxide convert 3-hydroxyquinaldine into 3-*methoxy-2-methylquinoline*, prisms, m. p. about 31°. The *hydrochloride* and *perchlorate* are deliquescent; the *chloroplatinate* (+H<sub>2</sub>O), and an abnormal *chlorostannate*, [OMe·C<sub>9</sub>H<sub>5</sub>MeN]<sub>2</sub>H<sub>2</sub>SnCl<sub>6</sub>, are described. Attempts to determine whether in this chlorostannate a dihydro compound of the base was present, resulting from the oxidation of the stannous chloride, gave no definite results. The *methiodide*, brown prisms, m. p. 196°, is obtained in poor yield, together with a *substance*, yellow needles, m. p. 84°, containing 2–3% of iodine, by heating 3-methoxyquinaldine with methyl iodide and methyl alcohol at 100°. 3-Ethoxy-2-methylquinoline (Königs and Stockhausen, *loc. cit.*), m. p. 74°, under similar conditions readily yields the *methiodide*, pale yellow needles (+1.5H<sub>2</sub>O), m. p. 207°. The latter is converted by silver oxide into a solution showing indications of ammonium base formation, but not of quinaldonium change as observed with the 4-methoxyquinaldines (Conrad and Eckhardt, A., 1889, 519).

3-Hydroxy-2-methylquinoline, on heating with benzaldehyde and zinc chloride, yields 3-*hydroxy-2-β-styrylquinoline*, chocolate-brown substance, m. p. 130°, sintering at 110° (*methiodide*, *hydrochloride*, and *chloroplatinate* are amorphous). 3-*Hydroxy-2-β-o-hydroxystyrylquinoline*, m. p. 220°, and 3-*hydroxy-2-β-p-hydroxystyrylquinoline*, brownish-yellow powder, m. p. 225°, were similarly obtained.

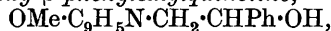
4-*Hydroxy-2-β-styrylquinoline* forms yellowish-white plates, m. p. 279° (*hydrochloride* and *chloroplatinate* described). *Hydroxy-2-β-o-hydroxystyrylquinoline*, bright yellow powder, darkening at 260°,

m. p. above  $300^{\circ}$ , is converted by sodium ethoxide and methyl iodide into 4-methoxy-2- $\beta$ -o-methoxystyrylquinoline, amorphous, yellow substance, m. p. above  $300^{\circ}$ , and by sodium ethoxide and benzyl chloride into the corresponding dibenzyl ether, brownish-yellow powder. 4-Hydroxy-2-methylquinoline, anisaldehyde, and zinc chloride, etc., yield 4-hydroxy-2- $\beta$ -p-methoxystyrylquinoline, greyish-yellow, amorphous product, m. p.  $266^{\circ}$ , yielding a yellow perchlorate; in the absence of zinc chloride, 4-hydroxy-2- $\beta$ -hydroxy- $\beta$ -p-methoxyphenylethylquinoline,

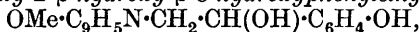


(not obtained crystalline) is produced. The chloroplatinate and chloraurate are described. 4-Methoxy-2- $\beta$ -styrylquinoline has m. p.  $297^{\circ}$  (hydrochloride, yellow). From 4-methoxy-2- $\beta$ -o-hydroxystyrylquinoline, ochreous powder, no crystalline derivatives could be obtained. 4-Methoxy-2- $\beta$ -p-methoxystyrylquinoline is a yellowish-white powder [hydrochloride sintering at  $120^{\circ}$ , m. p.  $165^{\circ}$ ; methiodide, m. p.  $168^{\circ}$  (decomp.)]. m-Methoxybenzaldehyde and 4-methoxy-2-methylquinoline yield lustrous crystals of a base, m. p.  $134.5^{\circ}$ , which has not been obtained pure, but is probably 4-methoxy-2- $\beta$ -m-methoxystyrylquinoline. Vanillin and 4-methoxy-2-methylquinoline yield 4-methoxy-2- $\beta$ -p-hydroxy-3'-methoxystyrylquinoline (yellow hydrochloride).

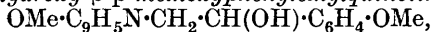
3-Methoxy-2-methylquinoline, benzaldehyde, and zinc chloride yield 3-methoxy-2- $\beta$ -styrylquinoline, a yellow, amorphous substance (hydrochloride, yellow plates), or in the absence of zinc chloride, 3-methoxy-2- $\beta$ -hydroxy- $\beta$ -phenylethylquinoline,



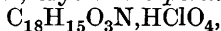
yellow needles, m. p.  $103^{\circ}$  (hydrochloride, decomp.  $105^{\circ}$ , chloroplatinate, and chloraurate described). Salicylaldehyde and 3-methoxy-2-methylquinoline yield an amorphous, yellow substance from which the golden-yellow perchlorate,  $\text{C}_{18}\text{H}_{15}\text{O}_2\text{N}\cdot\text{HClO}_4$ , of 3-methoxy-2- $\beta$ -o-hydroxystyrylquinoline is obtained; the corresponding alkine, 3-methoxy-2- $\beta$ -hydroxy- $\beta$ -o-hydroxyphenylethylquinoline,



is a flesh-coloured powder (diacetyl derivative, yellow, m. p.  $110^{\circ}$ ), which could not be crystallised. Anisaldehyde, 3-methoxy-2-methylquinoline, and zinc chloride yield 3-methoxy-2- $\beta$ -4'-methoxystyrylquinoline, yellowish-brown powder (hydrochloride, chloroplatinate, and perchlorate described), or in the absence of zinc chloride, 3-methoxy-2- $\beta$ -hydroxy- $\beta$ -p-methoxyphenylethylquinoline,



m. p.  $112^{\circ}$  (hydrochloride, chloroplatinate, and chloraurate described). Protocatechualdehyde and 3-methoxy-2-methylquinoline yield a brown, amorphous product, 3-methoxy-2- $\beta$ -mp-dihydroxystyrylquinoline, giving a brown, crystalline perchlorate,



whilst vanillin affords 3-methoxy-2- $\beta$ -p-hydroxy-m-methoxystyrylquinoline, dark red (perchlorate and sulphate described). 3-Methoxy-2-methylquinoline, piperonal, etc., yield a product giving an orange hydrochloride, from which on reduction no crystalline product was obtained.

R. B.

**Constitution and Colour. XI. Colour Variations shown by Acidic Organic Substances when Forming Salts with Bases.** F. KEHRMANN (*Helv. Chim. Acta*, 1925, 8, 31—35; cf. A., 1922, ii, 333).—Salt formation at a phenolic hydroxyl group causes an intensification of the colour of a substance. The auxochromic effect of the  $\cdot\text{ONa}$  group is of the same magnitude as that of the amino group, whilst hydroxyl is similarly equivalent to  $\text{NH}_2\cdot\text{HCl}$ . A similar equivalence in colour is found between the sodium salt of a hydroxyquinone (e.g., benzaurin) and the corresponding aminoquinone-imine hydrochloride (e.g., Doebner's violet). This relation holds with safranines, oxazines, thionines, and carbazines (dihydroacridines), and it is accounted for by the smaller auxochromic effect of the  $\cdot\text{C:NH}$  group as compared with the  $\text{C:O}$  group, being compensated by the intensification due to salt formation on the former. G. M. B.

**Allylcrotylbarbituric Acid.** L. TAUB, L. SCHÜTZ, and K. MEISENBURG (U.S. Pat. 1511919).—*Allylcrotylbarbituric acid* has m. p. 125—126°. CHEMICAL ABSTRACTS.

**Action of Formaldehyde on Alkylated Methyluracils.** K. SCHMEDES (*Annalen*, 1925, 441, 192—203; cf. Kircher, A., 1912, i, 53).—Under ordinary conditions, 1:4-dimethyluracil is either unattacked or is polymerised by treatment with formaldehyde. In concentrated hydrochloric acid, however, the product is 1:4-dimethyl-5-chloromethyluracil, which with boiling water or cold alkali gives a dimeride of dimethyluracil. With bromine water, it yields probably a dibromide, which readily loses bromine and formaldehyde to form 5-bromo-1:4-dimethyluracil, m. p. 231—233°. 1:4:5-Trimethyluracil is converted by formaldehyde, alone or in concentrated acid, into the dimeride,  $\text{C}_{14}\text{H}_{20}\text{O}_4\text{N}_4$ , m. p. 300—310°, which forms a dibromide, m. p. 249—251°. From the dibromide by treatment with lead hydroxide are obtained the corresponding oxide,  $\text{C}_{14}\text{H}_{18}\text{O}_5\text{N}_4$ , m. p. 291—293°, and a soluble by-product, m. p. 258—260°. C. H.

**Preparation and some Properties of Picrolonic Acid.** L. HUGOUNENQ, G. FLORENCE, and E. COUTURE (*Bull. Soc. Chim. biol.*, 1925, 7, 58—60).—Bertram's method for the preparation of picrolonic acid (*Diss.*, Jena, 1892) has been improved in some important particulars. Pure phenylmethylpyrazolone is treated with seven times its weight of cold nitric acid ( $d$  1.38), the product washed with water and treated with boiling 33% acetic acid. After filtration, crude picrolonic acid separates. It is dried in a vacuum, freed from resins by treatment with benzene, and crystallised from 90% alcohol (yield, 16%). C. T. G.

**Constitution and Colour. X. Constitution of Coloured Derivatives of Triphenylmethane.** F. KEHRMANN (*Helv. Chim. Acta*, 1924, 7, 1057—1062).—A theoretical discussion, the subject matter being classified under the following headings: (i) the *p*-quinonoid triphenylmethane dyes, which form imonium salts; (ii) the coloured (carbonium) salts afforded by triphenylcarbinol

and its derivatives, and (iii) the coloured free radicals, such as triphenylmethyl.

W. A. S.

**Preparation of Mauveine and Various Bases.** A. COBENZL (*Oesterr. Chem.-Ztg.*, 1925, 28, 25—28; cf. A., 1916, i, 77).—Mauveine is regarded as a regular safranine, formed from phenyl-*p*-phenylenediamine and 2 mols. of *o*-toluidine, and in confirmation details are given of its technical preparation by the oxidation of a mixture of these substances and aniline; *as*-phenylmethyl-*p*-phenylenediamine gives a redder dye, *as*-phenyl-*p*-tolyl-*p*-phenylenediamine a bluer one. Grey dyes are formed by heating nitroso-dimethyl- or -diethyl-aniline (or a mixture of these) with *as*-dimethyl- or -diethyl-*p*-phenylenediamine, and by oxidising nitrosodimethylaniline with aniline bases. Blue safranines are formed by oxidising a mixture of *as*-dimethyl-*p*-phenylenediamine and aniline or other bases; the former may be converted into other blue dyes either by fusion with *p*-phenylenediamine or diazotisation and coupling with  $\beta$ -naphthol. Sulphonated dyes related to Meldola's blue are made (1) by heating sodium  $\beta$ -naphthol-6-sulphonate with nitroso-dimethyl- or -diethyl-aniline and acetic acid; (2) by direct sulphonation of the dye. All are bluish-grey, and the *ethyl* compound,  $C_{26}H_{24}O_4N_3S$  is regarded (see original paper) as possessing a novel structure of the naphthaphenazine type.

6-Methylanilinoquinoline, a brown solid, has been prepared from *as*-phenylmethyl-*p*-phenylenediamine.

B. F.

**Varying Tendency of the Principal Aromatic Nuclei to Couple with Diazo Compounds.** G. R. LEVI (*Atti Congr. Naz. Chim. Ind.*, 1924, 271—274).—The predominance of azo dyes in which the coupling product is a derivative of naphthalene, especially  $\alpha$ -substituted naphthalene, rather than of benzene is shown to depend on the fact that, as regards their affinity for diazo compounds, the nuclei stand in the order  $\alpha$ -naphthyl,  $\beta$ -naphthyl, phenyl.

1- $\beta$ -Naphthyl-naphthylene-1:4-diamine,  $C_{20}H_{16}N_2$ , obtained by reduction of the product prepared from diazosulphanilic acid and  $\alpha$ : $\beta$ -dinaphthylamine in hydrochloric acid, forms an *acetyl* derivative, m. p. 180°. 2- $\alpha$ -Naphthyl-naphthylene-1:2-diamine, m. p. 195° (reddening), obtained from the same reagents but in acetic acid, forms an *acetyl* compound, m. p. 291°, and condenses readily with phenanthrenequinone to a base, which forms a crystalline *nitrate*,  $C_{34}H_{23}O_3N_3$ .

T. H. P.

**Octahydrophenazine.** M. GODCHOT (*Compt. rend.*, 1925, 180, 444—446).—Saturation of a cold absolute-alcoholic solution of 2-chlorocyclohexanone (cf. Bouveault and Chereau, A., 1906, i, 513) with dry ammonia produces 1:2:3:4:6:7:8:9-octahydrophenazine (yellow prisms, m. p. 107—108°), which yields the following derivatives: *dibromide*, m. p. about 70° (decomp.); *picrate*, m. p. 167—168°; *monomethiodide*, m. p. about 150° (decomp.); *chloroplatinate*,  $2C_{12}H_{16}N_2 \cdot H_2PtCl_6$ ; *monohydrochloride*, m. p. 116—117°.

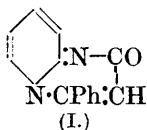
W. E. E.

**Constitution of the 4-Phenyl-1:8-naphthyrid-2-one of Palazzo and Tamburini. Tautomerism of 2-Aminopyridine.**

O. SEIDE (*Ber.*, 1925, 58, [B], 352—356).—By the action of sulphuric acid on 2-benzoylacetylamidopyridine Palazzo and Tamburini (*A.*, 1911, i, 327) have obtained a substance which they regarded as 4-phenyl-1:8-naphthyrid-2-one,  $C_6H_5N < \begin{smallmatrix} CPh:CH \\ NH-CO \end{smallmatrix}$ .

This compound is shown to be a pyrimidine derivative in which, as in analogous cases (cf. Tschitschibabin, *A.*, 1924, i, 987; this vol., i, 158; Finger and Kraft, this vol., i, 73), ring closure has occurred at the pyridine nitrogen atom and not at the 3-carbon atom.

2-Benzoylacetylamidopyridine, m. p. 111—112°, is conveniently prepared by heating ethyl benzoylacetate with 2-aminopyridine at 155—160°. The constitution of the compound as 2-benzoylacetylamidopyridine or 1-benzoylacetylamido-2-pyrimidine is established by the hydrolysis of its *methiodide*, m. p. 162°, to 1-methyl-2-pyrimidine. Ring closure to 4-*keto*-6-phenyl-1:2-divinylenedi-



*hydropyrimidine* (I), m. p. 151° (Palazzo and Tamburini's "4-phenyl-1:8-naphthyrid-2-one"), is effected with sulphuric acid (*d* 1.84) at 100°; the *hydrochloride*, m. p. 211—216° (decomp.), *chloroplatinate*, decomp. above 300° after blackening at 262°, and *picrate*, m. p. 183°, of the base are described. The constitution

ascribed previously to the compound is not compatible with its insolubility in cold alkali hydroxide and conversion by the hot reagent into acetophenone. With phosphorus pentachloride, it gives a *compound*,  $C_{14}H_9ON_2Cl$ , m. p. 164°. It is oxidised by permanganate to 4-*keto*-6-phenyldihydropyrimidine, m. p. 267°, identical with the synthetic product which will be described subsequently. H. W.

**Intramolecular Condensation Reactions of Aminoacetals and Aminoaldehydes. III. 2-Amino-3-methylpyridine and 1:2-Dihydronaphthyridine.** C. RATH (*Ber.*, 1925, 58, [B], 346—348; cf. Seide, this vol., i, 72).—3-Methylpyridine is converted

by sodamide in the presence of toluene at 120—130° into 2-amino-3-methylpyridine, b. p. 113—116°/11 mm., m. p. 103—104° (Seide, m. p. 24°); the hydrochloride, m. p. 177—178°, and picrate, m. p. 229°, are described. The base is transformed by bromoacetal at

250° into 1:2-dihydronaphthyridine,  $C_5H_5N < \begin{smallmatrix} CH:CH \\ NH-CH_2 \end{smallmatrix}$ , b. p. 112—117°/12 mm.; the non-crystalline *hydrochloride* is described.

H. W.

**Alkylation of Pyridyl-2-nitroamine. I. New Reaction Analogous to that of Kishner and Wolff.** A. E. TSCHITSCHIBABIN and G. P. MENSCHIKOV (*Ber.*, 1925, 58, [B], 406—408).

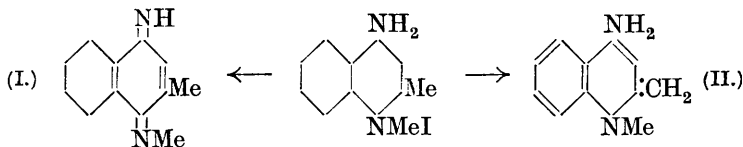
—Alkylation of pyridyl-2-nitroamine (Tschitschibabin and Razorenov, *A.*, 1915, i, 992) in aqueous alkaline solution by methyl sulphate or potassium methyl sulphate yields 1-methyl-2-pyridyl-nitroimine,  $C_5H_5NMe:N \cdot NO_2$ , m. p. 161° identical with the product obtained by the direct nitration of 1-methyl-2-pyrimidine (Tshi-

tschibabin and Kononov, unpublished work). The constitution of the product is further established by its decomposition by alkali hydroxide into nitrous oxide and 1-methyl-2-pyridone. The reaction is analogous to the Kishner-Wolff decomposition of hydrazones by alkalis and appears to be of general application. The similarity of the reaction to the decomposition of nitroamide by alkalis supports the constitution  $\text{NH}_2\cdot\text{NO}_2$  rather than  $\text{HO}\cdot\text{N}:\text{N}\cdot\text{OH}$  for nitroamide. 1-Ethyl-2-pyridylnitroimine has m. p.  $139^\circ$ . H. W.

**New Class of Indigoid Dyes.** F. REINDEL and H. RAUCH (*Ber.*, 1925, 58, [B], 393—397).—The author concurs with Finger and Kraft (this vol., i, 75) and Tschitschibabin (this vol., i, 158) in regarding "pyrindoxyl" (Reindel, A., 1924, i, 1236) as a glyoxaline derivative. Decarboxylation of pyridylglycine, from which the constitution of the compound is deduced, only proceeds smoothly to the production of 1-methyl-2-pyridimine if the latter is removed as it is formed, since otherwise it becomes isomerised to 2-methylaminopyridine. Addition of chloroacetic acid to 2-aminopyridine gives the *product*,  $\text{C}_5\text{H}_6\text{N}_2\cdot 2\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$ , m. p.  $87.5^\circ$ , from which pyridylglycine is quantitatively produced by treatment with warm sodium carbonate solution. Acetic anhydride and pyridylglycine give the *monoacetyl* compound ( $+\text{H}_2\text{O}$ ), m. p.  $300\text{--}301^\circ$  (decomp.), and the *diacetyl* derivative of the tautomeric form, m. p.  $195^\circ$ .

The dye obtained previously (*loc. cit.*) gives a crystalline *sodium* salt, whereby its bimolecular nature is established. H. W.

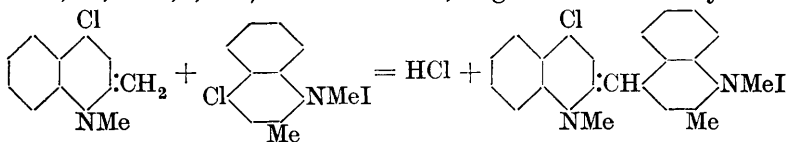
**Substituted 4-Aminoquinolines.** O. FISCHER, E. DIEPOLDER, and E. WÖLFEL (*J. pr. Chem.*, 1925, [ii], 109, 59—68).—A continuation of earlier work (A., 1916, i, 739), with the object of determining whether the elimination of hydrogen halide from 4-aminoquinaldinium salts is analogous to its elimination from the corresponding quinoline salts. The elimination of hydrogen iodide can take place in two ways, yielding either an imine base (I) or a methylene base (II); the latter reaction is considered the more



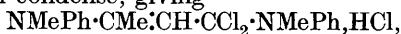
probable. 4-Chloroquinaldinium iodide reacts with aniline and (more slowly) with methylaniline, the product in the latter case giving rise to 4-phenylmethylamino-1-methyl-2-methylene-1:2-dihydroquinoline. 4-Hydroxyquinaldine, obtained in 16% of the theoretical yield by heating ethyl  $\beta$ -phenylamino- $\alpha$ -crotonate (cf. Conrad and Limpach, A., 1887, 679) with phosphorus pentachloride and oxychloride at  $110\text{--}115^\circ$ , is converted into 4-chloroquinaldine, the higher temperature and longer heating employed by Conrad and Limpach increasing the yield of a bluish-violet by-product. Similarly, a temperature of  $120^\circ$  suffices for the conversion of

4-chloroquinaldine into 4-anilinoquinaldine, m. p. 153–154° (cf. Conrad and Limpach, *loc. cit.*); alternatively the 4-chloroquinaldine may be treated with aniline in acetic acid solution. The *hydrochloride*, yellow needles, softening at 168°, resolidifying and melting at 252° (decomp.), the yellow *picrate*, and the yellow *methiodide*, darkening slightly at 240°, m. p. 254°, of 4-anilinoquinaldine are described. On warming with aqueous sodium hydroxide, the methiodide yields a yellow *base*,  $C_{17}H_{16}N_2$ , m. p. 162°, which with alcoholic hydrogen iodide is reconverted into the methiodide, and is probably 4-anilino-1-methyl-2-methylene-1:2-dihydroquinoline (*picrate*, m. p. 135°). Similarly 4-chloroquinaldine and methylaniline yield 4-*phenylmethylaminoquinaldine*, m. p. 76°, which affords a methiodide [yellow needles, darkening slightly at 215–225°, m. p. 235° (*picrate*, decomp. 159°)], identical with the product obtained from methylaniline and 4-chloroquinaldine methiodide, and apparently also with the product of addition of methyl iodide to the base  $C_{17}H_{16}N_2$  (m. p. 162°), obtained from 4-anilinoquinaldine and sodium hydroxide. 4-Chloroquinaldine and *as*-dimethylphenylenediamine similarly give a *base*,  $C_{18}H_{19}N_3$ , yellow, darkening at 250°, m. p. 268° (*hydrochloride*,  $C_{18}H_{20}N_3Cl$ , reddish-brown). With methyl iodide in the dark (cf. Conrad and Limpach, A., 1889, 519), 4-chloroquinaldine yields a *methiodide*, greenish-yellow needles, which turn blue at 200° and at 212° change to a bluish-black mass, with effervescence. Dissolved in alcohol and treated with sodium carbonate or dilute ammonia, the methiodide yields a violet solution which slowly deposits steel-blue crystals of a dye,  $C_{22}H_{20}N_2ClH$ . This dye, which is formed by loss of 1 mol. of hydrogen chloride and 1 mol. of hydrogen iodide, from 2 mols. of methiodide, is decolorised by acids and from its spectroscopic properties appears to be an *isocyanine*. The reaction is so sensitive that it can be easily used to detect the presence of atmospheric ammonia. The reaction is being further investigated (cf. following abstract). R. B.

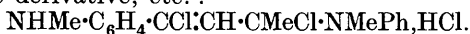
**Action of Phosphoryl Chloride on Aceto-methyl- and -ethyl-anilide. Synthesis of 4-Chloroisoquinocyanines.** O. FISCHER, A. MÜLLER, and A. VILSMEIER (*J. pr. Chem.*, 1925, [ii], 109, 69–87).—The dye obtained by treating 4-chloroquinaldine methiodide with ammonia (cf. Fischer, Diepolder, and Wölfel, preceding abstract) is identical with that obtained by Friedel (A., 1895, i, 423) by the action of phosphoryl chloride on acetomethyl-anilide, and has the composition  $C_{22}H_{20}N_2Cl_2$  and not  $C_{20}H_{20}N_2Cl_2$ , as stated by Friedel. Its formation from 4-chloroquinaldine methiodide is represented as due to loss of hydrogen iodide, yielding a methylene base, which then condenses (cf. Kaufmann and Vonderwahl, A., 1912, i, 502) as shown below, to give the chloro*isocyanine*.



The dye is thus a member of the ethyl-red group; this explains its spectroscopic properties, and its oxidation to 4-chloro-1-methyl-2-quinolone. A re-examination of Friedel's reaction shows that the acid solution obtained when the fused mass is dissolved in water contains no *isocyanine* dye but a considerable amount of 4-chloroquinaldine methochloride, from which the dye is produced on treatment with alkali. Methylaniline is also present in this solution, and it is suggested that phosphoryl chloride converts acetomethylanilide into the dichloro derivative,  $\text{NMePh}\cdot\text{CCl}_2\text{Me}$ , 2 mols. of which condense, giving



from which by ring closure and elimination of methylaniline the 4-chloroquinaldine is produced. Possibly 1 mol. of dichloro derivative may undergo rearrangement to a chlorinated *o*-amino-acetophenone derivative, etc.:



The *isocyanine* dye yields a *picrate*, decomp.  $193^\circ$ , and *chloroplatinate*. The mother-liquors from the dye, prepared by Friedel's reaction, contain small quantities of 4-methylanilinoquinaldinium chloride, isolated as the *picrate*, darkening at  $148\text{--}150^\circ$ , m. p.  $160^\circ$ , and the *iodide*, partly decomp. at  $215^\circ$ , wholly at  $235\text{--}238^\circ$ . Much less methylaniline is formed than is indicated by the above equations owing to interaction with the dichloride to give diphenyldimethylethenylamidinium chloride,  $\text{NMePh}\cdot\text{CCl}_2\text{Me} + \text{NHMePh} = \text{NMePh}\cdot\text{CMe}\cdot\text{NMePh} + \text{HCl}$ . This chloride is very soluble, but the difficultly soluble *iodide*, m. p.  $187\text{--}188^\circ$ , the *picrate*, and *chloroplatinate*, decomp.  $195^\circ$ , are readily obtained. The base itself on distillation yields a mixture of methylaniline and acetomethylanilide. This explains why Friedel obtained considerable methylaniline on basifying the liquors from the dye. Repetition of Hofmann's process, using acetic acid, methylaniline, and phosphoryl chloride, gives chiefly diphenyldimethylethenylamidinium chloride, whilst if part of the methylaniline is replaced by acetomethylanilide, an 80% yield of the amidinium iodide is obtained. Similarly, acetoethylanilide and phosphoryl chloride at  $125\text{--}130^\circ$  yield a gold or bronze *dye*,  $\text{C}_{24}\text{H}_{24}\text{N}_2\text{Cl}_2$ , decomp.  $185^\circ$  (yield 25%). The *iodide*, m. p.  $270^\circ$  (decomp.), is obtained by adding potassium iodide solution to an alcoholic solution of the chloride; on longer heating and with excess of potassium iodide, a blue solution is formed, which deposits a red *substance*. The *picrate*, m. p.  $210^\circ$  (decomp.), and *chloroplatinate*, m. p. above  $300^\circ$ , are also described. Oxidation with potassium permanganate yields 1-ethyl-4-chloroquinolone. The *isocyanine* obtained from acetoethylanilide is somewhat bluer than that from acetomethylanilide. R. B.

**Preparation of N-Aralkylated Iminazolyalkylamines [Aminoalkylglyoxalines].** O. GERNGROSS (D.R.-P. 392067, addition to D.R.-P. 332955; from *Chem. Zentr.*, 1924, ii, 890).—Halides of the type  $\text{Ar}\cdot\text{CH}_2\cdot\text{halogen}$  (where Ar=substituted or unsubstituted aryl groups) are allowed to react on the silver or alkali salts of iminazolyalkylamines or their *exo*-benzoyl deriv-



atives (cf. D.R.-P. 332955, and D.R.-P. 278884; A., 1915, i, 167; 1921, i, 454). Thus when the silver salt of histamine is heated with benzyl bromide in absolute alcohol the *hydrobromide* of N-exo-dibenzylhistamine (4- $\beta$ -dibenzylaminoethylglyoxaline), m. p. 152°, is obtained. The free base has m. p. 129°, and may also be obtained by heating a methyl-alcoholic solution of histamine and benzyl bromide at 100°. The silver salt of exobenzoylhistamine when heated with benzyl bromide in methyl alcohol affords isobenzylhistamine (4- $\beta$ -aminoethyl-1-benzylglyoxaline) as an oil; it is also formed in small amounts on benzylating the silver salt of free histamine. The products have a therapeutic action similar to that of ergot.

F. A. M.

**Preparation of Intermediate Products [Triazines].** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 220302).—The interaction of various cyanuric halides with  $\alpha$ -naphthol, in presence of a condensing agent, yields new compounds, in which the naphthol residues are linked to the cyanuric ring in their para positions. 2 : 4 : 6-Tri-p-hydroxynaphthyl-1 : 3 : 5-triazine (light yellow, m. p. above 300°); 2-anilino-4 : 6-di-p-hydroxynaphthyl-1 : 3 : 5-triazine (orange, m. p. 255—258°); 2 : 4-diamino-6-p-hydroxynaphthyl-1 : 3 : 5-triazine (colourless, m. p. 305—308°), and 2 : 4-diphenylamino-6-p-hydroxynaphthyl-1 : 3 : 5-triazine (m. p. 241—242°) have been obtained.

B. W. A.

**History of the Synthesis of Uric Acid.** R. BEHREND (*Annalen*, 1925, 441, 215—216).—Contrary to Horbaczewski's statement (A., 1883, 179; 1885, 1050; 1887, 918; 1888, 256), no uric acid is obtained by melting glycine or chloroacetic acid with carbamide. Horbaczewski remains, however, the discoverer of the first uric acid synthesis, for from trichlorolactamide and carbamide about 8% of uric acid is obtained.

C. H.

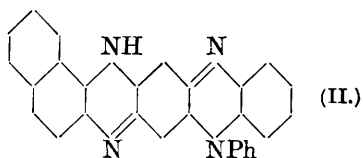
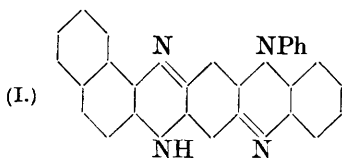
**Synthesis of Methylated Uric Acids by Behrend and Roosen's Method.** A. PRÜSSE (*Annalen*, 1925, 441, 203—215).—The Behrend-Roosen synthesis is applicable to 1-, 3-, and 7-methyl-, 1 : 7-, 3 : 7-, and 7 : 9-dimethyl-uric acids, but not to 9-methyl-, 1 : 3-, 1 : 9-, and 3 : 9-dimethyl-uric acids, nor to the tri- and tetra-methyluric acids. When methylcarbamide is used, the methyl group always takes up the 7-position. s-Dimethylcarbamide reacts only with isodialuric acid and not with its methyl derivatives. The synthesis of 7-methyl-, 7 : 9- and 3 : 7-dimethyl-, 1-methyl-, 1 : 7-, and 1 : 3-dimethyl-uric acids is described. Where no condensation with the carbamide occurs, the product of the reaction is the isobarbituric acid corresponding with the isodialuric acid used.

C. H.

**Fluorindines and Fluorindinium Salts.** F. KEHRMANN and J. A. SCHEDLER (*Helv. Chim. Acta*, 1925, 8, 3—8; cf. A., 1923, i, 488).—1 : 2-Naphthylenediamine hydrochloride condenses in aqueous solution with dihydroxybenzoquinone to give 2 : 3-dihydroxynaphthaphenazine,  $C_{10}H_6<\overset{N}{\parallel}\overset{N}{\parallel}C_6H_2(OH)_2$ , orange-yellow crystals

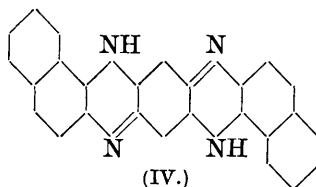
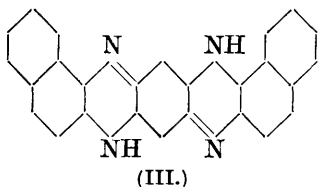
(diacetyl derivative, m. p. 217—218°), converted when heated with *o*-phenylenediamine in boiling benzoic acid into *naphthaphenfluorindine* (annexed formula). It is slowly oxidised in the air to a naphthaphendi-phenazine,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} > C_6H_2 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \approx C_6H_4$ .

Using *o*-aminodiphenylamine in place of *o*-phenylenediamine the products are *monophenyl-naphthaphenfluorindines* (I and II). The substance first isolated in microscopic red needles gives strongly fluorescent solutions, and from the nitrobenzene mother-



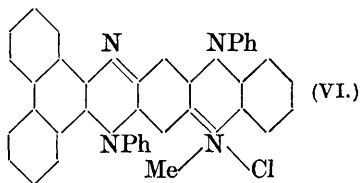
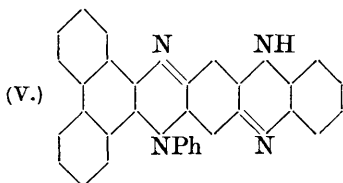
liquors a second isomeride is obtained (as its *hydrochloride*) which gives deep red, non-fluorescent solutions.

*Dinaphthadfluorindine* (III or IV) results from a similar condens-



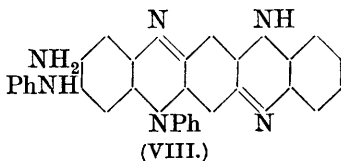
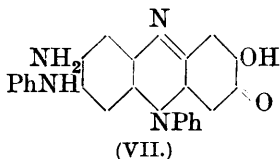
ation with 1 : 2-naphthylenediamine. The base (dark green *hydrochloride*) is unstable, being oxidised to a *dinaphthadiphenazine*,  $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} > C_6H_2 \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \approx C_{10}H_6$ .

1-Amino-2-anilino-7-hydroxyflavinduline, heated in fused benzoic acid with *o*-phenylenediamine, gives *N*-phenylphenanthraphenfluorindine (V), which gives intensely coloured solutions in various solvents but is not markedly fluorescent. In a similar manner, using *o*-aminodiphenylamine, *N*-diphenylphenanthraphenfluorindine is obtained, which is methylated by methyl sulphate, the product being isolated as *N*-diphenylmethylphenanthraphenfluorindinium chloride (VI), which gives bluish-green solutions.



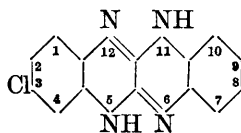
2-Amino-3-anilino-7-hydroxyaposafranon (VII) is produced by boiling diphenyltetra-aminobenzene dihydrochloride with dihydroxy-

benzoquinone in alcoholic solution, and is isolated as the *hydrochloride*. Condensed with *o*-phenylenediamine in boiling benzoic acid it is



converted into 2-amino-3-anilino-5-phenylfluorindine (VIII), isolated as the *nitrate*, almost black needles. G. M. B.

**Phenyl and Halogen Derivatives of Fluoflavine.** F. KEHRMANN and C. BENER (*Helv. Chim. Acta*, 1925, 8, 20—22).—6-Chloro-2:3-dihydroxyquinoxaline, m. p. above 350°, results from the condensation of 4-chloro-1:2-phenylenediamine hydrochloride with



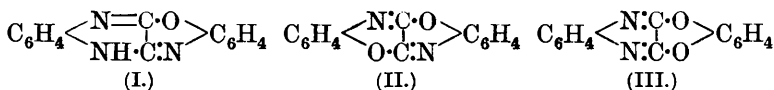
oxalic acid at 220°, and is converted by phosphorus pentachloride into 2:3:6-trichloroquinoxaline, m. p. 143—144°, colourless, but giving intensely yellow solutions in sulphuric acid. Condensation of chlorodihydroxyquinoxaline with *o*-phenylenediamine hydrochloride

in boiling benzoic acid yields 3-chlorofluoflavine (annexed formula, cf. Hinsberg and Pollak, A., 1896, i, 394), golden-yellow needles, m. p. above 350°.

Condensation of chlorodihydroxyquinoxaline with 4-chloro-1:2-phenylenediamine yields 3:8-dichlorofluoflavine, m. p. above 350°. The chlorine atoms in these chlorofluoflavines were found not to be replaceable by the anilido group. 5-Phenylfluoflavine, golden-yellow crystals, resulted from the condensation of phenylhydroxyquinoxalone with *o*-phenylenediamine. Its solutions have an intense green fluorescence. No quaternary salt was obtained with methyl sulphate. G. M. B.

**Syntheses of Oxygen Analogues of Fluoflavine.** F. KEHRMANN and C. BENER (*Helv. Chim. Acta*, 1925, 8, 16—20).—Oxygen analogues of fluoflavine (see above) are obtained by substituting *o*-aminophenols and pyrocatechol for *o*-phenylenediamine in its preparation. The substances are paler in colour as replacement of NH groups by oxygen proceeds, but all have halochromic properties, the salts being unstable to water.

*Diphenazineoxazine* (I), yellow needles, m. p. 311—312.5°, results from the condensation of dihydroxyquinoxaline and *o*-aminophenol in boiling benzoic acid, also by heating dichloroquinoxaline with *o*-aminophenol. The substance has a bluish-green fluorescence in solution and gives orange and greenish-yellow solutions in mineral



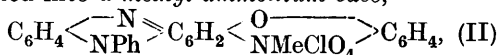
acids. From chlorodihydroxyquinoxaline by the above reaction, there was produced the corresponding *chlorodiphenazineoxazine*,

sulphur-yellow crystals, m. p. 298—299°. 1-Phenylhydroxyquin-oxalone,  $C_6H_4 \begin{smallmatrix} \text{N}=\text{C} \cdot \text{OH} \\ \text{NPh} \cdot \text{CO} \end{smallmatrix}$ , decomp. 302—303°, from *o*-aminodiphenylamine and oxalic acid, gave by a similar reaction *phenyl-diphenazineoxazine*, yellow plates, m. p. 207·5—208·5°, strongly fluorescent in solution.

*Diphendioxazine* (II), colourless crystals, m. p. 259—260°, is produced by the condensation of oxalic acid and *o*-aminophenol hydrochloride in benzoic acid. Its solutions in sulphuric acid are of a greenish-yellow colour, and in fuming sulphuric acid of an orange shade. Dichloroquinoxaline and pyrocatechol react when heated together to yield *diphenazineoxine* (III), colourless needles, m. p. 264—265°, giving a greenish-yellow solution in concentrated sulphuric acid. G. M. B.

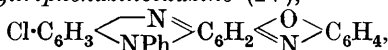
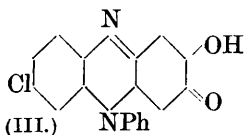
### Derivatives of Triphenazineoxazine and Triphenendioxazine.

F. KEHRMANN and J. A. SCHEDLER (*Helv. Chim. Acta*, 1925, 8, 9—12).—Hydroxyaposafranone condenses with *o*-aminophenol hydrochloride in boiling benzoic acid to give *N*-phenyltriphenazine-oxazine (I),  $C_6H_4 \begin{smallmatrix} \text{N} \\ \text{NPh} \end{smallmatrix} \begin{smallmatrix} \text{C} \\ \text{C} \end{smallmatrix} \begin{smallmatrix} \text{O} \\ \text{N} \end{smallmatrix} C_6H_4$ , decomp. 314°, which dissolves in solvents with a violet-red colour and a fiery-red fluorescence (*hydrochloride* and *perchlorate* described). On methylation, it is converted into a *methyl ammonium base*,



[*nitrate*, *perchlorate* (II), and *chloroplatinate* described]. This formula is preferred to that given by Diepolder (A., 1900, i, 191) to an identical product. The substance dyes mordanted cotton a violet-blue shade.

Dihydroxybenzoquinone and chloro-*o*-aminodiphenylamine yield 6-chloro-2-hydroxyaposafranone (III), brick-red needles, which is converted by *o*-aminophenol in boiling benzoic acid into *chlorophenyltriphenazineoxazine* (IV),

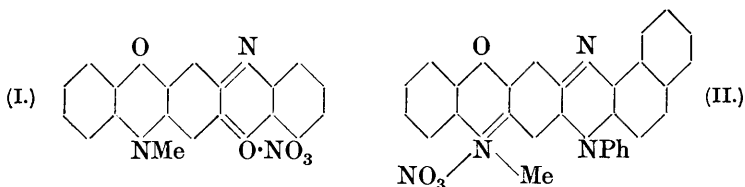


giving red, fluorescent solutions. Methylation of this base gave a *methylammonium base* (*nitrate* and *chloroplatinate* described) with dyeing properties. G. M. B.

**Condensation of Methylphenoxazine-*o*-quinone with *o*-Aminophenol and Alkylated *o*-Diamines.** F. KEHRMANN and G. WILD (*Helv. Chim. Acta*, 1925, 8, 13—15).—Condensation of methylphenoxazine-*o*-quinone with *o*-aminophenol hydrochloride in cold acetic acid produces the *methylammonium* compound of *triphendioxazine*, isolated as *nitrate* (I) (*chloroplatinate* described), also obtained in small quantity by methylation of triphenendioxazine, the methylation occurring, therefore, on the nitrogen atom.

The product from methylphenoxazine-*o*-quinone and *o*-aminodiphenylamine was found identical with the methylation product

of *N*-phenyltriphenazineoxazine (preceding abstract), which establishes its formula. The same *o*-quinone condensed with phenyl-



1 : 2-naphthylenediamine in boiling benzoic acid yielded an *ammonium* salt, isolated as *nitrate* (II) (*chloroplatinate* and *perchlorate* described). When 1 : 2-naphthylenediamine is substituted for its phenyl derivative a *substance* results which is probably the parent base,  $C_6H_4 \begin{smallmatrix} O \\ \diagup \quad \diagdown \end{smallmatrix} C_6H_2 \begin{smallmatrix} N \\ \diagdown \quad \diagup \end{smallmatrix} C_{10}H_6$ . G. M. B.

**Reactions of various Arylthiocarbamides with Sulphur and Aromatic Amines.** T. G. LEVI (*Atti Congr. Naz. Chim. Ind.*, 1924, 400—402).—That the aniline takes part in the reaction when arylthiocarbamides are heated with aniline and sulphur (A., 1924, i, 216, 1000) is shown by the fact that anilinobenzthiazole is not obtained when the aniline is replaced by an inert solvent, such as cymene, cumene, or naphthalene. When, however, the aniline is replaced by its homologues, the reaction proceeds differently. From toluidine and sulphur and thiocarbanilide, phenyltolylthiocarbamide, or ditolylthiocarbamide, dehydrothiotoluidine is obtained.

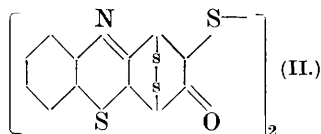
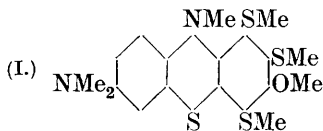
Dehydrothio-*o*-toluidine forms a *picrate*, m. p. 201—202°, an *acetyl* derivative, m. p. 121—122°, and a *chloroplatinate*, undergoing change at 230—240°; when fused with potassium hydroxide it yields anthranilic acid. Dehydrothio-*p*-toluidine forms a *picrate*, m. p. 204—206°, and a *chloroplatinate* which undergoes change at 230—240°, and gives *m*-aminobenzoic acid when fused with potassium hydroxide.

The product of the interaction of *m*-toluidine, sulphur, and *m*-tolylphenylthiocarbamide consists, not of either of the two possible dehydrothio-*m*-toluidines, but of *m*-toluidino-*m*-tolylthiazole,  $C_6H_3Me \begin{smallmatrix} N \\ \diagdown \quad \diagup \end{smallmatrix} S \begin{smallmatrix} N \\ \diagup \quad \diagdown \end{smallmatrix} C \cdot NH \cdot C_6H_4Me$ , m. p. 175°, which gives a *picrate*, m. p. 234—235°, an *acetyl* compound, m. p. 125—127°, and a *chloroplatinate*, and cannot be diazotised (cf. Hegershoff, A., 1903, i, 865). *Xylidino-m*-xylolthiazole,  $C_6H_2Me_2 \begin{smallmatrix} N \\ \diagdown \quad \diagup \end{smallmatrix} S \begin{smallmatrix} N \\ \diagup \quad \diagdown \end{smallmatrix} C \cdot NH \cdot C_6H_3Me_2$ , obtained similarly from *m*-xylidine, has m. p. 159°, and forms a *picrate*, m. p. 214°, and an *acetyl* compound, m. p. 131°.

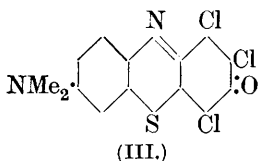
T. H. P.

**Constitution of Sulphur-blue.** A. BINZ and C. RÄTH (*Ber.*, 1925, 58, [B], 309—313).—Reduction of sulphur-blue (D.R.-P. 167012; cf. Bernthsen, *Chem.-Ztg.*, 1908, 32, 956) followed by

treatment of the product with diazomethane gives *pentamethyl-leucosulphur-blue* (I), from which the constitution (II) is deduced



for the reoxidised, de-alkylated dye. According to the patent, the dye is prepared by the interaction of chloranil, sodium sulphide, and dimethyl-*p*-phenylenediamine thiosulphonate without isolation of intermediate products. Attempts to follow the successive stages of the reaction were incompletely successful. Unexpectedly, the action of sodium sulphide on chloranil yields mainly *tetrachloroquinol*, m. p. 230—232°, the identity of which is confirmed by its



conversion into tetrachloro-*p*-dimethoxybenzene, m. p. 160°. Dimethyl-*p*-phenylenediamine thiosulphonate and tetrachloroquinol in faintly alkaline solution give trichloromethylene-violet (III), which is converted by sodium sulphide into chlorohydroxymethylene-violet disulphide,  $C_{28}H_{18}O_4N_4Cl_2S_4$ , from which the remaining chlorine atoms could not be removed by further treatment with sodium sulphide. H. W.

### Phenanthraquinonyl-3-azide and its Acid Decomposition.

K. BRASS and G. NICKEL (*Annalen*, 1925, **441**, 217—227).—Unlike the 2- and 4-azidophenanthraquinones, phenanthraquinonyl-3-azide yields no aminohydroxy or dihydroxy derivatives on treatment with dilute sulphuric acid (cf. A., 1924, i, 407). With sulphuric acid (2 vols. to 1 vol. of water), no substance soluble in alkali is produced but a black product which consists mainly of 3-aminophenanthraquinone together with insoluble by-products of high molecular weight. A more dilute acid (1 : 3) leaves much of the azide unattacked, whilst with 17% acid the azide is not attacked. Cold concentrated sulphuric acid affords 3-aminophenanthraquinone (yield, 70%) and the insoluble by-products. The different behaviour of the 3-azide is attributed to the para-relationship of azide and carbonyl groups (cf. Bamberger, A., 1921, i, 716; 1923, i, 1141). A quantitative study of the reaction shows that nitrous oxide is not produced and that the volume of nitrogen formed corresponds exactly with that calculated from the azide. In view of these results, it is probable that the remaining nitrogen is hydrogenated at the expense of the phenanthrene nucleus and that thereby the insoluble by-products result (cf. A., 1924, i, 953). 3-Nitrophenanthraquinone cannot be obtained by direct nitration of phenanthraquinone, but is obtained by the action of acetylnitric acid on 9 : 10-diaminophenanthrene (cf. Schmidt and Söll, A., 1908, i, 995). Reduction with alkaline sodium hyposulphite yields 3-aminophenanthraquinone, m. p. 256° (oxime, m. p. 247°), from

which *phenanthraquinonyl-3-diazonium perbromide*, red flocks, is obtained by the action of bromine in potassium bromide solution on the diazonium sulphate at 5°. The perbromide is converted by 10% ammonia solution into *3-azidophenanthraquinone*, brown needles, m. p. 186° (then exploding). *o*-Phenylenediamine and 3-azidophenanthraquinone yield *3-azidophenanthraphenazine*, yellow needles, m. p. 183°.

R. B.

**Preparation of Aromatic Carbonyl Compounds containing Tervalent Arsenic.** O. MARGULIES (Brit. Pat. 199091; F. Pat. 553300; Swiss Pat. 103553 and additions, 104479 and 104947; from *Chem. Zentr.*, 1924, ii, 1272—1273).—Aromatic or aliphatic-aromatic arsinic acids containing one or more non-cyclic carbonyl groups (aldehydo and keto), are treated with reducing agents such as sodium hyposulphite, phosphorus trichloride, phosphorous acid, sulphurous-hydriodic acid, sodium sulphite, etc., which reduce the acids to arsenious oxides or arseno compounds without attacking the carbonyl group; the products have valuable therapeutic properties and afford derivatives with strong trypanocidal and spirillicidal properties. Thus, an alkaline solution of benzaldehyde-*p*-arsinic acid on treatment at 60° with sodium hyposulphite and magnesium chloride affords *4:4'-dialdehydoarsenobenzene*, decomp. above 260°.

*3-Nitro-2-hydroxybutyrophenone-5-arsinic acid* in a similar way yields *3:3'-dinitro-4:4'-dihydroxy-5:5'-dibutyrylarsenobenzene*, which darkens, without melting, above 100°; acetophenone-*p*-arsinic acid yields *acetophenone-p-arsenious oxide*, m. p. 260—265°. Further reduction yields arsenoacetophenone, a yellow powder. Hydroxyacetophenonearsinic acid on reduction with hyposulphite and magnesium chloride affords *dihydroxydiacetylarsenobenzene* as a yellow powder.

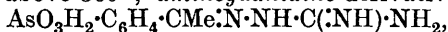
*3-Nitro-4-hydroxy-5-acetylphenylarsinic acid* is reduced by cold hydriodic acid and sulphur dioxide to *3-nitro-4-hydroxy-5-acetylphenylarsenious oxide*, m. p. 230—235° (decomp.). F. A. M.

**Preparation of Derivatives of Organic Arseno Compounds.** O. MARGULIES (Brit. Pat. 199092; F. Pat. 553301; Swiss Pat. 103775 and additions, 104480—4; from *Chem. Zentr.*, 1924, ii, 1273—1274).—Aliphatic-aromatic arsenic compounds containing non-cyclic carbonyl groups are treated with substances containing the hydrazino group. Suitable aliphatic-aromatic substances are, e.g., benzaldehyde-*p*-arsinic acid, acetophenone-*p*-arsinic acid, phenyl propenyl ketone-*p*-arsinic acid,  $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH} : \text{CHMe}$ , and the *p*-arsinic acids derived from methyl benzyl ketone, benzylideneacetone, and methyl benzyl diketone; suitable hydrazine derivatives are: methyl(? phenyl)hydrazine, phenylmethylhydrazine, carbohydrazide, and diaminoguanidine,



The products have powerful trypano- and spirillo-cidal properties. The following substances are described: *4-hydroxy-3-propionylphenylarsinic acid p-nitrophenylhydrazone*, yellow needles, m. p.

about 235° (decomp.). *Semicarbazone of 5-nitro-4-hydroxy-3-acetylphenylarsinic acid*, darkens above 240°. *Semicarbazone of benzylideneacetone-p-arsinic acid*, yellow needles, decomp. above 330°. *Diethylhydrazone of benzaldehyde-p-arsinic acid*, m. p. 140° (decomp.). *Phenylmethylhydrazone of benzaldehyde-p-arsinic acid*, yellow needles, m. p. 295° (decomp.). *Semicarbazone of 3:3'-dihydroxy-4:4'-diacetylarsenobenzene*, yellow, amorphous powder. The following derivatives of acetophenone-p-arsinic acid are described: *hydrazone*, colourless crystals darkening above 340°; *phenylhydrazone*, yellow leaflets, m. p. about 225° (decomp.); *aminobiuret* condensation product,  $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , brownish-yellow leaflets, m. p. above 360°; *aminoguanidine* derivative,



m. p. 300° (decomp.); *carbohydrazide* derivative, m. p. above 360°, *malonylhydrazide*, m. p. above 360°; *oxalylhydrazide*, m. p. above 360°; *semicarbazone*. The following are mentioned: *Semicarbazone of acetophenone-p-arsenious oxide*; *semicarbazone of 4:4'-diacetylarsenobenzene*; *semicarbazone of 3-hydroxy-4-acetylphenylarsinic acid*; *semicarbazone of 3-hydroxy-4-acetylphenylarsenious oxide*.

F. A. M.

**Preparation of Arsenious Oxides and Arseno Compounds of the Aromatic Series.** O. MARGULIES (Brit. Pat. 199093; F. Pat. 553302; Swiss Pat. 103980 and additions, 104720, 104721, 104946, 105164; from *Chem. Zentr.*, 1924, ii, 1274).—Condensation products of arsenic acids, containing non-cyclic CO groups, with hydrazine or its derivatives, are reduced to the corresponding arsenious oxides or arsenobenzene derivatives, or the corresponding condensation products of arsenious oxides are reduced to the arsenic acids; suitable reducing agents are sodium hyposulphite, phosphorus trichloride, phosphorous acid, sulphur dioxide-hydriodic acid, or sodium hydrogen sulphite. The following examples are given: *benzaldehyde-p-arsinic acid semicarbazone* is reduced by alkaline sodium hyposulphite in presence of magnesium chloride, to the yellow 4:4'-dialdehydoarsenobenzene semicarbazone. The semicarbazone of acetophenone-p-arsinic acid is reduced in ethyl acetate solution by means of phosphorus trichloride, or in aqueous solution by sodium hydrogen sulphite, to the semicarbazone of p-acetylphenylarsenious oxide. The malonylhydrazone of acetophenone-p-arsinic acid,  $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe} \cdot \text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , is reduced by alkaline sodium hyposulphite to the yellow malonylhydrazone of 4:4'-diacetylarsenobenzene, decomp. above 330°. The semicarbazone of 2-hydroxy-4-acetylphenylarsenious oxide is reduced by stannous chloride and hydrochloric acid to the semicarbazone of 2:2'-dihydroxy-4:4'-diacetylarsenobenzene, decomp. about 220°. The phenylhydrazone of 5-nitro-4-hydroxy-3-acetylphenylarsinic acid (decomp. 225°) on reduction with sulphur dioxide and hydriodic acid affords the phenylhydrazone of 5-nitro-4-hydroxy-3-acetylphenylarsenious oxide, a yellowish-brown powder, decomp. 260–270°. Reduction of a mixture of equivalent amounts of acetophenone-p-arsinic acid and m-hydroxyacetophenone-p-arsinic acid with



alkaline sodium hyposulphite or other reducing agents, affords the *arsenobenzene* derivative,

$\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{C}_6\text{H}_4\cdot\text{As}\cdot\text{As}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CMe}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ ,  
a yellow powder. F. A. M.

**Complex Compounds of Boron and the Asymmetry of Borosalicylic Acid.** J. BÖESEKEN (*Ber.*, 1925, 58, [B], 268—270).—A reply to Rosenheim and Vermehren (*A.*, 1924, i, 1194) and Rosenheim (this vol., i, 31). H. W.

**Fluorides of Organometallic Compounds. III. Thallium Alkyl and Aryl Fluorides.** E. KRAUSE and A. VON GROSSE.—(See i, 378.)

**Preparation of a Crystalline, Organic Lead Compound with Four Different Groups.** E. KRAUSE and O. SCHLÖTTIG (*Ber.*, 1925, 58, [B], 427—432).—Although lead tetra-alkyls with four different alkyl groups have been described previously (Grüttner and Krause, *A.*, 1917, i, 256), their attempted resolution into optically active forms has been rendered impossible by their low melting point and lack of ability to crystallise. The latter properties can be sufficiently improved by the introduction of phenyl and cyclohexyl groups. Among aromatic radicals, the heaviest groups are least firmly attached to the lead atom; in general, the order of (decreasing) firmness of attachment of groups is: *cyclohexyl*, *alkyl*, *aryl*.

The preparation of lead tetraphenyl and lead triphenyl bromide, which depends very greatly on experimental conditions, is described in detail. Lead triphenyl chloride is readily obtained on a small scale by heating an intimate mixture of lead tetraphenyl and ammonium chloride for 12 hours at 170—180°. *Lead triphenyl methyl*, m. p. 60°, prepared by the action of an excess of magnesium methyl bromide or chloride on lead triphenyl bromide, yields the compound,  $2\text{PhAg}\cdot\text{AgNO}_3$ , when treated with alcoholic silver nitrate. *Lead triphenyl p-phenoxyphenyl*,  $\text{PbPh}_3\cdot\text{C}_6\text{H}_4\cdot\text{OPh}$ , m. p. 127°, and *lead diphenyl di-p-xylyl*, m. p. 94°, are described. Lead triphenyl bromide is produced by the action of bromine on lead triphenyl *p*-tolyl, lead triphenyl *p*-xylyl, lead triphenyl *p*-phenoxyphenyl, or lead triphenyl  $\alpha$ -naphthyl. Lead diphenyl di-*p*-xylyl gives *lead diphenyl p-xylyl bromide*, m. p. 90°, which is converted by magnesium phenyl bromide into lead triphenyl *p*-xylyl. *Lead diphenyl cyclohexyl bromide*, m. p. 135°, prepared from lead triphenyl cyclohexyl, is reconverted by magnesium phenyl bromide into lead triphenyl cyclohexyl, m. p. 119—120°. *Lead diphenyl methyl bromide*, m. p. 118°, decomp. 124°, and *lead diphenyl ethyl bromide*, m. p. 119°, decomp. 130—135°, are described. *Lead diphenyl cyclohexyl methyl*, prepared from lead diphenyl cyclohexyl bromide and magnesium methyl bromide, is a colourless oil which is converted by bromine into *lead phenyl cyclohexyl methyl bromide*, m. p. 93—94° (decomp.). H. W.

**Melanotic Pigments.** H. HEINLEIN (*Biochem. Z.*, 1924, 154, 24—34).—A new method is outlined for freeing melanin from

protein impurities. Horse melanin and human sarcoma melanin thus purified and analysed gave fairly consistent results: C 55.9—56.3%, H 5.2—5.7%, N 8.5—9.4%, O 27.3—28.1%. These figures together with the analyses of artificially prepared melanins support the assumption that tyrosine is the parent substance. Oxidation of tyrosine by persulphate causes loss of nitrogen. The author is unable to confirm the statement that both prepigments and formed melanin reduce ammoniacal silver nitrate. Purified melanin differs from tissue melanin in not being decolorised by chlorine dioxide.

P. W. C.

**Constitution of Proteins.** R. O. HERZOG (*Z. physiol. Chem.*, 1924, **141**, 158—160).—Polemical against Abderhalden. The view that proteins may contain amino-acid anhydrides associated by means of subsidiary valencies (Abderhalden and Schwab, A., 1924, i, 1361) has previously been advanced by others (*e.g.*, Herzog and Kobel, A., 1924, i, 1007).

E. S.

**Proteins. IV. Hydrolytic Fission of 2:5-Diketopiperazines and Dipeptides.** M. LÜDTKE (*Z. physiol. Chem.*, 1924, **141**, 100—104).—In the hydrolysis of diketopiperazines by acids or alkalis, the first stage (formation of dipeptide) proceeds to completion, but the fission of the dipeptide appears to reach an equilibrium, the position of which depends on the temperature.

E. S.

**Combination of Proteins, Amino-acids, etc. with Acids and Alkalis and their Combining Weights as determined by Physico-chemical Measurements.** L. J. HARRIS (*Proc. Roy. Soc.*, 1925, **B**, **97**, 364—386).—The dissociation constants of methylene derivatives of amino-acids are shown to be of the order of  $10^3$  times greater than those of the corresponding amino-acids; " $p_H$ -combination curves" are obtained by plotting the  $p_H$  values of a protein solution against the alkali (or acid) added, after correcting the latter for the "hydrogen-ion error." This correction is made by subtracting from the amount of alkali (or acid) added, the amount of alkali (or acid) which would have to be added to a hypothetical blank consisting of water only in order to produce the same total volume of liquid having the same  $p_H$  as the amino-acid and alkali (or acid) mixture. Such curves may be used for determining the nature of denaturation and hydrolytic changes. The amount of acid or alkali (corrected for control) required by a protein solution over a given range of  $p_H$  is proportional to the amount of protein present.

The equivalent combining weights of protein can be found by adding successive amounts of acid or alkali to the protein and observing a physical constant of the resulting solution. When the values of the latter are plotted against the acid or alkali added the curve shows a sharp break at the point denoting the addition of a constant equivalent of acid or alkali.

It is considered that the free protein molecule of gelatin does not consist of a practically non-ionised molecule, but rather of a mixture

of basic or acidic ions, or probably as an ammonium salt, or a "zwitterion." O. O.

**Relation of Chemical Structure to Rate of Hydrolysis of Peptides. II. Hydrolysis with Erepsin.** P. A. LEVENE and H. S. SIMMS.—(See i, 473.)

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## Biochemistry.

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**Method of Transport of Oxidised Carbon from the Tissues to the Blood.** B. J. COLLINGWOOD (*Proc. Physiol. Soc.*; *J. Physiol.*, 1924, 59, xxii).—The exchange between tissue fluids and blood appears to be largely one of ions ( $\text{HCO}_3'$  and  $\text{CO}_3''$ ) and only to a small extent of dissolved carbon dioxide. CHEMICAL ABSTRACTS.

**Oxygen and Carbon Dioxide Contents of Arterial and Venous Blood in Dogs.** H. J. STEWART (*J. Biol. Chem.*, 1925, 62, 641—647).—By the use of a special cannula introduced through the right external jugular vein, mixed venous blood can be obtained directly from the right ventricle. The percentage oxygen saturation of the arterial blood of a normal resting dog is 92—95% and for any one dog is constant over long periods; that of the mixed venous blood under similar conditions is 72—80%. C. R. H.

**Detection of Gaseous Poisons in Blood.** E. KOHN-ABREST (*Compt. rend.*, 1924, 179, 903—906).—A form of apparatus for extracting and collecting all the volatile substances from a sample of blood is described. The whole is evacuated before use and the blood (50 c.c., if possible) poured into a 500 c.c. flask from a stoppered dropping funnel. The flask is kept at 80—85° and the volatile portions and dissolved gases are passed into a U-tube fitted with a central bulb. The water collects in the latter whilst such substances as hydrogen sulphide and hydrogen cyanide pass on and are trapped in a bubbler containing *N*/20-silver nitrate. The gaseous products are finally collected over mercury. Alcohol, if present, condenses with the water; if condensation is incomplete, the remainder is found in the silver nitrate. Any precipitate in the latter is separated by centrifuging and is examined for silver sulphide and cyanide; the excess of silver nitrate is determined volumetrically in a portion of the liquid. The gas is examined by the usual methods. Experiments carried out in this manner show that blood in contact with coal gas absorbs the cyanogen and hydrogen cyanide in proportions which may exceed 1 part in 5000 parts by volume. H. J. E.

**Adsorption of Protein Degradation Products by the Formed Elements of the Blood *in Vivo* and *in Vitro*.** IV. Adsorption of certain Amino-acids by the Red Blood-corpuscles. B. SBARSKY and A. MUCHAMEDOFF (*Biochem. Z.*, 1925, 155, 495—498).—Red blood-corpuscles adsorb from 10 to 40% of added glycine and alanine, whilst leucine and tyrosine are not adsorbed. J. P.

**Sinking of Red Blood-corpuscles in Flowing Blood.** L. BERCZELLER and H. WASTL (*Biochem. Z.*, 1924, **153**, 100—110).—The rate of sedimentation of red blood-corpuscles is more rapid in a stream of blood than in stationary blood. J. P.

**Viscosity of Suspensions of Blood-corpuscles. I.** L. BERCZELLER and H. WASTL (*Biochem. Z.*, 1924, **153**, 111—119).—The viscosity of suspensions of blood-corpuscles does not increase with increasing concentration as rapidly as does the viscosity of yeast-cell suspensions under like conditions. J. P.

**Blood Clotting. XII.** B. STUBER. **Detection of so-called Thrombin in Circulating Blood.** P. KUHN (*Biochem. Z.*, 1925, **155**, 477—484).—Thrombin is present as such in circulating blood, a result which supports the author's view of the colloidal nature of blood clotting (cf. A., 1923, i, 1151; this vol., i, 94). J. P.

**Clotting of Blood and Settling of Blood-corpuscles as a Problem of the Physical Chemistry of Fibrinogen. Does the Stability of Plasma Proteins Depend on their Isoelectric Points?** E. WÖHLISCH (*Z. ges. exp. Med.*, 1924, **40**, 137—166; from *Chem. Zentr.*, 1924, ii, 687; cf. A., 1924, i, 1013).—The stability of plasma proteins is unconnected with their isoelectric points. Fibrinogen has not the properties of an alkali hydrosol, since its isoelectric point is  $p_H$  4.85. Thrombin coagulation is thus an irreversible process. The isoelectric point of fibrin lies farther from neutrality than that of fibrinogen. Fibrinogen is normal in its stability relationships with salts. Supplementary to Höber's theory of the settling of blood-corpuscles, it is suggested that the fibrinogen adsorbed on the surface of the corpuscles undergoes a transformation resulting in a change in its isoelectric point.

G. W. R.

**Theory of the Action of Thrombin.** E. WÖHLISCH (*Biochem. Z.*, 1924, **145**, 279—285; from *Chem. Zentr.*, 1924, ii, 687; cf. preceding abstract).—The author disagrees with the theories of Stuber and Sano (A., 1923, i, 410—411). Schmidt's thrombin is unable to effect the clotting of a solution of fibrinogen when separated from it by a membrane impermeable to thrombin. G. W. R.

**Determination of Surface Tension [of Blood-serum] by the Ring Method (Torsion Balance).** P. L. DU NOÛY.—(See ii, 279.)

**Determination of Lipoids in the Blood-serum of Nervous Cases.** S. MINOVICI and (MISS) M. ILIESCO (*Bul. Soc. Chim. România*, 1924, **6**, 67—71).—Normal serum obtained in the morning contained between 1.30 and 1.57 g. of total cholesterol and between 4 and 5.90 g. of fatty acids per litre. In the sera of patients suffering from various nervous complaints, the cholesterol never amounted to 1 g. per litre, but the proportion of fatty acids was approximately normal. T. H. P.

**Cholesterol in Normal Infants.** BANU, NEGRESCO, and HERESCO (*Compt. rend. Soc. Biol.*, 1924, **91**, 730—732; from *Chem. Zentr.*, 1924, ii, 2177).—In the first three months of life the

cholesterol content of the blood of normal infants is approximately 0.05%, somewhat higher in breast-fed children and somewhat lower in those which are bottle-fed. The cholesterol content at 2 weeks is 0.007%, and at 8—10 months 0.055%.  
G. W. R.

**Gravimetric Micro-determination of Cholesterol.** T. TOMINAGA (*Biochem. Z.*, 1925, **155**, 119—122).—A modification of the digitonin method of cholesterol determination (A., 1923, ii, 344) so as to make it applicable to the determination of cholesterol in small amounts of blood. The error of the original method ( $\pm 3\%$ ) is reduced in the two experiments reported to  $+0.8\%$  and  $-0.6\%$ .  
P. W. C.

**Determination of Lecithin in Blood.** A. GRIGAUT (*J. Pharm. Chim.*, 1925, [viii], **1**, 97—104).—The residue after evaporating to dryness the alcohol-ether extract of 1 c.c. of serum, is extracted with anhydrous ether. The phosphorus of this extract is converted into orthophosphoric acid and the solution, after neutralisation and making up to known volume, is treated with standard solutions of ammonium molybdate in sulphuric acid, and stannous chloride; the resulting coloration is compared with that given by a standard phosphate solution treated in a similar manner, in a Duboscq colorimeter. By this method human serum is found to contain 0.17% and red corpuscles 0.25% of lecithin.  
H. J. C.

**Sugar Content of Blood-corpuscles.** F. HÖGLER and K. UEBERRACK (*Biochem. Z.*, 1925, **155**, 123—124).—Additional figures are brought in support of the authors' contention that the plasma contains a higher percentage of sugar than the corpuscles (A., 1924, i, 1124), and the results, therefore, of Richter-Quittner (A., 1925, i, 95) are discredited.  
P. W. C.

**Micro-determination of Blood-sugar.** C. J. DIAZ and B. S. CUENCA (*Biochem. Z.*, 1924, **153**, 97—99).—Preference is expressed for the original method of Hagedorn and Jensen (A., 1923, ii, 265, 440) as against the modifications of Dresel and Rothman (A., 1924, ii, 632).  
J. P.

**Determination of Dextrose, Non-protein Nitrogen, Uric Acid and Total Phosphorus in Normal Human Blood in Tropical Regions, and in the Blood of Birds suffering from Avitaminosis.** P. J. T. VAN BERKHOUT (*Reprint Rept. Dutch-Ind. Med. Civ. Ser.*, 1924, **4**, 326—343).—The blood of a healthy man in tropical regions does not differ from that of a subject in temperate regions in respect of dextrose, non-protein nitrogen, and uric acid, but is slightly higher in total phosphorus. The blood of cocks suffering from avitaminosis does not vary appreciably from that of normal birds. Pigeons in this condition, however, developed pronounced hyperglycæmia, and various deviations in the blood analyses were noted.  
O. O.

**Determination of Dextrose in Presence of Sucrose in Organic Liquids.** M. BUFANO (*Arch. Farm. sper. Sci. aff.*, 1924, **38**, 231—242).—The author has investigated various methods which

have been proposed for determining dextrose in presence of sucrose in organic liquids such as blood. The results obtained show that in no case is the preliminary purification of the liquid for the removal of proteins without effect on the sucrose, which undergoes hydrolysis to some extent and, in view of the small proportions of sugars present, introduces considerable error. T. H. P.

**Phosphoric Esterase of Blood at Various Hydrogen-ion Concentrations.** M. MARTLAND (*Biochem. J.*, 1925, **19**, 117—121).—Hydrolysis of the phosphoric ester of blood was observed when the  $p_H$  fell below 7.3. At a  $p_H$  above 7.35, synthesis takes place. S. S. Z.

**Glycolysis and Changes of the Inorganic Phosphorus in Blood *in Vitro*.** H. BIERRY and L. MOQUET (*Compt. rend. Soc. Biol.*, 1924, **91**, 250—252; from *Chem. Zentr.*, 1924, ii, 1358).—In defibrinated blood, formation of lactic acid and inorganic phosphates proceeds parallel with the disappearance of free sugar. The dextrose in the corpuscles is probably converted first into a hexose phosphate and then into lactic acid. This process may take place under the influence of insulin. R. B.

**Ammonia in Blood.** J. K. PARNAS and J. HELLER (*Compt. rend. Soc. Biol.*, 1924, **91**, 706—707; from *Chem. Zentr.*, 1924, ii, 2176).—Ammonia determinations by means of the apparatus of Parnas and Wagner (A., 1922, ii, 312) showed the following amounts (mg.) of ammonia in 100 g. of rabbit blood: well nourished adult males, 0.025—0.05; the same starved, 0.1—0.15; 2 months' old males, 0.08—0.15; pregnant females, >0.2; the same starved, up to 0.4. The whole of the ammonia may not be pre-formed since the content rises on keeping for a few hours up to 1.5—2.0 mg. per 100 c.c. This formation of ammonia is located principally in the red corpuscles, and takes place in an atmosphere of either oxygen or nitrogen. The temperature coefficient between 0° and 20° is 1.4, and between 20° and 40°, 1.8. G. W. R.

**Ammonia and Ammonia Production in Blood.** II. J. K. PARNAS (*Biochem. Z.*, 1925, **155**, 247—255).—The method described previously (Parnas and Heller, this vol., i, 323) and used for the determination of the ammonia content of rabbit's blood has been extended to other animals. Not only does the ammonia content of freshly-shed blood vary considerably from one species to another, but also the ammonia produced in the blood on keeping, the latter being fifteen times as much in the blood of the duck as in that of the horse. Gravimetric urea determinations (xanthhydrol precipitation) show that this ammonia is not produced at the expense of the blood urea. Urea is not present in hen's blood. H. D. K.

**Bromine Content of Blood. Detection of Minute Quantities of Bromine.** H. BERNHARDT and H. UCKO (*Biochem. Z.*, 1925, **155**, 174—186).—Guareschi's qualitative test for bromine (A., 1912, ii, 989) is modified and used for detection and determination of bromine in blood. The determination cannot be reduced to

volumetric or colorimetric methods, but is carried out by ascertaining the amount of blood which, after ashing with potash and liberating the bromine under standard conditions, would just give a violet coloration with the reagent. This amount of blood contains 0.05 mg. of bromine. By this and by the older indirect methods the bromine content of blood is shown to be 1—1.5 mg. %.

P. W. C.

**Determination of Chlorides in Blood.** C. BENGUEREL (*Ann. Chim. Analyt.*, 1925, [ii], 7, 39—40).—Excess of 0.1N-silver nitrate solution is added to the diluted and deproteinised blood (prepared with 20% trichloroacetic acid) and the excess titrated with 0.1N-thiocyanate solution.

D. G. H.

**Determination of Cyanates in Blood.** E. G. MONTGOMERY (*Biochem J.*, 1925, 19, 71—74).—The blood plasma of the cat contains 1.04 mg. % cyanic acid and that of the rabbit 0.78 mg. % some hours after a protein meal. It is suggested that cyanic acid may be a precursor of urea. The cyanate of the blood was converted by incubation with an ammonium salt solution into urea, and the latter determined by the xanthhydrol method.

S. S. Z.

**Mineral Composition of the Blood of Dogs (under Narcosis).** A. BLANCHETIÈRE and H. CARDOT (*Compt. rend. Soc. Biol.*, 1924, 90, 1017—1019; from *Chem. Zentr.*, 1924, ii, 485—486).—The following data, differing in some respects from those previously available, are given for the content of sodium, potassium, and calcium, respectively, expressed in mg. per 100 c.c. in the blood of dogs under different conditions. Individual 1, after administration of chloralose: jugular vein, 305.7—16.0—15.1; carotid, after 5 mins., 296.3—14.1—12.3; left heart, after 5 mins., 261.9—14.3—12.3. Individual 2, without narcosis: left heart, 258.7—17.9—12.4; after 15 mins., 223.2—19.4—12.1; the same dog without narcosis: left heart, 263.1—17.7—22.8; after 15 mins., 271.8—15.6—22.1; after a further 15 mins., 220.5—14.9—12.0.

G. W. R.

**Methæmoglobin.** J. B. CONANT and L. F. FIESER (*J. Biol. Chem.*, 1925, 62, 595—622).—Comparison of the results of electro-metric titration of methæmoglobin with sodium hyposulphite with determinations of total hæmoglobin and reduced hæmoglobin shows that 0.5 mol. of sodium hyposulphite is required for the reduction of 1 mol. of methæmoglobin. Results are given of the determination of the oxidation-reduction potentials of mixtures of hæmoglobin and methæmoglobin at varying  $p_H$ . The reaction between potassium ferri-cyanide and hæmoglobin was found to be reversible, the final equilibrium being determined by the tension of oxygen and the  $p_H$ ; at a low tension of oxygen or in alkaline solution, the conversion of hæmoglobin into methæmoglobin is almost complete, whereas in a neutral solution saturated with oxygen about 20% of the hæmoglobin is unchanged. The bearing of these results on the constitutional relationship of hæmoglobin and methæmoglobin is discussed.

C. R. H.

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**Determination of Methæmoglobin in the Presence of its Cleavage Products.** J. B. CONANT and L. F. FIESER (*J. Biol. Chem.*, 1925, **62**, 623—631).—The methæmoglobin is reduced to hæmoglobin by the sodium salt of anthrahydroquinone- $\beta$ -sulphonic acid and the increase in oxygen capacity of the solution is determined.  
C. R. H.

**Carbon Monoxide Dissociation Curve of Hæmochromogen.** M. L. ANSON and A. E. MIRSKY (*Proc. Physiol. Soc.; J. Physiol.*, 1924, **59**, xiii).—The curve can be expressed by the mass law equation  $K = [\text{Hb}][\text{CO}]/[\text{HbCO}]$ . The value of  $K$  at body temperature in very alkaline solution is  $0.00405 \pm 0.0004$  when the tension is measured in % atm.  
CHEMICAL ABSTRACTS.

**Molecular Weight of Cholesterol.** J. R. PARTINGTON and S. K. TWEEDY —(See ii, 273.)

**Cholesterol in the Cerebro-spinal Fluid.** F. LASCH (*Biochem. Z.*, 1924, **153**, 150—155).—In 40 normal and pathological cases (including syphilis and icterus) examined no cholesterol was detected in the cerebro-spinal fluid with one exception, and that was a hæmorrhagic fluid.  
J. P.

**Presence of Iodine in the Venous Blood of the Thyroid.** E. GLEY and J. CHEYMOL (*Compt. rend.*, 1924, **179**, 930—932).—Experiments on goats show that the iodine content of blood issuing from each lobe of the thyroid is related to the proportion of iodine in the lobe, but is affected by other causes. The blood examined gave a mean iodine content of 0.191 mg. per 1000 as compared with 0.120 mg. for the blood in general circulation.  
H. J. E.

**Unusual Type of Fatty Compound in a Product of Animal Origin.** S. KON and C. FUNK.—(See i, 230.)

**Calcium Content of the Growing Embryo.** E. SCHMITZ (*Arch. Gynäkol.*, 1923, **121**, 1—7; *Ber. ges. Physiol.*, 1924, **25**, 11—12; from *Chem. Zentr.*, 1924, ii, 854).—An examination of 2—6 months' old human fœti showed the youngest (before any bone formation) to contain 0.047 g. CaO. At 69 days, the percentage of calcium oxide in the ash was 19.58; at 100 days, 29.53%; at 150 days, 39%. The daily increase during the third month was 0.0015 g.; fourth month, 0.01 g.; fifth month, 0.041 g.; sixth month, 0.1 g.; seventh month, 10.44 g.; eighth month, 16.24 g.; ninth month, 0.39 g. This resembles the curve for the total increase in weight of the fœtus.  
F. A. M.

**Rôle of Calcium and Potassium Ions in the Development of Embryos.** P. MENDELÉEV and A. SLOSSE (*Compt. rend. Soc. Biol.*, 1924, **91**, 137—138; from *Chem. Zentr.*, 1924, ii, 1000; cf. Mendeléev, *Compt. rend. Soc. Biol.*, 1924, **90**, 985).—The different effects of placenta from embryos of varying age on the growth of embryonic tissue can be correlated with their potassium/calcium ratios.  
G. W. R.

**Changes in the Total, Amino-, and Ammoniacal Nitrogen of Hens' Eggs during Incubation.** A. AGGAZZOTTI (*Arch. ital. biol.*, 1923, **72**, 127—132; from *Chem. Zentr.*, 1924, ii, 694).—During incubation there is a transfer of water from white to yolk with consequent increase in the total nitrogen and amino-nitrogen of the white, calculated on fresh substance. Calculated on dry matter this increase is not shown. During the first half of the incubation period the ammonia increases to twice the initial value and then falls to the original value. The total nitrogen and amino-nitrogen of the yolk, calculated on the dry matter, remain unchanged, whilst the ammoniacal nitrogen decreases. In sterile eggs, no such changes are observed. G. W. R.

**Lipoids of the Ovarian Follicles in Human Beings and Cattle.** M. YAMAUCHI (*Z. Konstitutionslehre*, 1924, **10**, 28—66; from *Chem. Zentr.*, 1924, ii, 2181).—In the human primordial ovarian follicle, fat rarely occurs; in adolescent follicles, glycerol esters, cholesterol esters, and mixtures of cholesterol and fatty acids are found. In the follicles of adult women the same lipoids occur, but in the later stages of maturity, during pregnancy, their amount diminishes. In chronic wasting diseases, the lipoids of the ovaries gradually disappear. Similar data were obtained for calves and cows. G. W. R.

**Lipoids of the Ovaries of Cows during the Œstrous Cycle.** L. LANG (*Z. Konstitutionslehre*, 1924, **10**, 79—98; from *Chem. Zentr.*, 1924, ii, 2181).—Glyceryl esters, phosphatides, and cerebrosides are always found in the corpus luteum of cows. The lipid metabolism of the corpus luteum is of more importance than that of the ovarian follicle. G. W. R.

**Lipoids in the Testes of Cattle.** K. SORG (*Z. Konstitutionslehre*, 1924, **10**, 67—78; from *Chem. Zentr.*, 1924, ii, 2181).—Interstitial cells containing lipoids occur in very young calves. Lipoids are first found in the epithelia of the seminal ducts at pubescence. The lipoids, both in calves and in adult animals, are exclusively phosphatides and cerebrosides. G. W. R.

**Little Studied Constituents of Cow's Milk. II. The Water Soluble Yellowish-green Colouring Matter.** B. BLEYER and O. KALLMANN (*Biochem. Z.*, 1925, **155**, 54—79).—The fraction obtained from filtered boiled whey by precipitation with mercuric nitrate (cf. T., 1879, **35**, 530) consists of water-soluble albuminous material (formed during boiling) on which is adsorbed the true colouring matter (lactochrome) of milk. To obtain pure lactochrome, whey was evaporated in a vacuum at low temperature, treated with twice its volume of 96% alcohol, allowed to stand in ice for 2 days, centrifuged, separated, and evaporated in a vacuum to a syrup. By successive extractions with 96% alcohol and evaporating, a syrup free from albuminous matter is obtained. This is shaken repeatedly with four times its volume of a mixture of chloroform and 96% alcohol (2 : 1); the extracts are evaporated to

a syrup and shaken out with a chloroform-alcohol mixture (8 : 1). The substance obtained gives a positive xanthoproteic test, is definitely not urobilin (cf. A., 1903, ii, 500), and is probably allied to urochrome and alloxypoteic acid. A new method is adopted for dealing with large quantities of whey. Whey after evaporation in a vacuum to one-third its volume is dialysed against three times its volume of water at 25° for 9 hours. The dialysate is concentrated in a vacuum, saturated with ammonium sulphate, and extracted as above with chloroform-alcohol, evaporated, and treated with benzene to remove cholesterol. The raw product is then adsorbed on a suitable colloid (Aluminium oxydatum hydricum, Merck) and recovered by treatment with alcohol, ammonia, or both. Thiocyanate is a minor but constant constituent of milk.

P. W. C.

**Synthesis of Lecithin in the Animal Organism.** H. C. ECKSTEIN (*J. Biol. Chem.*, 1925, **62**, 743—757).—The lecithin content of the lymph from the thoracic duct of dogs was unchanged after the introduction of olive oil or of palmitic acid into the duodenum, and slightly increased after the introduction of oleic acid; this increase was probably a toxic effect of oleic acid, and not an indication of synthesis of lecithin. After the ingestion of lecithin itself, there was observed a small increase in the lecithin and a much more marked increase in the fatty acids of the lymph, which suggests a transformation of lecithin into neutral fat during the process of absorption.

C. R. H.

**Determination of the Free Acid of Gastric Juice.** H. SAHLI (*Schweiz. med. Woch.*, 1924, **54**, 1—6; from *Chem. Zentr.*, 1924, ii, 2192).—An aqueous solution of an indicator is titrated with 0.1*N*-hydrochloric acid until the colour matches that obtained with gastric juice containing the same indicator. For acid juices and for less acid juices, the indicators used are methyl-violet and litmus, respectively.

G. W. R.

**Secretion of Urine as Studied on the Isolated Kidney.** E. H. STARLING and E. B. VERNEY (*Proc. Roy. Soc.*, 1925, **B**, **97**, 321—363).—The mechanism of urinary secretion in mammals has been studied by perfusing the dog's kidney with the heart-lung preparation. Hydrocyanic acid suspends tubular activity. This action is reversible, and on reversion to perfusion with normal blood the tubule cells resume their function. Urea sulphate and, when present in the serum, phenolsulphonaphthalein, are secreted by the tubule cells into the glomerular filtrate, whilst water, chloride, hydrogen carbonate, and dextrose are reabsorbed by the tubule cells from the glomerular filtrate. Pituitrin has a direct influence on the kidney, and it is shown that this cannot be explained by its vascular action. It is suggested that substances such as pituitrin normally regulate the output of water and chloride in the intact animal, and that their absence accounts in a large measure for the characters of urine secreted by the isolated organ.

O. O.

**Ratio of the Amounts of Acetone and of  $\beta$ -Hydroxybutyric Acid Excreted in the Urine.** A. LUBLIN (*Deut. Arch. klin. Med.*, 1924, **145**, 15—21; from *Chem. Zentr.*, 1924, ii, 2179).—From daily observations on twenty-four individuals it was found that no constant proportion exists between acetone and  $\beta$ -hydroxybutyric acid in the urine, the ratio of the former to the latter varying from 1:1.5 to 1:9.6. The lowest ratios are found on days on which minimal amounts of acetone substances are excreted. Constancy in this ratio is not to be expected from physiological considerations. A similar variability in the ratio is also found in blood, where there is a smaller excess of  $\beta$ -hydroxybutyric acid than in urine. G. W. R.

**Determination of the Total Organic Acids of Urine. Their Relationship to Nitrogen Nutrition and to Ketonuria.** R. GOIFFON (*Arch. malad. l'appar. dig. nutrit.*, 1923, **13**, 869—881; from *Chem. Zentr.*, 1924, ii, 692).—The organic acids in the blood originate directly from the food, from fermentation in the intestine, or from metabolic processes. The nature of the acids and the degree to which they are oxidised affect their excretion in the urine. Administration of protein does not affect the ratio of organic acids to carbamide. Decrease in this ratio is due to decrease in the secretion or formation of such acids, or to their more complete oxidation. Increase in the ratio is due to causes other than the formation of acids from protein. The relationships in surgical acidosis are more complicated than formerly supposed. Such acidoses may occur without ketonæmia and may persist after disappearance of ketones from the blood. G. W. R.

**Effect of Neutral Salts on the Excretion of Acids in the Urine.** P. GYÖRGY (*Klin. Woch.*, 1924, **3**, 1225—1226; from *Chem. Zentr.*, 1924, ii, 693).—Oral administration of potassium chloride and sodium chloride, respectively, to infants on a milk diet resulted in increased acidity of the urine. In cases where a rise of temperature was produced by sodium chloride, the increased acidity of the urine was no longer observed and the reaction actually became more alkaline. G. W. R.

**Diazo Reaction in Urine.** G. HUNTER (*Biochem. J.*, 1925, **19**, 25—33).—The diazo reaction in sodium carbonate solution consists of two types. Type A reaction is characterised by a gradual development of colour until a stable maximum is reached. Type B reaction develops immediately a bright orange-red colour which disappears rapidly. Whilst all urines give type A reaction, type B reaction is only observed in pathological urines, especially in those from typhoid and measles. S. S. Z.

**Carnosine of Muscle and Iminazole Excretion in the Urine.** G. HUNTER (*Biochem. J.*, 1925, **19**, 34—41).—The carnosine of striated muscle in the cat can be lowered by starvation. It can be raised again by the ingestion of a meat diet. There is evidence of an increased excretion of iminazole in the urine when the carnosine disappears rapidly. S. S. Z.

**Detection of Chlorophyll Degradation Products in Urine.** M. HOFSTETTER (*Biochem. Z.*, 1925, **155**, 80—89).—After administration of chlorophyll (0.2—0.4 g. crude or 0.01—0.02 g. pure) by mouth to rabbits and to a less extent after chronic sulphonal and trional poisoning, porphyrins are detected in small quantities in the urine by chemical and spectroscopic (less trustworthy) tests. Rabbits excrete a little porphyrin when fed on fresh grass. The amount is greatly increased on giving extracted chlorophyll, and it is concluded that chlorophyll is absorbed much more readily when freed from cellulose. Porphyrin appears in the urine of patients 3 days after the administration of 6—8 “chlorosan” pastilles (6—16 mg. of pure chlorophyll) per day and also appears after insolation. P. W. C.

**Appearance of Red Colouring Matter (in the Urine) after Administration of Pure Chlorophyll. II.** A. P. GODINHO (*Biochem. Z.*, 1925, **155**, 90—96).—After administration of 0.05 g. of phäophytin (pure but magnesium-free chlorophyll), a red, fluorescent substance, not identical with hæmatoporphyrin, appears in the urine on the same and succeeding days. Larger doses may cause excretion lasting for several weeks. Administration of much greater amounts of chlorophyll in the form of green vegetables leads to the excretion of only a small amount of the colouring matter, cellulose apparently preventing, to a great extent, the absorption of the chlorophyll. P. W. C.

**Excretion of Chlorophyll Derivatives in the Urine. III.** Y. KITAHARA (*Biochem. Z.*, 1925, **155**, 97—112).—Porphyrin excretion, a measure of chlorophyll absorption, does not take place to any extent on administration of cooked or uncooked vegetable foodstuffs, *e.g.*, spinach up to 500 g. or cabbage up to 400 g., but does result from taking the uncooked juice obtained by fine maceration of these vegetables. For absorption, therefore, the chlorophyll of vegetables must be freed from the cellulose framework of the leaf, and under these conditions, the porphyrin appearing in the urine is proportional to the amount of chlorophyll administered. Numerous tables show the periods of porphyrin excretion after taking cooked and uncooked vegetables, vegetable juices, “chlorosan,” and phäophytin. P. W. C.

**Detection of Urobilin and Urobilinogen in Urine. C.** BENGUEREL (*Ann. Chim. Anal.*, 1925, [ii], 7, 40—41).—The urine, which has been slightly acidified with acetic acid, is shaken with an ethereal alcoholic solution of zinc acetate, and the fluorescence developed is examined with an arc light against a black background. The transformation of urobilinogen may take a few minutes. D. G. H.

**Urochromogen and Urochrome. The New Form of Urea.** W. O. MOOR (*Biochem. Z.*, 1924, **153**, 19—38).—Only 3—6% of the power of urine to decolorise permanganate is accounted for by the reducing action of the urine when tested with ferric chloride and potassium ferricyanide. The substance responsible for the

decolorisation gives a blue colour with ammonia and phosphotungstic acid, and is identified as the new form of urea (U) already described (A., 1924, i, 1134). The ratio of "U" to the normal form of urea was found to vary from 0.7 to 4.5 in urines of different specific gravity, and the clinical significance of such variations is discussed. In general, normal urines give a high and abnormal urines a low ratio. Urochrome occurs in urine as such in amounts varying from 0.3 to 0.4%, and a method of isolation is described. Urochrome is differentiated from the new form of urea. J. P.

**Fate of Hexamethylenetetramine in the Body.** F. DE EDS (*Arch. Intern. Med.*, 1924, **34**, 511—528).—Urinary excretion of hexamethylenetetramine, usually 32—85%, is increased, even up to 100%, by administration of sodium hydrogen carbonate. In phosphate buffer mixtures, decomposition of the substance is a function of hydrogen-ion concentration, but some occurs in alkaline mixtures. Decomposition is diminished by serum. Intravenous injection does not affect the urea or formic acid content of the blood. Normal persons excreted about 0.3% of the ingested dose as formic acid, but in a febrile case there was no increase in the excretion of formic acid. CHEMICAL ABSTRACTS.

**Determination of Diastase in Fæces.** N. FRANK and F. DOLESCHALL (*Biochem. Z.*, 1925, **155**, 125—132).—The Wohlge-muth method of diastase determination is applicable to fæces rich in fat only after ether extraction of the fæces emulsion. An ether-extractable component of the fæces, believed to be a fatty acid-soap complex, forms a sediment with starch which gives a blue coloration with iodine and masks the action of diastase even although present in normal amount. The result is of importance in cases of pancreatic deficiency. P. W. C.

**Biochemistry of Avitaminosis.** A. PALLADIN. II. **Nitrogen Metabolism (in particular Creatine Metabolism) in Experimental Scurvy.** A. PALLADIN and A. KUDRJAWZEWA (*Biochem. Z.*, 1924, **152**, 373—387). III. **Blood Enzymes in Experimental Scurvy.** P. NORMARK (*ibid.*, 420—425).—II.—In scorbutic conditions produced in guinea-pigs by lack of vitamin-C, an increased muscle and urinary creatine is found, the extent of the increases running more or less parallel to the severity of the symptoms. The excretion of ammonia is also increased.

III. In avitaminosed guinea-pigs, the blood catalase remains unaltered, proteases increase, whilst esterases diminish in the later stages. Peroxydase is at first increased but later returns to normal. J. P.

**Biochemistry of Avitaminosis.** A. PALLADIN. IV. **Calcium Excretion and Blood Calcium in Experimental Scurvy.** A. PALLADIN and E. SSAWRON (*Biochem. Z.*, 1924, **153**, 86—96).—In experimental scurvy, the excretion of calcium in urine and fæces begins to decrease during the first, second, or third week, whilst the blood calcium remains normal during the first and second weeks and sinks later. J. P.

**Respiration of Tissues in Avitaminosis and Inanition.** J. ROCHE (*Compt. rend.*, 1925, **180**, 467—469).—The respirations of the corresponding tissues of normal and starved pigeons *in vitro* are of the same intensity. Death from inanition cannot, therefore, be explained as due either to diminished cellular oxidation, or to deficient nourishment of the tissues. The intensity of respiration *in vitro* of the tissues of pigeons suffering from avitaminosis is strictly comparable with that of the corresponding tissues of normal pigeons. These facts are contrary to the theory of Abderhalden and Hess (A., 1922, i, 399, 607, 788). The cause of avitaminosis probably lies rather in failure to satisfy a special metabolic need than in diminution of the elementary respiration of the tissues. W. E. E.

**Cholesterolaemia and Cholesterolysis in Experimental Diabetes.** I. I. NITZESCU, C. POPESCU-İNOTESTI, and I. CADARIU (*Compt. rend. Soc. Biol.*, 1924, **90**, 1067—1069; from *Chem. Zentr.*, 1924, ii, 1006—1007).—After depancreatisation, the cholesterol content of the blood rises, but falls in the subsequent cachexia. The difference between the cholesterol contents of the right and left heart is less than under normal conditions. Cholesterol is also not decomposed by the lungs *in vitro*. G. W. R.

**Chemical Study of Defective Ossification in Rachitic Animals.** R. ROBISON and K. M. SOAMES (*Biochem. J.*, 1925, **19**, 153—161).—The blood of rats fed on diets containing a sufficiency of calcium and inorganic phosphate but deficient in the fat-soluble factor contains a normal amount of inorganic phosphate and of the phosphoric ester hydrolysable by the bone enzyme, and these are not increased by the addition of cod-liver oil to the diet. The amount of the phosphoric ester resistant to the action of the bone enzyme is usually increased by cod-liver oil or other sources of the fat-soluble factor, but there appears to be no direct connexion between this increase and the improvement in the calcification of the bones. The defective calcification of the skeleton resulting from such diets is probably not due to any deficiency of inorganic phosphate or of the specific phosphoric ester in the blood, or of the enzyme in the bone by which the ester is hydrolysed. An excess of hydrolysable esters (caused by the injection of sodium glycerophosphate) may, however, produce some improvement in the calcification of the bones. In rats fed on diet very deficient in inorganic phosphate, the concentrations of inorganic phosphate and of phosphoric esters in the blood are below normal. The inorganic phosphate level in the blood of such animals is raised almost to the normal by cod-liver oil, but the amounts of esters are not significantly increased. The ratios of Ca/P in the bones support the view that the defective calcification in such a case is due mainly to a deficiency of inorganic phosphate ions, whilst this is not the case when the defect is caused by a lack of the fat-soluble factor alone. S. S. Z.

**Sodium, Potassium, Calcium, and Magnesium in Blood Plasma in Renal Disease.** I. M. RABINOWITCH (*J. Biol. Chem.*, 1925, **62**, 667—673).—Of 23 cases of advanced cardio-renal disease

only 5 were found in which the ratios Na : K : Ca : Mg in the blood were abnormal; in these cases the chief abnormality was an increase in the potassium.

C. R. H.

**Mechanism of the Action of Bismuth in Syphilis.** C. LEVADITI, S. NICOLAU, J. SALGUE, and R. SCHOEN (*Compt. rend.*, 1924, 179, 939—942).—Bismuth, when injected in the form of a suspension of sodium potassium bismuthotartrate in oil, appears to be liberated from this compound in the form of metal under the influence of leucocytes. In this condition, it appears to combine with certain proteins of the cell and so become assimilable, forming a substance which, even when present in small quantities, reacts with spirochætes and destroys them.

H. J. E.

**Effect of Interpancreatic Administration of Dextrose on the Blood-sugar Curve.** E. C. ALBRITTON (*Science*, 1924, 60, 274).—Blood-sugar curves obtained after intravenous injection of dextrose differ materially from those following its alimentary administration. Some of the curves obtained when the pancreas was subjected to a higher concentration of sugar in the blood are interpreted as indicating a greater discharge of insulin than occurred on injection by a peripheral vein.

A. A. E.

**Synthesis and Degradation of Carbohydrates in the Organism.** A. GIGON (*Helv. Chim. Acta*, 1925, 8, 35—37).—In converting dextrose into glycogen the organism must, from Karrer's results (A., 1921, i, 313, 768; 1923, ii, 460), first produce an anhydride. The increased production of carbon dioxide after ingestion of dextrose is due to the complete combustion of about one-tenth of it, the energy liberated being in close agreement, according to Karrer's thermochemical measurements, with that required for anhydride formation for the remainder. The subsequent conversion of the anhydride into glycogen is slightly exothermic. More carbon dioxide is produced when lævulose is given to a fasting man than when an equal amount of dextrose is ingested; it is probable, therefore, that formation of the anhydride from the ketose involves a greater absorption of energy than in the case of dextrose.

G. M. B.

**Influence of the Parents' Diet on the Young. III. Influence on the Young of an Excessive Amount of Calcium in the Mother's Diet during Pregnancy.** V. KORENCHEVSKY and M. CARR (*Biochem. J.*, 1925, 19, 112—116).—There is a marked decrease in the disorders of general nutrition and in the rachitic changes in the skeleton produced in the young by a diet deficient in fat-soluble factor, even when the mother is kept on a deficient diet during lactation, if the mother's "normal" diet is enriched during pregnancy with cod-liver oil and an excess of calcium. This effect is not obtained if butter replaces cod-liver oil as a source of the fat-soluble factor.

S. S. Z.



**Effects of Calcium Glycerophosphate, Sodium Glycerophosphate, and Sodium Dihydrogen Phosphate on the Skeleton of Rats Kept on a Diet deficient only in Fat-soluble Factor.** V. KORENCHESKY and M. CARR (*Biochem. J.*, 1925, **19**, 101—111).—Subcutaneous injections of an aqueous solution of calcium glycerophosphate increases the degree of calcification of the skeleton of rats kept on a diet deficient in fat-soluble vitamins. The water content of the bone, however, remains the same or may even be higher. Sodium glycerophosphate has in most cases produced the same effect on calcification, only in a much smaller degree. This difference was particularly marked histologically, since no improvement could be detected in the rachitic changes in the skeleton of rats treated with the sodium salt; a slight improvement is observed in about 50% of rats which received calcium glycerophosphate injections. The ingestion of calcium glycerophosphate does not affect the rachitic calcium impoverishment of the skeleton of rats kept on a diet deficient in the fat-soluble vitamins, nor does the injection of sodium dihydrogen phosphate.

S. S. Z.

**Efficiency of Urea as a Source of Nitrogen in a Young Ruminant (Kid).** B. A. LAVROV, O. P. MOLTSCHANOVA, and A. J. OCHOTNIKOVA (*Biochem. Z.*, 1924, **153**, 71—85).—From a study of the nitrogen balance and respiratory exchange of a young well-nourished kid kept on a basal diet of chopped hay, potato paste, sugar, and mineral salts to which varying amounts of urea were added, it is concluded that whilst the protein synthesised from the urea in the intestine may suffice for maintaining nitrogen equilibrium in adult animals, such is not the case in young animals kept on a low basal diet. In the latter condition, growth ceases, appetite diminishes, and a negative nitrogen balance ensues. Urea is therefore only of use as a source of nitrogen to the growing animal if the other sources of protein are ample for growth requirements.

J. P.

**Possible Correlation between Dietary Protein and Loss of Fur in Young Growing Rats.** G. A. HARTWELL (*Biochem. J.*, 1925, **19**, 75—79).—Loss of fur in rats is caused when potato or white bread forms the sole source of the protein of their diet. The addition of gluten, gelatin, or caseinogen to the bread diet completely prevents the loss of fur. When brown bread or oatmeal is the sole source of protein, loss of fur does not occur.

S. S. Z.

**Behaviour of Amino-acids in the Blood. Significance of the Liver in Protein Metabolism.** S. ROSENBAUM (*Z. ges. exp. Med.*, 1924, **41**, 420—438; from *Chem. Zentr.*, 1924, ii, 689).—When amino-acids are injected intravenously into normal individuals no increase in the amino-nitrogen of the blood, sampled a few minutes later, occurs so long as the quantity injected does not exceed a certain amount; frequently, indeed, a decrease is observed. In grave hepatic disorders, the amino-nitrogen is raised by injection of amino-acids. This is also the case with dogs in which the liver

has been excluded from the circulation. The liver thus exerts a regulating effect on the intermediate metabolism of proteins.

G. W. R.

**Effect of Sodium Benzoate on Composition of Blood and Urine. Possible Synthesis of Glycine in the Body.** W. W. SWANSON (*J. Biol. Chem.*, 1925, 62, 565—573).—Ingestion of 3—10 g. of sodium benzoate is followed (in man) by a decrease in the excretion of urea and uric acid whilst the concentration of urea in the blood is unchanged and that of uric acid raised. It is suggested that these results may indicate a synthesis of glycine from some substances which are normally converted into urea. C. R. H.

**Administration of 1-Nitroanthraquinone.** H. JOHN (*Biochem. Z.*, 1925, 155, 161—162).—If 2.5 g. of 1-nitroanthraquinone mixed with the food are fed to mice over a period of 6 days in successive doses of 0.1 g., there appears in the urine a little unchanged nitroanthraquinone together with two other substances, probably amino- and hydroxy-anthraquinones. P. W. C.

**Sensitivity to Light of Trypaflavine.** H. JOHN (*Biochem. Z.*, 1925, 155, 159—160).—Trypaflavine, when injected subcutaneously or intravenously into mice in doses of 0.5 c.c. of a 0.005% solution, is very toxic only if the animal is exposed to light. If, however, the same solution is exposed to light and then injected, it is non-toxic. P. W. C.

**Fixation of Bismuth in the Organs after Administration of Soluble and Insoluble Salts of the Metal.** (MME.) A. LISSIEVICI-DRAGANESCU (*Bul. Soc. Chim. România*, 1924, 6, 86—91).—The determination of bismuth in animal organs is conveniently effected by destroying the organic matter in the manner described by Pouchet and utilising Aubry's reagent mixed with a little gum arabic, comparison being made with a series of tubes prepared from known quantities of the metal. Protracted administration of sodium potassium tartrobismuthate by intramuscular injection results in the fixation of the bismuth in small amounts (diminishing in magnitude in the following order) in the large intestine, kidneys, spleen, salivary glands, brain, and liver. When a toxic dose of ammoniacal bismuth citrate is rapidly administered, the order of fixation of the bismuth is as above, except that the liver takes up almost as much as the kidneys. Thus, the quantities of bismuth found in different organs are not related to the amounts of blood in these organs.

Bismuth, administered in therapeutic dose to man, is found in the urine and saliva, but never in the cerebro-spinal fluid. With animals the metal enters the urine, faeces, and milk, and, with a heavy dose, the cerebro-spinal fluid, but never the bile.

T. H. P.

**Chemical Condition of Circulating Lead.** L. SCREMIN (*Arch. exp. Path. Pharm.*, 1925, 105, 49—53).—When injected subcutaneously into the guinea-pig, lead iodide is quickly converted

into lead phosphate. Lead sulphide and chromate, however, remain unchanged for some time. In serum containing an excess of phosphate, lead iodide, carbonate, and sulphate are changed to the phosphate in a comparatively short time. When injected into rabbits, the iodide, sulphate, and carbonate are eventually found to be changed to phosphate, but the chromate remains unchanged. This is explained by the very low solubility of the chromate, which is almost as difficultly soluble as the phosphate. The toxicological action of lead salts is considered to be due to the lead ion.

O. O.

**Antiseptic Action of Mercuric Chloride in Solvents of Different Dielectric Constants.** W. HELLENBRAND and G. JOACHIMOGLU (*Biochem. Z.*, 1924, **153**, 131—135).—Mercuric chloride has no antiseptic action in solvents of low dielectric constant (chloroform, benzene, ether), whilst its antiseptic action is vigorous in solvents of high dielectric constant (nitrobenzene, glycerol, water). These findings are correlated with the extent of dissociation of the antiseptic in the various solvents.

J. P.

**Antiseptic Action of Mercury Compounds.** G. JOACHIMOGLU and N. KLISSIUNIS (*Biochem. Z.*, 1924, **153**, 136—143).—The antiseptic actions of mercuric bromide and cyanide decrease with increasing acidity and on the addition of sodium bromide to the former and potassium cyanide to the latter. The antiseptic action of mercuric bromide is apparent in nitrobenzene, glycerol, and chloroform, but not in benzene or ether. Chloroform, therefore, is an exception to the rule already enunciated (see preceding abstract).

J. P.

**Hyperthermic Action of the Phenoxyacetic Acids.** E. MAMELI and E. FILIPPI (*Atti Congr. Naz. Chim. Ind.*, 1924, 390—391).—For combating the temperature depression accompanying cholera, carbon monoxide poisoning, etc., useful results are obtained by the hypodermic administration of phenoxyacetic acid or one of its near homologues in doses of 0.2—0.3 g. per kg. body-weight. These compounds cause no toxic effects, so that their hyperthermic action may be prolonged or enhanced without danger.

T. H. P.

**Benzoylallylecgonine and Benzoylbenzylecgonine.** E. POULSON and G. WEIDEMANN (*Arch. exp. Path. Pharm.*, 1925, **105**, 58—62).—*Benzoylallylecgonine* has been prepared by heating an intimate mixture of anhydrous benzoylecgonine and allyl iodide in a closed tube at 105° for 4 hrs.; it has m. p. 98°, is almost insoluble in water, soluble in the usual organic solvents;  $[\alpha]_D^{20}$  in absolute alcohol —31.0°; *hydriodide*, m. p. 182°; *hydrochloride*, m. p. 176°, and  $[\alpha]_D^{20}$  in absolute alcohol —37.3°. *Benzoylbenzylecgonine*, prepared in an analogous manner, is an oil, insoluble in water but easily soluble in alcohol and ether. It has  $[\alpha]_D^{20}$  in absolute alcohol —27.0°; *hydrochloride*, m. p. 123°,  $[\alpha]_D^{20}$  in absolute alcohol —18.5°. When injected intravenously into frogs, rats, and rabbits, both alkaloids produce symptoms similar to those of cocaine poisoning and the lethal dose in each case is similar to that of cocaine. The

lethal dose of the benzyl compound, however, for guinea-pigs is about three times that of cocaine. For local anæsthesia the allyl compound acts at a minimum concentration of 0.25%. Cocaine is without effect at this dilution. From the results of twenty-five experiments on humans it appears that for local anæsthesia the allyl compound is superior to cocaine. O. O.

**Localisation in the Organism of Alkyl Derivatives of Barbituric Acid.** P. FREDET and R. FABRE (*Compt. rend.*, 1925, **180**, 469—471).—The distribution of intravenously injected 5:5'-diethyl- (veronal) and 5:5'-allylisopropyl-barbituric acids in the blood and organs of the dog is determined. In each case, the hypnotic was administered as the diethylamine salt in aqueous solution. Both compounds are conveyed chiefly by the blood-corpuscles. They become localised in the brain and spinal cord.

W. E. E.

**Oxidation of Benzyl Alcohol and Benzyl Esters in the Human Organism.** J. SNAPPER, A. GRÜNBAUM, and S. STURKOP (*Biochem. Z.*, 1925, **155**, 163—173).—Substances containing benzyl groups, *e.g.*, papaverine and benzyl alcohol, are known to relieve muscular spasm in surviving organs and have therefore been administered orally. Benzyl alcohol, acetate, cinnamate, and hydrocinnamate are, however, oxidised when taken orally and excreted as hippuric acid as rapidly and as completely (80—90% of the theoretical) as benzoic acid, which is pharmacologically inactive. This explains why the oral administration of these substances has been attended with unsatisfactory results.

P. W. C.

**"Butesin" Picrate, a New Type of Anæsthetic-Antiseptic.** F. K. THAYER (*Amer. J. Pharm.*, 1925, **97**, 39—42).—Records the preparation and properties of *n*-butyl *p*-aminobenzoate ("butesin") picrate,  $C_6H_2(NO_2)_3(OH) \cdot 2NH_2 \cdot C_6H_4 \cdot CO_2Bu$ , yellow, m. p. 109—110°, which may be useful in the treatment of burns and similar injuries.

B. F.

**Chloralose and Parachloralose.** J. CHEVALIER and A. CHERBULIEZ (*Compt. rend. Soc. Biol.*, 1924, **91**, 642—644; from *Chem. Zentr.*, 1924, ii, 2186).—Pure chloralose has m. p. 187°. On injection, it exerts an anæsthetic effect similar to that of chloral or chloroform, but does not increase nervous irritability. The latter property, shown by commercial preparations, is to be attributed to the presence of parachloralose, which diminishes the anæsthetic effect of chloralose.

G. W. R.

**Local Anæsthetic and Anti-spasmodic Actions of some Ethers and Esters of Saligenin.** H. H. JENSEN and A. D. HIRSCHFELDER (*J. Pharm. Expt. Ther.* 1925, **24**, 423—448).—The synthesis and chemical properties of the ethers and esters used have been described by Hart and Hirschfelder (*A.*, 1922, i, 38). Except the butyl ether, which is too irritating for practical use, they have less local anæsthetic action than saligenin itself. The aromatic

ethers and esters (benzyl, benzoyl, and dibenzoyl) have greater toxicity, anti-spasmodic action, and depressant action on the circulation and respiration than the alkyl ethers and esters (ethyl, butyl, *iso*amyl, and acetyl), but all are more active than saligenin itself, and the aromatic ethers are most active of all. All, however, are too pungent and irritating for clinical administration either by mouth or subcutaneously. The effects seem to be due to a summation of the effects of saligenin and the substance liberated by hydrolysis.

C. P. S.

**Quantitative Investigation in Biological Fluids of Substances with great Surface Activity.** R. BRINKMAN and J. V. D. VELDE (*Biochem. Z.*, 1925, 155, 187—196).—The inadequacy of drop-counting methods is demonstrated, and a new method is described, with details of the apparatus used. The method consists in the preparation of a unimolecular film of the active substance and the measurement of the surface area of this film. H. D. K.

**Electroendosmosis through Mammalian Serous Membranes. I. Hydrogen-ion Reversal Point with Buffers containing Multivalent Anions.** S. MUDD (*J. Gen. Physiol.*, 1925, 7, 389—415).—When an electric current is passed through a mammalian serous membrane bathed in dilute buffer solution, electroendosmosis causes a flow of fluid through the membrane. This flow is towards the cathode when the  $p_H$  of the fluid is greater than a certain critical value—the reversal point. On the acid side of the reversal point, the flow is towards the anode. A method is described for studying quantitatively this electroendosmotic effect.

With buffer solutions containing only univalent ions, the reversal points were somewhat higher. The membranes used and their reversal points were: mesenteries of living animals (dog, cat, rabbit),  $p_H=4.4$ ; *post mortem*,  $p_H=4.8$ ; cat pleuræ, *post mortem*,  $p_H=4.3$ ; dog pleuræ, *post mortem*,  $p_H=5.0$ ; lean and fat pericardia, *post mortem*,  $p_H=5.1$ ; human pericardia, *post mortem*,  $p_H=5.0$ .

Discussing the bearing of these results on the question of the chemical composition of the water-pervious channels through the membranes, the author concludes that even in the fat cells the surfaces contain protein in important amounts.

C. P. S.

**Selective Vital Staining.** J. GICKLHORN and R. KELLER (*Biochem. Z.*, 1924, 153, 2—13).—Methods are described for the specific intravital staining of given organs and tissues whereby their oxidative or reductive activity may be studied. The strong reducing action of active nerve-fibres on the dye is noted. Using a combination of an alkaloid and dye (*e.g.*, cocaine and methylene-blue) it is possible to stain selectively living neurones, receptors, fibres, and ganglia of the central nervous system.

J. P.

**Enzymes and Light. VI. Influence of Iodides on Irradiated Enzymes.** L. PINCUSSEN (*Biochem. Z.*, 1924, 152, 406—415).—The action of malt diastase on soluble starch is inhibited, more especially in acid solution, by ultra-violet irradiation in the

presence of potassium iodide. Under the same conditions, iodide has little influence on the enzyme in the dark. On the other hand, the actions of salivary and taka-diaestases are increased by irradiation, especially in alkaline solution, whilst pancreatic diaestases show a similar but very much less marked behaviour. The results are correlated with a balance between the protective action of potassium iodide and the inhibitory action of iodine liberated from it by the ultra-violet irradiation. J. P.

**Enzymes and Light. VII. L. PINCUSSEN. Influence of Iodides on Irradiated Enzymes. II. N. KLISSIUNIS** (*Biochem. Z.*, 1924, 152, 416—419).—The inhibitory action of ultra-violet irradiation on trypsin is maximal in the absence of iodides of the alkali or alkaline-earth metals. Little or no difference was detected in the influence of previously irradiated or non-irradiated salts on enzyme solutions kept in the dark. J. P.

**Autolysis of the Muscle of the Cod Fish. E. H. CALLOW** (*Biochem. J.*, 1925, 19, 1—6).—The autolysis of cod muscle at 37°, whether previously frozen rapidly to -19° or not, is practically complete after 7 days. At 1°, the change is very slight even after 12 months. The autolysis of thawed muscle previously frozen slowly in air at -11° proceeds at a slightly greater rate than that of unfrozen muscle. On thawing cod muscle a fluid ("drip") separates out. This fluid contains a higher percentage of soluble nitrogen and autolyses to a greater extent than normal cod muscle. Cod muscle contains a protein which coagulates at 37°. S. S. Z.

**Kinetics of the Decomposition of Hydrogen Peroxide by Catalase. J. H. NORTROP** (*J. Gen. Physiol.*, 1925, 7, 373—387).—Having found, in studying the kinetics of trypsin digestion, that the anomalous results were caused by the inactivation of the enzyme (A., 1924, i, 805), the author has applied the formula derived for trypsin to the experiments of Morgulis on catalase (A., 1921, i, 751). The decomposition of hydrogen peroxide by liver-catalase at 20°, the peroxide being present in excess and in relatively high concentration, is accounted for by the assumptions: (1) The rate of formation of oxygen is independent of the peroxide concentration if the latter is greater than 0.10M. (2) The rate of decomposition of peroxide is proportional at any time to the amount of catalase present. (3) The catalase undergoes spontaneous unimolecular decomposition which is independent of the concentration of catalase, and inversely proportional to the original concentration of hydrogen peroxide up to 0.4 M. From these assumptions, the equation  $K = 1/t \cdot \log a/(a-x)$  is derived and found to fit accurately the results obtained by Morgulis ( $x$ =amount of oxygen liberated in time  $t$ ;  $a$ =total amount of oxygen liberated; and  $K$ =inactivation constant of the enzyme). C. P. S.

**Diaestase. W. SYNIEWSKI** (*Bull. Internat. Acad. Pol. Sci. Lettres*, 1924, 131—143).—It has been shown previously that the diaestase present in barley extract hydrolyses only the  $\alpha$ -carbonyl linkings of the starch molecule and is hence an  $\alpha$ -diaestase, setting

free all the maltose residues from the starch and leaving only the non-reducing limit dextrin I, which with iodine gives a blue coloration equal in intensity to that given by starch.  $\alpha$ -Diastase is destroyed by heating the extract at 60° for 20 mins. The  $\beta$ -diastase of malt arises only during malting, and is not completely destroyed until a temperature of 80° is reached. That this  $\beta$ -diastase is a natural enzyme and not an artificial product is shown by the fact that the action on starch of a mixture of barley extract with malt extract previously heated at 78° corresponds exactly with that of non-denatured malt extract. T. H. P.

**Action of  $\alpha$ -Diastase on the so-called Amylopectin.** W. SYNIEWSKI (*Bull. Internat. Acad. Pol. Sci. Lettres*, 1924, 145—148).—The existence of the author's non-reducing "limit dextrin I," which is the source of the dextrans formed when starch is hydrolysed with diastase (see i, 368), might be regarded as a proof of Maquenne's amylose-amylopectin theory of the constitution of starch granules. The author finds, however, that Gatin-Gruzewska's amylopectin is hydrolysed by the  $\alpha$ -diastase of barley extract in exactly the same way as Maquenne's amylose (the author's amylo-dextrin, identical with soluble starch), the products consisting of maltose and the author's non-reducing limit dextrin I; identity between the latter and amylopectin is, therefore, impossible. T. H. P.

**Variability of the Optimum Temperature for the Diastatic Action of Germinated Barley on Cooked and Uncooked Starchy Materials.** R. LECOQ (*Bull. Soc. Chim. biol.*, 1925, 7, 26—30).—The optimum temperature for the diastatic action of extracts of malt varies from 50° to 75° and depends on the condition of the malt and on whether the starchy materials to be acted upon are cooked or uncooked. [Cf. B., 1925, 257.] C. T. G.

**Diastatic Breakdown of Starch.** L. DE HOOP and J. A. VAN LAER (*Biochem. Z.*, 1925, 155, 235—244).—It is possible to obtain practically quantitative yields of maltose from starch if an amylase is used which is rich in co-enzyme, but most malt amylases, and all dialysed preparations, yield a mixture of approximately 80% maltose and 20% dextrin. By evaporating the reaction mixture to dryness, dissolving the residue in pyridine, and pouring into 96% alcohol, the dextrin comes out of solution and may be freed from maltose by two reprecipitations. The purified dextrin has reducing properties, an  $[\alpha]_D^{20}$  of 178.5°, and is very resistant toward malt extracts and commercial diastase preparations. It does not appear to be a trihexosan. H. D. K.

**Source of Error in the Use of Lintner's Starch Solution for Determining Diastatic Power.** W. SYNIEWSKI (*Bull. Internat. Acad. Pol. Sci. Lettres*, 1924, 149—151).—When Lintner's starch is used for the determination of diastatic activity, low values for the latter are obtained, as an appreciable quantity of diastase may be present without hydrolysis occurring. The error introduced in this way increases with the age of the starch solution, and appears

to depend on adsorption of diastase by suspended colloidal particles of reversion products of the starch.  
T. H. P.

**Laccase and the Laws of Enzyme Action.** P. FLEURY (*J. Pharm. Chim.*, 1925, [viii], 1, 105—116).—The relations existing between the amount of substrate transformed and time, concentration of enzyme, and  $p_H$ , have been studied by methods previously described (cf. A., 1924, i, 594), and it is found that laccase obeys the general laws followed by hydrolytic enzymes. A theory is put forward to explain the cause of the variation of the optimum  $p_H$  with the concentration of guaiacol.  
H. J. C.

**Enzymes present in the Latex of *Ficus carica*.** I. Esterases. S. VISCO (*Arch. Farm. sper. Sci. aff.*, 1924, 38, 243—250).—The latex of *Ficus carica* contains an esterase capable of hydrolysing mono- and tri-butyryns, although it is without action on triolein. The observed instability of the emulsions of latex and triolein may be the cause of the lack of action in this case.  
T. H. P.

**Enzyme Action. XXIX. Lipolytic Actions of Rabbit Tissues.** H. M. NOYES and K. G. FALK (*J. Biol. Chem.*, 1925, 62, 687—695). **XXX. Lipolytic Action of Tissues of Different Animals.** K. G. FALK, H. M. NOYES, and K. SUGIURA (*ibid.*, 697—709).—XXIX.—A study of the lipolytic activity of extracts of the different tissues of the rabbit towards various esters shows that the activity decreases in the order, liver, lungs, testes, kidney, brain, leg muscle.

XXX.—No general similarity could be observed in the curves representing the relative lipolytic activities of extracts of the same tissue taken from different animals towards the same series of esters except in the case of the brain. In absolute activity, the tissues of the rat were the richest, followed in descending order by those of the rabbit, ox, and man.  
C. R. H.

**Determination of Lipase in Body Fluids and in Tissues.** P. RONA and A. LASNITZKI (*Biochem. Z.*, 1924, 152, 504—522).—A method is described for measuring the lipolytic activity of surviving tissues, which depends on the determination of the carbon dioxide liberated from a Ringer bicarbonate solution by the acid derived from the substrate—glyceryl tributyrates. The lipase of serum (1 : 1000) acting on the substrate gives a linear curve over a period of 2 hrs.  
J. P.

**Oxidising Enzymes in the Constituents of the Seeds of French and Soya Beans.** J. J. NITZESCU and J. COSMA (*Compt. rend. Soc. Biol.*, 1924, 89, 1247—1250; from *Chem. Zentr.*, 1924, ii, 672).—Dehydrogenase is present in the meal of both beans. The embryo is richest in the enzyme, whilst the cotyledons and husk contain little or none.  
G. W. R.

**Iron, the Oxygen-carrying Component of the Oxidative Enzyme.** O. WARBURG (*Biochem. Z.*, 1924, 152, 479—494).—A review, more particularly of the author's own recent work, of the rôle of iron as an oxidative catalyst.  
J. P.



**Isolation of the Perhydridase (Schardinger's Enzyme) of Milk.** B. SBARSKY and D. MICHLIN (*Biochem. Z.*, 1925, **155**, 485—494).—For the determination of perhydridase the nitrate reduction method of Bach is preferred to the methylene-blue method. The enzyme is associated with the cream and occurs only in traces in skimmed milk and in butter, butter-milk being a convenient source of the enzyme. The precipitate obtained on treating butter-milk with acetone is dried and extracted with light petroleum. The resulting powder is strongly active, reducing nitrates to nitrites and methylene-blue to its leuco-base. It is insoluble in water, but dissolves in  $N/200$ -hydrochloric acid to give a solution 480 times as active as milk. Perhydridase has a temperature optimum of  $60^{\circ}$ . Aldehydes, xanthine, hypoxanthine, and protein degradation products act as oxygen acceptors to the isolated enzyme, which is regarded as being identical with Schardinger's enzyme and with purine-oxydase. J. P.

**Influence of Oxygen on the Production of Urea by Enzymes of the Liver and Spleen.** R. A. McCANCE (*Biochem. J.*, 1925, **19**, 134—140).—From experiments on the effect of oxygen on the formation of urea in autolysis of liver and of spleen, it is found that this gas inhibits the rate of urea production in autolysis by tissue enzymes. Where other factors such as hydrogen-ion concentration and accumulation of amino-acids are concerned, the effect of oxygen may also be to reduce the total amount of urea formed. S. S. Z.

**Enzymes of the Skin.** J. WOHLGEMUTH and Y. YAMASAKI (*Klin. Woch.*, 1924, **3**, 1113—1114; from *Chem. Zentr.*, 1924, ii, 673).—Appreciable amounts of diastase and catalase are found in all layers of the skin. A lipase also occurs which is not sensitive to either quinine or atoxyl. Only one autolytic ferment of moderate intensity was found. G. W. R.

**Enzymic Synthesis of Protein. II. Effect of Temperature on Synthesising Action of Pepsin.** H. BORSOOK and H. WASTENEYS (*J. Biol. Chem.*, 1925, **62**, 633—639. **III. Effect of  $p_H$  on Peptic Synthesis.** H. WASTENEYS and H. BORSOOK (*ibid.*, 675—686; cf. this vol., i, 102).—II.—Boiling, or the addition of alkali, destroys both hydrolytic and synthetic properties of pepsin; in concentrated solutions at  $p_H$  4.0 of the peptic hydrolysates of egg-albumin the synthesising action of pepsin is progressively increased by raising the temperature up to  $72^{\circ}$ , at which temperature the enzyme is destroyed.

III.—The optimum  $p_H$  for peptic synthesis is 4.0. The curve representing the relation of  $p_H$  to amount of protein synthesised resembles in form the primary dissociation curve of a dibasic acid or the curve representing the undissociated residue of an amphoteric electrolyte. No evidence could be obtained of auto-destruction of the enzyme at any of the reactions employed, nor was the relation between amount of enzyme and amount of protein synthesised a linear one; it is therefore concluded that the effect of the  $p_H$  on the

reaction is due to the ionisation, not of the enzyme, but of a dibasic acid or an amphoteric electrolyte contained in the substrate.

C. R. H.

**Nephelometric Investigations on the Enzymic Hydrolysis of Proteins. III. Determination of Peptic and Tryptic Digestion of Casein.** P. RONA and H. KLEINMANN (*Biochem. Z.*, 1925, 155, 34—53).—A method (cf. A., 1923, i, 1145; this vol., i, 103) for the rapid determination of casein solutions is described and modified to follow quantitatively the rate of hydrolysis of casein during peptic and tryptic digestion. Phosphate-buffered sodium acetate-casein solutions are precipitated with hot, saturated quinidine hydrochloride solution, made up to standard volume, and after 10 mins. are compared with standards nephelometrically. The error of the method is 1—2%.

P. W. C.

**Standards for the Colorimetric Determination of Trypsin.** J. A. SMORODINZEV and A. N. ADOVA (*Biochem. Z.*, 1924, 153, 14—18).—The method of Palladin for determining tryptic activity (*Pflüger's Arch.*, 1910, 134, 337) is improved by staining the fibrin with a 0.05% solution of diphenylrosaniline in glycerol instead of in alcohol, and by using water-glycerol in place of aqueous colour standards.

J. P.

**Liberation of Ammonia in Tryptic Digestion.** A. HUNTER and R. G. SMITH (*J. Biol. Chem.*, 1924, 65, 649—665).—In the tryptic hydrolysis of casein, gliadin, and Witte's peptone, the production of ammonia is relatively very much slower than the formation of free amino-nitrogen; the results indicate that the amide linkings are far more resistant to this enzyme than the peptide linkings; the result with Witte's peptone further shows that preliminary peptic digestion does not render the amide linkings more susceptible to attack by trypsin.

C. R. H.

**Effect of Lecithin, Cholesterol, and Cholesterol Derivatives on Tryptic Digestion.** F. STANDENATH (*Biochem. Z.*, 1925, 155, 245—246).—Lecithin strongly inhibits tryptic digestion; cholesterol and cholesterol derivatives have no influence on it. H. D. K.

**Relation of Chemical Structure to Rate of Hydrolysis of Peptides. II. Hydrolysis with Erepsin.** P. A. LEVENE and H. S. SIMMS (*J. Biol. Chem.*, 1925, 62, 711—724; cf. A., 1924, i, 1360).—In general, ereptic hydrolysis of peptides follows a similar course to that already described for acid hydrolysis; with erepsin, as with acid, glycylsarcosine shows anomalous behaviour. From the results, it is concluded that the strength of any peptide or anhydride linking is a function of the acidic or basic dissociation constants of the group involved.

C. R. H.

**Tyrosinase-Tyrosine Reaction. II. Theory of Deamination.** H. S. RAPER and A. WORMALL (*Biochem. J.*, 1925, 19, 84—91).—The following evidence is produced to show that there is no intermediate deamination of tyrosine by tyrosinase as suggested by Bach. There is no production of ammonia during the oxidation

of tyrosine by tyrosinase. The removal of all the ammonia initially present in the solutions or formed by any part of the oxidation process does not affect the formation of the intermediate and final products of the action of the enzyme, which is contrary to Bach's hypothesis that melanin is formed as a result of oxidation of the deaminised tyrosine accompanied by condensation with ammonia. Tyrosinase has no action on solutions of *p*-hydroxy-phenylpyruvic acid either with or without the necessary ammonia for recondensation. Melanin contains 8.40% of nitrogen (tyrosine 7.73%). Some properties of melanin are given. S. S. Z.

**Tyrosinase-Tyrosine Reaction. III. Supposed Deaminising Action of Tyrosinase on Amino-acids.** F. C. HAPFOLD and H. S. RAPER (*Biochem. J.*, 1925, **19**, 92—100).—Further evidence in support of the view that tyrosinase has no intermediate deaminising action is produced (see preceding abstract). There is no aldehyde formation, liberation of ammonia, or diminution in amino-nitrogen when potato tyrosinase acts on glycine, alanine, or phenyl-glycine. When tyrosinase acts on tyrosine to form melanin or its precursors, oxygen is absorbed. No such absorption occurs when equivalent molecular solutions of glycine or alanine replace tyrosine. The ammonia formation observed by Chodat and Schweizer by the action of tyrosinase on amino-acids takes place only when *p*-cresol, phenol, or pyrocatechol is present. Resorcinol, quinol, and *p*-benzoquinone have not this effect; *o*-benzoquinone alone causes deamination of amino-acids in the same way as the system *p*-cresol-tyrosinase. It is suggested that certain phenols in the presence of amino-acids form a preliminary *o*-quinone derivative which attacks the amino-acids with the liberation of ammonia. S. S. Z.

**Mechanism of the Tyrosine-Tyrosinase Reaction.** R. A. GORTNER (*Proc. Soc. Exp. Biol. Med.*, 1924, **21**, 543—545).—When tyrosinase is removed from a tyrosine solution by filtration (using an insoluble form of the enzyme prepared from meal-worms, cf. T., 1910, **97**, 110), after the initial rose colour has developed, the solution remains unchanged and the black pigment is not formed. The presence of the enzyme is necessary for the initiation of each stage of the reaction (cf., however, Raper and Wormall, A., 1923, i, 1146). Further, the action of tyrosinase, soluble or insoluble, on tyrosol does not go beyond the production of the rose colour even on long keeping. The formation of the black oxidation colours appears to require the presence of an amino group (absent from tyrosol). C. T. G.

**Plant Tyrosinases (with Particular Regard to the Action of Quinine).** F. BOAS and F. MERKENSCHLAGER (*Biochem. Z.*, 1925, **155**, 197—227).—The organs (leaves, tubers, seeds) of certain plants become black if placed in a solution of quinine sulphate, of a concentration of not less than about 0.05%. This is consequent on the setting free of tyrosinase from the cells damaged by the quinine. It is possible to protect the cells by addition of sodium

or potassium hydrogen phosphate to the quinine-containing medium, and comparison is made with the beneficial effect of phosphate injection on the excretion of pigmented urine which may occur in malaria patients after large doses of quinine. Pigmentation similar to that produced by quinine salts is brought about in the same plants in the absence of quinine when their cells are damaged by cold or heat or narcosis or by other agents, and the influence is described of a large number of organic and inorganic substances on this pigmentation in the potato. The use of quinine sulphate in the investigation of infectious diseases of plants is suggested.

H. D. K.

**Influence of Acidity on the Action of Yeast Extracts on Concentrated Solutions of Dextrose.** R. KUHN and G. E. VON GRUNDHERR.—(See i, 203.)

**Alcoholic Zymase and a more Exact Interpretation of its Activity.** G. PARIS (*Atti Congr. Naz. Chim. Ind.*, 1924, 446—449).—The results now obtained, in conjunction with those previously published, show that in an acid or neutral medium the fermentation of dextrose by yeast proceeds regularly and to completion, ethyl alcohol being the final product. In presence of sodium sulphite, fermentation remains incomplete owing to the interception of the acetaldehyde; the acceptor for the hydrogen of fermentation being thus rendered unavailable, glyceraldehyde takes its place and is converted into glycerol. Under these conditions, the ratio aldehyde : glycerol is approximately that expressed by the equation:  $C_6H_{12}O_6 = CH_3 \cdot CHO + CO_2 + C_3H_8O_3$ . In an alkaline medium, acetaldehyde undergoes simultaneous oxidation and reduction (Cannizzaro's reaction) under the influence of yeast, giving rise to alcohol and acetic acid; that yeast generates aldehydomutase is shown by the fact that other aldehydes also are converted into the corresponding alcohol and acid.

In accordance with these results, the author advances the following modified conception of the action of zymase, which must be regarded as composed of a number of independent enzymes. The work of the latter begins with depolymerisation of the sugar and ends with the formation of alcohol. The phenomenon of fermentation consists, indeed, not of three separate reactions as supposed by Neuberg, but of a single continuous process: (1)  $C_6H_{12}O_6 \rightarrow 2OH \cdot CH_2 \cdot CH(OH) \cdot CHO$ ; (2)  $\rightarrow CH_3 \cdot CO \cdot CHO, H_2O$ ; (3)  $\rightarrow CH_3 \cdot CO \cdot CO_2H + H_2$ ; (4)  $CH_3 \cdot CO \cdot CO_2H \rightarrow CO_2 + CH_3 \cdot CHO$ ; (5)  $CH_3 \cdot CHO + H_2 \rightarrow CH_3 \cdot CH_2 \cdot OH$ . If the acetaldehyde is fixed, reaction (5) does not take place, and the glyceraldehyde undergoes reduction to glycerol.

T. H. P.

**Action of Ultra-violet Rays on Alcoholic Fermentation and on Yeast.** R. and R. DE FAZI (*Atti Congr. Naz. Chim. Ind.*, 1924, 449—450).—The influence of ultra-violet rays on fermenting wort (cf. A., 1916, i, 236; 1922, i, 1219) results in decreased time of fermentation and maturation, and in enhanced keeping properties, of the beer. [Cf. B., 1925, 257.]

T. H. P.

**Relation between Alcoholic Fermentation and Hydrogen-ion Concentration.** I. E. HÄGGLUND and A. M. AUGUSTSON (*Biochem. Z.*, 1925, **155**, 334—347).—Taking the rate of evolution of carbon dioxide to indicate the velocity of fermentation of sucrose, dextrose, and maltose by yeast, the optimum reaction for this fermentation at 30°, in presence of various buffer mixtures—of phosphates, of lactic acid and sodium lactate, of acetic acid and sodium acetate, of pyruvic acid and sodium pyruvate—has been found to be in the neighbourhood of  $p_H$  4.5. The optimum  $p_H$  varies somewhat with the nature and concentration of the buffer substances. Alcoholic fermentation is extraordinarily sensitive to free acetic acid, whilst free phosphoric acid is relatively inactive.

H. D. K.

**Artificial and Natural Formation of Sugar Phosphates.** C. NEUBERG and M. KOBEL (*Biochem. Z.*, 1925, **155**, 499—506).—The oxidation of lævulose by molecular oxygen in the presence of phosphate (Warburg and Yabusoe, A., 1924, i, 713; Meyerhof and Matsuoka, *ibid.*, 1045) is not accompanied by the intermediate formation of hexose-phosphates. The formation of the latter in dextrose solutions in the presence of yeast or yeast juice at  $p_H$  6.4 to 8.4 is but slightly slowed by the addition of considerable amounts of cyanide, from which it is concluded that the latter process is not dependent on the catalytic action of a heavy metal as is the oxidation of lævulose in the presence of phosphate. J. P.

**Yeast Metabolism.** I. A. K. BALLS and J. B. BROWN (*J. Biol. Chem.*, 1925, **62**, 789—821). II. **Carbon Dioxide and Alcohol.** J. B. BROWN and A. K. BALLS (*ibid.*, 823—836).—I. Bakers' yeast (*Saccharomyces cerevisiae*) was grown in a medium consisting of beet-sugar molasses and ammonium salts, the mixture being aerated. The growth, determined by measuring the dry weight of the yeast at intervals, was found to be logarithmic; at the end of the 8th hour, however, there was a sharp transition in the rate of growth, the velocity constant falling to 1/10 of its previous value. This point of transition was coincident with the disappearance of sugar from the medium and with the occurrence of the maximum concentration of alcohol; the slackening of growth could be prevented by addition of fresh sugar. No evidence was obtained of the production of growth-inhibiting substances in the medium. A definite relation was found to exist between concentration of yeast and rate of fermentation, but not between concentration of yeast and rate of inversion. The total nitrogen remained unchanged throughout the whole period of growth, but the soluble nitrogen decreased progressively and independently of the rate of growth of the yeast; atmospheric nitrogen was therefore not fixed and the soluble nitrogen was used only for building up yeast cells. After the disappearance of the sugar, there remained an unidentified reducing substance in the medium which was constant in amount throughout the remainder of the experiment.

II.—The ratio of alcohol to carbon dioxide produced under the conditions described above was found to be considerably less than

that required by the accepted equation for the fermentation of a hexose, although the excess of carbon dioxide was not equivalent to the alcohol which had disappeared. Similarly, if solutions of alcohol containing yeast were aerated, alcohol disappeared, and carbon dioxide (less than the equivalent of the alcohol lost) was produced, whilst the yeast increased in weight. It is concluded that, in presence of excess of oxygen, alcohol is oxidised by yeast, partly to carbon dioxide and partly to some substance utilised by yeast in its growth.

C. R. H.

**Effect of Nitrates on Yeast.** A. FERNBACH and S. NICOLAU (*Compt. rend. Soc. Biol.*, 1924, 91, 8—10; from *Chem. Zentr.*, 1924, ii, 995).—Potassium nitrate exerts an accelerating effect on zymase. With prolonged contact, nitrate is changed to nitrite, which depresses the activity of the yeast. Nitrate has no effect on the other enzymes of yeast. In the absence of a supply of nitrogen other than nitrate, yeast does not multiply.

G. W. R.

**Metabolism of Acid-fast Bacteria. IV. Metabolism of the Human and Bovine Types of Tubercle Bacillus.** S. KONDO (*Biochem. Z.*, 1925, 155, 148—158).—An investigation (cf. A., 1924, i, 804) of the growth of the tubercle bacillus types humanus, bovinus, and gallinaceus in nutrient media containing various sources of carbon (organic acids, alcohols, and carbohydrates) and nitrogen (ammonia, amino-acids, urea, and uric acid) revealed little difference in metabolism amongst the three types, each being characterised by the utilisation of only a narrow range of simple substances.

P. W. C.

**"Intestinal" Anthrax.** G. SANARELLI (*Compt. rend.*, 1924, 179, 937—939).—Gastric juice from adult guinea-pigs and rabbits kills the non-sporing bacteria in 5 or 10 mins., whilst with that from new-born animals the time is usually 2 mins. Intestinal secretions, even when dilute, inhibit the germination of anthrax spores, although the development of *proteus*, *Staphylococcus*, and other microbes is in no way hindered. The action, especially marked in the case of fresh material, falls off in old or heated specimens; it is impaired by pathological conditions of the intestinal tract.

H. J. E.

**Globulin and Albumin Fractions of Blood Plasma of Cows and Calves in Relation to Infection with *Bacillus abortus*.** P. E. HOWE and E. S. SANDERSON (*J. Biol. Chem.*, 1925, 62, 767—788).—Subcutaneous inoculation of living cultures of *Bacillus abortus* or of rabbits' blood corpuscles into calves produced no permanent changes in the distribution of the blood proteins, although a temporary increase in the fibrinogen and a rise or fall in the total globulin might be observed. No change was observed in the plasma proteins of cows during normal pregnancy, but after intravenous inoculation with *B. abortus* and in cows which had aborted there was found constantly an increase in the globulin and in 50% of the cases a decrease in the albumin. Certain further changes in

the distribution of plasma proteins both of cows and calves are described, which appear to be dependent on changes in environment.

C. R. H.

**Bacterial Autolysis. Acidification due to the Formation of  $\beta$ -Hydroxybutyric Acid.** LEMOIGNE (*Ann. Inst. Pasteur*, 1925, **39**, 144—173).—Aqueous emulsions of bacillus M (probably *Bacillus megatherium* de Bary) rapidly become acid, the final acidity being 6—7 times that at the commencement; 1 g. of dry bacteria represents an acidity of 16—18 c.c. of an *N*/10-solution, 60—75% of this acidity being due to  $\beta$ -hydroxybutyric acid. This occurs also in the absence of oxygen and without the production of gases. As in all such phenomena, there is elimination of soluble phosphates.

I. E. B.

**Action of Bacteria on Bile Acids.** H. LICHT (*Biochem. Z.*, 1924, **153**, 159—164).—Various bacteria (*coli*, *proteus*, *typhus*, *pyocyaneus*, *Streptococcus*, *Staphylococcus*, and *fæcal*) do not bring about the scission of bile acids into cholic acid and their respective amino-acids, but they do alter the cholic acid residue in such a way that the gravimetric determination of the bile acids cannot be carried out by Exner and Heyrovsky's method.

J. P.

**Destruction of Uric Acid by Bacteria and Moulds.** J. L. MORRIS and E. E. ECKER (*J. Infect. Dis.*, 1924, **34**, 592—598).—Ulpiani's uric acid bacterium, isolated from fæces, destroys uric acid, but not owing to the presence of uricase. In simple media, the following pathogenic moulds destroyed uric acid: *Epidermophyton inguinale*, *Mastigocladium blochi*, a nail *Blastomyces*, *Achorion violaceum*, and *Sporotrichum shenkii*.

CHEMICAL ABSTRACTS.

**Nitroprusside Reaction of Bacteria.** A. B. CALLOW and M. E. ROBINSON (*Biochem. J.*, 1924, **19**, 19—24).—*Bacillus alcaligenes*, *B. proteus*, *B. pyocyaneus*, *B. prodigiosus*, and *B. fluorescens* give strong nitroprusside reactions. The substance responsible for this reaction has not yet been identified. The iodine equivalents in each case are given. *B. coli*, *B. sporogenes*, *Sarcina aurantiaca*, *Staphylococcus aureus*, *Streptococcus acidilactici*, and the Timothy grass bacillus failed to give the nitroprusside reaction.

S. S. Z.

**Bacterial Fermentation, particularly in the *Coli-Typhosus* Group.** W. C. DE GRAAFF and A. J. LE FÈVRE (*Biochem. Z.*, 1925, **155**, 313—332).—Neuberg's method of fixation with sodium sulphite has been extensively employed in an investigation of the production of acetaldehyde during the fermentation of a large number of sugars and polyhydric alcohols by various members of this group of bacteria. Acetaldehyde is invariably found wherever gas or acid formation takes place. Many of the simpler sugars and related compounds, *e.g.*, glyceraldehyde, glycerol, glyceric acid, dihydroxyacetone, pyruvic acid, ethylene glycol, are fermented by certain of the colon organisms with intermediate production of

acetaldehyde. Support is given to Neuberg's view as to the importance of pyruvic acid as an intermediate substance during bacterial fermentation.

The basal medium employed was peptone water containing sodium sulphite, with calcium carbonate in suspension. The fermentation of glycol, pyruvic acid, and glycerol by *Bacillus coli* was followed quantitatively and a carbon balance sheet prepared. Carbon dioxide, acetic acid, and hydrogen were the main products; only in the case of glycerol were appreciable quantities of succinic and lactic acids formed. The succinic acid is probably formed from pyruvic acid.

H. D. K.

### Causes of $p_H$ Variation in Cultures of *Bacillus diphtheriae*.

G. ABT and G. LOISEAU (*Ann. Inst. Pasteur*, 1925, **39**, 114—143).—*Bacillus diphtheriae* grown in Martin broth produces much carbon dioxide, more than half of which is liberated during growth, the remainder being partly free and partly as bicarbonate, in the medium. The dissolved carbon dioxide is partly ionised, and tends to increase the acidity. There is, however, no definite relationship between the  $p_H$  at any given time and the amount of carbon dioxide dissolved. *B. diphtheriae* destroys acetic acid preferably, then butyric and lactic acids, whilst formic acid is the most resistant. Simultaneous formation and destruction of the acids takes place during the growth of the organism, the former predominating in the first 2 days, the two processes being about equal for the next 2 days, after which the latter predominates. This process together with the accumulation of carbon dioxide in the medium explains the initial phase of acidity of cultures made in alkaline media. Alkalinity is produced by three causes: production of ammonia, conversion of salts of organic acids into hydrogen carbonates, and the change of primary to secondary phosphates. In acid media, the rapid destruction of the organic acids and the buffering action of the bicarbonate suppress the phase of acidification.

I. E. B.

**Utilisation of Paraffin by Micro-organisms.** W. O. TAUSSEON (*Biochem. Z.*, 1925, **155**, 356—368).—A mould, allied to *Aspergillus flavus*, has been isolated which is capable of utilising paraffin wax or vaseline as sole source of carbon. Grown aerobically in a synthetic medium, 75% of the paraffin is decomposed in six weeks. The optimum  $p_H$  for growth lies between 7.0 and 8.0. A mixture of esters of higher fatty acids with alcohols of high molecular weight is formed as an intermediate product. Other fungi and bacteria having similar properties are described.

H. D. K.

**Biochemistry of *Vibrio cholerae*.** J. HIRSCH (*Z. Hyg. Infekt.-Krankh.*, 1924, **102**, 503—516; from *Chem. Zentr.*, 1924, ii, 684).—In aqueous peptone cultures *Vibrio cholerae* reduces nitrate quantitatively to nitrite. The reduction is independent of the initial development of the vibrio. The velocity of reaction increases with the time and with the concentration of nitrate up to 0.3%. Oxygen from the nitrate cannot replace deficient atmospheric oxygen.

G. W. R.



**Influence of Carbohydrates on Hydrogen Sulphide Production by *Bacillus ærtrycke* (Mutton).** H. HEAP and B. H. E. CADNESS (*J. Hyg.*, 1924, 23, 77—93).—The effect of carbohydrates in accelerating bacterial multiplication is parallel to the effect on the rate of formation of hydrogen sulphide. The rate of formation of amino-nitrogen, however, remains stationary. Apparently, in presence of dextrose the sulphur portion of the complex is attacked more readily than the nitrogen portion. CHEMICAL ABSTRACTS.

**Nitrification in Acid Solutions.** T. GAARDER and O. HAGEM (*Bergens Museums Aarbok.*, 1922—1923; *Naturvidensk. række*, No. 1, 26 pp.; from *Chem. Zentr.*, 1924, ii, 2173).—By selective culture, strains of bacteria have been obtained which can produce nitrites from ammonium sulphate at various hydrogen-ion concentrations. The following bacteria have been distinguished: *Bact.*- $\alpha$ , optimum  $p_H$  7.7—7.9, minimum  $p_H$  7.0—7.1; *Bact.*- $\beta$ , optimum  $p_H$  6.8—7.0, minimum  $p_H$  6.6; *Bact.*- $\gamma$ , optimum  $p_H$  6.5—6.6, minimum  $p_H$  6.0—6.1; probably also a bacterium with optimum  $p_H$  7.0—7.2. It is not certain if the nitrification in acid solutions is the work of one or of two bacteria. G. W. R.

**Utilisation of Energy Liberated by Oxidations.** E. AUBEL and R. WURMSER (*Compt. rend.*, 1924, 179, 848—851).—The theory that the mechanical energy of living beings arises from reactions involving oxidation and reduction (Wurmser, *Bull. Soc. Chim. biol.*, 1923, 5, 487) was tested in order to ascertain whether there exists any relation between rate of development and susceptibility of the medium to biological oxidation (cf. Gompel, Mayer, and Wurmser, A., 1924, i, 605). *Aspergillus niger* was grown in a series of solutions containing ammonium chloride and citric acid of similar respective concentrations but with different amounts of sodium hydroxide added to each to bring about differences in hydrogen-ion concentration. The rates of development of the mould were closely related to the respective velocities of oxidation of the citric acid. H. J. E.

**Effect of the Mineral Composition of the Culture Medium on the Structure of *Aspergillus niger*.** M. MOLLIARD (*Compt. rend.*, 1924, 178, 1865—1867; from *Chem. Zentr.*, 1924, ii, 682).—When the chlorides are substituted for the sulphates of magnesium, iron, and zinc in cultures of *Aspergillus niger* the growth of the mycelium becomes slower. A certain amount of citric acid is formed. Lævulose is more rapidly utilised than dextrose, the opposite being the case under normal conditions. Decrease in the potassium content of the medium produces marked changes in the hyphæ and, as is the case when acids are added, causes sterility and the formation of giant cells. The effect of acids is probably due to the removal of potassium from the organism. G. W. R.

**Effect of the Nature of Sugar on the Formation of Organic Acids by *Aspergillus niger* in Unbalanced Media.** M. MOLLIARD (*Compt. rend. Soc. Biol.*, 1924, 90, 1395—1397; from *Chem. Zentr.*, 1924, ii, 682; cf. preceding abstract).—By the addition

of increasing amounts of lævulose to cultures of *Aspergillus niger* containing the same concentration of dextrose, the amount of gluconic acid formed increases until the concentration of lævulose in the medium is equal to that of dextrose. Of the other sugars, only maltose leads to the production of appreciable amounts of acid, apparently gluconic acid. Sucrose yields the largest amounts of oxalic and citric acids. G. W. R.

**Agents for the Transformation of Toxins into Anatoxins.** A. BERTHELOT and G. RAMON (*Compt. rend.*, 1925, 180, 340—342).—Diphtheria toxin may be converted into anatoxin by treatment with acraldehyde, crotonaldehyde, acetaldehyde, or hexamethylenetetramine; the first two substances exert an irritating action on living tissues, but the last two, especially acetaldehyde, have no such disadvantage. (See also A., 1924, i, 463.) T. H. P.

**Colorimetric Determination of Oxygen.** W. W. EFIMOFF (*Biochem. Z.*, 1925, 155, 371—375).—A method for determining oxygen in solution (culture media), of wider applicability than that of Winkler, is described. The leuco-base of indigo-carmin is added, by means of a special pipette which avoids contact of the base with air, to the solution under investigation, and the resulting blue colour is compared with a series of standard solutions of the dye. J. P.

**Hormonal Regulation of Intermediate Carbohydrate Metabolism. I. Importance of Adrenaline and Insulin in the Utilisation of Dextrose by Warm-blooded Animals.** A. GOTTSCHALK (*Biochem. Z.*, 1925, 155, 348—355).—Adrenaline hinders the formation of acetaldehyde during the aërobic autolysis of muscle in Tyrode's solution in presence of calcium sulphite. Insulin has the opposite effect and increases acetaldehyde formation in these circumstances, whilst simultaneous addition of adrenaline and insulin gives intermediate results. H. D. K.

**Hormonal Significance of Ammonia. Antagonism and Synergism of Ammonium and Magnesium Ions in the Organism.** W. W. PRÁWDICZ-NEMINSKI (*Biochem. Z.*, 1924, 152, 388—405).—The hormonal action of ammonia and its derivatives is reviewed from the point of view of their influence on the rhythmic movements of the intestine and on the rhythm and tone of the heart in relation to an antagonism between ammonium and calcium or magnesium ions. The literature is extensively quoted. The possible clinical significance of the antagonistic actions of ammonia and magnesium is discussed. J. P.

**Influence of Adrenaline on the Concentration of Carbamide in the Blood.** C. DUBOIS and M. POLONOVSKI (*Compt. rend. Soc. Biol.*, 1924, 91, 293—295; from *Chem. Zentr.*, 1924, ii, 1363).—The concentration of carbamide in the blood is increased by adrenaline, apparently by a similar mechanism to that increasing the sugar content. R. B.

**Insulin and the Oxidation of Dextrose.** G. AHLGREN (*Berl. klin. Woch.*, 1924, **3**, 1158—1160; from *Chem. Zentr.*, 1924, ii, 1007).—Finely-divided frog muscle in the presence of methylene-blue oxidises dextrose only over a certain range of concentration of insulin ( $10^{-9}$  to  $10^{-13}$ ). At higher concentrations, oxidation of dextrose is inhibited. The muscle must be examined immediately after removal from the body in order to detect the glycolysis induced by insulin during life.

G. W. R.

**Insulin and the Oxydases of Muscle.** I. I. NITZESCU and I. COSMA (*Compt. rend. Soc. Biol.*, 1924, **90**, 1077—1078; from *Chem. Zentr.*, 1924, ii, 1007; cf. preceding abstract).—Insulin investigated by Thunberg's methylene-blue method accelerates the decomposition of  $\beta$ -hydroxybutyric and pyruvic acids.

G. W. R.

**Effect of Insulin on the Composition of the Blood.** P. MAZZOCCO and V. MORERA (*Compt. rend. Soc. Biol.*, 1924, **91**, 30; from *Chem. Zentr.*, 1924, ii, 1008).—After administration of insulin to dogs the total nitrogen, inorganic phosphorus, and alkaline reserve of the blood decrease. No decrease occurs in residual nitrogen, calcium, potassium, or magnesium. Normal composition is restored after a few hours.

G. W. R.

**Effect of Insulin on the Phosphorus of the Blood.** E. SAVINO (*Compt. rend. Soc. Biol.*, 1924, **91**, 29; from *Chem. Zentr.*, 1924, ii, 1008).—The inorganic phosphorus of the blood of sheep falls concomitantly with sugar, from 9 mg. % to 5 mg. % in  $3\frac{1}{2}$  hrs. The decrease of sugar but not of phosphorus is arrested by administration of dextrose.

G. W. R.

**Insulin and its Action. III. Lactic Acid Content of Muscle in Death due to Insulin or to Starvation.** H. BAUR and R. KÜHN (*Münch. med. Woch.*, 1924, **71**, 541—544; from *Chem. Zentr.*, 1924, ii, 710; cf. Baur, Kühn, and Wacker, *Münch. med. Woch.*, 1924, **71**, 187).—The lactic acid content of the skeletal muscle of rabbits killed by insulin is less than that of normal animals and does not exhibit the usual *post-mortem* rise. Lower figures still are obtained for the lactic acid content of the muscles of animals killed by starvation.

G. W. R.

**Secretin and Insulin.** H. PENAU and H. SIMONNET (*Bull. Soc. Chim. biol.*, 1925, **7**, 17—25).—A method, previously used for the preparation of insulin (Penau, A., 1924, i, 1150), has been applied to the extraction of secretin from the mucous membrane of the duodenum of the pig. After fractional precipitation with alcohol, the product is dissolved in dilute hydrochloric acid and further purified by precipitation with sodium chloride and dialysis. The material so obtained, when injected into normal dogs and rabbits, produces abundant secretion of pancreatic juice, has no appreciable depressor action on the blood pressure, and, further, acts like insulin in causing marked hypoglycæmia. The latter action also followed injection into a depancreatized dog. Com-

parative injections of purified insulin showed no secretory activity. Secretin, prepared in this way, appears to be a colloidal complex of a protein nature; but it is not yet known whether the secretory and hypoglycæmic activities are associated with one or with two substances.

C. T. G.

**Intermediate Carbohydrate Metabolism in the Liver.**  
**VIII. Phosphatase and Phosphate of Hexosediphosphoric Acid in the Liver with regard to Insulin.** T. BRUGSCH and H. HORSTERS (*Biochem. Z.*, 1925, 155, 459—476).—Phosphatase, capable of converting hexosediphosphoric acid into *d*-fructose and phosphoric acid, is present in the liver of both normal and depancreatized dogs, its activity in the latter case being somewhat less than in the former. The activity of the phosphatase is not appreciably affected by the presence of insulin even when the latter has been administered in amount sufficient to produce hypoglycæmic convulsions in the animal. The active constituent of insulin is a kinase of phosphatase (Euler, A., 1911, i, 105) and promotes the synthesis of fructosediphosphoric acid.

J. P.

**Insulin-like Behaviour of Oat Bran Extract.** E. BODEN, P. NEUKIRCH, and F. WANKELL (*Klin. Woch.*, 1924, 3, 1396—1397; from *Chem. Zentr.*, 1924, ii, 1365).—An alcoholic-acetic acid extract of oat-bran contains a substance which decreases the blood-sugar in rabbits, normal and diabetic humans, and diminishes the ketonuria in diabetics. The action persists several hours after intravenous injection.

R. B.

**Early Action of Insulin in the Diabetic.** L. LAWN and C. G. L. WOLF (*Biochem. J.*, 1925, 19, 122—133).—From experiments on the respiratory exchange and blood-sugar levels of four cases of diabetes as influenced by the administration of food, with and without protection from insulin, the authors conclude that insulin probably first converts dextrose into glycogen and then enables the organism to mobilise and burn the glycogen in the normal way.

S. S. Z.

**Presence of Vitamin-A in Yeast Fat.** E. M. LUCE and I. S. MACLEAN (*Biochem. J.*, 1925, 19, 47—51).—Fat extracted from yeast by ether promotes growth in rats subsisting on a diet deficient in the fat-soluble vitamins. If the extracted yeast is boiled with hydrochloric acid, dried, and again extracted with ether a fat is obtained which has no growth-promoting properties. Ordinary dried yeast and dried yeast obtained from organisms incubated in carbohydrate solution to increase the fat content, do not promote growth in daily doses of 0.5 g. This is most probably due to the insufficient quantity of yeast fat administered. It is suggested that vitamin-A is possibly synthesised directly by the yeast-cell.

S. S. Z.

**Changes in the Percentage of Vitamin-A and in the Nature of Albumin during the Germination of Seeds of *Phaseolus radiatus*, L. (Katjang Idjo).** W. F. DONATH (*Repts. Dutch Ind. Med. Civ. Ser.*, 1924, 344—362; Reprint).—The vitamin-A content

of the ungerminated seeds (katjang idjo) of *Phaseolus radiatus*, L., of the short sprouts (tao geh—used as a staple food in the Dutch East Indies) grown therefrom in the dark, and of longer sprouts grown out of doors has been investigated on rats. A synthesis of fat-soluble vitamin occurs during the first few days of growth in the dark and a much greater increase in the seedlings grown in sunlight. An increase in the nutritive albumin content occurs under the same conditions. L. F. H.

**Oxidation of Vitamin-A during the Preparation of Butter from Cream.** J. B. PLATON (*Biochem. Z.*, 1925, 155, 228—234).—Butter was made (1) in presence of air, (2) in an atmosphere of carbon dioxide. Fed to young rats, there was found to be no difference in the content of vitamin-A in the two butters. The minimum quantity of butter required to maintain normal growth in young rats was considerably less than that believed necessary by earlier workers. H. D. K.

**Influence of Storage on the Antiscorvy Value of Fruits and Vegetable Juices.** E. M. DELF (*Biochem. J.*, 1925, 19, 141—152).—The whole fruits of oranges and lemons and the whole roots of swedes retain their antiscorbutic activity on storage as long as the tissue remains living. The expressed juice of oranges and lemons stored for 5 years in frozen condition retains about half its original antiscorbutic potency. Swede juice, stored in a similar way, loses the greater part of its value in less than 2 years. Canned orange and tomato juices retain much of their value even after storage for 4 years at laboratory temperature, canned tomato being the less stable. Lemon juice containing potassium hydrogen sulphite as a preservative and stored at laboratory temperature for 4½ years, loses about five-sixths of its original value. Orange and lemon juices can be preserved satisfactorily for 1 to 3 years at laboratory temperature in presence of their own rind oil. S. S. Z.

**Fat-soluble Vitamins. XXI. Alleged Growth-promoting Properties of Air Irradiated with Ultra-violet Light.** E. M. NELSON and H. STEENBOEK (*J. Biol. Chem.*, 1925, 62, 575—593).—The following results were obtained with rats kept on a diet lacking the anti-rachitic factor. Non-irradiated animals showed normal growth when placed in the same cage with irradiated animals, or when placed in a jar of which the false bottom (galvanised iron wire screen) had been irradiated, but not when kept in a jar of which the air only had been irradiated (cf. Hume and Smith, A., 1923, i, 728). The screen effect was not obtained with new screens and is, therefore, probably due to a slight (although invisible) contamination of the latter by the animals previously kept on them; it is necessary for the animals to be actually in contact with the irradiated screen, and the possibility is therefore suggested that the effect is brought about by the ingestion by the animals of traces of excreta, adherent to the screens, and rendered active by irradiation.

C. R. H.

**Influence of Ultra-violet Radiations on Accessory Food Factors.** S. S. ZILVA (*Biochem. Z.*, 1925, 155, 333).—Spinka's suggestion (this vol., i, 212) that the failure to grow of mice given irradiated butter as sole source of vitamin-A was not necessarily due to destruction of this vitamin by the ultra-violet light, is not in accordance with experimental data previously brought forward (see A., 1919, i, 461; 1921, i, 475). H. D. K.

**Effect of Irradiation and Diet on Calcium and Phosphorus Metabolism.** J. M. HENDERSON (*Biochem. J.*, 1925, 19, 52—62).—One hour's irradiation daily for 24 days with a carbon-arc lamp definitely increased the calcium and phosphorus retention in a pig fed on a diet badly balanced particularly with respect to phosphorus, calcium, and magnesium, as compared with a control animal fed on a similar diet but kept in the dark. The calcium and phosphorus in the urine rose both actually and relatively to their excretion in the faeces. No concomitant increase in body-weight was observed. In the case of pigs fed on a well-balanced diet, no significant difference in the retention of calcium and phosphorus was recorded between irradiated animals and pigs kept in the dark. S. S. Z.

**Physiological Equilibria in Plants. Dependence of the Growth Constant of Maize on Nitrogen Nutrition.** A. RIPPEL and O. LUDWIG (*Biochem. Z.*, 1925, 155, 133—147).—The course of growth of maize is followed in a constant mixture of sand, potassium dihydrogen phosphate, and potassium sulphate with varying amounts of ammonium nitrate and the growth formula of Robertson modified by Rippel is applied. Both this constant and the curvature of the growth curve increase directly with the amount of nitrogen present. P. W. C.

**Determination of Chlorides and Sulphates in Expressed Plant-tissue Fluids.** R. A. GORTNER and W. F. HOFFMAN (*Bot. Gaz.*, 1924, 77, 96—102).—Wetmore's method for determination of chlorides in blood (cf. A., 1921, ii, 126) is applicable, with slight modification, to their determination in plant sap. Sulphates are determined by the Benedict-Denis method for determining sulphur in urine (cf. Benedict, A., 1909, ii, 827; Denis, A., 1911, ii, 66). This does not, however, distinguish between organic and inorganic sulphur. Both methods are rapid, accurate, and simple to carry out. Full details are given. C. T. G.

**Plurality of the Products of Photosynthesis Deduced from a Study of the Gaseous Exchanges between the Atmosphere and the Whole Plant.** P. MAZÉ (*Compt. rend.*, 1925, 180, 306—309).—Consideration of the results previously obtained by the author (A., 1902, ii, 345, 346; 1903, ii, 36; 1921, i, 209), Schloesing (A., 1893, ii, 137, 180; 1894, ii, 110; 1901, ii, 31), and others leads to the conclusion that the ratio of photosynthetic assimilation by plants, that is, oxygen liberated : carbon dioxide absorbed, is always greater than 1. Thus, it may be assumed that the products of the photosynthesis comprise, in addition to carbohydrates, substances more highly reduced than the latter. Since the total products are,

on the whole, less rich in oxygen than the carbohydrates, respiration can fix oxygen in plants although the ratio between the weights of hydrogen and oxygen is greater than 1 : 8. T. H. P.

**Spectrum of Chlorophyll in the Living Leaf.** J. WLODEK. (See ii, 258.)

**Regeneration of Amylogenous Excitability of Plastids during Hydrolysis.** A. MAIGE (*Compt. rend.*, 1924, **179**, 838—840).—The amyliiferous plastids which have lost their starch-forming activity after prolonged amylogenesis recover it during the process of amyolysis, the recovery being more marked in the case of the more active amylytic cells. In the same cell, the transformation of starch takes place with a velocity depending on the plastids involved. Those which effect slow transformation have, in comparison with those which act rapidly, a more marked amylogenous activity which appears to correspond with a stronger inhibition of the action of amylase. This inhibiting effect should be regarded as one of the forms of amylogenous activity with regard to the amount of sugar in the cell: it controls the starch transformation in each plastid during hydrolysis. H. J. E.

**Rôle of the Mineral Constituents in Plants. II. Influence of Neutral Salts on Peroxydase.** A. J. SMIRNOV (*Biochem. Z.*, 1925, **155**, 1—33).—The influence of neutral salts on peroxydase activity (cf. A., 1924, i, 1265) in aqueous extracts of wheat of known  $p_H$  is investigated, pyrogallol serving as oxidisable substrate and the energy of oxidation being measured by the amount of purpurogallin formed. The elements found in the ash of the peroxydase at concentrations realised in the cell cause increased activity. Activity is optimum at  $p_H$  8.8 and falls away slowly on the acid side down to  $p_H$  3.5, but very rapidly on the alkaline side. The action is determined by the cation, and for alkaline-earth metals increases with increasing atomic weight. Concentrations of calcium chloride at  $N/80$ — $N/800$ , strontium chloride at  $N/8000$ , and barium chloride at  $N/800$  give the maximal increased activity, the action being still pronounced at  $N/8000$ ,  $N/40,000$ , and  $N/40,000$  respectively. The positive action of magnesium chloride, however, rapidly becomes negative on dilution (due probably to hydrolysis). Zinc chloride inhibits peroxydase activity; mercuric chloride shows only slight inhibition and may at a dilution of  $N/10^7$  cause increased activity. Sodium, potassium, and rubidium chlorides possess about equal inhibitory action;  $N/20$ -lithium chloride has a positive effect, but loses it at  $N/100$ ; ammonium chloride is almost inactive. The inhibitory effect of alkali chlorides is smaller than the stimulating effect of alkaline-earth chlorides. Manganous chloride shows inhibition which increases on dilution. These salts act directly on the peroxydase, since they do not show these effects on the ( $Fe^{++} + H_2O_2$ ) system. Salts of the iron series only act in fairly high concentration in presence of hydrogen peroxide. Phosphates and nitrates (optimum concentration  $N/80$ ) have a large, sulphates a smaller stimulatory effect. P. W. C.

**Nitrogenous Groups of Plant Nucleic Acid.** W. JONES and M. E. PERKINS (*J. Biol. Chem.*, 1925, **62**, 557—564).—Among the products of the hydrolysis of yeast-nucleic acid at the ordinary temperature with 1% sodium hydroxide (which process involves no formation of free phosphoric acid or purine bases and no deamination) there have been isolated the nucleotides of guanine, adenine, and cytosine, but not that of uracil; it is concluded that the uracil derivatives previously obtained from yeast-nucleic acid must have been formed secondarily from cytosine by deamination. C. R. H.

**Plant Phosphatides. I. Lecithin and Cephalin of the Soya Bean.** P. A. LEVENE and I. P. ROLF (*J. Biol. Chem.*, 1925, **62**, 759—766).—The fatty acids of the lecithin of soya bean contain less saturated acids than similar material of animal origin. In the saturated acid fraction there were isolated palmitic and stearic acids; by bromination of the mixed unsaturated acids di-, tetra-, and hexa-bromostearic acids were obtained. In addition to the oleic, linolic, and linolenic acids thus identified, the unsaturated fraction also contained a substance, insoluble in light petroleum, which appeared to be a mixture of hydroxy-fatty acids. The cephalin from the soya bean showed no marked difference from cephalins of animal origin. C. R. H.

**Extraction of Maltose from Tubers of *Mercurialis perennis*.** L. M. P. GILLOT (*J. Pharm. Chim.*, 1925, [viii], **1**, 205—207).—Maltose, previously isolated and characterised by its osazone (cf. A., 1923, i, 1163), has now been obtained in a crystalline condition. After a preliminary treatment of the aqueous extract of the plant with a yeast, which destroys sucrose and dextrose but not maltose, the latter is finally purified through its barium salt. I. E. B.

**Extraction and Properties of Gein, the Glucoside containing Eugenol, of *Geum urbanum*.** L. H. HÉRISSEY and J. CHEYMOL (*Compt. rend.*, 1925, **180**, 384—386; cf. A., 1905, ii, 345).—By extraction of the roots of herb-Bennet, gein is obtained as a colourless substance, m. p. 146—147°,  $[\alpha]_D^{20}$ —53° to 54.4° in aqueous solution. On hydrolysis with mineral acids or with gease, the rotation changes sign and reducing sugars and eugenol are produced. It is suggested that on hydrolysis with acid gein gives 1 mol. of eugenol, 1 of dextrose, and 1 of *l*-arabinose, whereas gease converts it into a sugar composed of [1 mol. dextrose+1 mol. *l*-arabinose—H<sub>2</sub>O], which may be vicianose. F. M. H.

**Glucosides of Several Species of Indigenous Orchids.** P. DELAUNEY (*Compt. rend.*, 1925, **180**, 224—225).—Loroglossoside (loroglossine) is present in four other species of orchids, viz., *Goodyera repens*, R. Br., *Limodorum abortivum*, Sw., *Spiranthes autumnalis*, Rich., and *Orchis ustulata*, L., besides those previously investigated (A., 1923, i, 1046). W. A. S.

**Leaf Pigments of *Potamogeton*.** S. PRÁT (*Biochem. Z.*, 1924, **152**, 495—497).—From the leaves of *Potamogeton natans* and *P. crispus*, in addition to chlorophyll derivatives, were extracted the



carotinoid pigments xanthophyll and rhodoxanthin (cf. Monteverde and Lubimenko, quoted by Palmer in "Carotinoids and Related Pigments," Chem. Catalog Co., New York. 1922). J. P.

**Blackening of Orobanches in the Course of their Desiccation.** M. BRIDEL and C. CHARAUX (*Compt. rend.*, 1925, **180**, 387—388).—The blackening which occurs during drying of the plants is attributed to enzymic oxidation, without hydrolysis, of their special glucoside, now named orobanchoside (cf. A., 1924, i, 976). F. M. H.

**Basic Constituents of the Rye Plant: the Ergot Question.** F. HOLTZ and H. MÜLLER (*Arch. exp. Path. Pharm.*, 1925, **105**, 27—37; cf. A. Kiesel, A., 1924, i, 698).—The stalks of green rye plants, the straw of ripe rye, and the ripe ears did not contain histidine, arginine, lysine, histamine, agmatine, putrescine, or cadaverine. Betaine was found in all three materials, and choline in the green stalks and ears. For the first time neosine, identified as chloraurate, was found in plant-tissue. What Kiesel considered to be agmatine was isolated in the present instance from the green stalks and straw and identified by means of its chloraurate as adenine. O. O.

**Action of Nitrites on the Growth of Plants. II.** D. FÉHÉR and I. VÁGI (*Biochem. Z.*, 1924, **153**, 156—158).—Sodium nitrite has no toxic action on plants when present in soil in amounts up to 1 g. per kg. of soil. J. P.

**Has Silicic Acid an Influence on the Morphological and Anatomical Structure of Rye Straw, where there is a Deficiency of Phosphatic Food?** H. WIESSMANN (*Z. Pflanz. Düng.*, 1925, **4**, A, 73—83).—Considerable increases in the yield of rye grain and straw resulted from the addition of colloidal silicic acid to a nutrient solution deficient in phosphate. The plants had a largely increased proportion of silica in the straw and a small increase in the grain. In spite of this, the anatomical structure of the straw was unaffected. There were, however, a greater number of nodes in straws receiving silicic acid, although some straws were incompletely developed. A. G. P.

**Neutral Salt Decomposition by Silicic Acid.** O. NOLTE (*Z. Pflanz. Düng.*, 1925, **4**, A, 191—192).—A reply to Hummelchen and Kappen (*ibid.*, 1924, **3**, A, 289). A. G. P.

**Interaction between Silica and Electrolytes in its Relation to Theories of Soil Acidity.** J. N. MUKHERJEE (*Nature*, 1925, **115**, 157—158).—Experiments with carefully purified hydrated silica confirm the previous observations (A., 1922, ii, 689; cf. Joseph and Hancock, T., 1923, **123**, 2022) that hydrated silica adsorbs acids, and that anions are preferentially adsorbed, although the actual values now obtained are smaller. The view that interaction between silica and salt solution is of a chemical nature is not accepted. It is incidentally recorded that on interaction of solutions of potassium sulphate ( $p_H$  6.8) and barium chloride ( $p_H$  6.6), the liquid shows an acid (up to  $p_H$  2) or alkaline (up to  $p_H$  11) reaction

according as barium chloride or potassium sulphate, respectively, is in excess. A. A. E.

**Bases as [Plant] Growth-promoting Substances and the Pickling of Seed with Bases and Other Substances.** T. BOKORNY (*Z. Pflanz. Düng.*, 1925, 4, A, 178—190).—Sodium hydroxide solutions at great dilution (at which potassium hydroxide has an indifferent or favourable effect) caused injury to plant seedlings. Injury to seedlings by bases was greater with peas and beans than with cereals. Ammonia proved more injurious than the other bases. Improvements in germination and growth of seedlings resulted from the pickling of seed in solutions of the bases at certain great dilutions. The strength of the base solution and the period of treatment are of the highest importance and differ with the nature of the seed. Brief contact of seed with more concentrated solutions of the bases resulted, in some cases, in an improved germination. A. G. P.

**Experiments with Copper Sulphate [on Plants].** A. DENSCHE and HUNNIUS (*Z. Pflanz. Düng.*, 1924, 3, A, 369—386).—Field trials with moderate dressings of copper sulphate as a plant stimulant showed considerable crop increases. The effect was less marked on peat soils. Laboratory investigations indicated that copper sulphate increased chlorophyll production, and treated plants contained a smaller proportion of iron. It is suggested that copper may replace iron in the functional activities of chlorophyll. Increased production of organic material due to copper manuring appeared to centre round an improved carbohydrate synthesis, there being no apparent effect on protein production. Copper absorbed by the plants was stored mainly in the stems. The treatment of seed with copper sulphate previous to sowing produced similar effects. A. G. P.

**Some Insecticidal Properties of the Fatty Acid Series.** E. H. SIEGLER and C. H. POPENOE (*J. Agric. Res.*, 1924, 29, 259—261).—Emulsions of fatty acids with lubricating oils proved efficacious against several forms of aphids. Toxicity appeared to increase with the molecular weight of the acid. Emulsions containing the free acids were more effective than the corresponding alkali salts. [Cf. B., May 1st.] A. G. P.

**Chemical Analysis of Soil.** K. K. GEDROIZ (*Russ. Com-missariat Agric.*, 1923, A, 3, 1—258).—A critical manual of soil analytical methods. Except in the case of dolomite, the amounts of calcium and magnesium respectively present as carbonate may be determined by heating the soil at 550°, when only the latter is decomposed. Methods for determining lithium, rubidium, caesium, titanium, zirconium, and vanadium are given.

#### CHEMICAL ABSTRACTS.

**Determination of the Acidity of Mineral Soils.** G. HAGER (*Z. Pflanz. Düng.*, 1925, 4, A, 159—177).—A comparative criticism of the various methods for determining soil acidity, put forward from time to time, is given. A. G. P.

**Influence of Humic Acids on Bacterial Life in Moor Soils, and a Method of Determining Soil Acidity.** T. ARND (*Z. Pflanz. Düng.*, 1925, 4, A, 53—72).—The activity of certain types of soil organisms in acid soils treated with varying proportions of lime was determined. Ammonification and denitrification were most active at the neutralisation point of soils with lime, and the point of inflexion of curves relating ammonification (or denitrification) with the amount of lime added may be taken as indicating the true lime-requirement (as in the Tacke-Süchting method). The method of Gully gives higher figures, and that of Daikuhara considerably lower figures than the above. In nitrification experiments, the activity of the organisms began at the neutralisation point of the soil. A. G. P.

**Lime Requirement of Soils from the Point of View of Plant Physiology. II. Soil Reaction and the Growth of the Higher Plants.** O. ARRHENIUS (*Z. Pflanz. Düng.*, 1925, 4, A, 30—52).—A number of the common farm crops were grown in soils artificially rendered more acid or alkaline than normal. Curves illustrating the relationship between plant growth and the  $p_H$  value of the soil invariably showed two maxima. It is suggested that the intake of foodstuffs by the plant is affected by the concentration of both hydrogen and hydroxyl ions. In addition to the crop yields, the composition of the ash of the plants was affected by the reaction of the soil. A. G. P.

**Ternary Systems,  $\text{CaO-Fe}_2\text{O}_3\text{-CaSO}_4$  and  $\text{CaO-Al}_2\text{O}_3\text{-CaSO}_4$ , as Explaining the Retention of Sulphates by Heavily-limed Soil.** W. H. MACINTYRE and W. M. SHAW (*Soil Sci.*, 1925, 19, 125—151).—Ignited silica, ferric and aluminium oxides, and ignited soil showed no tendency to adsorb appreciable amounts of sulphate. Lime and freshly-precipitated oxides of iron and aluminium in aqueous suspension combined in the proportions  $3\text{CaO-Fe}_2\text{O}_3$  and  $3\text{CaO-Al}_2\text{O}_3$ , respectively. These substances adsorbed calcium sulphate. Aqueous suspensions of aluminium hydroxide adsorbed lime and calcium sulphate in molecular proportions with the formation of  $3\text{CaO-Al}_2\text{O}_3\text{-3CaSO}_4$ . The crystallography of this substance and of calcium aluminate and ferrate is described. The triple compound was decomposed by calcium hydrogen carbonate, giving calcium sulphate with a deposition of alumina. A. G. P.

**Saturation Capacity of Mineral Soils.** D. J. HISSINK (*Z. Pflanz. Düng.*, 1925, 4, A, 137—158).—The theory of the "saturation capacity" of soils is further developed and additional methods for the practical determination of the degree of saturation of soils are described. The effect of variations in the degree of saturation on the physical properties of soils is discussed, and its bearing on the determination of the lime requirement explained. Conductometric methods indicate that the equivalent weight of humus is approximately 180 and that of the clay substance of the order of 1150. Replaceable bases in soil, represented as percentages of the clay substance present, bear a close relationship to the degree of saturation of the soil. A. G. P.

**Conversion of Calcium Oxide into Calcium Carbonate in the Soil and the Causes of its Combination.** E. BLANCK and F. SCHEFFER (*Z. Pflanz. Düng.*, 1925, 4, B, 66—69).—The conclusion previously arrived at that calcium oxide is converted quantitatively into carbonate in the soil (cf. this vol., i, 223) is shown to be incorrect. The amount of carbon dioxide finally found varied with soils of different types but did not exceed about 80% of the total required to account for the calcium oxide added. Sodium-, potassium- or calcium-permutite mixed with the soil did not retard the formation of carbonate, nor did previous extraction of the soil with hydrochloric acid affect it. Zeolitic compounds are not therefore concerned in the reaction. The addition, however, of silica-gel (but not alumina-gel) appreciably depressed the formation of calcium carbonate from oxide; and it is considered that combination with the silicic acid of the clay to form calcium silicate is the explanation of the fate of that part of the calcium oxide added which is not accounted for by conversion into carbonate. For details, cf. Scheffer, *Diss.*, 1925, Göttingen. C. T. G.

**Fixation of Nitrogen by *Azotobacter* in a Displaced Solution and in the Soil Residue Therefrom.** C. B. LIPMAN and L. J. H. TEAKLE (*Soil. Sci.*, 1925, 19, 99—103).—The efficiency of *Azotobacter chroococcum* in displaced soil solutions and in the residual soil was greater than in culture media rich in sugar or alcohol, being greater than 1 part of nitrogen per 40 parts of carbon in the solution and greater than 1 : 70 in the soil residue. The activity of the organism in both media is greater in pure culture than in unsterilised soil. The bearing of these results on the practical inoculation of field soils with *Azotobacter* is discussed. A. G. P.

**Influence of Urea, used as Fertiliser, on the Reaction of the Soil.** C. BRIOUX (*Compt. rend.*, 1924, 179, 915—917).—Urea, when used as a fertiliser, behaves towards the soil as an alkali owing to its rapid transformation into ammonium carbonate, maximum alkalinity being reached in 48 hours. When nitrification occurs, the soil becomes progressively acid; after the lapse of 76 days the  $p_H$  value was 5.35 in comparison with 6.45 for the original soil. H. J. E.

**Losses of Ammonia from Soil by Volatilisation.** G. R. CLARKE and C. G. T. MORISON (*Nature*, 1925, 115, 423—424).—Preliminary experiments show that during simultaneous desiccation and aëration, considerable amounts of ammonia are volatilised from soil. A. A. E.

**Determinations of the Degree of Humification of Soil Organic Matter.** G. W. ROBINSON and J. O. JONES (*J. Agric. Sci.*, 1925, 15, 26—29; cf. A., 1922, ii, 888).—Oxidation with hydrogen peroxide is proposed as the basis of a method for distinguishing the humified from the non-humified organic matter in soils. It is shown that fibrous materials such as cellulose and lignins are not appreciably attacked by hydrogen peroxide. The

highest ratios of humified to total organic matter were found in uncultivated soils containing high proportions of the latter constituent. G. W. R.

**Relation between the Vapour Pressure and Water Content of Soils.** A. N. PURI, E. M. CROWTHER, and B. A. KEEN (*J. Agric. Sci.*, 1925, **15**, 68—88).—The water contents of different soils in equilibrium with atmospheres of different degrees of humidity were determined by two methods which gave concordant results. The water content of soils in equilibrium with atmospheres of high relative humidity varies comparatively little from 20° to 40°. For lower degrees of humidity, water absorption decreases with increasing temperature. The vapour pressure relationships of soils show marked hysteresis effects. Attention is directed to the large variations in moisture content at low and high degrees of humidity and to the consequent difficulty of defining the "dry" state and also the hygroscopic coefficient. The moisture content of a soil exposed to an atmosphere of 50% humidity might be expected to be more easily determined. The effect of various treatments and additions on the vapour pressure relationships of soils is studied. G. W. R.

**Sulphofication in Soils.** A. A. KALUSHSKI (*Ann. Inst. agron. Saratov*, 1923, **1**, 88—97; from *Chem. Zentr.*, 1924, ii, 749).—The sulphate content of soil was found to increase from May to September, and to decrease from then to the following spring. These changes are attributed to activity within the soil itself. G. W. R.

**Sulphur as an Accessory Fertiliser.** A. A. KALUSHSKI (*Ann. Inst. agron. Saratov*, 1923, **1**, 99—104; from *Chem. Zentr.*, 1924, ii, 749—750; cf. preceding abstract).—In experiments with millet, sulphur used in conjunction with mineral phosphate had a favourable effect on yield. G. W. R.

**General Occurrence of Nickel and of Cobalt in Arable Land.** G. BERTRAND and M. MOKRAGNATZ (*Compt. rend.*, 1924, **179**, 1566—1569; cf. *A.*, 1922, i, 975).—Nickel and cobalt have been found in each of 33 samples of soil from different geological formations and from different parts of France and of Europe (cf. *A.*, 1924, ii, 62), the largest amounts being found in alluvial soil. Generally the quantity of nickel is 3—5 times that of the accompanying cobalt. Nickel varies from 5.5 to 38.6, cobalt 0.3 to 11.7 mg. per kg. of soil. Comparative analyses of the same soil at different depths show sensible variations, but the number of determinations made are considered insufficient to draw any definite conclusions. An observation of Tissandier (cf. *Compt. rend.*, 1876, **83**, 75) that fine particles containing iron and nickel (cobalt doubtful) fall on the surface of the earth from interplanetary space, is suggested as a possible explanation of the comparative constancy of the amounts of these metals in the soils examined. A. C.

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## Organic Chemistry.

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**Direct Synthesis of Higher from Lower Hydrocarbons.** S. C. LIND and D. C. BARDWELL (*Science*, 1924, **60**, 364—365).—When exposed to  $\alpha$ -radiation from radium emanation, ethane is partly converted into a liquid which is possibly octane, together with hydrogen. A mechanism of the reaction is suggested.

A. A. E.

**Isomerisation in Olefinic Compounds.** P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1924, [v], **10**, 492—503).—With compounds containing in their molecules a double linking, the most stable molecular arrangement may be foreseen from Werner's theory of variable affinity, which also indicates, in a case of possible isomerisation, the course this will take. A number of examples are given in illustration of these considerations.

T. H. P.

**Diacetylene.** LESPIEAU and C. PRÉVOST (*Compt. rend.*, 1925, **180**, 675—678).—The action of sodium ethoxide (1 mol.) in cold solution on erythrene tetrabromide gave *dibromobutadiene*,  $\text{CH}_2\text{:CBr}\cdot\text{CBr}\cdot\text{CH}_2$ , b. p.  $44^\circ/10$  mm., m. p.  $-21.5^\circ$ ,  $d^{15}_4$  1.961,  $n^{15}_D$  1.5723. It had a normal molecular weight in glacial acetic acid, but became polymerised to a white solid on keeping for several days. When either of the erythrene tetrabromides was heated at  $150$ — $160^\circ$  with an excess of alcoholic potassium hydroxide a small yield was obtained of Baeyer's diacetylene,  $\text{CH}\text{:C}\cdot\text{C}\text{:CH}$ , a colourless gas, condensed to a liquid, b. p.  $10^\circ$ ,  $d^5_4$  0.7107,  $n$  1.4198. Alcoholic silver nitrate gave a lemon-yellow, violently explosive substance,  $\text{CH}\text{:C}\cdot\text{C}\text{:C}\text{Ag}\cdot\text{AgNO}_3$ . From the alcohol recovered from the above experiment, after a preliminary fractional precipitation with cuprous chloride, silver nitrate gave a substance  $\text{CH}_2\text{:CBr}\cdot\text{C}\text{:C}\text{Ag}\cdot\text{AgNO}_3$ .

G. M. B.

**Reaction between Disubstituted Acetylenic Hydrocarbons and the Grignard Reagent.** H. GILMAN and J. B. SHUMAKER (*J. Amer. Chem. Soc.*, 1925, **47**, 514—515; cf. A., 1923, i, 285).—Addition of magnesium ethyl bromide or iodide to several typical disubstituted acetylenic hydrocarbons could not be observed.

F. G. W.

**Relation between the Structure of Organic Halides and the Speeds of their Reaction with Inorganic Iodides. II. Alkyl Chlorides.** J. B. CONANT and R. E. HUSSEY (*J. Amer. Chem. Soc.*, 1925, **47**, 476—488; cf. A., 1924, i, 273).—The rates of reaction of twenty alkyl chlorides with potassium iodide have been measured in acetone solution by the method previously reported. With the exception of ethyl chloride, all normal primary aliphatic chlorides have the same reactivity within 20%, ethyl chloride being about twice as reactive. Secondary and tertiary chlorides have reactivities

only 0.01—0.05 times that of the normal compounds, a result in general agreement with other data (cf. Haywood, T., 1922, 121, 1904). *cyclo*Hexyl chloride showed a reactivity of less than 0.0001 times that of the normal primary chlorides. The rates of reaction of five different chlorides with potassium, lithium, and sodium iodides were the same, indicating that the reaction takes place between the organic chloride and the iodide ion. The reaction constants, calculated as for a bimolecular reaction, are independent of the original concentrations of the reactants (cf. A., 1924, ii, 240).

F. G. W.

**Relation between the Structure of Organic Halides and the Speeds of their Reaction with Inorganic Iodides. III. Influence of Unsaturated Groups.** J. B. CONANT, W. R. KIRNER, and R. E. HUSSEY (*J. Amer. Chem. Soc.*, 1925, 47, 488—501; cf. preceding abstract).—Measurements of the rates of reaction, with potassium iodide in acetone solution, of compounds of the type  $A\cdot CH_2Cl$ , where A is an unsaturated group, indicate that the activity of the chlorine atom is roughly proportional to the acidity of the corresponding  $A\cdot OH$  derivative, to the activity of the  $\alpha$ -hydrogen atom in the  $A\cdot CH_3$  compounds, and inversely to the basicity of the amines  $A\cdot NH_2$ . The activation due to the unsaturated groups  $R\cdot CO\cdot$ ,  $CN\cdot$ , and  $Ph$  is in this order. The correspondence of activity of the chlorine with acidity of the hydroxyl replacing the  $CH_2Cl$  group is contrary to the prediction of the polarity theory. In the series  $A\cdot [CH_2]_n\cdot Cl$ , the activation of the chlorine atom is not appreciable when  $A=Ph$  or  $CO_2Et$ , if  $n$  is more than 1, but when  $A=Bz$ , the activation of the chlorine persists, but is a minimum when  $n=2$ . When  $A=OAc$  an alternation of activity is observed, the activity of the chlorine, when  $n=2$ , being slightly less than that of the chlorine in butyl chloride. In the substituted benzyl chlorides, the activities of the 4-nitro and 2:4-dinitro derivatives are in line with the acidities of the corresponding phenols, whilst the 2- and 4-chloro- and bromo-benzyl chlorides show activities much greater than would correspond to the enhancement of acidity in the corresponding phenols (cf. Franzen, A., 1921, i, 233; Olivier, A., 1923, i, 197, 769).

2:4-Dinitrobenzyl iodide, m. p. 69.5—70°, is described.

F. G. W.

**Addition of Gaseous Hydrogen Chloride and Hydrogen Bromide to Ethylene and Propylene under the Influence of Catalysts.** J. P. WIBAUT, J. J. DIEKMANN, and A. J. RUTGERS (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 671—685).—Bismuth and antimony trichloride and tribromide act as excellent catalysts for the additions under investigation. Whereas in presence of asbestos, charcoal, burned clay, and asbestos impregnated with barium chloride, no addition takes place between hydrogen chloride and ethylene at 270°, the reaction occurs slowly at the ordinary temperature in presence of bismuth trichloride, and proceeds rapidly between 120° and 200° without formation of by-products. The addition of hydrogen bromide to ethylene takes place more readily;

without a catalyst, the reaction becomes perceptible at  $140^{\circ}$ , whilst with bismuth bromide as catalyst, it proceeds rapidly at  $20^{\circ}$ . The reactions with propylene are still more rapid. [Cf. *B.*, 1925, 336.]  
L. L. B.

### Molecular Compounds of Iodoform and Quaternary Salts.

II. W. STEINKOPF and R. BESSARITSCH (*J. pr. Chem.*, 1925, [ii], 109, 230—264; cf. Steinkopf and Schwen, *A.*, 1922, i, 118). —Molecular compounds of iodoform with various quaternary salts have been prepared to ascertain the conditions of their formation. The central atom of the compound, the substituent hydrocarbon radicals, and the ionic halogen, as well as the iodoform component itself have been varied in those described. In all previously recorded compounds of this class (*loc. cit.*) the ratio of quaternary compound to iodoform is 1 : 1. This is generally the case here, but when phenyl and benzyl radicals are both present the ratio is 2 : 3. The molecular compounds are usually prepared by mixing hot alcoholic solutions of the components. On cooling they separate out (in most cases) in the solid state. In other cases, the tertiary base, halogen alkyl, and iodoform are brought together in solution, whilst in a few cases combination takes place in the absence of solvents. The following compounds are in the 1 : 1 ratio: *tetraethylammonium iodide-iodoform*  $\text{I}[\text{Et}_4\text{N}] \cdots \text{I}_3\text{CH}$ , m. p.  $198-200^{\circ}$  after darkening at about  $180^{\circ}$ . *Tetrapropylammonium iodide-iodoform* has m. p.  $181-182^{\circ}$ . *Tetrapropylammonium iodide-bromoform*, m. p.  $76-77^{\circ}$ . *Tetrapropylammonium iodide-chloroform*. *Dipropyldiallylammonium iodide-iodoform*, m. p. about  $153^{\circ}$ , from *dipropylallylammonium iodide*, decomp.  $211^{\circ}$ . *Tetra-allylammonium iodide-iodoform*, m. p.  $161-162^{\circ}$ . The corresponding chloroform compound could not be obtained. *Benzyltriethylammonium iodide-iodoform*, m. p.  $105^{\circ}$ , was made from *benzyltriethylammonium iodide*, m. p.  $168.5^{\circ}$ . *Phenylbenzyltrimethylammonium iodide-iodoform* (2 : 3); the quaternary component has m. p.  $156^{\circ}$  and not  $165^{\circ}$  as recorded in the literature. *Phenyldiethylallylammonium iodide-iodoform* was obtained as a hard crust which could not be recrystallised. *Diphenyldimethylammonium iodide-iodoform*, m. p. about  $98^{\circ}$  to dark orange liquid,  $102^{\circ}$  green liquid (decomp.). *Tribenzylammonium iodide* adds iodoform in the ratio 2 : 3, forming *tribenzylammonium iodide-iodoform*, m. p.  $108^{\circ}$ . *Tribenzylmethylammonium iodide-iodoform* (2 : 3) has m. p.  $161-162^{\circ}$ . *Antipyrine methiodide-iodoform*, m. p.  $128^{\circ}$  (decomp.). *Quinoline ethiodide-iodoform*, m. p.  $165-166^{\circ}$ . *Quinoline ethiodide-bromoform* (1 : 1), m. p.  $146-147^{\circ}$ . Triphenylamine, trimethylammonium chloride, and trimethylammonium bromide formed no additive products with iodoform. Triisobutylamine does not react with allyl iodide in the cold, but on warming forms *diisobutylammonium iodide*, m. p.  $272-273^{\circ}$ . Similarly, triisobutylamine and allyl iodide gave *diisobutylammonium iodide*, decomp. above  $260^{\circ}$  after softening at  $250^{\circ}$ , and trimethylamine and octyl iodide gave *dimethylammonium iodide*, m. p.  $172-174^{\circ}$ . The following new sulphonium compounds (all having the ratio 1 amine : 1 iodo-



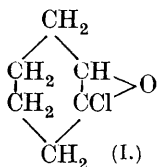
form) are described. *Ethyl-di-n-propylsulphonium iodide*, m. p. 163°, from dipropyl sulphide and ethyl iodide; *ethyl-di-n-propylsulphonium iodide-iodoform*, m. p. 98—100°; *di-n-propylallylsulphonium iodide*,  $(C_3H_5)(C_3H_7)_2S \cdot I$ , m. p. 79—80°; *di-n-propylallylsulphonium iodide-iodoform*, m. p. 77—78°; *triallylsulphonium iodide-iodoform*, m. p. 82—84°. Of the arsonium salts, only one, *phenylbenzyl-dimethylarsonium iodide-iodoform*, m. p. 88°, vivid yellow needles, had the 2 : 3 ratio; the component *phenylbenzyl-dimethylarsonium iodide* has m. p. 119—120°; Burrows and Turner (T., 1921, 117, 1378) give 114—115°. *Ethylallyl-diisobutylarsonium iodide-iodoform*, m. p. 83°, was prepared from *ethylallyl-diisobutylarsonium iodide*, m. p. 146—148°. *Benzylethyl-di-n-propylarsonium iodide-iodoform*, m. p. 144°, forms *benzylethyl-di-n-propylarsonium iodide-iodoform*, m. p. 75°. *Phenylmethyl-n-propylallylarsonium iodide* was obtained as a very deliquescent, uncrystallisable solid, which forms no additive compound with iodoform. *Phenylmethyl-ethylallylarsonium iodide* was obtained as an uncrystallisable liquid. *Diphenylbenzylmethylarsonium iodide-iodoform* has m. p. 116—117°. *Diphenylmethylallylarsonium iodide-iodoform* has m. p. 56—60°, and was prepared from the *arsonium iodide*, m. p. 144—145°. *Diphenyldimethylarsonium iodide-iodoform*, m. p. 94°, vivid, orange-yellow prisms. Diphenyldiethylarsonium iodide and iodoform scarcely showed change of colour in alcohol, but *diphenyldiethylarsonium tri-iodide*, m. p. 63—64°, was isolated from the product. *Triphenylbenzylarsonium iodide-iodoform*, m. p. 129°, was obtained from *triphenylbenzylarsonium iodide*, m. p. 162°; the mother-liquors yielded *triphenylbenzylarsonium tri-iodide*, m. p. 136°. *Diphenylmethyl-ethylarsonium bromide*, m. p. 147—148°, and *diphenyldiethylarsonium bromide*, m. p. 166—167°, gave no iodoform products like phenyltrimethylarsonium bromide (cf. Steinkopf and Schwen, *loc. cit.*). An attempt was made to prepare co-ordination isomerides of these molecular compounds by acting on an additive product of a tertiary base with an alkyl iodide according to the equations:  $I[R_4N] + I_3CH = I[R_4N] \cdots I_3CH$  and  $[R_3N \cdots I_3CH] + RI = [R_3N \cdots I_3CH] \cdots RI$ . *Triethylamine-iodoform*,  $2NEt_3, 3CHI_3$ , m. p. 81—83° (contrast Dehn and Conner, A., 1912, i, 834), did not react with ethyl iodide. Other secondary and tertiary amines which were tried did not react with iodoform. *Triethylpropylphosphonium iodide* has m. p. 178—180°; *benzyltriethylphosphonium iodide-iodoform*, m. p. 105°, from *benzyltriethylphosphonium iodide*, m. p. 135°. The additive compound from triethylphosphine and carbon disulphide when treated with iodoform lost carbon disulphide and formed *triethylphosphine-iodoform*,  $2Et_3P \cdots 3I_3CH$ , m. p. 122—123°. The ease with which the carbon disulphide is displaced is better expressed by the formula  $Et_3P \cdots \left\{ \begin{smallmatrix} S \\ S \end{smallmatrix} \gg C \right.$  than by that of Hantzsch and Hibbert (A., 1907, i, 496). Triethylphosphine sulphide did not add iodoform, but the methiodide gave *triethylphosphine sulphide methiodide-iodoform*,  $I[Et_3PSMe] \cdots 2I_3CH$ , m. p. 84° (the only instance of the ratio 1 : 2). The lability of the iodine in ethylene iodide (cf. Finkel-

stein, A., 1910, i, 453) is shown by the behaviour of the compound towards the hydriodides of the amines when ethylene is liberated and a tri-iodide formed,  $R_4NI + C_2H_4I_2 = R_4NI_3 + C_2H_4$ . Methylammonium iodide and ethylene iodide give *methylammonium tri-iodide*, m. p. 35—37°; *dipropylammonium iodide*, m. p. 230—235° (decomp.), gives *dipropylammonium tri-iodide*, m. p. 58—59°; *diisobutylammonium tri-iodide* has m. p. 57—58°; *tribenzylammonium tri-iodide*,  $C_{21}H_{22}NI_3$ , has m. p. 133°. Pyridine hydriodide, m. p. 190—195°, and not 268° as recorded in the literature, gives *pyridine hydriodide di-iodide*, m. p. 129—130°. *Tetrapropylammonium tri-iodide*,  $C_{12}H_{28}NI_3$ , has m. p. 98°. Antipyrine methiodide and ethylene iodide gave *antipyrine methiodide di-iodide*, m. p. 132—133°. Diphenyldimethylarsonium iodide, m. p. 209—211°, and not 190°, gives diphenyldimethylarsonium tri-iodide, m. p. 70—72°. Trimethylsulphonium iodide and ethylene iodide give trimethylsulphonium tri-iodide, m. p. 38—39°, which with iodoform gives trimethylsulphonium iodide-iodoform, m. p. 160—162°. The reaction between quinones and quaternary salts does not proceed normally. *p*-Benzoquinone and tetraethylphosphonium iodide in acetic acid yield a mixture of quinhydrone and tetraethylphosphonium tri-iodide due to the formation of hydrogen iodide. Corresponding compounds are formed from dimethyl- and diethyldiphenylarsonium iodides. Chloranil and quinoline ethiodide react in acetic acid to form tetrachloroquinol and a very unstable molecular compound, for which the formula  $I_2 \cdots OC_6Cl_4O \cdots [C_{11}H_{12}N]I$  is suggested. No general rules can be deduced from the investigation. The iodoform compounds are more stable than those of bromoform and chloroform, the strength of the co-ordinative linking being conditioned by the residual valencies of the three halogen atoms.

A. C.

**Action of Chlorine Monoxide on Organic Compounds.** S. GOLDSCHMIDT and H. SCHÜSSLER (*Ber.*, 1925, 58, [B], 566—571).—Chlorine monoxide is prepared by the action of chlorine on mercuric oxide obtained by the action of an excess of pure sodium hydroxide solution on mercuric nitrate, washed frequently with water, dried at 110°, and finally heated for 10 mins. at 280°. The gas is condensed in a suitable flask, from which it is transferred by a current of carbon dioxide to the substance under investigation, cooled to -20° and either used in large excess or dissolved in carbon tetrachloride, whereby risk of explosion is avoided. With saturated organic compounds, the products appear to be identical with those obtained by the use of chlorine, oxygenated compounds not being isolated; thus chloroacetone, ethyl chloroacetoacetate, and chlorinated cyclohexanes are produced from acetone, ethyl acetoacetate, and cyclohexane, respectively. Trichloroethylene yields chloral, pentachloroethane, and octachlorodiethyl ether,  $(CCl_3 \cdot CHCl)_2O$ , m. p. 40—42°, which is converted by hydriodic acid into ethane. The above constitution is preferred to the alternative structure,  $(CHCl_2 \cdot CCl_2)_2O$ , since the solid compound is accompanied by a liquid of the same analytical composition the existence of which is

accounted for by the presence of two asymmetric carbon atoms in the molecule and the consequent production of two inactive isomerides. Tetrachloroethylene yields hexachloroethane and, possibly trichloroacetyl chloride. *cyclo*Hexene gives a substance,  $C_6H_5OCl$ , b. p. 66–67°/9 mm., which could not be freed completely from dichloro*cyclo*hexane; it is formed by loss of hydrogen chloride from the primary additive product of chlorine monoxide, and appears to have the constitution I. Dichlorodicyclohexyl ether, m. p. 69°, is also produced.



Indene yields a *chloroindene oxide*,  $C_9H_7OCl$ , b. p. 106–115°/5 mm., and a substance,  $C_{18}H_{24}O_{10}Cl_3$ , m. p. 125°, which appears to be derived in a complex manner from two indene molecules.

H. W.

**Preparation of Pure Methyl Alcohol.** H. HARTLEY and H. R. RAIKES (*J. Chem. Soc.*, 1925, 127, 524–527).—Methyl alcohol is dehydrated by twice fractionating (<2 drops/sec.) through a Hempel column having an effective length of 1.3 metres, then refluxed under the column with aluminium-amalgam (3 g. per litre), and again fractionated. For the removal of ammonia, the dehydrated alcohol is refluxed for 6 hrs. under a column packed with freshly-dehydrated copper sulphate, and then rapidly distilled through this column. Methyl alcohol having a specific conductivity of 0.04 reciprocal megohm is obtained. Distillation of the pure alcohol over silver nitrate, in order to remove reducing agents, is not necessary.

To test for acetone in technical methyl alcohol a concentrated solution of mercuric cyanide in 6*N*-sodium hydroxide is mixed with an equal volume of the sample, and the mixture warmed to boiling. A white precipitate indicates the presence of a ketone; a mixture of ketone and aldehyde produces a precipitate which darkens when kept. When the impurities are present singly, 0.002% of acetone or 0.004% of formaldehyde may be detected.

For the rapid determination of water with an accuracy of 0.02% the method of Weaver (*A.*, 1915, ii, 21) is convenient. Density measurements allow the determination of water to at least 0.01%; the mean value  $d_4^{25}=0.78641$  was obtained, using different samples of pure alcohol. Relative viscosity determinations may also be used, when the limit of accuracy is 0.025%; the absolute viscosity of methyl alcohol was found to be 0.00545 at 25° (water 0.00895). The most sensitive test for water is the determination of the electrical conductivity of a dilute alcoholic solution of hydrogen chloride;  $\Lambda^{25}$  at 0.001*N* was depressed from 181.5 to 181.0 by less than 0.01% of water.

C. J. S.

**isoPropyl, Propyl, and Ethyl Alcohols : Refractive Indices.** C. T. BENNETT and D. C. GARRATT (*Perf. and Essent. Oil Rec.*, 1925, 16, 18).—The densities and refractive indices of mixtures of isopropyl, propyl, and ethyl alcohols and water are tabulated.

B. F.

### Influence of Constitution on the Rotatory Power of Optically Active Substances. XIX. Influence of Acetylenic Linkings.

H. RUPE and F. VONAESCH (*Annalen*, 1925, 442, 74—92).—The rotatory powers of the esters of  $\beta$ -methyl- $\Delta^7$ -butinen- $\beta$ -ol and  $\gamma$ -methyl- $\Delta^8$ -pentinen- $\gamma$ -ol, and of the corresponding olefinic and saturated alcohols, with five optically active acids, campholic acid, bornylenecarboxylic acid, camphanecarboxylic acid, camphorylideneacetic acid, and camphorylacetic acid have been determined. The campholic esters of the two acetylenic alcohols show pronounced anomalous dispersion and differ markedly from the corresponding olefinic esters. In these esters, the carboxyl group is one of the groups attached to the asymmetric carbon atom and the acetylenic linking is thus near enough to the latter to exercise a disturbing influence (cf. A., 1917, i, 538). A similar but much less pronounced anomaly appears in the two acetylenic esters of camphanecarboxylic acid, in which, owing to the presence of three asymmetric carbon atoms in the molecule, the slighter anomalous dispersion may simply express the resultant of different dispersion effects produced with the separate asymmetric carbon atoms (cf. A., 1920, i, 748). The camphorylideneacetic esters of the two acetylenic alcohols can be obtained in a solid form showing normal rotatory dispersion and normal rotatory power. The liquid form of these esters is a mixture of this solid form with a lower-melting form having a much smaller specific rotatory power, and the absence of anomaly in these cases also is probably to be attributed to opposite effects producing a normal dispersion curve.

$\gamma$ -Methyl- $\Delta^8$ -pentinen- $\gamma$ -ol,  $\text{OH}\cdot\text{CMeEt}\cdot\text{C}\equiv\text{CH}$ , b. p. 120—121°,  $d_4^{20}$  0.8665, was obtained by the action of sodamide on a mixture of acetylene and methyl ethyl ketone. The following esters were prepared by interaction of the alcohol with the acid chloride in pyridine solution.  $\gamma$ -Methylbutinenyl campholate, b. p. 120—121°/10 mm.,  $d_4^{20}$  0.9398,  $[\alpha]_D^{20}$  21.96°;  $\gamma$ -methylbutenyl campholate, b. p. 119—120°/10.5 mm.,  $d_4^{20}$  0.9255,  $[\alpha]_D^{20}$  31.76°;  $\gamma$ -methylbutyl campholate, b. p. 123—124°/11 mm.,  $d_4^{20}$  0.9185,  $[\alpha]_D^{20}$  31.98°;  $\gamma$ -methyl- $\Delta^8$ -pentinenyl campholate, b. p. 137—138°/13 mm.,  $d_4^{20}$  0.9416,  $[\alpha]_D^{20}$  23.91°;  $\gamma$ -methyl- $\Delta^8$ -pentenyl campholate, b. p. 134—135°/10.5 mm.,  $d_4^{20}$  0.9305,  $[\alpha]_D^{20}$  33.14°;  $\gamma$ -methylpentyl campholate, b. p. 139—140°/11 mm.,  $d_4^{20}$  0.9236,  $[\alpha]_D^{20}$  31.85°; the ester of bornylene-carboxylic acid with  $\gamma$ -methylbutinenol has b. p. 130—130.5°/9 mm.,  $d_4^{20}$  0.9795,  $[\alpha]_D^{20}$  104.52°; with  $\gamma$ -methylbutenol, b. p. 130—131°/10 mm.,  $d_4^{20}$  0.9596,  $[\alpha]_D^{20}$  100.05°; with  $\gamma$ -methylbutan- $\gamma$ -ol, b. p. 130—130.5°/8.5 mm.,  $d_4^{20}$  0.9480,  $[\alpha]_D^{20}$  98.31°; with  $\gamma$ -methyl- $\Delta^8$ -pentinen- $\gamma$ -ol, b. p. 143°/8.5 mm.,  $d_4^{20}$  0.9757,  $[\alpha]_D^{20}$  100.25°; with  $\gamma$ -methyl- $\Delta^8$ -penten- $\gamma$ -ol, b. p. 142°/10 mm.,  $d_4^{20}$  0.9589,  $[\alpha]_D^{20}$  96.23°; with  $\gamma$ -methylpentan- $\gamma$ -ol, b. p. 142—143°/9 mm.,  $d_4^{20}$  0.9488,  $[\alpha]_D^{20}$  95.40°; the ester of camphanecarboxylic acid with  $\gamma$ -methyl- $\Delta^8$ -pentinen- $\gamma$ -ol, has b. p. 145—146°/8.5 mm.,  $d_4^{20}$  0.9755,  $[\alpha]_D^{20}$  40.61°; with  $\gamma$ -methyl- $\Delta^8$ -penten- $\gamma$ -ol, b. p. 144—145°/8.5 mm.,  $d_4^{20}$  0.9626,  $[\alpha]_D^{20}$  44.03°; with  $\gamma$ -methylpentan- $\gamma$ -ol, b. p. 144—145°/8.5 mm.,  $d_4^{20}$  0.9539,  $[\alpha]_D^{20}$  39.67°; with  $\gamma$ -methylbutinen- $\gamma$ -ol, b. p. 130—131°/9 mm.,  $d_4^{20}$  0.9788,  $[\alpha]_D^{20}$  45.44°; with  $\gamma$ -methylbuten- $\gamma$ -ol, b. p. 130—

131°/11 mm.,  $d_4^{20}$  0.9604,  $[\alpha]_D^{20}$  56.18°; with  $\gamma$ -methylbutan- $\gamma$ -ol, b. p. 130—130.5°/9 mm.,  $d_4^{20}$  0.9503,  $[\alpha]_D^{20}$  56.34°.

$\gamma$ -Methyl- $\Delta^{\gamma}$ -butinenyl camphorylideneacetate has b. p. 94—96° (in high vacuum), m. p. 48—50°. The oil,  $d_4^{20}$  1.0413, has  $[\alpha]_D^{20}$  155.98°; benzene solution,  $[\alpha]_D^{20}$  60.68°. The solid in benzene has  $[\alpha]_D^{20}$  131.40°.  $\gamma$ -Methyl- $\Delta^{\gamma}$ -butenyl camphorylideneacetate, b. p. 93—95° (in high vacuum) has  $d_4^{20}$  1.0233,  $[\alpha]_D^{20}$  150.31°, and in benzene  $[\alpha]_D^{20}$  127.70°.  $\gamma$ -Methylbutyl camphorylideneacetate, b. p. 95—96° (high vacuum),  $d_4^{20}$  1.0063,  $[\alpha]_D^{20}$  153.71°, has in benzene  $[\alpha]_D^{20}$  132.80°.  $\gamma$ -Methyl- $\gamma$ -pentinyl camphorylideneacetate, b. p. 105° (high vacuum), m. p. 36°, has  $d_4^{20}$  1.0330,  $[\alpha]_D^{20}$  150.03°, and in benzene solution  $[\alpha]_D^{20}$  65.37°. The solid in benzene has  $[\alpha]_D^{20}$  126.18°.  $\gamma$ -Methyl- $\Delta^{\gamma}$ -pentenyl camphorylideneacetate, b. p. 103—104° (high vacuum), has  $d_4^{20}$  1.0286,  $[\alpha]_D^{20}$  151.21°, and in benzene,  $[\alpha]_D^{20}$  129.53°; and  $\gamma$ -methylpentyl camphorylideneacetate, b. p. 103—104° (high vacuum),  $d_4^{20}$  1.0052,  $[\alpha]_D^{20}$  146.91°; and in benzene,  $[\alpha]_D^{20}$  127.37°.  $\gamma$ -Methyl- $\Delta^{\gamma}$ -butinenyl camphorylacetate, has b. p. 178—180°/11.5 mm., 92—93° in high vacuum,  $d_4^{20}$  1.0376,  $[\alpha]_D^{20}$  60.25°; the  $\gamma$ -methyl- $\Delta^{\gamma}$ -butenyl ester has b. p. 92—93° (high vacuum),  $d_4^{20}$  1.0212,  $[\alpha]_D^{20}$  64.79°; the  $\gamma$ -methylbutyl ester, b. p. 178—180°/10.5 mm., 93—94° in high vacuum,  $d_4^{20}$  1.0042,  $[\alpha]_D^{20}$  65.42°; the  $\gamma$ -methyl- $\Delta^{\gamma}$ -pentinyl ester, b. p. 188°/13.5 mm., 102—103° (high vacuum),  $d_4^{20}$  1.0279,  $[\alpha]_D^{20}$  63.27°;  $\gamma$ -methyl- $\Delta^{\gamma}$ -pentenyl ester, b. p. 188—190°/14.5 mm.,  $d_4^{20}$  1.0283,  $[\alpha]_D^{20}$  65.30°; and the  $\gamma$ -methylpentyl ester, b. p. 188—190°/12.5 mm., 102—103° in high vacuum,  $d_4^{20}$  1.0047,  $[\alpha]_D^{20}$  64.26°. The values for  $[\alpha]_C^{20}$ ,  $[\alpha]_{H_2O}^{20}$ , and  $[\alpha]_F^{20}$  are quoted in all cases. R. B.

**Constitution of the Boric Acids and some of their Derivatives.** P. H. HERMANS (*Z. anorg. Chem.*, 1925, 142, 83—110).—The work is chiefly concerned with compounds of boric acid with polyhydroxy-alcohols and acids, but their constitution has served to throw light on that of the polyboric acids. The experimental results and theories of previous workers are discussed at some length. The view is held that the boric acids are co-ordination compounds, boron having the co-ordination number 4. Thus metaboric acid is  $[O:B(O)H]$  and orthoboric acid  $[(HO)_2B(O)H]$  but the latter can also exist in the tautomeric form  $B(OH)_3$ , which is predominant in organic solvents, giving rise to esters such as  $B(OAc)_3$ , and in aqueous solution thus explaining its weakly acid nature. The compounds of boric acid with  $\alpha\beta$  and  $\alpha\gamma$  glycols are probably mixtures of  $[(RO)_2B(O)H]$  with the tautomeric form  $(RO)_2B\cdot OH$ . The former explains the weakly acid properties and the latter the volatility and solubility in organic solvents. To account for the increase of acidity brought about by treating boric acid with aqueous solutions of certain polyhydroxy compounds such as pyrocatechol and citric acid, it is assumed that derivatives of a hypothetical acid  $[(HO)_2B(OH)_2]H$  are formed, but that this only happens when the hydroxyl groups of the hydroxy compounds are (after Böeseken's theory) "favourably" oriented in space. The following compounds are described.  $\beta\delta$ -Dimethylpentane- $\beta\delta$ -diol boric acid, m. p. 102°, b. p. 228°;  $\beta\delta$ -dimethylhexane- $\beta\delta$ -diol

*boric acid*, m. p. 43—45°, b. p. 99—100°/5 mm.; *pentane-βδ-diol boric acid*, m. p. 68°; *pinacone boric acid*, m. p. about 70°; mono- and di-potassium *cis-cyclohexane-1:2-diol borate*; *dipotassium cis-cyclopentanediol borate*; *monopotassium cis-1:2- and 2:3-tetrahydronaphthalenediol borate*; *potassium cis-1:2-indandiol borate*; *monopotassium phenylglycol borate*; *potassium dicitric borate*; *potassium dipyrocatechol borate*; *zinc disalicyclic borate*; *dicyclopentane-1-hydroxy-1-carbonyl boric acid*, m. p. 225°; *monopotassium cis-cyclopentane-1:2-diol borate*. N. H. H.

**Purification of Glycerol from Volatile Fatty Acids and their Esters.** A. KAILAN and R. OBIGI (*Monatsh.*, 1925, 45, 215—222).—A number of samples of glycerol to which 0.2% of butyric acid had been added were distilled under diminished pressure with and without the addition of sodium hydroxide (*a*) by means of superheated steam, (*b*) in a current of hydrogen, and the distillates collected in two receivers in series. The acid value of the original glycerol was 0.04, but in no case was the acid value of the glycerol in the first receiver (practically all) less than 0.07 to 0.09, even when the equivalent of alkali hydroxide added was three times that of the acid present. The ester content of the distillate was increased by the addition of alkali hydroxide to the distilling flask, especially in the case of superheated steam. This is considered to be due to ester formation by the action of glycerol on the sodium butyrate (glycerolysis). The residue in no case contained more than half of the free or esterified fatty acid originally present, as sodium salt. [Cf. *B.*, 1925, 325.] A. C.

**Solubility Curves in the Systems Mannitol-Boric Acid-Water and *cis*-Tetrahydronaphthalene-1:2-diol-Boric Acid-Water at 25°.** P. H. HERMANS (*Z. anorg. Chem.*, 1925, 142, 111—115; cf. i, 500).—At 25°, neither system shows the formation of a compound. A mutual increase in the solubility of the components occurs in both cases but is much greater in the first system. N. H. H.

**Preparation of Ethers.** H. WUYTS (*Compt. rend.*, 1925, 180, 671—673).—Details of the preparation of ethers from propyl, butyl, and amyl alcohols are given (cf. *A.*, 1924, i, 710) and the following azeotropic mixtures, involved in the separation of the products, have been characterised: binary mixture, b. p. 117.25°, containing 88% of *n*-butyl alcohol, b. p. 117.5°, and 12% of *n*-butyl ether, b. p. 141.9°; ternary mixture, b. p. 74.8°, 20.2% of *n*-propyl alcohol, b. p. 97.3°, 11.7% of water, and 68.1% of *n*-propyl ether, b. p. 90.7°; ternary mixture, b. p. 91°, 42.9% of *n*-butyl alcohol, 29.3% of water, and 27.7% of *n*-butyl ether; ternary mixture, b. p. 94.4°, of *iso*amyl alcohol, b. p. 131.5°, water, and *iso*amyl ether, b. p. 171°; ternary mixture, b. p. 95.9° of *n*-amyl alcohol, b. p. 138°, water, and *n*-amyl ether, b. p. 188. G. M. B.

**Hypochlorous Acid and the Alkyl Hypochlorites.** M. C. TAYLOR, R. B. McMULLIN, and C. A. GAMMAL (*J. Amer. Chem. Soc.*, 1925, 47, 395—403).—A stable solution of ethyl hypochlorite is

obtained by passing chlorine into a stirred suspension of calcium carbonate (25 g.) in water (1 litre) until 25 g. of chlorine are absorbed. The excess of carbonate is removed by filtration and the filtrate shaken with a 2% solution of ethyl alcohol in carbon tetrachloride. Ethyl hypochlorite is formed and remains dissolved in the carbon tetrachloride, which can be freed from chlorine by washing with sodium hydrogen carbonate solution. The solution loses chlorine slowly, and ethyl acetate is formed in good yield. Ethyl hypochlorite reacts with alkali hydroxides to form hypochlorites free from chlorides. Hypochlorites of glycerol, glycol, or ethylene chlorohydrin could not be obtained. Ethyl hypochlorite is hydrolysed in saturated aqueous solution (0.464*M*) to the extent of 69%, and to more than 90% in dilute aqueous solution. The distribution of ethyl hypochlorite between carbon tetrachloride and water was studied, and the results were applied to the determination of ethyl alcohol in spirituous liquors. [Cf. *B.*, 1925, 297.] F. G. W.

### Reactions of Ethyl Hypochlorite with Organic Substances.

S. GOLDSCHMIDT, R. ENDRES, and R. DIRSCH (*Ber.*, 1925, 58, [B], 572—577).—Ethyl hypochlorite frequently undergoes spontaneous and vigorous decomposition with production of ethyl acetate and chlorinated acetaldehyde when preserved at the atmospheric temperature, but its solutions in carbon tetrachloride are sufficiently stable at a low temperature to permit its action on organic compounds to be examined. In general, it appears to undergo hydrolysis to ethyl alcohol and hypochlorous acid with subsequent addition of the latter at an aliphatic double bond; thus amylene, cyclohexene, and indene yield the corresponding *chlorohydrins*, the first and third of which have b. p. 141—143° and 101—102°/2 mm., respectively. Direct addition of ethyl hypochlorite is observed in the case of 1:4-dihydronaphthalene, which yields a mixture of 3-chloro-2-ethoxy-1:2:3:4-tetrahydronaphthalene and 2:3-dichloro-1:2:3:4-tetrahydronaphthalene. Phenylacetylene yields exclusively  $\omega\omega$ -dichloroacetophenone, b. p. 138—140°/13 mm., which is identified by oxidation to benzoic acid and conversion into the dioxime of phenylglyoxal. The double bond of aromatic compounds reacts very sluggishly with ethyl hypochlorite. Benzene and anisole remained unaffected under widely varied conditions, whereas the more reactive phenol and quinol yield *o*- and *p*-chlorophenol and 2:3-dichloroquinol, respectively. The possibility that change occurs owing to the preliminary formation of phenyl hypochlorite is excluded by the observation that *o*-nitrophenol does not react with ethyl hypochlorite. The ester is particularly suitable for the chlorination of primary and secondary amines; thus ethylamine yields ethyldichloroamine. Acetaldehyde gives a mixture of chloroacetaldehyde and its acetals, whereas monochloroacetone and benzoyl chloride are obtained from acetone and benzaldehyde, respectively; it is possible that chlorine, formed by secondary action, takes part in these changes.

Chlorine monoxide, existing in equilibrium with hypochlorous acid (cf. Goldschmidt, A., 1919, ii, 227) appears to be the effective

agent in the action of aqueous hypochlorous acid on benzene (cf. van der Linden, A., 1912, i, 174). H. W.

**Certain Xanthates.** B. CECCHETTI (*Gazzetta*, 1925, 55, 104—105).—The formation of molybdenum xanthate,  $\text{Mo}(\text{S}\cdot\text{CS}\cdot\text{OEt})_2$ , m. p.  $108^\circ$  (decomp.), when carbon disulphide is treated with alcoholic potassium hydroxide and then with ammonium molybdate and dilute sulphuric acid, is confirmed. *Cadmium xanthate*, similarly obtained, turns orange-red at  $159^\circ$ , and becomes brown, and decomposes without melting at  $270^\circ$ . T. H. P.

**Preparation of Organic Acids by the Grignard Reaction.** D. IVANOV (*Bull. Soc. chim.*, 1925, [iv], 37, 287—296).—Carboxylic acids are obtained in good yield by the action of carbon dioxide on Grignard reagents at low temperatures and with agitation. Thus with magnesium butyl chloride (or bromide), valeric acid is obtained in 80% (or 86%) of the theoretical yield by reaction for 1 hr. at  $-20^\circ$ . At low temperatures, the principal by-product is dibutyl ketone (14%), together with some tributylcarbinol. At higher temperatures, tributylcarbinol is obtained in yields amounting to 45—51%, whilst the yield of valeric acid falls to 8—9%. Similarly the following acids have been obtained, in the yield indicated, by reaction for 1 hr. at  $-20^\circ$ : propionic acid, 72%; *n*-butyric acid, 77%; phenylacetic acid, 79%; benzoic acid, 80%.

*Tributylcarbinol*,  $(\text{C}_4\text{H}_9)_3\text{C}\cdot\text{OH}$ , m. p.  $20^\circ$ , b. p.  $120^\circ/10$  mm.,  $230\text{—}235^\circ/760$  mm. (with partial dehydration),  $d_4^{20}$  0.844,  $n_D^{18}$  1.4448, obtained as a by-product in the preparation of valeric acid, or by the action of magnesium butyl bromide on dibutyl ketone, on dehydration with oxalic acid gives  $\alpha\alpha$ -dibutylpent- $\Delta^2$ -ene [ $\epsilon$ -butyl- $\Delta^6$ -nonene],  $\text{CBu}_2\cdot\text{CH}\cdot[\text{CH}_2]_2\cdot\text{Me}$ , b. p.  $90^\circ/10$  mm.,  $215.5\text{—}216.5^\circ/760$  mm.,  $d_4^{20}$  0.7745,  $n_D^{20}$  1.4375. On hydrogenation in ethereal or acetic acid solution in the presence of platinum-black, the latter yields *tributylmethane* [ $\epsilon$ -butyl-nonane], b. p.  $217.5\text{—}218.5^\circ$ ,  $d_4^{18.5}$  0.7635,  $n_D^{18.5}$  1.4273 (cf. Gilman and Parker, this vol., i, 228). R. B.

**Decomposition of Acids in the presence of Metallic Chlorides.** A. MAILHE (*Bull. Soc. chim.*, 1925, [iv], 37, 305—311).—The vapours of saturated fatty acids are readily decomposed when passed over metallic chlorides at  $570\text{—}600^\circ$ , and the decomposition proceeds more readily as the number of carbon atoms in the acid molecule increases. Thus acetic acid is only slightly decomposed by sodium chloride at  $580^\circ$ , and less still by calcium chloride. The decomposition, as in the presence of copper powder (A., 1922, i, 803), appears to proceed in two ways. The main reaction yields a symmetrical ketone. With the lower members of the series, which yield diethyl ketone and acetone, this ketone largely escapes further decomposition and is collected in the liquid products of reaction. With the higher fatty acids, from butyric acid and *isovaleric* acid onwards, the ketone formed undergoes decomposition into carbon monoxide and ethylenic hydrocarbons. The second mode of decomposition yields carbon dioxide and saturated hydrocarbons. With *isobutyric* acid and sodium chloride



this mode of decomposition does not occur, and in the case of hexoic acid, where it is at a maximum, the gases collected only contain 14% of saturated hydrocarbons. Liquid olefines first appear with *isovaleric* acid. Oleic acid with calcium chloride yields a gas containing 30% of olefines, together with a liquid containing unsaturated acids as well as olefines, whilst the residual calcium chloride is contaminated with viscous polymerisation products; with barium chloride the gas contains 45% of olefines, whilst the liquid contains a smaller proportion of unsaturated acids. The composition of the reaction products varies slightly with the different chlorides used, but the variations may possibly be due to the difficulty of temperature regulation. Thus metallic chlorides do not exert the hydrogenating influence on olefines that finely-divided copper does.

R. B.

**Conditions of Maximum Stability for some Organic Substances.** I. BOLIN.—(See ii, 411.)

**Electrolysis of Alkali Acetates in Methyl-alcoholic Solution.**

J. SALAUZE (*Compt. rend.*, 1925, **180**, 662—664).—The substitution of methyl alcohol for water as the solvent in the electrolysis of sodium, potassium, or ammonium acetate increases the yield of ethane to 90—95%, and prevents any oxidation of the material. The electrolysis is best conducted with an anode of polished platinum in a solvent containing 30% of free acetic acid, which maintains the concentration of the acetate.

G. M. B.

**Thallium Salts of the Higher Fatty Acids.** D. HOLDE and M. SELIM (*Ber.*, 1925, **58**, [B], 523—528).—Thallium stearate, m. p. 119° (corr.), *thallium palmitate*, m. p. 115—117°, and thallium oleate, m. p. 83° (corr.), are prepared by neutralising an alcoholic solution of the requisite acid with approximately 0.1N-aqueous thalious hydroxide solution. At their melting points, they yield turbid liquids owing to the presence of air bubbles. They are not hydrolysed to a considerable extent in aqueous solution. Their solubilities in water and alcohol (96%) have been measured. Thallium oleate is uniformly more soluble than the stearate or palmitate, and the differences are particularly marked in 96% alcohol at a higher temperature (about 45°). A possible, ready method for the separation of oleic from stearic and palmitic acids is thus indicated.

H. W.

**$\Delta^a$ -Hypogæic Anhydride.** G. O. GABEL (*Ber.*, 1925, **58**, [B], 579).— $\Delta^a$ -Hypogæic anhydride,  $(C_{15}H_{29}CO)_2O$ , m. p. 60°, is prepared by the action of acetic anhydride on  $\Delta^a$ -hypogæic acid at 160—170°.

H. W.

**Fatty Acid Constituents of some Natural Fats. II. Palm-kernel Oil.** E. F. ARMSTRONG, J. ALLAN, and C. W. MOORE (*J. Soc. Chem. Ind.*, 1925, **44**, 143—144t).—Oil from the kernel of the West African palm (*Elæis guineensis*) having saponification equivalent 230.2 and iodine value 15.8 gave fatty acids having

equivalent 218.1 and iodine value 16.0; these were esterified and the esters subjected to fractional distillation under diminished pressure in the manner previously described (this vol., i, 353). The composition of the fatty acids from palm-kernel oil is heptonic acid 3, octonic acid 3, lauric acid 52, myristic acid 15, palmitic acid 7.5, stearic acid (?) 2.5, oleic acid 16, linoleic acid 1%.

F. B.

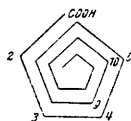
### Structure of Monobasic Unsaturated Acids and their Behaviour on Oxidation with Sulphuric-Chromic Acid.

L. J. SIMON (*Compt. rend.*, 1925, **180**, 833—836).—It has been shown that total oxidation of the carbon in unsaturated dibasic acids by sulphuric-chromic acid mixture takes place only in those acids with a terminal unsaturated linking (this vol., i, 511). It is found that the same applies to the monobasic acids.  $\Delta^7$ -Pentenoic acid behaves exceptionally owing, it is suggested, to the formation of a  $\gamma$ -lactone in the presence of strong sulphuric acid. Undecenoic acid behaves as though it does not contain the  $\text{CH}_2\cdot$  group, and it is suggested that the question of the structure of this acid should be reconsidered.

L. F. H.

### Configuration of the Higher Unsaturated Fatty Acids and their Salts.

J. KLIMONE (*J. pr. Chem.*, 1925, [ii], **109**, 265—272).—An attempt is made to explain why oleic acid does not readily take up oxygen whilst the unsaturated acids, linoleic and linolenic, having a like number of carbon atoms, do so readily. An



open ring in the form of a spiral is suggested for the structure of these acids in which the double bond in oleic acid is similarly situated to the  $\gamma : \delta$  or lactone position with regard to the carboxy group, which may therefore protect the bond from oxidation and so cause the relative stability of olive oil. The

striking solubility of the salts of the higher fatty acids (especially when unsaturated) in ether and solvents for fats make it very probable that the acids are of the *pseudo* type. The lead salts of oleic, linoleic, and linolenic acids cannot be the salts of true acids as dilute sulphuric acid only decomposes them into fatty acid and lead sulphate after the lapse of some time, even on warming. The solubility of the salts of the unsaturated fatty acids is influenced by the m. p. of the salts and of the corresponding acid. The lead salts of the polyunsaturated acids are much more soluble than that of oleic acid, since the former acids have a lower solidifying point. These solubility conditions only hold for salts of *pseudo*-acids, and not for salts the components of which are ionically combined. The stronger *pseudo* character of oleic acid as compared with stearic acid is deduced from the relative solubility of the lithium salts in water and alcohol. Further evidence showing how a double bond may increase the *pseudo* character of an acid is obtained from the investigations of Feigl (cf. A., 1923, ii, 880), in which it is shown that the copper salts of the oximes of the group  $\text{R}-\text{CH}(\text{OH})-\text{C}(\text{N}\cdot\text{OH})-\text{R}$  are soluble in ammonia if

the oxime contains only alkyl radicals, but not if phenyl radicals are present.

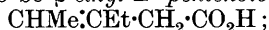
[With C. B. VON MOLTINI and (MISS) I. BENEDIK.]—The following metallic salts of unsaturated fatty acids are described: *Calcium oleate*, m. p. 83–84°; *mercury elaidate*, m. p. 115°; *silver elaidate*; *calcium elaidate*, m. p. 137°; *calcium linolenate*, m. p. 74° (indefinite); *calcium erucate*, m. p. 102–103°; *calcium palmitate*; *copper palmitate*, m. p. 138° after becoming transparent above 103°; *iron palmitate*, m. p. about 182°; *calcium stearate*, m. p. 179–180°; *calcium laurate*.  
A. C.

**Chemistry of the Three-carbon System. III.**  $\alpha\beta$ - $\beta\gamma$  **Change in Unsaturated Acids.** G. A. R. KON and R. P. LINSTAD (*J. Chem. Soc.*, 1925, 127, 616–624).—The change from  $\alpha\beta$  to  $\beta\gamma$  form,  $\begin{smallmatrix} -\text{CH}_2 \\ -\text{CH}_2 \end{smallmatrix} > \text{C}:\text{CHX} \rightarrow \begin{smallmatrix} -\text{CH}_2 \\ -\text{CH} \end{smallmatrix} > \text{C}:\text{CH}_2\text{X}$ , has been examined, in the case of acids possessing a low degree of mobility, with a view to ascertain the point of equilibrium. *cycloPentylideneacetic acid*, I, when treated with concentrated aqueous potassium hydroxide, passes into  $\Delta^1$ -*cyclopenteneacetic acid*, II.



*cycloPentanolacetic acid*, previously described by Harding and Haworth (T., 1910, 97, 486) as melting at 76° and as a semihydrate, is anhydrous and has m. p. 77°.

An acid, b. p. 217–218°, previously described by Fichter, Kiefer, and Bernouilli (A., 1910, i, 88) and stated to be  $\alpha\beta$ -diethylacrylic acid, is now shown to be  $\beta$ -ethyl- $\Delta^{\beta}$ -pentenoic acid,

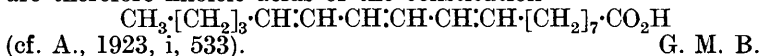


it has b. p. 133–134°/24 mm. or 217°/763 mm.,  $d_4^{22.7}$  0.9727,  $n_D^{22.7}$  1.45073,  $[\text{R}_L]$  35.44; *acid chloride*, b. p. 60–61°/14 mm.; *p-toluidide*, m. p. 94°; *amide*, m. p. 113–114°; *ethyl ester*, b. p. 183°/755 mm.,  $d_4^{17.5}$  0.9134,  $n_D^{17.5}$  1.43668,  $[\text{R}_L]_D$  44.75. The acid readily absorbs bromine to form a *dibromide*, and when boiled with 50% sulphuric acid yields  $\beta$ -ethylvalerolactone. The isomeric  $\beta\beta$ -diethylacrylic acid [ $\beta$ -ethyl- $\Delta^{\alpha}$ -pentenoic acid],  $\text{CEt}_2:\text{CH} \cdot \text{CO}_2\text{H}$ , has b. p. 129°/23 mm.,  $d_4^{21.2}$  0.9682,  $n_D^{21.2}$  1.46270,  $[\text{R}_L]_D$  36.42; *acid chloride*, b. p. 85°/25 mm.; *p-toluidide*, m. p. 80.5°; *amide*, m. p. 89°; *ethyl ester*, b. p. 87–88°/23 mm., 187–188°/755 mm.,  $d_4^{16.6}$  0.90955,  $n_D^{16.6}$  1.44542,  $[\text{R}_L]_D$  45.72. When oxidised with alkaline permanganate  $\beta\beta$ -diethylacrylic acid yields diethyl ketone and oxalic acid, and reacts very incompletely with bromine. Treated with 60% aqueous potassium hydroxide, the  $\beta\beta$ -acid gave a considerable quantity of the  $\beta\gamma$ -isomeride; when the  $\beta\gamma$ -acid was treated similarly only a small amount of the  $\beta\beta$ -acid was formed, thus showing that the point of equilibrium is very much on the side of the  $\beta\gamma$ -isomeride.

$\beta$ -Methyl- $\Delta^{\beta}$ -pentenoic acid,  $\text{CHMe}:\text{CMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , has b. p. 116°/23 mm.,  $d_4^{23.2}$  0.97845,  $n_D^{23.2}$  1.44692,  $[\text{R}_L]_D$  31.15; *acid chloride*, b. p. 57°/25 mm.; *p-toluidide*, m. p. 84°; *ethyl ester*, b. p. 62°/13 mm.,  $d_4^{18.8}$  0.91633,  $n_D^{18.8}$  1.43638,  $[\text{R}_L]_D$  40.58. When oxidised with

alkaline permanganate, the acid yields acetic acid.  $\beta$ -Methyl- $\beta$ -ethylacrylic acid [ $\beta$ -methyl- $\Delta^a$ -pentenoic acid],  $\text{CMeEt}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , has b. p.  $121\text{--}122^\circ/22\text{ mm.}$ , m. p.  $45^\circ$ ; acid chloride, b. p.  $65^\circ/25\text{ mm.}$ ; *p*-toluidide, m. p.  $66\text{--}67^\circ$ ; amide, m. p.  $92\text{--}93^\circ$ ; ethyl ester, b. p.  $67^\circ/24\text{ mm.}$ ,  $d_{4}^{17.9} 0.91413$ ,  $n_{\text{D}}^{17.9} 1.44110$ ,  $[\text{R}_\text{L}]_{\text{D}} 41.06$ . Both the acid and the ester give on oxidation methyl ethyl ketone. On treatment with potassium hydroxide  $\beta$ -methyl- $\beta$ -ethylacrylic acid forms the  $\beta\gamma$ -isomeride, whereas the reverse change from  $\beta\gamma$  to  $\alpha\beta$  only occurs to a slight extent, but probably somewhat greater than in the case of the higher homologue. C. J. S.

**Refractive Index of Chinese Wood Oil and the Structure of  $\alpha$ - and  $\beta$ -Elæostearic Acids.** J. BÖSEKEN and (MLLE.) H. J. RAVENSWAAY (*Rec. trav. chim.*, 1925, **44**, 241—243).—Chinese wood oil ( $d_{4}^{17} 0.942$ ,  $n_{\text{D}}^{17} 1.5220$ ) consisting, to the extent of 90%, of the glyceride of  $\alpha$ -elæostearic ( $\alpha$ -elæomargaric) acid, m. p.  $47^\circ$ ,  $d_{4}^{50} 0.8980$ ,  $n_{\text{D}}^{50} 1.5080$  (ethyl ester,  $d_{4}^{50} 0.8968$ ,  $0.9074$ ,  $n_{\text{D}}^{50} 1.5038$ ), is converted, by exposure for 48 hrs. to the light of a mercury vapour lamp, into *glyceryl tri- $\beta$ -elæostearate*, m. p.  $58.5^\circ$ ,  $d_{4}^{80} 1.1199$ ,  $n_{\text{D}}^{80} 1.5051$ .  $\beta$ -Elæostearic acid, m. p.  $67^\circ$ ,  $d_{4}^{80} 0.8839$ ,  $n_{\text{D}}^{80} 1.4970$ . Elæostearic acid has hitherto been regarded as an isomeride of linoleic acid, since its iodine value (160—170) indicates the presence in the molecule of two double bonds. The molecular refractivity of the  $\alpha$ - and  $\beta$ -glycerides and of the free acids and the  $\alpha$ -ethyl ester show far too high an exaltation, however, for two double bonds even if these be conjugated. The exaltation is of the right order of magnitude for three conjugated double bonds, as is shown by a comparison with the figures for substances such as hexatriene and octatriene. Pure linoleic acid,  $d_{4}^{15} 0.9050$ ,  $n_{\text{D}}^{15} 1.4710$  (from tetrabromostearic acid), shows no such exaltation. The high degree of unsaturation suggested is confirmed by hydrogenation experiments with finely-divided nickel as catalyst, the wood oil absorbing 7.0—7.9 mols. and ethyl  $\alpha$ -elæostearate (distilled in a high vacuum) 2.4—2.8 mols. of hydrogen. The elæostearic acids are therefore linoleic acids of the constitution



**Dependence of Rotatory Power on Chemical Constitution. XXIV. Further Experiments on the Walden Inversion.** J. KENYON, H. PHILLIPS, and H. G. TURLEY (*J. Chem. Soc.*, 1925, **127**, 399—417).—Sodium “*d*”-lactate with ethyl *p*-toluenesulphonate gives ethyl “*d*”-lactate, b. p.  $50^\circ/10\text{ mm.}$ ,  $d_{4}^{23} 1.0345$ ,  $n_{5461}^{13} 1.4176$ ,  $[\alpha]_{\text{D}}^{23} +11.29^\circ$  (in 80% yield), which with *p*-toluenesulphonyl chloride forms ethyl “*d*”- $\alpha$ -*p*-toluenesulphonoxypropionate, b. p.  $164\text{--}166^\circ/0.5\text{ mm.}$ ,  $d_{4}^{20} 1.2010$ ,  $[\alpha]_{5461}^{20} +53.9^\circ$  (together with a little laevorotatory ethyl  $\alpha$ -chloropropionate, the yield of which is increased by modifying the conditions); “*d*”- $\alpha$ -*p*-toluenesulphonoxypropionic acid has m. p.  $108^\circ$ ,  $[\alpha]_{5461}^{25} +41.6^\circ$  in ethyl alcohol; “*d*”- $\alpha$ -*p*-toluenesulphonoxypropionamide, m. p.  $105\text{--}106^\circ$ ,  $[\alpha]_{5461}^{25} +40.4^\circ$  in ethyl alcohol. Ethyl “*d*”- $\alpha$ -*p*-toluenesulphonoxypropionate with potassium benzoate gives ethyl “*d*”- $\alpha$ -benzoyloxy-

propionate, b. p.  $153^{\circ}/12$  mm.,  $d_4^{20}$  1.112,  $n_{5461}^{13}$  1.5006,  $[\alpha]_D^{20} +24.56^{\circ}$  (ethyl "*l*"- $\alpha$ -benzoyloxypropionate as prepared from benzoyl chloride and ethyl "*d*"-lactate has b. p.  $149^{\circ}/10$  mm.,  $d_4^{23}$  1.114,  $n_{5461}^{15}$  1.5010,  $[\alpha]_D^{20} -24.60^{\circ}$ ), whereas with potassium acetate or phenylacetate there is inversion (cf. T., 1923, 123, 44); ethyl "*l*"- $\alpha$ -acetoxypropionate, b. p.  $71-72^{\circ}/10$  mm.,  $d_4^{18}$  1.0442,  $n_D^{19}$  1.4096,  $[\alpha]_D^{18} -47.63^{\circ}$  (acetyl chloride and ethyl "*d*"-lactate give ethyl "*d*"- $\alpha$ -acetoxypropionate,  $[\alpha]_D^{22} +51.54^{\circ}$ ); ethyl "*l*"- $\alpha$ -phenylacetoxypionate, b. p.  $160-162^{\circ}/14$  mm.,  $d_4^{19}$  1.001,  $n_D^{16}$  1.4920,  $[\alpha]_D^{18} -37.61^{\circ}$  (ethyl "*d*"- $\alpha$ -phenylacetoxypionate,  $[\alpha]_D^{22} +38.54^{\circ}$ ). Ethyl "*d*"- $\alpha$ -bromopropionate and potassium acetate give ethyl  $\alpha$ -acetoxypropionate,  $[\alpha]_D^{18} -23.1^{\circ}$ . It is concluded that the inversion of configuration occurs during the interaction of potassium benzoate with the ester, and the unsaturated nature of the  $\text{CO}_2\text{K}$  group may be the main factor favouring the indirect reaction. It seems that the nature of the ionised salt is important, and, in the following cases, although a change of sign occurs, there is great loss of rotatory power: the "*l*"-ester with lithium chloride gives ethyl  $\alpha$ -chloropropionate,  $[\alpha]_D^{25} +2.82^{\circ}$ , whilst the "*d*"-ester with sodium bromide gives ethyl  $\alpha$ -bromopropionate,  $\alpha_D^{16} -0.58^{\circ}$ , and with potassium iodide gives ethyl  $\alpha$ -iodopropionate,  $[\alpha]_D^{20} -0.12^{\circ}$ . The reaction of the ester with Grignard reagents takes place according to the equation  $\text{MgR}\cdot\text{X} + \text{CHMe}(\text{O}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7)\cdot\text{CO}_2\text{Et} = \text{CHMeX}\cdot\text{CO}_2\text{Et} + \text{R}\cdot\text{MgO}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7$ ; thus from ethyl  $\alpha$ -*p*-toluenesulphonoxypropionate ( $\alpha_D^{25} -6.94^{\circ}$ ) are prepared ethyl  $\alpha$ -bromopropionate,  $[\alpha]_D^{30} +17.80^{\circ}$  (by use of magnesium ethyl bromide), or  $[\alpha]_D^{20} +15.84^{\circ}$  (by use of magnesium phenyl bromide), and ethyl  $\alpha$ -iodopropionate,  $\alpha_D^{22} +1.88^{\circ}$  (by use of magnesium ethoxyiodide). The action of alkylating agents on the ester is accompanied by loss of rotatory power: thus sodium ethoxide gives inactive ethyl  $\alpha$ -ethoxypropionate, but sodium phenoxide gives ethyl "*l*"- $\alpha$ -phenoxypropionate,  $[\alpha]_D^{23} -14.56^{\circ}$ . The mechanism suggested for the action of sodium ethoxide is also applied to the action of potassium carbonate on the "*l*"-ester, yielding ethyl  $\alpha$ -ethoxypropionate,  $\alpha_D^{20} -8.7^{\circ}$ , and to the interaction of ethyl "*d*"-lactate and ethyl *p*-toluenesulphonate, yielding ethyl  $\alpha$ -ethoxypropionate,  $\alpha_D^{21} +1.94^{\circ}$ , whereas a different explanation accounts for the high rotatory power of the phenyl ether. Hydrolysis of ethyl  $\alpha$ -*p*-toluenesulphonoxypropionate ( $\alpha_D^{20} -7.26^{\circ}$ ) with sodium hydroxide, potassium hydroxide, or silver oxide occurs without inversion of configuration, but with variable loss in rotatory power.

It is suggested that the key atom in the *p*-toluenesulphonoxy radical is the ester oxygen atom, and on these lines the resemblance with the organic esters of the halogen acids is accounted for. It is concluded that ethyl "*l*"- $\alpha$ -bromopropionate has the same configuration as ethyl "*l*"- $\alpha$ -*p*-toluenesulphonoxypropionate and therefore as dextrorotatory lactic acid, whence it follows that the action of magnesium ethyl bromide on the sulphonic ester is indirect. The ability of the sulphonic esters to break at the O-S linking accounts for their hydrolysis without inversion of configuration. The rotatory powers of ethyl "*d*"- $\alpha$ -*p*-toluenesulphonoxyprop-

ionate are given for various temperatures and wave-lengths and in the case of the corresponding acid the data with different solvents are given. It is curious that this ester, unlike ethyl "*d*"-lactate, exhibits simple rotatory dispersion.

F. M. H.

**Certain Organo-molybdc Complexes.** A. HONNELAITRE (*Ann. Chim.*, 1925, [x], 3, 5—71).—The investigations of Darmois (A., 1921, i, 539; 1922, i, 220, 522; 1923, i, 299, 300, 535; ii, 831; 1924, ii, 618) have been extended by the author, who has followed the course of the neutralisation by a base of a mixture in varying proportions of molybdc acid and another acid, both polarimetrically and by measurement of the  $p_H$  of the solution. Binary mixtures of molybdc acid with malic, oxalic, succinic, tartaric, mandelic, citric, lactic,  $\beta$ -hydroxybutyric, gallic, and salicylic acids, and with pyrocatechol, pyrogallol, and mannitol have been studied by these means.  $\beta$ -Hydroxybutyric acid forms no complex compounds with molybdc acid, the reaction being specific for the  $\alpha$ -hydroxy-acids.

The forms of the curves representing the optical rotation or the value of  $p_H$  in relation to the extent of the neutralisation indicate the formation of various complex molybdc compounds. Of these, the ammonium mandelate compound,  $\text{MoO}_3 \cdot 2\text{C}_6\text{H}_7\text{O}_3\text{NH}_4$ , which is of the same type as the compounds obtained by Henderson with other hydroxy-acids (T., 1896, 69, 1455; 1899, 75, 542), has been obtained crystalline and exhibits the constant specific rotation,  $[\alpha]_D$  3·8°, at high dilutions.

Ammonium dimolybdomalate (cf. Darmois, *loc. cit.*) is highly sensitive towards the action of acids, which cause the rotation to change in sign and tend towards a negative limit, which is independent of the nature of the acid used. On the other hand, the addition to an acid solution of this complex salt of more alkali than suffices to neutralise it, causes a sudden fall in the rotation, owing to the decomposition of the complex. Thus, ammonium dimolybdomalate serves as an indicator of neutrality, its high rotation and the great accuracy of polarimetric measurements rendering possible very accurate titration with its help. This salt may be employed in a similar manner as a reagent for compounds capable of forming complex derivatives with molybdc acid.

T. H. P.

**Ring-chain Tautomerism. XII. Derivatives of  $\beta\beta$ -Dimethyl- $\alpha$ -ethylglutaric Acid.** G. A. R. KON, L. F. SMITH, and J. F. THORPE (*J. Chem. Soc.*, 1925, 127, 567—573).—The influence of the presence of an  $\alpha$ -alkyl group in the  $\beta\beta$ -dimethylglutaric acids on their tendency to ring formation has been further studied. The bromo derivatives of the  $\alpha$ -ethyl acid exhibit little tendency to pass into derivatives of caronic acid, and there is no evidence of the existence of ring-chain tautomerism between a keto ring and a hydroxy ring such as is shown by the glutaric acids without an  $\alpha$ -substituent. There is, however, a strong tendency for the molecule to undergo disruption with the formation of  $\beta$ -methyl- $\alpha$ -ethylbutenoic acid.

When  $\beta\beta$ -dimethyl- $\alpha$ -ethylglutaric acid is treated with potassium hydroxide or with sulphuric acid (70% by volume), butyric and acetic acids are eliminated, and, probably, a lactone (m. p.  $82^\circ$ ) is formed. When the dibrominated product of the acid is esterified with alcohol there is produced a lactonic acid,  $\text{Me}_2\text{C} < \begin{array}{c} \text{CEt}(\text{CO}_2\text{H}) \cdot \text{O} \\ \text{CH}_2 \text{---} \text{CO} \end{array}$ , and a neutral fraction consisting of  $\alpha\gamma$ -dibromo-ester, which cannot be purified by distillation, since it loses ethyl bromide and is partly converted into bromolactonic ester.

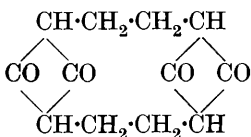
When the dibromo-acid chloride is poured into anhydrous formic acid, there separates a solid substance from which, by fractional separation with benzene, there are obtained *trans*- $\alpha\gamma$ -dibromo- $\beta\beta$ -dimethyl- $\alpha$ -ethylglutaric acid, m. p.  $178^\circ$  (decomp.), and *cis*- $\alpha\gamma$ -dibromo- $\beta\beta$ -dimethyl- $\alpha$ -ethylglutaric acid, m. p.  $145^\circ$  (decomp.). The mother-liquors from which the *cis*- and *trans*-acids separate give a bromolactone, m. p.  $154$ — $155^\circ$ , which is also the chief product when aqueous formic acid is used instead of the anhydrous acid.

Hydrolysis of either the dibromo-ester, the dibromo-acid, or the dibromolactone with dilute sodium carbonate yields a mixture of hydroxylactones, and when aqueous potassium hydroxide is employed  $\beta$ -methyl- $\alpha$ -ethylbutenoic acid, m. p.  $49.5^\circ$ , is produced, together with oxalic acid and a small quantity of a solid, m. p.  $208^\circ$  (decomp.).

C. J. S.

#### Action of Triethylamine on Adipyl and $\beta$ -Methyladipyl Chlorides.

E. WEDEKIND, M. MÜLLER, and C. WEINAND (*J. pr. Chem.*, 1925, [ii], **109**, 161—174).—A well-dried benzene solution of triethylamine reacts vigorously with adipyl chloride, forming triethylamine hydrochloride (96% yield) and *tricyclo*-(2,2,1,1,1,1)-*dodecane*-5 : 10 : 11 : 12-*tetraone* (annexed formula), m. p.  $141$ — $142^\circ$ ; loss by carbonisation, even at  $0.1$ — $0.2$  mm., reduces the yield to 10—15%. The condensation was carried out in an atmosphere of dry hydrogen. The suggested structure is supported by the fact that only two of the  $\text{:CO}$  groups react with



phenylhydrazine, the remaining two being sterically protected. The *diphenylhydrazone*,  $\text{C}_{24}\text{H}_{24}\text{O}_2\text{N}_4$ , m. p.  $182$ — $184^\circ$ , gives characteristic colorations with ferric chloride and potassium dichromate in concentrated sulphuric acid solution. Oxidation of the *tricyclododecanetetraone* with hydrogen peroxide or sodium peroxide gave a dibasic acid,  $\text{C}_{10}\text{H}_{14}\text{O}_4$ , m. p.  $171^\circ$ , the constitution of which has not been determined. Potassium and lead salts were prepared. Further oxidation led to a mixture from which a saturated acid, m. p.  $81$ — $82^\circ$ , was isolated. An attempt to reduce the diketone with amalgamated zinc and hydrochloric acid (Clemmensen's method) gave adipic acid. Hydrochloric acid alone also gave adipic acid. No hydrogenation took place in the presence of palladium. Pyridine reacts with adipyl chloride to form adipic acid, but no condensation product. Adipyl chloride reacts with ether in the presence of zinc to form ethyl adipate (cf. Wedekind

and Haeussermann, A., 1901, i, 536).  $\beta$ -Methyladipyl chloride did not give the corresponding cyclodecane under similar conditions, but yielded  $\beta$ -methyladipic anhydride,  $C_7H_{10}O_3$ , b. p. 225—227°/20 mm.; the reaction was much less vigorous and the result was in agreement with the behaviour of the monocarboxyl chlorides where polymerisation products with tertiary bases are only capable of isolation when the reaction is rapid and violent, otherwise the least trace of moisture results in the formation of the corresponding acid anhydrides. A. C.

**Relation between Structure and the Sulphochromic Oxidation.** L. J. SIMON (*Compt. rend.*, 1925, **180**, 673—675; cf. A., 1924, i, 481, 567).—The oxidation of a series of acids such as tartaric, malic, citric, and the unsaturated acids derived from them and their derivatives by the sulphochromic mixture with and without silver, gives results in accord with the generalisation previously announced. G. M. B.

**Hydrated mesoTartaric Acid.** M. AMADORI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 244—246).—The monohydrate of mesotartaric acid crystallises in the pinacoidal class of the triclinic system,  $a : b : c = 1.5461 : 1 : 1.2051$ ,  $\alpha = 83^\circ 13'$ ,  $\beta = 90^\circ 24'$ ,  $\gamma = 104^\circ 42'$ . T. H. P.

**l-Arabinolactone and some of its Derivatives.** L. J. SIMON and V. HASENFRATZ (*Compt. rend.*, 1924, **179**, 1165—1168).—l-Arabinolactone, when heated with three parts of methyl alcohol for a few minutes, readily yields methyl arabonate (cf. Böddener and Tollens, A., 1910, i, 460). Ribonolactone, m. p. 84—86° (cf. Ekenstein and Blanksma, A., 1913, i, 445), is unaffected by similar treatment. When heated at 110°, the methyl ester loses alcohol and is reconverted quantitatively into arabinolactone. Ethyl arabonate, m. p. 126.5°, is prepared similarly to the methyl ester; it is feebly dextrorotatory. Arabonolactone yields a triacetyl derivative, m. p. 67°,  $[\alpha]_D^{20} - 67.2^\circ$ , and is converted by benzoyl chloride in presence of pyridine into dibenzoyl and tribenzoyl derivatives, m. p. 200°,  $[\alpha]_D^{20} - 37.65^\circ$ , and m. p. 120°,  $[\alpha]_D^{20} + 24^\circ$ , respectively. Methyl and ethyl arabonates both yield tetra-acetyl derivatives, m. p. 129.5—131°,  $[\alpha]_D^{20} - 34.1^\circ$ , and m. p. 68°,  $[\alpha]_D^{20} - 26.7^\circ$ , respectively. H. J. E.

**Certain Aliphatic Carboxylic Acids.** E. PHILIPPI and R. SEKA [with E. HAGER and M. LANDAU] (*Monatsh.*, 1925, **45**, 273—279).—The methods available for the preparation of ethane- and ethylene-tetracarboxylic acids and their esters have been investigated. Alkyl ethylenecarboxylates are obtained so readily and in such good yields by Blank and Sampson's method (cf. A., 1899, i, 484), that reduction of these substances appears to give the best method for preparing the corresponding ethanecarboxylates. Reduction of fumaric acid by aluminium amalgam gives succinic acid in 50% yield, whilst ethyl ethylenetetracarboxylate was reduced in 75% yield; with the free acid, however, the yields were



only 10%; this is attributed to the occluding action of the aluminium hydroxide as well as to probable salt formation with the tetracarboxylic acid.

Skita's method (cf. A., 1908, i, 855), using colloidal platinum, gave nearly quantitative yields of succinic acid with fumaric acid, but the yield of ethanetetracarboxylic acid from ethylenetetracarboxylic acid could not be raised above 10% by this method of reduction (cf. also Mannich and Ganz, A., 1923, i, 13).

*Potassium ethanetetracarboxylate*,  $C_6H_2O_8K_4 \cdot 2H_2O$ , was prepared by the action of potassium hydroxide on the ethyl carboxylate (cf. Conrad and Guthzeit, A., 1883, 46). The anhydrous form was obtained on long drying at  $120^\circ$  in a vacuum; suspended in benzene, it reacted with well-dried hydrogen chloride to form the free acid in 80% yield, which is reduced by the slightest trace of water. No variation of the method was successful. Buchner's method (cf. A., 1892, 824) for ethanetetracarboxylic acid gives 50% yields and can only be used for small amounts. *Sodium ethanetetracarboxylate* ( $+3H_2O$ ), becomes anhydrous at  $110^\circ$ ; it could not be converted into the free acid as above. *Potassium aminoethanetetracarboxylate*,  $C_6H_3O_8N \cdot 8H_2O$ , loses only  $3H_2O$  in a vacuum at  $110^\circ$ ; further drying causes decomposition. Ethylenetetracarboxylic acid did not form an anhydride on heating with acetic anhydride (cf. Staudinger and Kreis, A., 1923, i, 438). A. C.

**Oxidation of *d*- $\beta$ -Thiolbutane to *d*-Butane- $\beta$ -sulphonic Acid; Rotations of Thio- and Sulpho-carboxylic Acids and their Salts.** P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1925, 63, 85—93).—The oxidation of *d*- $\beta$ -thiolbutane to *d*-butane- $\beta$ -sulphonic acid involves a reversal of the optical rotation; this result is similar to that obtained on oxidising *d*-amyl alcohol to the corresponding valeric acid, and is considered to be generally true of such oxidations of alcohols and mercaptans. A consideration of the optical properties of  $\alpha$ -thio- and  $\alpha$ -sulpho-acids and their mono- and di-basic salts, in relation to the respective strengths of the acidic groups involved, leads to the conclusion that an  $\alpha$ -sulphonic acid belongs to the same optical series, with respect to the carboxyl group, as the thio-acid from which it has been formed by oxidation, although the substitution by a metal of the hydrogen of the thio group and of the sulphonic group has an opposite effect in the two cases. *d*- $\beta$ -Thiolbutane, prepared by the action of alcoholic potassium hydrogen sulphide on *d*- $\beta$ -iodobutane, has  $[\alpha]_D^{20}$   $15.71^\circ$ ; *d*-butane- $\beta$ -sulphonic acid, by oxidation of the above compound with nitric acid, has, as barium salt,  $[\alpha]_D^{20}$   $-3.06^\circ$ , as free acid  $[\alpha]_D^{20}$   $-3.18^\circ$ . The monosodium salt of *d*- $\alpha$ -thiolpropionic acid has  $[\alpha]_D^{20}$   $-4.36^\circ$ ; the disodium salt,  $[\alpha]_D^{20}$   $7.32^\circ$ . *d*- $\alpha$ -Sulphopropionic acid has  $[\alpha]_D^{20}$   $8.94^\circ$ ; monosodium salt,  $[\alpha]_D^{20}$   $7.30^\circ$ ; disodium salt,  $[\alpha]_D^{20}$   $-1.66^\circ$ . Xanthopropionic acid has  $[\alpha]_D^{20}$   $55.51^\circ$ ; sodium salt,  $[\alpha]_D^{20}$   $20.86^\circ$ . Xanthosuccinic acid has  $[\alpha]_D^{20}$   $38.92^\circ$ ; monosodium salt,  $[\alpha]_D^{20}$   $16.87^\circ$ ; disodium salt,  $[\alpha]_D^{20}$   $3.07^\circ$ . Thiolsuccinic acid has  $[\alpha]_D^{20}$   $48.71^\circ$ ; monosodium salt,  $[\alpha]_D^{20}$   $22.12^\circ$ ; disodium salt,  $[\alpha]_D^{20}$   $25.04^\circ$ ; trisodium salt,  $[\alpha]_D^{20}$   $19.49^\circ$ . Sulphosuccinic acid has

$[\alpha]_D^{20}$  26.03°; *monopotassium* salt,  $[\alpha]_D^{20}$  20.88°; *dipotassium* salt,  $[\alpha]_D^{20}$  13.83°; *tripotassium* salt,  $[\alpha]_D^{20}$  25.67°. C. R. H.

**Electronic Theory of Valency and Electrolytic Oxidation of Formaldehyde.** C. DEL FRESNO.—(See this vol., ii, 267.)

**Acyclic Acetals and their Azeotropic Properties.** J. BÉDOWÉ (*Bull. Soc. chim. Belg.*, 1925, **34**, 41—55).—The author has applied the method used by Ghysels (cf. A., 1924, i, 490) for the preparation of formals of primary alcohols to the preparation of the corresponding acetals,  $\text{CH}_3\cdot\text{CH}(\text{OR})_2$ , from methyl, ethyl, propyl, butyl, *isobutyl*, amyl, and *isoamyl* alcohols. A mixture of the alcohol (5 mols.) and paraldehyde (2 mols.) with 1—2½% of the total mass of sulphuric, hydrochloric, or, better, *p*-toluene-sulphonic acid (which prevents the formation of crotonaldehyde) is heated under reflux for 10—12 hours, the mixture neutralised with the corresponding sodium alkoxide, and fractionally distilled, using a Crismer column. Only in the case of methyl alcohol is the direct distillation method possible. In the case of methyl- and ethyl-acetals, the acetal and the alcohol form a binary azeotropic mixture from which the acetal is separated by the addition of carbon disulphide, which forms a further azeotropic mixture with the acetal. In the other cases, most of the acetal remains in the residual fraction, the alcohol and water being removed as azeotropic mixtures during the distillation. The yields vary from 60 to 65%. Heterogeneous, binary azeotropic mixtures are formed by all the acetals with water, and homogeneous mixtures by methyl- and ethyl-acetals with the corresponding alcohol, whilst ternary azeotropic mixtures are produced by ethyl and propyl acetals, water, and the corresponding alcohol, which are homogeneous and heterogeneous, respectively. The compositions and boiling points of these mixtures are given. Two acetals have not been previously prepared: *di-n-butylacetal*, b. p. 188.8°/760 mm.,  $d_4^{20}$  = 0.8493,  $d_4^{20}$  0.8326,  $n_D^{20}$  1.4071; and *di-n-amylacetal*, b. p. 225.3°/760 mm.,  $d_4^{20}$  0.8532,  $d_4^{20}$  0.8374,  $n_D^{20}$  1.4169. J. W. B.

**$\gamma$ -Hydroxy- $\beta$ -ethylhexaldehyde and  $\beta$ -Ethyl- $\Delta^8$ -hexenaldehyde.** V. GRIGNARD and A. VESTERMAN (*Bull. Soc. chim.*, 1925, [iv], **37**, 425—430).—On shaking *n*-butaldehyde in ethereal solution with an aqueous solution of potassium hydroxide, a 65—70% yield of  $\gamma$ -hydroxy- $\beta$ -ethylhexaldehyde (cf. this vol., i, 111) is obtained. This substance gradually polymerises, being completely converted into the dimeride, a white solid, in 6 months. When slowly distilled with a trace of iodine (cf. Hibbert, A., 1915, i, 640)  $\gamma$ -hydroxy- $\beta$ -ethylhexaldehyde gives a 75—80% yield of  $\beta$ -ethyl- $\Delta^8$ -hexenaldehyde (Raupenstrauch, A., 1887, i, 794; Gorhan, A., 1905, i, 171). On addition of the above aldehydes to ethereal solutions of magnesium methyl bromide,  $\gamma$ -ethylheptane- $\beta\delta$ -diol, b. p. 126°/10 mm.,  $d_4^{14}$  0.9281,  $n_D^{14}$  1.4498, and  $\gamma$ -ethyl- $\Delta^7$ -hepten- $\alpha$ -ol, b. p. 84—86°/13 mm.,  $d_4^{14}$  0.8559,  $n_D^{14}$  1.4522, respectively, are obtained. On addition to ethyl magnesium bromide, the aldehydes yield the homologues,  $\delta$ -ethyloctane- $\gamma\epsilon$ -diol, b. p. 131°/14 mm.,

$d_4^{44}$  0.9225,  $n_D^{44}$  1.4524, and  $\delta$ -ethyl- $\Delta^8$ -octen- $\gamma$ -ol, b. p. 83—86°/8 mm.,  $d_4^{42}$  0.8571,  $n_D^{42}$  1.4536.

The dehydration of the ethylenic alcohols is not accomplished satisfactorily by the use of iodine or by the use of sulphuric acid, but by passing over heated aluminium an almost quantitative yield of the unsaturated hydrocarbons is obtained. By this catalytic method were prepared  $\gamma$ -ethyl- $\Delta^7$ -heptadiene, b. p. 84—86°/102 mm.,  $d_4^{15}$  0.7913,  $n_D^{15}$  1.4614, and  $\delta$ -ethyl- $\Delta^8$ -octadiene, b. p. 105—107°/90—95 mm.,  $d_4^{15}$  0.7981,  $n_D^{15}$  1.4655. The exaltations of the molecular refractivities of the hydrocarbons due to the conjugated systems of double bonds are notable.

L. F. H.

**Syntheses by means of the Sodium and Magnesium Derivatives of Propinine.** YVON (*Compt. rend.*, 1925, 180, 748—749).—Methyl  $\Delta^1$ -propinenyl ketone,  $\text{CMe:C:COMe}$ , obtained by the action of the sodium compound,  $\text{CMe:CNa}$ , on acetyl chloride, has b. p. 132.5—133.5°/772 mm.,  $d^{22}$  0.910,  $n^{22}$  1.141; by the action of sulphuric acid it yields acetylacetone. With hydrazine it condenses to dimethylpyrazole. The action of trioxymethylene on the propinine in presence of magnesium ethyl bromide gives  $\Delta^8$ -butinen- $\alpha$ -ol,  $\text{CMe:C:CH}_2\text{:OH}$ , b. p. 52—53°/14 mm., 141—143°/760 mm.,  $d^{21}$  0.958,  $n^{21}$  1.453; by the action of acetic anhydride, this yields the acetate, b. p. 156—158°,  $d^{20}$  0.995,  $n^{20}$  1.434. Using chloromethyl ether instead of trioxymethylene, the ether,  $\text{CMe:C:CH}_2\text{:OMe}$ , b. p. 100—101°/760 mm.,  $d^{21}$  0.854,  $n^{21}$  1.423, is obtained.

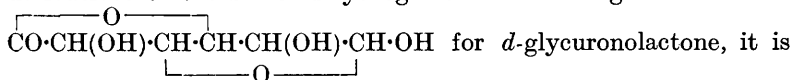
S. I. L.

**Higher Methyl Ketones.** G. T. MORGAN and E. HOLMES (*J. Soc. Chem. Ind.*, 1925, 44, 108—110r).—Methyl  $n$ -heptyl,  $n$ -octyl,  $n$ -decyl,  $n$ -undecyl,  $n$ -dodecyl,  $n$ -tridecyl,  $n$ -tetradecyl,  $n$ -pentadecyl,  $n$ -hexadecyl,  $n$ -heptadecyl,  $n$ -octadecyl, and  $n$ -nonadecyl ketones (the two last-named being new compounds, m. p. 61° and 58°, respectively) were obtained in about 60% yield by the dry distillation of the barium salt of the corresponding acid with 3 mols. of barium acetate, in a vacuum, in an iron pot, glass vessels not giving satisfactory results. Certain of the ketones were oxidised to the carboxylic acids containing one less carbon atom by sodium dichromate in sulphuric acid solution.

L. F. H.

**Relations between Rotatory Power and Structure in the Sugar Group. VIII. Some Terpene Alcohol Glycosides of Glucose, Glycuronic Acid, Maltose, and Lactose.** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1925, 47, 537—543; cf. this vol., i, 232).—Agreement in the values for the rotation of the terminal carbon atom of the carbohydrate chain in menthylglucosides (cf. Fischer and Bergmann, A., 1917, i, 467) and menthylglycuronic acids (*ibid.*, and Fischer, A., 1911, i, 217) calculated, on the principle of optical superposition, from both series of derivatives, indicates that this principle applies to these groups, and probably also to the bornylglucosides (cf. Fischer and Raske, A., 1909, i, 365; Hämäläinen, A., 1913, i, 639). Rotations of menthyl-maltosides and -lactosides, calculated using the values, for the

terminal carbon atoms and the menthyl group, derived from the rotations of the glucosides and glycuronic acids, are in good agreement with published data. From similar considerations, it is concluded that the anhydromenthylglucoside and the anhydromethylglucoside of Fischer and Zach (A., 1912, i, 239) are not derivatives of the same anhydroglucose. Assuming the structure



pointed out that this compound, as well as many derivatives of glycuronic acid, should occur in  $\alpha$ - and  $\beta$ -forms. F. G. W.

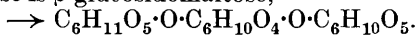
**Synthesis of Phosphoric Acid Esters. II. Synthesis of some Glucose Monophosphoric Acid Esters and their Behaviour towards Yeast.** S. KOMATSU and R. NODZU (*Mem. Coll. Sci. Kyoto*, 1924, 7, 377—387).— $\alpha$ -,  $\gamma$ -, and  $\zeta$ -Glucose hydrogen phosphates are not fermentable by living yeast but the  $\alpha$ - and  $\gamma$ -esters are rapidly fermented by zymin at a rate comparable with the fermentation of dextrose in the presence of phosphates. These two esters accelerate the rate of fermentation of dextrose by zymin, and the  $\gamma$ -ester accelerates the fermentation of dextrose by zymin washed free from the co-enzyme. The esters, therefore, would seem to play an important rôle in fermentation, but their rotatory powers are not the same as that of the phosphate isolated from the fermentation product of dextrose by Robison (A., 1923, i, 86). The *barium*  $\alpha$ -glucosephosphate obtained by the action of phosphoryl chloride and barium hydroxide on penta-acetylglucose in ether, is a white powder,  $[\alpha]_D^{25} + 14.9^\circ$ , which reduces Fehling's solution only on long boiling or hydrolysis with acids; the hydrolysis yields a strongly dextrorotatory product. The ester gives an *osazone*, m. p. 203—204°.  $\gamma$ -Glucose hydrogen phosphate was obtained by the partial hydrolysis of  $\gamma$ -diisopropylideneglucose phosphate and converted into its *barium* salt,  $[\alpha]_D + 29.2^\circ$  in water, which reduces Fehling's solution readily.  $\zeta$ -Glucose hydrogen phosphate was prepared in a similar manner to the corresponding hydrogen sulphate (A., 1922, i, 986; 1923, i, 441) by the action of phosphoryl chloride on dextrose in pyridine, and converted into the *barium* salt, which had  $[\alpha]_D + 19.1^\circ$  in water, and readily reduced Fehling's solution. Evidence is adduced to support the view that Neuberg's phosphoric ester (A., 1910, i, 610) has the constitution assigned to the last-named ester. L. F. H.

**Degradation of Mercaptals of Monosaccharides and a New Synthesis of Alkyl Glucosides.** E. PACSU (*Ber.*, 1925, 58, [B], 509—513).—*d*-Glucosedi-benzylmercaptal (cf. Lawrence, A., 1896, i, 272; Pacsu, A., 1924, i, 712) when treated with mercuric chloride (1 mol.) in hot, absolute ethyl-alcoholic solution gives  $\alpha$ -benzylthioglucoside, m. p. 112—114°,  $[\alpha]_D^{20} + 176.1^\circ$  in aqueous solution, in about 81% yield (cf. Schneider and Sepp, A., 1916, i, 792; 1918, i, 252). A mixture of  $\alpha$ - and  $\beta$ -methylglucosides, in combined yield of 90.5%, is produced when *d*-glucosedi-benzylmercaptal is heated with an excess of mercuric chloride in absolute methyl-alcoholic

solution; after removal of precipitated benzylthiolmercurichloride, the filtrate is treated with hydrogen sulphide to remove excess of mercury, filtered, neutralised with silver carbonate, and evaporated under diminished pressure.  $\alpha$ -Methylglucoside predominates greatly in the product of the reaction, but the precise ratio of the  $\alpha$  to  $\beta$  compound appears to depend largely on the duration of heating.

H. W.

**Starch. II. Constitution of Polymerised Amylose, Amylopectin, and their Derivatives.** A. R. LING and D. R. NANJI (*J. Chem. Soc.*, 1925, 127, 629—636).—When a solution of "amylose" is treated with a small quantity of barley or malt diastase at  $p_H$  4.5, it is converted rapidly and quantitatively into maltose, the optimum temperature for barley diastase being  $45^\circ$ , and for malt diastase  $30$ — $40^\circ$ . Scarcely any action occurs at  $70^\circ$ . By the action of maltase at  $38^\circ$  on the osazone of the trihexose derived from amylopectin, there are produced glucosazone and isomaltose, and by the action of emulsin, at the same temperature, maltosazone and dextrose are formed. It is therefore concluded that the trihexose is  $\beta$ -glucosidomaltose,



The product obtained by the action of malt diastase at  $70^\circ$  on amylopectin, and consequently on  $\alpha\beta$ -hexa-amylose, consists of  $\beta$ -glucosidomaltose only.

In starches containing amylose and amylopectin only, these are present in the proportion 66.6% and 33.3%, respectively. The low result obtained by other investigators is due to the fact that about 25% of the amylose in the starch granules is in a crystalloidal phase which is readily extracted by water or dilute alkali, whilst the remainder is in a colloidal phase uniformly dispersed in the amylopectin layers and resists extraction. By the action of barley diastase at  $50^\circ$ , the amylose is converted into maltose, which may be determined by its reducing power, and the amylopectin is dephosphated and depolymerised, whilst any hemicellulose is left unaltered and may be removed by filtration. C. J. S.

**Starch. III. Nature and Genesis of the Stable Dextrin and of the Maltodextrins.** A. R. LING and D. R. NANJI (*J. Chem. Soc.*, 1925, 127, 636—651).—When  $\alpha\beta$ -hexa-amylose is treated with malt diastase between  $30^\circ$  and  $70^\circ$  in the absence or presence of maltose, it gives a series of intermediate compounds between this and  $\beta$ -glucosidomaltose (cf. preceding abstract). In the absence of maltose, the products are 1 part of maltose and 2 parts of isomaltose, whereas in the presence of maltose the products depend on several factors, but the limit is 2 parts of maltose to 1 part of isomaltose. The optimum temperature is about  $50^\circ$ . In the presence of maltose, amylopectin undergoes hydrolysis with malt diastase, one-third being converted into maltose and the remainder into stable dextrin. Stable dextrin is not produced by the hydrolysis of  $\alpha\beta$ -hexa-amylose with malt diastase under these conditions.

Stable dextrin has been isolated in almost theoretical yield from

the products of the action of malt diastase on starch at 40°, as a white powder having  $[\alpha]_D$  185° and  $R$  14. It appears to be a mixture of two substances, as it can be fractionated by 86% alcohol into a soluble portion having  $[\alpha]_D$  174.6°,  $R$  38.7, and  $M=693$ , almost identical with the maltodextrin- $\beta$  of Ling and Baker (T., 1895, 67, 702, 739); the other component has a much higher molecular weight and probably contains  $C_{24}$ . The components are believed to be present in the proportion of 1 part of the substance corresponding with maltodextrin- $\beta$  and 2 parts of the tetra-amylose. The fundamental unit of stable dextrin is regarded as composed of four hexose residues and consists partly of a closed-chain and partly of an open-chain complex. When stable dextrin is hydrolysed, there is no appreciable difference in the velocity of reaction whether maltose is present or absent. When hydrolysed with malt diastase in the presence of 80% of maltose equal parts of maltose and isomaltose are formed. Stable dextrin is acted on slowly by maltase to form isomaltose, and by emulsin, giving isomaltose and dextrose. C. J. S.

**Starch. IV. Nature of the Amylohemiacellulose Constituent of certain Starches.** A. R. LING and D. R. NANJİ (*J. Chem. Soc.*, 1925, 127, 652—656).—The hemicellulose present in certain starches, such as barley, wheat, rice, etc., is not acted on by the diastase of unmalted barley at 50°, whilst the other two constituents of the starches are hydrolysed or rendered soluble by this enzyme. By this means, "amylohemiacellulose" may be isolated from starch. Hemicellulose is a white powder practically insoluble in water, and when hydrolysed with dilute mineral acids silica separates from the liquid; it contains 1.2—1.3% of ash, consisting mainly of calcium, magnesium, iron, silica, and phosphoric acid. The amounts of calcium, magnesium, and phosphoric acid vary considerably, but the silica content remains between 0.83% and 0.92%. Hemicellulose is regarded as a calcium-magnesium or iron salt of a silicic ester. Malt diastase causes hydrolysis of the hemicellulose, with the production of maltose as the sole final product; the optimum temperature of the conversion lies between 50° and 55°, and scarcely any hydrolysis occurs at 70°. This behaviour on hydrolysis is taken as indicating that hemicellulose is a derivative of  $\alpha$ -hexa-amylose, possibly formed from this by esterification with silicic acid.

Amylohemiacellulose occurs in rice, wheat, and barley starches in the proportions 19.15%, 10.0%, and 7.68%, respectively. C. J. S.

**Cellulose. XI. Trimethylcellulose-A and its Scission.** K. HESS and W. WELTZIEN (*Annalen*, 1925, 442, 46—60).—By increasing the alkali concentration in the latter stages of the methylation (cf. A., 1924, i, 146) to the proportion sodium hydroxide/water=2/1, and using a large excess of alkali over the methyl sulphate, the authors have obtained a trimethylcellulose-A containing approximately 45% of methoxyl. Extensive hydrolysis of the methyl sulphate is avoided by working at lower temperatures (50—60°), whilst the insolubility of the methylated product prevents

its destruction or alteration by the excess of alkali, its solubility in alkali decreasing as the methoxyl content increases. The state of division of the original cellulose is immaterial, but improved results are obtained if the initial material is dissolved in water and solid sodium hydroxide added, thereby precipitating the methylated product in a finer state of division. It is probable, however, that a decrease in the acid character of the cellulose molecule with progressive methylation as well as the alteration in solubility is the cause of the difficulty experienced in obtaining a product having a methoxyl content corresponding with three methoxyl groups. The yield amounts after 10 methylations to about 47.5% of the theory on the cellulose-*A* used, and identical products are obtained whether the first four methylations are performed with barium hydroxide and methyl sulphate as previously described (*loc. cit.*) or not. The trimethylcellulose-*A* (OMe = 45.1%) appears to be identical with the product similarly obtained from hydrocellulose. These results are confirmed by similar figures obtained on attempting to fractionate the substances with cold water; the trimethyl derivative from cellulose-*A* gives slightly higher rotatory powers throughout than the corresponding fractions from hydrocellulose. The solution of trimethylcellulose-*A* in water, however, appears not to be a true solution but a colloidal dispersion with fluctuating aggregates. On treatment with 1% methylalcoholic hydrogen chloride, both trimethylcellulose-*A* and trimethylhydrocellulose are immediately converted into trimethylglucose methylglucoside (yield 88%), identical with the product obtained by Irvine (T., 1923, 123, 518) from insoluble trimethylcellulose. Accordingly, trimethylcellulose is regarded as possessing a characteristic  $\alpha$ -configuration, a conclusion supported by the conversion of trimethylglucose (under similar conditions) into the  $\alpha$ -glucoside. Hydrolysis with 5% hydrochloric acid at 100° converts the methylglucoside into  $\beta\gamma\delta$ -trimethylglucose (yield 96%), corresponding in properties with that described by Denham and Irvine (T., 1917, 111, 248). The final rotatory values for the trimethylglucose on the addition of alkali do not agree with those obtained by Irvine. On treatment with acetyl bromide and hydrogen bromide at 0°, trimethylcellulose-*A* yields a product, b. p. 160—180°/1 mm., OMe about 25%, indicating that at least one methyl group has been eliminated.

In view of the above results, the difference between the soluble cellulose-*A* and the more stable alkali-cellulose from cotton is attributed to the greater insolubility of the natural cellulose in alkali. The greater reaction surface afforded by the soluble cellulose-*A* also tends to promote its chemical change. Accordingly, either no profound chemical change takes place in the formation of trimethylcellulose, or such change, if proceeding, occurs exactly to the same extent, in addition to the alkylation, in both the soluble and insoluble forms.

R. B.

**Cellulose of Jute.** A. LEHNE and W. SCHEPMANN (*Z. angew. Chem.*, 1925, 38, 93—98).—An average sample of clean jute showed :

moisture, 11.42; ash, 0.73; fat and resin (benzene-alcohol extract), 1.03; aqueous extract, 3.84; cellulose, 69.63; lignin, 18.83. Raw jute gave 11.38% of furfuraldehyde, crude jute cellulose prepared by Sieber and Walter's method, 8.35, and purified jute cellulose freed from hemicelluloses, 2.41%, all calculated on dry material. Purification of the jute cellulose was effected by treatment with 17% sodium hydroxide solution. On complete saccharification with 41.4% hydrochloric acid at 23° according to Willstätter and Zechmeister's method under identical conditions, jute cellulose yields the same amount of dextrose as cotton cellulose, and the rate of saccharification is identical at every stage for the two celluloses. Under the same conditions, raw jute yields cupric-reducing sugar equivalent to the cellulose contained; no products of saccharification are contributed by the lignin. The rate of saccharification stands in constant ratio of 10 : 6 to that of cotton cellulose, the increased velocity corresponding with the higher concentration of hydrolysing agent per unit of hydrolysed product. The identity of the law of saccharification of raw jute as compared with cotton cellulose points to the absence of chemical union between the lignin and cellulose in jute. J. F. B.

**Action of Dilute Acids on Wood Cellulose.** R. SIEBER (*Papier-Fabr.*, 1925, 23, 127—131).—The "baryta-resistance value" is taken as a measure of the normal undegraded cellulose in wood cellulose. By suitable treatment of bleached sulphite-cellulose, a purified pulp was prepared having a baryta resistance value of 98.3%. This pulp was boiled with sulphuric acid of different concentrations for 4 hours and the progressive hydrolysis of the resistant cellulose was measured by the decrease in the baryta-resistant cellulose and the formation of baryta-soluble cellulose and soluble carbohydrates and sugars. With concentrations below *N*-sulphuric acid, the formation of fermentable sugar was relatively small, the degradation of the resistant cellulose yielding mainly baryta-soluble cellulose and non-fermentable sugars. Above that concentration, the formation of fermentable sugar increased considerably, but at the expense of the soluble non-fermentable carbohydrates. The conversion of baryta-resistant into baryta-soluble cellulose increased as the concentration of the hydrolysing acid was increased. The hydrolysis of the pentosans was inconsiderable until a concentration of 3*N*-sulphuric acid was employed. Hydrolysis of ordinary unpurified sulphite-celluloses yielded practically the same products as the purified, so far as the relation between the concentration of hydrolysing acid and the proportion of the total cellulose converted into non-resistant cellulose and sugar were concerned. J. F. B.

**Hydro- and Oxy-cellulose.** K. HESS (*Papier-Fabr.*, 1925, 23, 122—127).—The hydrocellulose of Knoevenagel and Busch prepared from viscose-cellulose appears to be homogeneous in that it is completely soluble in 8% sodium hydroxide solution and quantitatively precipitated by acidifying the solution. Nevertheless, it is possible to fractionate this substance by precipitating the



solution by ammonia and to obtain from it cellulose-A with a low cupric-reducing value. This cellulose-A (cf. this vol., i, 118) is structurally intact cellulose and in "cuprammonium" solution it has the same optical activity as the original cellulose. Hydrocellulose is therefore a mixture of cellulose or cellulose-A with cellulose-dextrins. These latter are of unknown constitution and themselves are probably complex mixtures. The first definite product of hydrolysis of cellulose which has been characterised is *isocellobiose* of Ost and Prosiegel, which, however, is a true sugar. The position with regard to oxycellulose is very similar. No definite product of oxidation can be characterised in the solid oxycellulose; the only true oxidation products, such as saccharic acid and carbon dioxide, are found externally in the medium. Any attached oxidised groupings existing in the products cellulose or cellulose-A are entirely uncharacterised and in such minor quantities as to be regarded as mechanically adherent. The strong development of carbonyl groups has indeed still to be accounted for, but the hypothesis which presumes the formation of a glycuronic acid residue on the basis of the furfuraldehyde reaction is unacceptable on experimental grounds. J. F. B.

**Alkali-cellulose. I.** E. HEUSER and W. NIETHAMMER (*Cellulose-Chem.*, 1925, 6, 13—18; cf. this vol., i, 119).—The indirect method of Vieweg is generally applicable to the study of the reaction between cellulose and alkali hydroxide, and in the hands of several investigators has led to the definite establishment of the formation of the compound  $(C_6H_{10}O_5)_2 \cdot NaOH$ . A similar compound with potassium hydroxide is also produced. Gladstone's direct method by washing with alcohol is only applicable under certain conditions. The use of alcohol tends to concentrate the alkali hydroxide on the fibre otherwise than by chemical combination. This effect can be counteracted and consistent lower results obtained by washing the alkali-cellulose with cold 90% alcohol and then extracting in a Soxhlet apparatus with warm absolute alcohol at 50°. The flattening in the absorption curve indicative of chemical combination is then distinctly shown at concentrations of about 16 g. of sodium hydroxide per 100 c.c. By this method also, the absorption of sodium hydroxide by various types of modified cellulose may be studied. These modified derivatives all absorb considerably more alkali hydroxide than normal cellulose, and the quantity increases as the degree of modification or depolymerisation is more profound. Cellulose regenerated from "cuprammonium" solution and Girard's hydrocellulose are modifications which are not very far depolymerised, absorbing more than normal cellulose and about equal amounts. Various oxycelluloses are further degraded and give higher values, whilst the highest absorptions are shown by the hydrocellulose prepared from viscose by the method of Knoevenagel and Busch. [Cf. also this vol., i, 369, 370.] J. F. B.

**Alkali-cellulose. II.** E. HEUSER and R. BARTUNEK (*Cellulose-Chem.*, 1925, 6, 19—26).—The formation of the compound  $(C_6H_{10}O_5)_2 \cdot NaOH$  is well established, but the existence of the

higher stage of chemical combination indicated by Vieweg as  $C_6H_{10}O_5$ , NaOH is not confirmed, and the phenomena which suggest it are more probably due to adsorption. In the case of lithium and potassium hydroxides, the limit of chemical combination is definitely marked in the proportions of  $2C_6H_{10}O_5$  to 1 mol. of base and with rubidium and caesium hydroxides at  $3C_6H_{10}O_5$  to 1 mol. of base; in all these cases, there are no signs of higher combination with largely increased concentrations. Swelling of the fibre measured microscopically proceeds with increase of concentration up to the point corresponding with the formation of the chemical compound in each case. The maximum amount of swelling is reached with these different alkali hydroxides at the same concentrations as the maximum electrical conductivities of their solutions and varies with the degree of hydration of the alkali ions. The ions with lowest atomic volumes are associated with the highest number of water molecules, and it appears that when the alkali ion enters into combination with the cellulose molecule it carries with it its associated water and distends the cellulose. Thus the maximum swelling with lithium hydroxide is 97; with sodium, 78; with potassium, 64; with rubidium, 53; with caesium, 47%. After the whole of the cellulose molecules have reacted with the alkali ions to form alkali-cellulose, further increase in concentration induces a lowering of the degree of swelling and of hydration, and this decrease takes place in the same order, namely, lithium most and caesium least. The fact that the alkali-cellulose compound is not formed in alcoholic solutions supports the view as to the ionic nature of the alkali-cellulose reaction.

J. F. B.

**Conversion of Lignin, Cellulose, and Wood into Humic Substances by Fungi.** C. WEHMER (*Brennstoff-Chem.*, 1925, 6, 101—106).—Previous work (A., 1915, i, 197) on the degradation of lignin, cellulose, and wood by fungi (e.g., *merulius*, *conioophora cerebella*, *polyporus vaporarius*) has been extended. Cellulose is decomposed but lignin in the free state is not attacked. Experiments with wood paper and wood, however, show that the ligno-cellulose is decomposed, the cellulose disappears, and the lignin is converted into humic acids. A microscopic section shows an alteration in the structure of the cell-wall. In coal and peat formation, it is suggested that a similar decomposition of the plant tissues by fungi takes place.

A. C. M.

**Humic Acids. VII. Properties and Reactions of Humic Acids and Humins.** W. ELLER [with G. HELMRICH, D. KLEMM, E. HAUBOLD, and A. SCHÖPPACH] (*Annalen*, 1925, 442, 160—180; cf. A., 1923, i, 542, 543, 544).—The carbon content of the products of the action of molten potassium hydroxide on humin from lignite and quinol-humic acid or on natural, quinol-, nitrogenous quinol-, or carbohydrate-humic acids is uniformly considerably higher than that of the initial materials, so that the hypothesis that humins are transformed into humic acids by molten potassium hydroxide cannot be accepted. The ash content of the natural products is greatly diminished by the process, and in some cases completely

removed. The loss of nitrogen is only partial, thus affording evidence of a mainly constitutive and not absorptive union of the element. Attempts to remove ammonia from humic acids by intensive dialysis did not lead to a diminution of the nitrogen content, whilst distillation of humic acid from aminophenols or quinol in ammoniacal solution or of nitrogen-free humic acids which had been treated with ammonia with concentrated potassium hydroxide solution caused the elimination of only 8—32% of the nitrogen as ammonia. Treatment of natural, quinol-, and carbohydrate-humic acids with phosphorus and hydriodic acid under pressure yields an insoluble residue, an acid substance, and a mixture of hydrocarbons which are closely similar among themselves and also with the products obtained by Willstätter and Kalb (A., 1922, i, 989) from lignin and carbohydrates. It is considered that this similarity is due to the decomposition of the different molecules under the drastic experimental conditions into similar fragments which probably suffer subsequent condensation amongst themselves and not to the analogous constitution of the original molecules. Dry distillation of quinol-, carbohydrate-, or natural humic acids gives only a very small proportion of tar consisting mainly of acidic substances, probably phenols.

H. W.

#### Relation between Constitution and Taste of $\alpha$ -Amino-acids.

A. HEIDUSCHKA and E. KOMM (*Z. angew. Chem.*, 1925, **38**, 291—294; cf. Cohn, "Die organischen Geschmacksstoffe," Berlin, 1914, and Paul, A., 1923, i, 167).—By careful comparison with graded standard solutions of sucrose, quantitative values for the "degree of sweetness" and the "molecular degree of sweetness" of glycine, sarcosine, *dl*-alanine, and *d*-alanine were obtained. The results showed that the connexion between molecular weight and degree of taste is not a simple one, and that stereochemistry must be taken into consideration. [Cf. B., May 29th.]

B. W. A.

**Relatively Asymmetric Synthesis in the Case of Complex Salts of Heavy Metals.** J. LIFSCHITZ (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 721—725).—From pure *d*-alanine, the red *isomeride* of the tri-*d*-alanine cobaltic salt was obtained by boiling with cobaltic hydroxide (Ley's method). From the mother-liquor, the  $\alpha$ -salt (+H<sub>2</sub>O) was obtained. The mother-liquor of the  $\alpha$ -salt contained an extremely soluble and a more deeply coloured  $\alpha'$ -salt, which was isolated with some difficulty by repeated precipitation from a fairly concentrated solution in 97% alcohol. Curves are given for the rotations of the three salts in water and in 50% sulphuric acid. From an analysis of both the  $\alpha$  and the  $\alpha'$  complexes, it was found that both salts are trialanine complexes, differing only in the degree of hydration. Cryoscopic measurements of the molecular weight of the  $\alpha'$  salt gave values in accordance with a uninuclear constitution. It is concluded that the  $\alpha$  and  $\alpha'$  compounds are the partly asymmetric antipodes *d*-[Co-*d*-alanine<sub>3</sub>] and *l*-[Co-*d*-alanine<sub>3</sub>], a relatively asymmetric synthesis of such inorganic compounds, occurring as if they are prepared from an inactive metallic salt and active co-ordinating molecules, thus being realised.

This conclusion is strongly supported by a study of the rotation curves.  
L. L. B.

**New Hydroxyurethanes and Chromoisomeric Silver Salts of their Acyl Derivatives.** R. E. OESPER and W. A. COOK (*J. Amer. Chem. Soc.*, 1925, **47**, 422—428).—The *n*-propyl, *n*-butyl, and isoamyl derivatives of carboxyhydroxamic acid,  $\text{NH}(\text{OH})\cdot\text{CO}_2\text{R}$ , prepared by Jones' method (A., 1898, i, 172), formed pale yellow oils which could not be purified. Their benzoyl esters (cf. A., 1914, i, 1168) were also oils. The following substituted benzoyl derivatives, obtained by the interaction of sodium salts of the acids and the substituted benzoyl chlorides in ethereal suspension, are described: *p*-chlorobenzoyl carbethoxyhydroxamate, m. p. 75—76° (silver salt, m. p. 210°; *N*-ethyl derivative, liquid); *p*-chlorobenzoyl carbo-*n*-propoxyhydroxamate, m. p. 38° (*N*-ethyl derivative, liquid); *m*-nitrobenzoyl carbethoxyhydroxamate, m. p. 88—89° (*N*-ethyl derivative, m. p. 67—68°); *m*-nitrobenzoyl carbo-*n*-propoxyhydroxamate, m. p. 59° (*N*-ethyl derivative, m. p. 38°); *m*-nitrobenzoyl carbo-*n*-butoxyhydroxamate, m. p. 44° (*N*-ethyl derivative, m. p. 57°); *p*-nitrobenzoyl carbethoxyhydroxamate, m. p. 92° (*N*-ethyl derivative, liquid); *p*-nitrobenzoyl carbo-*n*-propoxyhydroxamate, m. p. 75° (silver salt, m. p. 235°; *N*-ethyl derivative, m. p. 43°); and *p*-nitrobenzoyl carbo-*n*-butoxyhydroxamate, m. p. 74° (*N*-ethyl derivative, liquid). Certain of the above silver salts exhibit chromoisomerism, but in those cases where the two modifications could be isolated, the same *N*-ethyl derivatives were obtained from both forms by the action of ethyl iodide. Benzoyl carboisoamyloxyhydroxamate (A., 1914, *ibid.*) gave a yellow silver salt, m. p. 141—142° after becoming paler at 88°. The dibenzoyl derivative has m. p. 65°, and it is concluded that the product originally described is derived from an isomeric amyl alcohol. Certain *N*-benzyl derivatives of the above benzoyl carbalkoxyhydroxamates were prepared by heating the appropriate silver salts with benzyl chloride in chloroform. As the constitution of the above *N*-ethyl derivatives could only be deduced from their hydrolysis products, and as the possibility of migration of an alkyl group, during hydrolysis, from nitrogen to oxygen, is not excluded, certain isomeric *o*-alkyl ethers,  $\text{OEt}\cdot\text{C}(\text{OR})\cdot\text{NBz}$ , were prepared according to the scheme  $\text{NH}\cdot\text{C}(\text{OEt})(\text{CN}) + \text{NaOR} \rightarrow \text{NH}\cdot\text{C}(\text{OEt})(\text{OR})$  (cf. A., 1896, i, 71);  $\text{NH}\cdot\text{C}(\text{OEt})(\text{OR}) + \text{NH}_2\text{OH}\cdot\text{HCl} \rightarrow \text{C}(\text{OEt})(\text{OR})\cdot\text{NOH}$  (cf. A., 1913, i, 958);  $\text{C}(\text{OEt})(\text{OR})\cdot\text{NOH} + \text{Ph}\cdot\text{COCl} + \text{NaHCO}_3 \rightarrow \text{C}(\text{OEt})(\text{OR})\cdot\text{N}\cdot\text{O}\cdot\text{COPh}$  (cf. A., 1886, 216). Ethyl *n*-propyl-, m. p. 151—152°; ethyl *n*-butyl-, m. p. 148—149°, and ethyl isoamyl-benzoyloximidocarbonate, m. p. 156—157°, are described, all of which gave hydroxylamine on hydrolysis, whilst the above *N*-ethyl derivatives all yielded similarly  $\beta$ -ethylhydroxylamine.  
F. G. W.

**Configuration of  $\alpha$ -Aminohexonic Acids and of  $\alpha$ -Amino-hexoses.** P. A. LEVENE (*J. Biol. Chem.*, 1925, **63**, 95—101).—A theoretical discussion of the known optical properties of the hexonic and  $\alpha$ -aminohexonic acids and their derivatives, together

with arguments by analogy from the behaviour of the  $\alpha$ -thio- and  $\alpha$ -sulpho-acids leads to the conclusion that those hexonic and aminohexonic acids should be classified as *d*-acids the salts of which are more strongly dextrorotatory than the free acids, and, conversely, the *l*-acids are those the salts of which are more strongly lævorotatory. The adoption of this classification would involve the assumption that the deamination by nitrous acid of an amino-hexonic acid proceeds without Walden inversion. C. R. H.

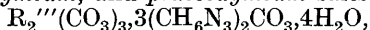
**Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. IV. Influence of Substitution in the Amide Group on the Reactivity of the Halogen Atom in Bromomalonamide.** R. W. WEST (*J. Chem. Soc.*, 1925, 127, 748—753).—Determinations of the velocity coefficients of the reaction  $\text{:CHBr} + \text{HI} = \text{:CH}_2 + \text{IBr}$ , when applied to substituted malonamides, show that the reactivity of the bromine atom is influenced by the proximity of certain common groups, which can be arranged in the following ascending order:  $\text{NH}_2$ ,  $\text{NHMe}$ ,  $\text{NHEt}$ ,  $\text{NHPr}^s$ ,  $\text{NH}\cdot\text{C}_4\text{H}_9(\text{iso})$ ,  $\text{NH}\cdot\text{CH}_2\text{Ph}$ ,  $\text{OH}$ ,  $\text{OEt}$ ,  $\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}(p)$ ,  $\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}(p)$ .

The values of  $k_3$  at  $25^\circ$ , calculated from the empirical formula,  $\log k_3 = 0.9 \log k_1 + 0.474 \log k_2$ , where  $k_2 < k_1$ , are in good agreement with the experimental figures. At  $30.2^\circ$ , the experimental results are expressed approximately by the equation  $\log k_3 = 0.7 \log k_1 + 0.522 \log k_2$ .

During the course of the investigation a number of new compounds were prepared: *Malondiisopropylamide*, m. p.  $114^\circ$ ; *malonethylamide*, m. p.  $123^\circ$ ; *malonisopropylamide*, m. p.  $129^\circ$ ; *malonisobutylamide*, m. p.  $83^\circ$ ; *malonethylisopropylamide*, m. p.  $98^\circ$ ; *malonphenylmethylamide*, m. p.  $154^\circ$ ; *malon-p-tolylmethylamide*, m. p.  $183^\circ$ ; *malon-p-tolyloethylamide*, m. p.  $176^\circ$ ; *malon-p-tolylisopropylamide*, m. p.  $192^\circ$ ; *malon-p-tolylisobutylamide*, m. p.  $177^\circ$ ; *malonbenzyl-p-tolylamide*, m. p.  $188^\circ$ . From these compounds the following bromo derivatives were prepared: *Bromomalondiisopropylamide*, m. p.  $204^\circ$ ; *bromomalon-p-bromophenylmethylamide*, m. p.  $187^\circ$ ; *bromomalon-p-tolylmethylamide*, m. p.  $186^\circ$ ; *bromomalon-p-tolyloethylamide*, m. p.  $178^\circ$ ; *bromomalonbenzyl-p-tolylamide*, m. p.  $167^\circ$ ; *bromomalonethylamide*, m. p.  $161^\circ$ ; *bromomalonisobutylamide*, m. p.  $156^\circ$ ; *bromomalon-p-bromophenylethylamide*, m. p.  $179^\circ$ ; *bromomalon-p-tolylisopropylamide*, m. p.  $179^\circ$ ; *bromomalon-p-tolylisobutylamide*, m. p.  $148^\circ$ ; *bromomalonisopropylamide*, m. p.  $192^\circ$ ; *bromomalonethylisopropylamide*, m. p.  $172^\circ$ ; *bromomalon-p-tolylamide*, m. p.  $202^\circ$ ; *bromomalondi-p-tolylamide*, m. p.  $217^\circ$ .

C. J. S.

**Double Carbonates of Guanidine with Rare-earth Metals.** G. CANNERI (*Gazzetta*, 1925, 55, 39—44).—Successive quantities of the freshly-precipitated hydroxide of the rare-earth metal are digested with a cold, saturated guanidine carbonate solution and the clear liquid finally obtained is allowed to crystallise. *Yttrium*, *lanthanum*, *neodymium*, and *praseodymium* salts,



are thus prepared. Thorium hydroxide dissolves freely in concentrated guanidine carbonate solution, yielding *thorium guanidine carbonate*,  $\text{Th}(\text{CO}_3)_2 \cdot 3(\text{CH}_6\text{N}_3)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ . W. E. E.

### Double Acetates of Rare-earth Metals with Organic Bases.

G. CANNERY (*Gazzetta*, 1925, **55**, 33—39).—The rare-earth metals of the cerium and yttrium group give isomorphous compounds of the type  $\text{R}'''(\text{OAc})_3 \cdot \text{C}(\text{NH})(\text{NH}_2)_2 \cdot 2\text{CH}_3 \cdot \text{CO}_2\text{H}$ . The following double salts, obtained by crystallising mixed solutions of their constituents, are of this class: *Cerous guanidine acetate*, *lanthanum guanidine acetate*, *neodymium guanidine acetate*, *praseodymium guanidine acetate*, *yttrium guanidine acetate*. A solution containing guanidine acetate in excess yielded a second *neodymium guanidine acetate*,  $\text{Nd}(\text{OAc})_3 \cdot 2\text{C}(\text{NH})(\text{NH}_2)_2 \cdot 2\text{CH}_3 \cdot \text{CO}_2\text{H}$ . By vacuum concentration over sulphuric acid of thorium hydroxide dissolved in an acetic acid solution of guanidine, *thorium guanidine acetate*,  $\text{Th}(\text{OAc})_4 \cdot 2\text{C}(\text{NH})(\text{NH}_2)_2 \cdot 2\text{CH}_3 \cdot \text{CO}_2\text{H}$ , is obtained. *Cerous carbamide acetate* and *lanthanum carbamide acetate* are obtained by spontaneous evaporation of the rare-earth metal acetate in presence of very little carbamide acetate. *Neodymium carbamide acetate* is obtained in the same way as neodymium guanidine acetate. The above three compounds are of the type  $\text{R}'''(\text{OAc})_3 \cdot 3\text{CO}(\text{NH}_2)_2$ , and are probably isomorphous.

Fractional crystallisation of the acetates of the elements of the cerium group with guanidine acetate in dilute acetic acid solution promises to afford a method of separating these metals.

W. E. E.

### Electrolytic Preparation of Semicarbazide Sulphate. L. J.

BIRCHER, A. W. INGERSOLL, B. F. ARMENDT, and G. COOK (*J. Amer. Chem. Soc.*, 1925, **47**, 391—394).—A suspension of nitrocarbamide (50 g.) in 20% sulphuric acid (600 c.c.), vigorously stirred, forms the catholyte of a two-fluid cell, the cathode being a layer of mercury of area 215 cm.<sup>2</sup> The anolyte is 20% sulphuric acid, with a coiled strip of lead, of the same area as the cathode, for anode. The cell is maintained at 5—10°, and a current of 0.06 amp./cm.<sup>2</sup> passed through the cell until the nitrocarbamide has all dissolved, and for 30 mins. longer, the total time required being about 4½ hrs. The catholyte is filtered, and evaporated to 150 c.c. under reduced pressure, below 45°. Semicarbazide sulphate separates on cooling, in a yield of 67—70% (cf. T., 1901, **79**, 1326; A., 1912, i, 339; 1922, i, 723). Crude, washed, and air-dried nitrocarbamide, as obtained from carbamide nitrate by the method of Thiele and Lachmann, may be used in the above preparation with only slight reduction of yield. F. G. W.

**Derivatives of Cyanamide.** E. FROMM.—(See i, 594.)

**Action of Ammonia on Cyanamide.** A. COUDER (*Compt. rend.*, 1925, **180**, 926—928).—Ammonia is energetically absorbed by cyanamide at the ordinary temperature to form a colourless liquid which appears to be a solution of cyanamide in liquid

ammonia, from which crystals of dicyanodiamide are slowly deposited, the change to the dimeride being complete at 0° in about 20 days. Various physical determinations demonstrate the absence of any polymerisation in the freshly-prepared solution, yet if the ammonia be driven off, the residue is dicyanodiamide. This is interpreted on the assumption that ammonia and cyanamide form a complex which dissociates irreversibly into ammonia and dicyanodiamide.

J. S. C.

**Action of Hydrogen on Calcium Cyanamide.** W. BOBROW-NICKI (*Przemysł Chem.*, 1924, 8, 7—14; from *Chem. Zentr.*, 1924, ii, 1740—1741).—In the preparation of calcium cyanamide by the action of nitrogen on calcium carbide, appreciable amounts of hydrogen are formed owing to the action of the moisture present on calcium, calcium silicide, and magnesium silicide, also occurring as impurities in the calcium carbide. At 400°, hydrogen reacts with calcium cyanamide, yielding ammonia,  $\text{CaCN}_2 + 3\text{H}_2 = \text{Ca} + \text{C} + 2\text{NH}_3$ . The side reactions,  $\text{Ca} + \text{H}_2 = \text{CaH}_2$ , and  $3\text{Ca} + 2\text{NH}_3 = \text{Ca}_3\text{N}_2 + 3\text{H}_2$ , also occur. At 600°, the formation of hydrogen cyanide begins. The liberation of nitrogen increases as a linear function of the temperature from 500° to 900°. The formation of ammonia reaches a maximum at about 600°, whilst that of hydrogen is at maximum at 650°. The assumption that calcium, calcium hydride, and calcium nitride are formed is rendered probable, since these substances are known to catalyse the combination of hydrogen with nitrogen at 600°. Calcium hydride is responsible for the presence of methane in the gaseous products. Ammonia is produced by the action of nitrogen on calcium cyanamide previously treated with hydrogen. The small yield of ammonia under such conditions is attributed to the effect of excess of nitrogen on the reversible reaction,  $3\text{H}_2 + \text{N}_2 \rightleftharpoons 2\text{NH}_3$ .

G. W. R.

**Potassium Ferrocyanide from Sodium Ferrocyanide and Potassium Chloride.** W. DOMINIK (*Przemysł Chem.*, 1924, 8, 97—108; from *Chem. Zentr.*, 1924, ii, 1740).—It should be advantageous to prepare sodium ferrocyanide from ferrous sulphate and sodium cyanide, subsequently converting it into the potassium salt by the action of potassium chloride, but the solubility relationships of the salts in question render this difficult. Better results may be obtained in aqueous ethyl-alcoholic solution. A 100% excess of potassium chloride is required. In an aqueous solution of potassium and sodium chlorides, the required excess of potassium chloride is generally greater than this, and increases with decrease in the temperature of crystallisation.

G. W. R.

**A Nitroprusside of Bivalent Iron.** A. UNGARELLI (*Gazzetta*, 1925, 55, 118—127).—The action of sodium hyponitrite on Hofmann's sodium aquoferropentacyanide (A., 1896, i, 517; 1900, i, 591) yields *sodium hyponitritoferropentacyanide*,  $[\text{Fe}(\text{CN})_5\text{NO}]\text{Na}_4 + 5\text{H}_2\text{O}$ , which responds to the reactions common to all ferropenta-

cyanides. Attempts to oxidise this compound to  $[\text{Fe}(\text{CN})_5\text{NO}]\text{Na}_3$  proved unsuccessful.

T. H. P.

**Additive Compound of Triethylphosphine and Carbon Disulphide.** J. P. WIBAUT (*Rec. trav. chim.*, 1925, **44**, 239—240).—The additive compound,  $\text{PET}_3\text{CS}_2$ , described by Hofmann (*Ann. Suppl.*, 1861, **1**, 26) melts at  $121\text{--}122^\circ$  (after sintering at  $118\text{--}119^\circ$ ), and not at  $95^\circ$  as recorded in the literature.

G. M. B.

**Bismuth Compounds.** E. MASCHMANN (*Arch. Pharm.*, 1925, **263**, 99—107).—From a consideration of the relative positions of arsenic, antimony, and bismuth in the periodic classification, and a survey of the chemico-therapeutical literature, the conclusion is reached that organic derivatives of bismuth are not necessarily those in which the element displays its most useful therapeutical properties, but that these are to be sought in compounds in which the metallic nature of the element is only slightly masked. The following substances, all prepared from bismuth nitrate, and all solids, are described (in the sugar and alcohol derivatives the group  $\text{BiNO}_3$  replaces two hydrogen atoms in the original sugar or alcohol): *sodium tribismuthyl tartrate*,  $\text{C}_6\text{H}_2\text{O}_9\text{Bi}_3\text{Na}\cdot 2\text{H}_2\text{O}$ ; *xylose*, *arabinose*, *sucrose*, *maltose*, and *mannose bismuth nitrates*, and the *sodium salt* of the latter; *erythritol*, *arabitol*, *sorbitol*, and *dulcitol bismuth nitrates*, and the corresponding *alkali-bismuth oxide-alcohols*, obtained by the action of alkali hydroxide on the nitrates.

B. F.

**Constitution of Grignard's Magnesium Compounds. II.** J. MEISENHEIMER (*Annalen*, 1925, **442**, 180—210; cf. Meisenheimer and Casper, A., 1921, i, 654).—According to Hess and Rheinboldt (A., 1921, i, 777), the primary product of the action of magnesium ethyl bromide on benzaldehyde is an additive compound,  $\text{Ph}\cdot\text{CHO}\cdots\text{MgEtBr}$ , which yields phenylethylcarbinol when decomposed by water, but passes in the presence of boiling benzene into ethylene and the compound  $\text{Ph}\cdot\text{CHO}\cdots\text{MgHBr}$ , from which benzyl alcohol is obtained on addition of water; similar observations are recorded with crotonaldehyde and cinnamaldehyde (Hess and Wustrow, A., 1924, i, 859). It is difficult, however, to perceive in what manner the primary additive compound yields phenylethylcarbinol instead of regenerating the aldehyde, particularly as the similar compounds from acetomesitylene and magnesium ethyl iodide (cf. Klages, A., 1902, i, 666) and from ethylene oxide and magnesium ethyl bromide (cf. Blaise, A., 1902, i, 357; Grignard, A., 1903, i, 552) yield acetomesitylene and ethylene oxide, respectively, when treated with water. Hess' conception also does not explain the observation that the formation of benzyl alcohol is not observed even in boiling benzene if an excess of magnesium ethyl halide is used. The action of benzaldehyde on magnesium alkyl halides has therefore been reinvestigated. Benzyl alcohol and phenylethylcarbinol are determined in mixtures by taking advantage of the fact that the primary alcohol is converted by *p*-nitrobenzoyl chloride into the corresponding ester,



whereas the carbinol is esterified to only a slight extent and transformed mainly into  $\alpha$ -chloro- $\alpha$ -phenylpropane. The process is sufficiently accurate if the mixture contains not less than 10% of benzyl alcohol, whereas the results obtained by fractional distillation are untrustworthy. The action of molecular proportions of magnesium ethyl bromide or iodide and benzaldehyde in ice-cold ethereal solution leads, if the duration of the action is short, mainly to phenylethylcarbinol; much benzaldehyde remains unattacked, whilst benzyl alcohol and by-products of high boiling point are not formed. After 3 hours at the atmospheric temperature, the presence of benzyl alcohol can be detected, the amount of unchanged aldehyde is diminished and that of the carbinol increased; after 24 hours, very little aldehyde remains, but the production of a greater proportion of benzyl alcohol could not be established with certainty. If the ether is removed immediately after addition of the reactants is complete and the residue is boiled for 3 hours with benzene, the products contain benzyl alcohol (10—20% of the aldehyde used) and a large proportion of constituents of high boiling point. If the Grignard reagent and aldehyde are used in the proportion 3 : 2, phenylethylcarbinol is obtained in excellent yield from the cold solution after 24 hours, whereas benzyl alcohol and by-products of high b. p. are not produced; if, however, the aldehyde is in excess (3 : 2) much benzyl alcohol (more than 30%) is formed, and this proportion can be increased if the ether is removed and the residue boiled with benzene; in spite of the large excess, very little or no aldehyde can be recovered and the proportion of residue of high b. p. is very considerable. The use of ether-free, organo-magnesium compounds with benzene as solvent leads uniformly to higher yields of benzyl alcohol. If the mixture is decomposed immediately after addition of the reactants is complete, little or no benzyl alcohol is produced and much aldehyde is recovered. After 3 hours, little aldehyde remains and the yield of benzyl alcohol is 10—15%, whilst after 24 hours the aldehyde has disappeared and the yield of benzyl alcohol increased to 15—22%; the residue of high b. p. is insignificant. Boiling the benzene solution increases greatly the formation of by-products without greatly affecting the yield of benzyl alcohol. With an excess of magnesium ethyl iodide, the production of benzyl alcohol and by-products is not observed even under these conditions, and the yield of phenylethylcarbinol is excellent. When aldehyde is in excess relatively little phenylethylcarbinol is formed, but much benzyl alcohol and by-products. Replacement of magnesium ethyl halides by magnesium *isobutyl* bromide invariably causes increased production of benzyl alcohol. In general, the temperature of the reaction has relatively little influence on the yields of benzyl alcohol, the main factors being the nature of the solvent and, above all, the relative proportions of the reactants. The course of the reaction is readily explained by the assumption of the formation of a moderately stable, additive compound,  $\text{Ph}\cdot\text{CHO}\cdots\text{MgEtBr}$ , which normally becomes transformed into the substance  $\text{Ph}\cdot\text{CHEt}\cdot\text{O}\cdot\text{MgBr}$ , but can also com-

bine with a hydrogen atom of the ethyl group, thus giving  $\text{Ph}\cdot\text{CH}_2\text{O}\cdot\text{MgBr} + \text{C}_2\text{H}_4$ . The action of an excess of benzaldehyde is more readily explained by assuming the formation of an additive compound,  $(\text{Ph}\cdot\text{CHO})_2 \cdots \text{MgEtBr}$ , which subsequently decomposes into  $\text{Ph}\cdot\text{CH}_2\text{O}\cdot\text{MgBr} + \text{Ph}\cdot\text{CHO} + \text{C}_2\text{H}_4$ . It is remarkable that the yield of alkylene in no case approximates even to that of benzyl alcohol. The action of magnesium ethyl bromide on acetone does not lead under any conditions to the production of isopropyl alcohol, whilst propaldehyde and magnesium phenyl bromide yield exclusively phenylethylcarbinol.

The previous supposition (Meisenheimer and Caspar, *loc. cit.*), that magnesium is co-ordinatively quadrivalent in the etherates, cannot be maintained; the metal appears to be usually trivalent.

The authors fail to confirm the observation of Hess and Wustrow (*loc. cit.*) that the production of cinnamyl alcohol from the additive product of cinnamaldehyde and magnesium ethyl bromide can be followed analytically by the loss in weight of the isolated product due to the evolution of ethylene. The proof that the magnesium chloride alcoholate of styrylisobutylcarbinol is not identical with the additive compound of cinnamaldehyde and magnesium isobutyl chloride is shown to be invalid.

H. W.

### Electrolytic Properties of Magnesium Organic Compounds.

I. N. W. KONDYREW (*Ber.*, 1925, 58, [B], 459—463).—Electrolysis of a solution of magnesium ethyl bromide in ether with a platinum cathode and magnesium anode results in the deposition of metallic magnesium on the cathode. With a zinc anode, magnesium is only deposited initially and is replaced subsequently by zinc. A copper anode, on the other hand, is not appreciably dissolved, whilst magnesium is deposited on the platinum cathode. With an aluminium anode, magnesium is deposited on the cathode. Similar observations are made during the electrolysis of solutions of magnesium *n*-propyl bromide with platinum cathodes and magnesium or zinc anodes and of magnesium phenyl bromide between platinum and zinc electrodes. Solution of the anode, when occurring, takes place in accordance with Faraday's laws. Electrolysis is not due to the etherates of magnesium halides even if they are present in the solutions.

H. W.

### Electrolytic Properties of Magnesium Organic Compounds.

II. Electrical Conductivity of Magnesium Ethyl Bromide in Ethereal Solutions. N. W. KONDYREW and D. P. MANOJEW (*Ber.*, 1925, 58, [B], 464—467; cf. preceding abstract).—Measurements of the electrical conductivity of magnesium ethyl bromide dissolved in diethyl ether at 13°, 15°, 20°, 25°, and 30°, show that the equivalent conductivity increases with decreasing concentration, the change being proportional to the square root of the dilution. The sign of the temperature coefficient depends on the concentration of the solutions.

H. W.

Organo-metallic Compounds of Aluminium. P. LEONE (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 497—502).—Aluminium

alkyl halides may be readily prepared by boiling the perfectly dry alkyl halides with aluminium, the reaction commencing after about 15 mins. and rapidly becoming so violent that external cooling is necessary; the action is catalysed by a small proportion of anhydrous ether. *Aluminium ethyl iodide*,  $\text{Al}_2\text{Et}_3\text{I}_3$ , is obtained as a dark brown liquid which fumes strongly in the air and is decomposed by atmospheric moisture or violently by water, with formation of ethane and aluminium iodide and hydroxide. *Aluminium propyl iodide* has similar properties. *Aluminium isoamyl iodide* forms colourless crystals which effloresce rapidly in the air. *Aluminium octyl bromide* is a viscous mass and *aluminium phenyl iodide* a very dense liquid (cf. Spencer and Wallace, T., 1908, **93**, 1827).

T. H. P.

**Organo-metallic Compounds of Aluminium.** P. LEONE (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 229—232; cf. preceding abstract).—The action of the organo-metallic compounds of aluminium on ammonia and on primary and secondary amines is analogous to that of the corresponding magnesium compounds, the hydrocarbon being liberated and the nitrogen becoming attached directly to the metal:  $\text{Al}_2\text{R}_3\text{I}_3 + 3\text{NH}_3 = 3\text{RH} + \text{Al}_2\text{I}_3(\text{NH}_2)_3$  (cf. Meunier, A., 1903, ii, 544). The reaction proceeds readily and with development of heat in the case of ammonia and the primary and secondary aliphatic amines, only with difficulty with aromatic amines, and not at all with alkylanilines. Tertiary amines, owing to their lack of substitutable hydrogen, do not react in this way. The compounds obtained were:  $\text{Al}_2\text{I}_3(\text{NH}_2)_3, \text{Et}_2\text{O}$ , from aluminium ethyl iodide and ammonia;  $\text{Al}_2\text{I}_3(\text{NHEt})_3, \text{Et}_2\text{O}$ , from aluminium propyl iodide and ethylamine;  $\text{Al}_2\text{I}_3(\text{NMe}_2)_3, \text{Et}_2\text{O}$ , from aluminium propyl iodide and dimethylamine, and  $\text{Al}_2\text{I}_3(\text{NHPh})_3, \text{Et}_2\text{O}$ , from aluminium ethyl iodide and aniline. All form white, microcrystalline powders, and contain 1 mol. of either ether or benzene of crystallisation, which cannot be removed at temperatures below that of incipient decomposition. These compounds are readily decomposed by moisture, ammonia being liberated. T. H. P.

**Interactions of Tellurium Tetrachloride and Acetic Anhydride.** G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1925, **127**, 531—538).—Tellurium tetrachloride and a large excess of acetic anhydride (6 mols.) in chloroform condense to form, as main product, *dichlorotelluridiacetic acid*,  $\text{Cl}_2\text{Te}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , m. p. 160—161°, which on reduction with alkali metabisulphite is converted quantitatively into *tellurodiacetic acid*,  $\text{Te}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , m. p. 140—141°, a substance which is dichroic and exhibits dimorphism. The *diammonium*, *disodium*, *disilver*, and *copper* salts of the latter acid were prepared.

With 1.75 to 3 mols. of acetic anhydride, the condensation results in the formation of a mixture of trichlorotelluriacetic acid,  $\text{TeCl}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and acetanhydrobistelluritrichloride,  $(\text{TeCl}_3\cdot\text{CH}_2\cdot\text{CO})_2\text{O}$ .

The product, when reduced, is converted into *ditellurodiacetic acid*,

$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{Te}:\text{Te}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $144^\circ$ , which forms soluble *alkali* salts and an insoluble *silver* salt.

The mother-liquors from the telluro- and ditelluro-acetic acids contain *methylene bistellurotrichloride*,  $\text{CH}_2(\text{TeCl}_3)_2$ , m. p.  $173^\circ$ , which is converted into oxide or oxychloride in contact with moist air or water, and readily condenses with methyl ketones, yielding compounds such as *methylenebistelluriacetone dichloride*,



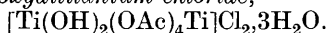
m. p.  $181^\circ$ . When methylene bistellurotrichloride is reduced with

bisulphite there is formed *ditelluromethane*,  $\text{CH}_2\begin{matrix} \text{Te} \\ ||| \\ \text{Te} \end{matrix}$ , which is

converted into a black powder at  $40^\circ$ , and explodes when heated more strongly. Ditelluromethane is converted into methylene bistellurotrichloride by the action of chlorine. C. J. S.

### Chloro-acetato Compounds of Quadrivalent Titanium.

M. GIUA and E. MONATH (*Z. anorg. Chem.*, 1925, **143**, 383—393).—Titanium tetrachloride reacts vigorously with acetic acid, hydrochloric acid being evolved and a solid compound obtained which was assumed by Bertrand to be a double anhydride of titanic and acetic acids. The product, however, still contains chlorine and by varying the conditions a number of substances can be obtained the compositions of which are best expressed by the formulæ given below. They are readily soluble in water and alcohol, probably with decomposition, and titanic acid is quantitatively precipitated when the aqueous solutions are heated. The following compounds are described; similar compounds are formed with other fatty acids: *Tetra-acetoxydichlorodititanium chloride*,  $[\text{TiCl}_2(\text{OAc})_4\text{Ti}]_2\text{Cl}_2\cdot\text{H}_2\text{O}$ . *Triacetoxydihydroxychlorodititanium chloride*,  $[\text{TiCl}(\text{OH})_2(\text{OAc})_3\text{Ti}]_2\text{Cl}_2$ . *Tetra-acetoxydihydroxydititanium chloride*,  $[\text{Ti}(\text{OH})_2(\text{OAc})_4\text{Ti}]_2\text{Cl}_2$ . *Tetra-acetoxydihydroxydititanium chloride*,



*Dioxydihydroxydiacetoxydititanium*,  $[\text{TiO}_2(\text{OH})_2(\text{OAc})_2\text{Ti}]$ , or  $\text{TiO}(\text{OH})\cdot\text{OAc}$ .

A. G.

### Action of Chlorine Monoxide on Organic Compounds.

S. GOLDSCHMIDT and H. SCHÜSSLER.—(See i, 497.)

### Reactions of Ethyl Hypochlorite with Organic Substances.

S. GOLDSCHMIDT, R. ENDRES, and R. DIRSCH.—(See i, 502.)

**Constitution of Aromatic Substances and their Chemical and Physical Properties.** I. A. PASTAK (*J. Chim. physique*, 1925, **22**, 48—58).—The relation between the constitution of benzene derivatives and their melting points is considered. In the disubstituted derivatives of the type  $\text{C}_6\text{H}_4\text{R}_2$  (with the exception of a few phenolic and acidic derivatives) the para isomeride has the highest melting point, and the meta the lowest. In the exceptional cases, the melting points rise from the ortho, through the meta to

the para derivative. This rule applies to the tetra- and hexa-substituted derivatives of the types  $C_6H_2R_4$ ,  $C_6R'_2R_4$ , if these are regarded as ortho, meta, or para according to the positions of the hydrogen atoms or  $R'$  radicals. Polynuclear hydrocarbons such as phenanthrene and anthracene may be included if regarded as tetrasubstituted derivatives of benzene. Trisubstituted derivatives,  $C_6H_3R_3$ , are included under the rule by postulating that the influence of two similar substituents in the meta positions is equivalent to that of a similar radical acting in the direction of the resultant of the two former. Thus symmetrical  $C_6H_3R_3$  is regarded as a para and asymmetrical  $C_6H_3R_3$  as a meta isomeride. Application of this postulate to the tetrasubstituted derivatives leads to the results given above.

F. G. T.

**New Process of Nitration with the Aid of Nitrogen Oxides from Air or Ammonia.** II. A. SCHAARSCHMIDT, H. BALZER-KIEWICZ, and J. GANTE (*Ber.*, 1925, **58**, [B], 499—502; cf. this vol., i, 123).—Fluorobenzene is practically unattacked by nitrogen tetroxide under conditions which give yields of 7.3, 6.5, and 45% of the corresponding nitro compounds from chloro-, bromo-, and iodo-benzene. The ratio, para:ortho compound, is greater in the cases of bromo- and iodo- than of chloro-benzene. Dimethylaniline is more readily attacked by nitrogen peroxide than is iodo-benzene, yielding *p*-nitrodiphenylamine. Pyridine and nitrogen peroxide yield the known additive compound, which could not be transformed into nitropyridine. Thiophen yields only uninviting products. In the presence of aluminium chloride, fluoro-, bromo-, and iodo-benzene yield complexes similar to that obtained previously with chlorobenzene (the compound from bromobenzene has the composition  $2AlCl_3 \cdot 3N_2O_4 \cdot 3PhBr$ ). The halogenonitrobenzenes obtained from them are mixtures of the para and ortho derivatives, in which the former predominate to an even greater extent than is the case with the chloronitrobenzenes. With pyridine, substitution in the nucleus does not occur in the presence of aluminium chloride. *pseudo*Nitrosites do not appear to be formed from benzene, nitrogen peroxide, or aluminium chloride after prolonged contact.

H. W.

**Reactions of Sodium Mono-, Di-, and Tri-sulphides with 1-Chloro-2-nitro-, 1-Chloro-4-nitro-, and 1:4-Dichloro-2-nitro-benzene.** H. H. HODGSON and J. H. WILSON (*J. Chem. Soc.*, 1925, **127**, 440—444).—The behaviour of sodium monosulphide with these chloronitrobenzenes is complex; in each case the yields of chloroaniline, sulphides, disulphides, and mercaptans, as obtained under varying conditions, are tabulated. Sodium di- and trisulphides yield, with the chloronitrobenzenes, disulphides and sometimes sulphur. In agreement with Blanksma (*A.*, 1901, i, 462), two forms of 4:4'-dinitrodiphenyl disulphide are isolated, but it is suggested that his 2:2'-dinitrodiphenyl trisulphide and tetrasulphide were mixtures of the disulphide with sulphur. From 1-chloro-4-nitrobenzene is obtained 4:4'-diaminodiphenyl tri-

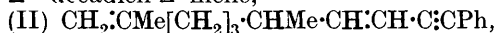
*sulphide*, m. p. 122° (*hydrochloride*, m. p. 200°), which is converted by boiling aqueous sodium monosulphide (or aniline) into 4 : 4'-diaminodiphenyl disulphide.

F. M. H.

**Influence of Constitution on the Rotatory Power of Optically Active Substances. XVIII. Influence of Acetylenic Linkings.** H. RUPE and R. RINDERKNECHT (*Annalen*, 1925, 442, 61—73).—Continuing earlier work (A., 1924, i, 647; this vol., i, 274), the rotatory powers of substances containing both acetylenic and ethylenic linkings have been compared.  $\kappa$ -Phenyl- $\beta\zeta$ -dimethyl- $\Delta^{\alpha}$ -decen- $\Delta^{\epsilon}$ -inen- $\theta$ -ol,



containing an ethylenic and an acetylenic linking at opposite ends of the chain, shows normal rotation dispersion, as does the  $\kappa$ -phenyl- $\beta\zeta$ -dimethyl- $\Delta^{\alpha\omega}$ -decadien- $\Delta^{\epsilon}$ -inene,



obtained from it, in spite of the presence of a conjugated ethylenic and acetylenic linking. The corresponding decatene (III),  $\text{CH}_2:\text{CMe}[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CHPh}$ , in which two ethylenic linkings are conjugated, shows anomalous dispersion.  $\kappa$ -Phenyl- $\beta\zeta$ -dimethyl- $\Delta^{\alpha\omega}$ -decadiene,

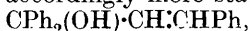


obtained by reduction of (II) (cf. Rupe and Jäger, A., 1914, i, 131), shows normal rotatory dispersion, whilst the  $\kappa$ -phenyl- $\beta\zeta$ -dimethyl- $\Delta^{\alpha}$ -decene (IV) obtained from it on reduction, like the isomeric reduction product from (II), show strong anomalous dispersion, which, however, is accompanied by a very small specific rotatory power, much smaller than that of dihydrocitronellol, an observation in harmony with previous observations on the relative influence of phenyl and alkyl groups at the remote end of a chain attached to an asymmetric carbon atom (cf. A., 1909, i, 927). Conjugation of the ethylenic and acetylenic linkings, however, as in (II), appears to produce a high specific rotation and refractivity, this compound having a molecular exaltation midway between that of phenylacetylene and Moureu's pentinene. Magnesium phenylacetylene bromide with citronellol yields  $\kappa$ -phenyl- $\beta\zeta$ -dimethyl- $\Delta^{\alpha}$ -decen- $\Delta^{\epsilon}$ -inen- $\theta$ -ol, b. p. 124°/0.01—0.05 mm.,  $d_{20}^4$  0.9547,  $[\alpha]_D^{20}$  6.35°. By distillation over aluminium phosphate at 210—240°/10 mm., it gave a crude product which on fractionation yielded phenylacetylene, a citronellal, and  $\kappa$ -phenyl- $\beta\zeta$ -dimethyl- $\Delta^{\alpha\omega}$ -decadien- $\Delta^{\epsilon}$ -inene, b. p. 172—175°/10 mm., 95°/0.05 mm.,  $d_4^{20}$  0.9318,  $[\alpha]_D^{20}$  84.35°,  $n_D$  1.55378. By reduction with a zinc-copper couple and aqueous acetic acid in alcoholic solution (cf. Straus, A., 1906, i, 77), the decadieninene is converted into  $\kappa$ -phenyl- $\beta\zeta$ -dimethyl- $\Delta^{\alpha\omega}$ -decatene, b. p. 170—173°/10 mm., 95°/0.05 mm.,  $d_4^{20}$  0.9273,  $[\alpha]_D^{20}$  52.85°. On reduction of the decadieninene with hydrogen and nickel in alcohol and acetic acid, one mol. of hydrogen is rapidly absorbed, a second and a third mol. more slowly, yielding  $\kappa$ -phenyl- $\beta\zeta$ -dimethyl- $\Delta^{\alpha}$ -decene, b. p. 166—168°/10 mm., 102°/0.05 mm.,  $d_4^{20}$  0.8794,  $[\alpha]_D^{20}$  -1.16°. The product differs only slightly in its physical constants from the hydrocarbon, b. p. 168—170°/10 mm., 93°/0.05 mm.,  $d_4^{20}$  0.8814,

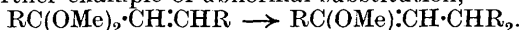
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$[\alpha]_D^{20} - 3.74^\circ$ , obtained by the similar reduction of Rupe and Jäger's decadiene (*loc. cit.*).  
R. B.

**Diphenylstyrylcarbinol and the Constitution of Dimeric Triphenylallene. XI. Distyryl Ketone and Triphenylmethane.** F. STRAUS and M. EHRENSTEIN (*Annalen*, 1925, **442**, 93—118; cf. Ziegler, Grabbe, and Ulrich, this vol., i, 131).—The unsaturated keto-chlorides obtained by the action of phosphorus pentachloride on phenyl styryl ketone and distyryl ketone react with magnesium phenyl bromide as derivatives of allyl chloride, replacement of halogen by phenyl, *e.g.*,  $\text{CHPhCl}:\text{CH}:\text{CPhCl} \rightarrow \text{CHPh}_2:\text{CH}:\text{CPhCl}$ , yielding chlorides in which the halogen atom is less reactive and showing remarkable halochromism in sulphuric acid. These chlorides do not react abnormally with sodium methoxide (A., 1912, i, 989), and the expected diphenylstyrylcarbinol ether,  $\text{CPh}_2(\text{OMe}):\text{CH}:\text{CHPh}$ , was not obtained, but the methyl ethers  $\text{CPh}_2:\text{CH}:\text{CHPh}:\text{OMe}$  (I) and  $\text{CPh}_2:\text{CH}:\text{CH}:\text{CH}:\text{CHPh}:\text{OMe}$  (II). The ether (I), which is identical with the  $\alpha\gamma\gamma$ -triphenylallyl methyl ether described by Ziegler (*loc. cit.*) and is accompanied by a stereoisomeride, shows characteristic halochromism in sulphuric acid, sulphur dioxide, and other solvents; the colour of these solutions disappears more or less rapidly, through the formation of dimeric triphenylallene (cf. A., 1922, i, 148). The conversion of the ether (I) into the chloride,  $\text{CPh}_2:\text{CH}:\text{CHPhCl}$ , by hydrogen chloride (cf. Ziegler, *loc. cit.*) is prevented by apparently inconsiderable variations in the experimental conditions with formation of the dimeric triphenylallene. A re-examination of the behaviour of Meyer and Schuster's diphenylstyrylcarbinol (A., 1922, i, 540) with hydrogen chloride proves it to be identical with the methyl ether (I), and accordingly in the reaction by which it is formed migration of hydroxyl or methoxyl has occurred. The configuration  $\text{CPh}_2:\text{CH}:\text{CHPh}:\text{OH}$  is accordingly more stable than



but the reaction affords fresh evidence of the uncertainty in this field of conclusions in regard to constitution based on decomposition reactions (cf. A., 1912, i, 989). A further attempt to obtain the methyl ether of diphenylstyrylcarbinol by the action of magnesium phenyl bromide on the acetal of phenyl styryl ketone (A., 1918, i, 501) yielded  $\alpha\gamma\gamma$ -triphenylpropenyl methyl ether, b. p.  $182-185.5/0.3$  mm.,  $d_4^{25} 1.0823$ ,  $n_D^{18.5} 1.62353$ . The constitution of this ether is established by its conversion by hydrogen chloride into  $\beta\beta$ -diphenylpropiophenone, and by its oxidation to benzophenone, methyl benzoate, and benzoic acid. Its formation thus affords a further example of abnormal substitution,



The oxidation of dimeric triphenylallene with chromic acid in acetic acid yields a product containing 20% of resin, 30% of *o*-dibenzoylbenzene, and 25—30% of benzophenone, together with benzoic acid and a bright red substance, m. p.  $177-178^\circ$ . These results, especially the production of benzophenone, which does not arise from the further oxidation of *o*-dibenzoylbenzene, are incon-

sistent with the formulæ ascribed to dimeric triphenylallene by Ziegler (*loc. cit.*), and the structures  $\text{CPh} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh} \cdot \text{CHPh} \cdot \text{CH} : \text{CPh}_2$  or  $\text{CPh} \begin{smallmatrix} \text{CH} \\ \text{C}_6\text{H}_4 \end{smallmatrix} \text{CPh} \cdot \text{C}(\text{CH}_2\text{Ph}) : \text{CPh}_2$  are suggested, the first of which explains why 1 : 3-diphenylindene does not polymerise to dimeric triphenylallene.

$\alpha\gamma$ -Dichloro- $\alpha\gamma$ -diphenyl- $\Delta^{\beta}$ -propylene and magnesium phenyl bromide give in 80—85% yield  $\gamma$ -chloro- $\alpha\alpha\gamma$ -triphenyl- $\Delta^{\beta}$ -propylene, m. p. 84.5—85.5°, giving a golden-yellow solution in sulphuric acid (cf. Staudinger, A., 1909, i, 905), together with diphenyl and  $\alpha\zeta$ -dichloro- $\alpha\gamma\delta\zeta$ -tetraphenylhexa- $\Delta^{\alpha\epsilon}$ -diene.  $\alpha\gamma\gamma$ -Triphenylallyl methyl ether forms white needles, m. p. 99—100°, identical with Ziegler's compound, and lustrous needles, m. p. 78.5—79°, which in methyl alcohol are converted by a trace of sulphuric acid into the higher-melting form. Both isomerides and the corresponding chloride give halochromic solutions in sulphur dioxide, sulphuric acid, and perchloric acid, and with stannic chloride in benzene.

$\alpha\gamma$ -Dichloro- $\alpha\epsilon$ -diphenylpenta- $\Delta^{\beta\delta}$ -diene,  
 $\text{CHPhCl} \cdot \text{CH} : \text{CCl} \cdot \text{CH} : \text{CHPh},$

with magnesium phenyl bromide yields  $\gamma$ -chloro- $\alpha\alpha\epsilon$ -triphenylpenta- $\Delta^{\beta\delta}$ -diene, m. p. 72—73°, which reacts more readily with sodium methoxide than the corresponding propylene derivative, and gives the *methyl ether* (II), which could not be crystallised.

Reduction of  $\alpha\gamma\gamma$ -triphenylpropenyl methyl ether with palladium and hydrogen in methyl alcohol yields  $\alpha\gamma\gamma$ -triphenylpropyl methyl ether, b. p. 235°/18 mm.,  $d_4^{25}$  1.0619,  $n_D^{18.53}$  1.58319, also obtained by the reduction of the ether (I). The *dimethyl acetal* of phenyl  $\beta$ -phenylethyl ketone has b. p. 188.5—189.5°/18 mm.,  $d_4^{23}$  1.0425,  $n_D^{22.95}$  1.54068.

R. B.

**Reduction of Aromatic Nitro Compounds.** R. W. WEST (*J. Chem. Soc.*, 1925, 127, 494—495).—Reduction is effected by addition of iron filings to a boiling solution of the nitro compound in methylated spirit and hydrochloric acid. The amino compound may be purified by steam distillation or isolated as its hydrochloride, and it is claimed that the method gives good yields of pure products.

F. M. H.

**Action of Hydrogen Peroxide on Magnesium Arylamines.**

J. F. DURAND and R. NAVES (*Compt. rend.*, 1925, 180, 521—522).—As hydrogen peroxide acts on magnesium alkyl halides to yield primary alcohols (cf. Oddo and Binaghi, A., 1922, i, 314), so it reacts with magnesium arylamine halides to yield  $\beta$ -hydroxylamines. By the action of an anhydrous, ethereal solution of hydrogen peroxide on magnesium aniline bromide,  $\text{NHPh} \cdot \text{MgBr}$  at  $-25^\circ$ ,  $\beta$ -phenylhydroxylamine is obtained in 80% yield. In one experiment, *p*-aminophenol was produced instead of the expected compound. The results can be best interpreted by giving hydrogen peroxide the formula  $\text{HO} \cdot \text{OH}$ .

J. W. B.

**Interaction of Ethylene Oxide and Aniline.** G. O. GABEL (*Ber.*, 1925, 58, [B], 577—579).—The course of the action of

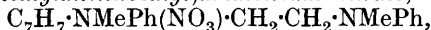
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ethylene oxide on aniline tends mainly towards the production of di- $\beta$ -hydroxyethylaniline,  $\text{NPh}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})_2$ , even under conditions which appear favourable to the formation of  $\beta$ -hydroxyethylaniline. The tertiary base, m. p.  $58^\circ$  [Rindfusz and Harnack (A., 1920, i, 681) record m. p.  $53.5\text{--}54^\circ$ ], yields a *chloroplatinate*, m. p.  $150\text{--}152^\circ$  (decomp.), a *picrate*, m. p.  $118^\circ$ , and a non-crystalline hydrochloride. H. W.

**Catalytic Action. VIII. Catalytic Reduction of  $\beta$ -Naphthylamine.** T. HARA (*Mem. Coll. Sci. Kyoto*, 1924, [A], 7, 403—407).—When passed over finely-divided nickel at  $200^\circ$ ,  $\beta$ -naphthylamine yields  $\beta$ -*ar*-tetrahydronaphthylamine, di- $\beta$ -*ar*-tetrahydronaphthylamine, naphthalene, and reduced naphthalenes. From the proportions of these products formed, it is concluded that the primary reaction product consists of 76% of *ar*-isomerides and 24% of *ac*-isomerides (cf. A., 1923, i, 782). L. F. H.

**Asymmetric Nitrogen Atom. III. Dependence of the Rate of Decomposition of an Optically Active Aminoammonium Nitrate on the Presence of Primary, Secondary, and Tertiary Amines.** E. WEDEKIND and H. UTHE (*Ber.*, 1924, 58, [B], 470—475; cf. Wedekind and Mayer, A., 1909, i, 186).—*Phenylbenzylmethyl-(methylanilinoethyl)ammonium nitrate*,



is not completely stable in chloroform solution, and its decomposition can be followed polarimetrically or by measurement of the electrical conductivity of the solution. The action is accelerated by the presence of *s*-dimethylanilinoethane, mono-, di-, or triethylamine, aniline, or methylaniline, but scarcely by dimethylaniline. For some unexplained reason, the secondary amines are particularly active. It remains undecided whether inactivation is due to catalytic racemisation or chemical decomposition of the nitrate. The latter substance is not present in appreciable amount in the optically inactive solutions, from which well-defined products have not been isolated. The aminoammonium nitrate does not decompose more rapidly when dissolved in aniline or methylaniline than in chloroform solution in the presence of relatively small quantities of these bases. Under these conditions, however, the electrical conductivity is observed to sink to a minimum, after which a gradual rise occurs. The phenomenon is explained by the hypothesis that the nitrate decomposes primarily and irreversibly into *s*-dimethylanilinoethane and benzyl nitrate and the latter substance reacts with aniline to form benzylaniline nitrate (which has been isolated), thus causing the increase in conductivity of the solution. H. W.

**Oxalic Acid as an Agent for Splitting Off Alcohol Groups.** E. WASER and K. SANDER (*Helv. Chim. Acta*, 1925, 8, 106—111).—When *cyclohexyl* alkyl ethers react with anhydrous oxalic acid, the *cyclohexene* formed may be partly reduced, giving a trace of *cyclohexane*, as in the case of hexahydroanisole. Aliphatic ethers are very reluctant to react at all with oxalic acid. The

mixed aromatic-aliphatic ethers differ in their reactivity. Whilst anisole and phenyl butyl ether fail to react, phenyl propyl ether, phenetole, and both methyl and ethyl ethers of  $\alpha$ - and  $\beta$ -naphthol give phenol or naphthol respectively and the corresponding alkyl oxalate. M. J.

**The Two 1 : 3-Dimethylcyclohexan-4-ones and the Corresponding Dimethylcyclohexanols.** M. GODCHOT and P. BEDOS (*Compt. rend.*, 1925, **180**, 751—754).—The second geometrical isomeride of the ketone is obtained by the action of magnesium methyl iodide on the chloromethylcyclohexanone of b. p. 110—112° (see Godchot and Bedos, this vol., i, 258), as an odorous liquid, b. p. 171° (corr.),  $d_4^{16}$  0.9004,  $n_D^{16}$  1.4429; *semicarbazone*, m. p. 136°, *oxime*, oily; this is presumably the *trans* form, the isomeride previously known being probably the *cis* form. With each of these isomeric ketones, two geometrically isomeric alcohols correspond; the *cis-trans* and *cis-cis* alcohols corresponding with the first isomeric ketone are already known. Reduction of the second or *trans*-ketone by sodium in presence of sodium hydrogen carbonate gives a 1 : 3-dimethylcyclohexan-4-ol, b. p. 176—177°,  $d_4^{16}$  0.9004,  $n_D^{16}$  1.4536; *phenylurethane* compound, oily; *allophanate*, m. p. 149°; reduction by platinous oxide in acetic acid gives a mixture of this alcohol with a second, much more soluble, m. p. 135—136°.

S. I. L.

**Preparation of cycloHexenols by Catalytic Dehydration of cycloHexanediols.** J. B. SENDERENS (*Compt. rend.*, 1925, **180**, 790—793).—*cycloHexanediols*, when dehydrated by sulphuric acid trihydrate under certain conditions, yield considerable amounts of *cyclohexenols* in addition to *cyclohexadienes* (cf. A., 1924, i, 40). The dehydration of *cyclohexane-1 : 4-diol* gives a 54% yield of  $\Delta^1$ -*cyclohexen-3-ol*, b. p. 165—166°,  $d_4^{19}$  0.993; *phenylurethane*, m. p. 79°; *acetate*, a pleasant-smelling liquid, b. p. 178—180° (slight decomp.). This compound is probably identical with the *cyclohexenol* obtained by Baeyer (A., 1894, i, 175). *cycloHexane-1 : 3-diol* yields the same  $\Delta^1$ -*cyclohexen-3-ol* and no isomeride, together with  $\Delta^{1,4}$ - and  $\Delta^{1,3}$ -*cyclohexadienes* in the proportion of 1 of the former to 5 of the latter. The dehydration of *cyclohexane-1 : 2-diol* is difficult and no *cyclohexenol* could be isolated. L. F. H.

**Action of Sulphuryl Chloride on Aminophenols.** W. ELLER and V. LORENZ (*Ber.*, 1925, **58**, [B], 494—497).—Chloranil, a by-product in the conversion of *p*-aminophenol by means of sulphuryl chloride into 2 : 3 : 5 : 6-tetrachloro-4-dichloroaminophenol (cf. Eller and Klemm, A., 1922, i, 448), is not a primary product, but is formed from the last-mentioned compound by the action of ethyl alcohol used for its recrystallisation. The change is facilitated by the addition of water, but does not appear to take place in other solvents, even methyl alcohol. The nitrogen of the dichloroamino group is evolved in the elementary state.

The final product of the action of sulphuryl chloride on *o*-aminophenol is 1 : 2 : 3 : 3 : 6 : 6-hexachloro- $\Delta^1$ -*cyclohexene-4 : 5-dione*, b. p. 170°/18 mm. (the corresponding monohydrate, m. p. 98°,

and *dihydrate*, m. p.  $93^{\circ}$ , are described). *m*-Aminophenol is converted into a *substance*,  $C_5H_3OCl_5$ , m. p.  $154^{\circ}$ , which is regarded as 2 : 2 : 3 : 4 : 5-pentachlorocyclopentanone. H. W.

**Changes in the Sweetening Power of Dulcin (*p*-Phenetyl-carbamide) by Chemical Modification.** H. THOMS (*Deuts. Zuckerind.*, 1924, 49, 1056; from *Chem. Zentr.*, 1924, ii, 2801).—Replacement of one of the amino-hydrogen atoms in *p*-phenetyl-carbamide by an alkyl group decreases the sweetness. Introduction of a second carbamido group in the ortho-position to the first causes a similar loss of sweetening power. Accordingly, it is concluded that for the production of flavour the presence of one or more "sapiphoric" groups alone is not sufficient, but these groups must occupy definitely related positions (cf. Bergmann, Camacho, and Dreyer, A., 1923, i, 203). R. B.

**Molecular Compounds of the Phenols. I. Behaviour of the Cresols towards Alcohol, Ether, and Acetone.** G. WEISSENBERGER and L. PIATTI (*Monatsh.*, 1925, 45, 187—206).—Conflicting views as to the existence of complexes between cresol and various solvents (cf. Berl and Schwebel, A., 1922, i, 932; C. and W. von Rechenberg, *ibid.*) are discussed. Measurements of the vapour pressure of solutions of the three cresols have been made at various concentrations with different solvents. With alcohol as solvent, the pressures are lower in each case than those calculated from van't Hoff's formula until the composition of the mixture reaches 2 mols. of alcohol : 1 mol. of cresol, after which the observed and calculated pressures agree. Curves obtained by plotting the differences between these pressures against the molar concentration of the alcohol and cresol show a maximum lowering at 0.5 mol. of alcohol : 1 mol. of cresol corresponding with 29.7% of alcohol to 70.3% of cresol for each isomeride, the ratios of the depressions being  $o : p : m = 5.5 : 4.8 : 3.6$  in mm. of mercury. If the lowering of the vapour pressure be taken as an expression of the strength of the residual valencies, these numbers are a measure of the relative field strengths of the isomerides engaged in forming molecular complexes with alcohol. Parallel conditions hold for the solvents acetone and ether, the composition of the mixture for the maximum lowering of vapour pressure being again 0.5 mol. of solvent to 1 mol. of each isomeride, corresponding with 65.3% of cresol to 34.7% of acetone and 59.6% of cresol to 40.4% of ether. The comparative strengths of the residual valencies are, for acetone  $o : p : m = 34.9 : 34.1 : 31.4$ , for ether, 78.2 : 74.3 : 69.2 (mm. mercury), indicating more stable complexes than in the case of alcohol. It is considered that the field of force of the oxygen atom in these compounds is not completely saturated and can exert its action on other fields of force, the intensity of which varies according to constitutional influences. Measurements of the viscosity of the cresol isomerides were made in the same solvents at various concentrations. Curves connecting the viscosity and the molar concentration showed no irregularities or characteristic points. It is considered from the nature of the curves that the

formation of molecular compounds need not express itself in alterations of viscosity and that the absence of minima or maxima (cf. Rechenberg, *loc. cit.*) does not indicate the absence of such compounds. The specific gravities of the molecular compounds are very near to or identical with those of the corresponding mixtures (cf. Berl and Schwebel, *loc. cit.*) and appear to cause no deviation in the calculated curves. The surface tensions ( $\sigma$ ) as measured by the drop method were not lowered by the presence of molecular compounds. The curves ( $\sigma$  against concentration) in general showed a normal course, indicating that the presence of molecular compounds has no effect on the surface tension. In the cases of *m*-cresol-acetone and *p*-cresol-acetone, however, maxima were found for the mixtures consisting of 0.5 mol. of cresol : 1 mol. of acetone, whilst the curves for *m*-cresol-ether and *p*-cresol-ether were straight lines up to the composition 1 mol. of ether : 1 mol. of cresol, after which they became normal. The values of  $\sigma$  for the isomerides (in dynes per cm.) are *o* : *p* : *m* = 33.5 : 33.5 : 31.9 (water, 73.0). It is concluded that the relative intensities of the residual valencies displayed by the isomeric cresols are always the same, and that, as a consequence, the cresols afford a standard for measuring the strength of the residual valencies in other organic compounds. A. C.

**Molecular Compounds of the Phenols. II. Behaviour of Cresols towards Aromatic Hydrocarbons.** G. WEISSENBERGER and L. PIATTI (*Monatsh.*, 1925, 45, 281—285; cf. preceding abstract).—The vapour pressures, viscosities, and surface tensions of mixtures of benzene with the isomeric cresols have been determined at 18° over a wide range and the sets of values plotted against the concentrations of the mixtures. The viscosity and surface-tension curves are normal and agree with the form calculated for mixtures. The values for the vapour pressures, on the other hand, are in all cases much higher than those calculated from the van't Hoff formula. As a result of this, the curves show a positive deviation from the normal. The differences between the observed and calculated pressures plotted against the concentrations give curves which are the converse of those described for alcohol. Each of the three curves shows a maximum when the corresponding mixture consists of 1 mol. of cresol : 1 mol. of benzene (54.1% of cresol : 45.88% of benzene), after which they run nearly parallel and at (nearly) equal distances apart. Assuming with Dolezalek that only negative isotherms indicate the formation of molecular compounds, the curves are difficult to explain. Neither association of the cresol molecules nor of benzene (cf. Traube, A., 1895, ii, 308; Ramsay and Shields, T., 1893, 63, 1089) would appear to give a satisfactory explanation for the deviations from the calculated values. A. C.

**Some Bromo Derivatives of *p*-Cresol and the Mobility of their Bromine Atoms.** V. M. KOHN and J. WIESEN (*Monatsh.*, 1925, 45, 251—259; cf. Kohn and Jawetz, this vol., i, 135).—Tetrabromo-*p*-cresol heated with aluminium chloride in

benzene at 100° yields bromobenzene and 2:6-dibromo-*p*-cresol, b. p. 280—286° (uncorr.), m. p. 97°, the meta position of the bromine atoms to the hydroxyl group being assumed from the behaviour of the corresponding *o*-cresol derivative (cf. Kohn and Jawetz, *loc. cit.*). If the heating is continued too long, the meta bromine atoms are also eliminated. The benzoyl derivative,  $C_{14}H_{10}O_2Br_2$ , has m. p. 64°.

2:3:5-Tribromo-*p*-cresol, m. p. 102° (cf. Zincke, A., 1902, i, 284), on similar treatment, lost all its bromine and formed *p*-cresol, m. p. 194—198°; no modification of the conditions of the reaction enabled the expected *o*-bromo-*p*-cresol to be prepared in this way. 3:5-Dibromo-*p*-hydroxybenzyl bromide prepared by the method of Auwers (cf. A., 1903, i, 621) also gave *p*-cresol under like conditions with probable intermediary formation of the dibromodiphenylmethane derivative,  $C_6H_2Br_2(OH) \cdot CH_2Ph$ . 3:5-Dibromo-*p*-hydroxybenzyl bromide heated with quinol in the presence of aqueous potassium hydroxide yielded 3:5-dibromo-4:2':5'-trihydroxydiphenylmethane, m. p. 200° (decomp.), tribenzoyl derivative, m. p. 150°; with resorcinol, 3:5-dibromo-4:2':4'-trihydroxydiphenylmethane, m. p. 182—183°, tribenzoyl derivative, m. p. 175—177°; with pyrocatechol, 3:5-dibromo-4:3':4'-trihydroxydiphenylmethane, m. p. 147—148° (darkening), tribenzoyl derivative, m. p. 65—68°. A. C.

**2-Nitro-*m*-cresol and 2-Amino-*m*-cresol.** H. H. HODGSON and H. G. BEARD (*J. Chem. Soc.*, 1925, 127, 498).—If the nitration of *m*-cresol (cf. Gibson, T., 1923, 123, 1269) is modified by using stronger fuming sulphuric acid in the disulphonation, purification by acetylation becomes unnecessary. Conversion of 2-nitro-*m*-cresol into 2-nitro-3-methoxytoluene and of this into 2-bromo-3-methoxytoluene is mentioned, whilst reduction of the nitro compound with sodium hyposulphite gives 2-amino-*m*-cresol.

F. M. H.

**Amines. X. Formation of Tyramine by Decarboxylation of Tyrosine from Silk.** T. B. JOHNSON and P. G. DASCHAVSKY (*J. Biol. Chem.*, 1925, 62, 725—735).—Tyrosine was prepared in large quantities by the hydrolysis, in 25% sulphuric acid, of crude silk fibroin; the yield was 7%. The amino-acid was decarboxylated by heating for 40 minutes at 260° in a mixture of equal parts of diphenylmethane and diphenylamine; the yield of crude tyramine was 95% of the theoretical. C. R. H.

**Bromo- $\alpha$ -naphthols and Orientation of certain Classes of Disubstituted Naphthalene Derivatives.** R. C. FUSON (*J. Amer. Chem. Soc.*, 1925, 47, 516—518).—*m*- and *p*-Bromophenylparaconic acids, m. p. 164—165° and 140—140.5°, respectively, were obtained by condensing the corresponding bromobenzaldehydes with succinic anhydride (cf. Fuson, this vol., i, 253). From these, 7-bromo- $\alpha$ -naphthol, m. p. 105.5—106.5°, and 6-bromo- $\alpha$ -naphthol, m. p. 129—130°, were obtained, respectively, by distillation (cf. A., 1883, 595). The bromo- $\alpha$ -naphthols form useful

points of reference in elucidating the orientation of naphthalene derivatives.  
F. G. W.

**Preparation of Alkylresorcinols and Aralkylresorcinols.** SHARP AND DOHME, INC., and A. R. L. DOHME (Brit. Pats. 219922 and 223190).—Alkyl- or aralkyl-resorcinols are obtained by condensing resorcinol with an aliphatic or aromatic acid in presence of zinc chloride, and reducing the resulting ketone with zinc amalgam and hydrochloric acid. 2:4-Dihydroxyphenyl isopropyl ketone has b. p. 176—180°/9 mm.; 2:4-dihydroxyisobutylbenzene, m. p. 58—60°, b. p. 156°/9 mm. 2:4-Dihydroxyphenyl isobutyl ketone has b. p. 172—175°/9 mm.; 2:4-dihydroxyisoamylbenzene, m. p. 64—65°, b. p. 172—175°/9 mm. 2:4-Dihydroxyphenyl n-butyl ketone has b. p. 185—195°/9 mm.; 2:4-dihydroxy-n-amylbenzene, m. p. 56°, b. p. 176°/8 mm. 2:4-Dihydroxy-n-hexylbenzene has m. p. 58—60°, b. p. 178—180°/8 mm. 2:4-Dihydroxybenzophenone has m. p. 142—143° and 2:4-dihydroxydiphenylmethane, m. p. 78—79°, b. p. 220—222°/10 mm. The new alkylresorcinols have antiseptic and germicidal properties.  
E. H. R.

**Complex Compounds of Boric Acid. I. Dipyrocatecholboric Acid, some Salts and Derivatives. II. Salts of Borosalicylic Acid.** J. MEULENHOF (Rec. trav. chim., 1925, 44, 150—165).—I. The increase in acidity of boric acid in presence of pyrocatechol and related substances is ascribed to the formation, by union of 2 mols. of pyrocatechol with 1 mol. of boric acid, of a complex compound of the type  $\left[ \text{C}_6\text{H}_4 \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{B} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \text{C}_6\text{H}_4 \right] \text{H}$  (cf. Hermans, A., 1923, i, 557). By addition of a base to an aqueous solution of pyrocatechol and boric acid, salts of dipyrocatecholboric acid are obtained as colourless compounds, usually possessing no melting point, hydrolysed in aqueous solution, decomposed by acid, and not oxidised by air, and of these the following are described: *aniline* (yield 94%), *p-chloroaniline*, *dimethylaniline*, *pyridine*, m. p. 122—123°, *ammonium* (ammonium carbonate may be used in the preparation), *sodium*, and *potassium* salts. By heating the salt of an amine at 100°/1—2 mm., most of the base is removed, and subsequent sublimation at 180—200°/1—2 mm. yields *dipyrocatecholboric acid*, but the ammonium salt sublimes without decomposition.

A modification of Weselsky and Benedikt's method of nitrating pyrocatechol (A., 1882, 1200) is used to prepare 3-nitropyrocatechol, m. p. 86.5°, and 4-nitropyrocatechol, m. p. 177°. The specific conductivity of boric acid and pyrocatechol is increased by introduction of a nitro group into the pyrocatechol, and more so by the 3- than by the 4-nitro group. The *aniline*, *ammonium*, and *potassium* salts of each bis-nitropyrocatecholboric acid are described. The aniline salt of the 3-acid loses aniline more readily than does that of the 4-acid, but in neither case is the pure bis-nitropyrocatecholboric acid obtained. In presence of excess of ammonia, the *monoammonium* salt of the 3-acid crystallises as a red, dichroic substance, easily sublimed.

The *pyridine* salt and *aniline* salt, m. p. 225°, of dipyrogallolboric

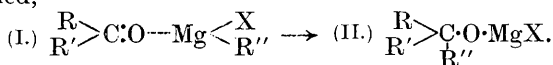
acid have been prepared; these only slowly lose base when heated in a vacuum, forming the free *dipyrogallolboric acid*, to which the increase in conductivity and solubility of boric acid in presence of pyrogallol is attributed.

II. It was not found possible to repeat Foelsing's preparation of borodisalicyclic acid (A., 1916, i, 314). By addition of the calculated quantity of a base or carbonate to a concentrated aqueous solution of boric acid and salicylic acid (or the method may be modified by use of a borate or salicylate), its salts are prepared; they have an acid reaction and bitter taste and are decomposed by water. The *aniline* salt, m. p. 229—231°, and *pyridine* salt, m. p. 82—83° (+H<sub>2</sub>O), of borodisalicyclic acid are stable at 140°/1 mm. The following borodisalicylates are described: *sodium*, *potassium*, *ammonium*, *silver*, *copper* (+10H<sub>2</sub>O bluish-green, and anhyd., green), *cobalt* (+10H<sub>2</sub>O salmon pink, and anhyd.), *manganese*, *calcium*, *magnesium* (these three +10H<sub>2</sub>O and anhyd.), *lead*, *strontium*, and *barium*; the water of crystallisation is considered to be attached to the anion. An amorphous product, which is regarded as the *sodium* salt of boromonosalicylic acid, has been isolated.

F. M. H.

**Reducing Action of Organo-magnesium Halides.** H. RHEINBOLDT and H. ROLEFF (*J. pr. Chem.*, 1925, **109**, 175—190; cf. Hess and Rheinboldt, A., 1921, i, 777).—Ordinary ether solutions of Grignard reagents bring about the reduction of benzaldehyde to benzyl alcohol but in much smaller yields than are obtained on using "individual" magnesium ethyl iodide (Hess and Rheinboldt, *loc. cit.*). Only small amounts of benzyl alcohol are formed when magnesium ethyl halides act on benzaldehyde in the cold (cf. Schorigin, A., 1908, i, 881), but the reduction increases greatly with rise of temperature. The mixture of carbinols obtained by heating the additive product of benzaldehyde and magnesium ethyl bromide in boiling ether for 1 hour contained 11% of benzyl alcohol; replacing the ether by benzene raised the yield to 22%, but in toluene, owing to the formation of resinous products, the yield fell to 17%. The greatest reducing action occurs when the aldehyde is added direct to the boiling Grignard solution, in ether 34%, benzene 40%, toluene 27%. The yields of benzyl alcohol were very similar when the Grignard reagent was added to a boiling solution of the aldehyde or when ethyl bromide was added to a solution of benzaldehyde in boiling ether and magnesium. Increasing the length of time of heating in benzene to 2 hours doubled the yield of benzyl alcohol (42%), but in 10 hours there was only a slight further increase (44%). The reducing action of magnesium *cyclohexyl* chloride shows a similar dependence on the temperature and on the solvent. Comparative yields of benzyl alcohol were, in the cold 7%, in boiling ether 18%, in anisole 23%, in benzene 57%. Magnesium *isobutyl* bromide gave a 25% yield in the cold, 55% in boiling ether, 57% in benzene, but varying the method of bringing the reactants together had no appreciable effect on the yield. In the reaction between magnesium *cyclohexyl* chloride and benzaldehyde, dibenzylidenecyclohexanone, m. p. 117°, was isolated. This sub-

stance becomes brilliant red in bromine vapour; similarly, di-cinnamylidenecyclohexanone becomes deep green. Both substances show intense halochromism with acids and certain salts. The reducing action of Grignard reagents on ketones has also been examined. It was expected, from statements of Sabatier and Mailhe (A., 1904, i, 809, etc.), that magnesium cyclohexyl bromide would reduce benzophenone to benzhydrol at the ordinary temperature. This was not the case even on heating, and under varied experimental conditions diphenylcyclohexylcarbinol, which the above workers were unable to isolate, was always found in addition to benzhydrol. Phenyl cyclohexyl ketone with magnesium cyclohexyl bromide yielded phenyldicyclohexylcarbinol, which exhibited no halochromism as opposed to diphenylcyclohexylcarbinol. Magnesium isobutyl bromide reduces benzophenone quantitatively to benzhydrol in the cold, and phenyl isobutyl ketone to phenylisobutylcarbinol, no tertiary carbinol being found. The reduction product with pinacolin amounted to 66% in the cold and 72–73% when heated, isobutylene being evolved. The results are explained on the assumption that an additive, molecular compound (I) is first formed,



The redistribution of the valencies may result in the loosening of the bond of the radical  $R''$  and the splitting off of an unsaturated hydrocarbon, leaving  $Mg < \begin{array}{c} X \\ \diagdown \\ H \end{array}$  which brings about reduction; or molecular rearrangement with formation of (II) may take place. The latter results in a tertiary alcohol and no reduction. The direction of the change depends on the radical  $R''$  and on the temperature, whilst steric influences also play a part. An unsaturated hydrocarbon is only split off when  $R''$  is attached to the magnesium (I), and not if (II) has been formed. The more quickly molecular rearrangement takes place, the less likelihood is there of the formation of reduction products. If a co-ordination position on the magnesium atom is occupied by the ether molecule, molecular rearrangement is accelerated, which explains why with the ordinary Grignard reagent much less reduction product is obtained than with the ether-free "individual" organo-magnesium halides. A. C.

**Constitution of Grignard's Magnesium Compounds. II.**  
J. MEISENHEIMER.—(See i, 527.)

**Action of Magnesium Phenyl Bromide on Organic Acids.**  
F. N. PETERS, jun., E. GRIFFITH, D. R. BRIGGS, and H. E. FRENCH (*J. Amer. Chem. Soc.*, 1925, **47**, 449–454).—When oxalic, malonic, succinic, or adipic acid is boiled under reflux with ethereal magnesium phenyl bromide, the only products obtained are phenol and diphenyl. Using excess of the magnesium phenyl bromide, benzoic and propionic acids react readily with formation of triphenylcarbinol and diphenylethylcarbinol, respectively. Phenylacetic acid yielded, similarly, a substance, m. p. 196°, which afforded benzoic acid and benzophenone on oxidation with alkaline per-



manganate, and deoxybenzoin when heated above its m. p. *iso*-Butyric acid, treated with 8 equivalents of magnesium phenyl bromide, gave an oil,  $C_{16}H_{18}O$ , b. p.  $170^{\circ}/21$  mm., identical with that obtained by the action of magnesium propyl iodide on benzophenone. Diphenylacetic acid yielded similarly only a small quantity of a *substance*, m. p.  $233$ — $234^{\circ}$ , insoluble in alkali, most of the acid not reacting.  $\beta\beta$ -Diphenylpropionic acid and magnesium phenyl bromide yielded a *substance*,  $C_{27}H_{24}O$ , m. p.  $97$ — $98^{\circ}$ . Benzoylformic acid yielded similarly benzoic acid and triphenylmethane, whilst pyruvic acid afforded  $\alpha$ -phenyl-lactic acid. Chloroacetic acid gave a *substance*,  $C_{14}H_{14}O_2$ , m. p.  $121^{\circ}$ , which yielded carbon dioxide and benzophenone on oxidation, with a trace of, probably, chloroacetophenone.  $\alpha$ -Bromopropionic acid yielded similarly a *substance*,  $C_{15}H_{16}O_2$ , m. p.  $93^{\circ}$ , which gave acetic acid and benzophenone on oxidation. Mandelic acid yielded  $\alpha\beta$ -dihydroxy- $\alpha\beta\beta$ -triphenylethane. No reaction was observed between benzoic acid and magnesium phenyl bromide. Cinnamic acid and magnesium phenyl bromide yielded  $\beta\beta$ -diphenylpropionic acid, whilst with magnesium methyl iodide a small quantity of an oil, apparently styryl methyl ketone, was obtained. F. G. W.

**Isomerism of Ethylene Oxides with Migration [of Groups]. Mechanism of Molecular Transpositions.** M. TIFFENEAU, A. OREKHOV, and J. LÉVY (*Compt. rend.*, 1924, 179, 977—980; cf. A., 1923, i, 213, 788, 789).—The substituted ethylene oxides of the type  $\begin{matrix} \text{CHAR} \\ \text{CRR} \end{matrix} > O$  can undergo isomeric change on being heated

and yield by a semihydrobenzoin transposition the aldehydes  $CArRR'\text{-CHO}$ . This is regarded as confirmatory of the authors' view that the migration of the aromatic group does not constitute the first change in the transposition which occurs on dehydrating  $\alpha$ -glycols, but is preceded by the elimination of water. The migration follows the breaking of one of the oxygen linkings in an unstable intermediate compound.  $\alpha$ -Anisyl- $\beta$ -methylpropylene oxide, b. p.  $150$ — $160^{\circ}/30$  mm., on distillation readily isomerises into  $\alpha$ -anisyl- $\alpha$ -methylpropaldehyde, b. p.  $260$ — $265^{\circ}$  (*semicarbazone*, m. p.  $184^{\circ}$ ). The same aldehyde was prepared from phenyl anisyl dimethylglycol; its isomerides, anisyl isopropyl ketone and  $\beta$ -anisylbutan- $\gamma$ -one, may be readily differentiated by the melting points of their *semicarbazones*,  $212$ — $213^{\circ}$  and  $159$ — $160^{\circ}$ , respectively. H. J. E.

**Preparation of Plastic Material from Cellulose Esters.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING, and G. BALLE ('D.R.-P. 395704; from *Chem. Zentr.*, 1924, ii, 2623—2624).—The *methoxy* derivative of *oo'*-dihydroxymethyl-*p*-cresol has m. p.  $106^{\circ}$ , the *triacetyl* derivative, b. p.  $212^{\circ}/12$  mm., and *oo'*-*diacetoxy-methyl-p-tolyl p-toluenesulphonate*, m. p.  $63^{\circ}$ . These are good gelatinising agents for cellulose esters. R. B.

**Influence of Experimental Conditions on the Decomposition of Benzoyl Peroxide.** W. DIETRICH (*Helv. Chim. Acta*, 1925, 8, 149—154).—Whether exploded alone or in the presence

of organic solvents at 200° in a steel bomb, benzoyl peroxide is decomposed into carbon dioxide and diphenyl, together with small quantities of benzoic acid and *p*-diphenylbenzene (cf. Fichter and Fritsch, A., 1923, i, 438). Decomposition follows exactly the same course when the peroxide is boiled with high-boiling organic solvents such as paraffin (b. p. 300°), nitrobenzene, phenol, and anisole, the temperature being rapidly raised at the outset. The solvents are recovered unchanged. With lower-boiling solvents such as toluene and *m*-xylene, there are indications of a secondary reaction, in which the solvent is participating, although diphenyl is still the main product. When the decomposition is conducted more slowly, at water-bath temperatures, this secondary reaction becomes predominant and, in the case of toluene, for example, *p*-phenyltoluene, associated with a little ortho isomeride, is the main product (cf. Lippmann, A., 1887, 151; Böeseken and Gelissen, this vol., i, 30). In boiling aniline, the decomposition does not follow the ordinary course, but the peroxide acts exclusively as an oxidising agent, with production of azobenzene and aniline-black.

M. J.

**Syntheses by means of Organic Peroxides. II. Action of Benzoyl Peroxide on Toluene.** H. GELISSEN and P. H. HERMANS (*Ber.*, 1925, 58, [B], 476—479; cf. this vol., i, 379).—Benzoyl peroxide and toluene at 100° yield mainly benzoic acid, carbon dioxide, and a mixture of *o*- and *p*-methyldiphenyl. A subsidiary reaction gives carbon dioxide, benzene, and tolyl benzoate. The yield of benzoic acid is considerably less than that expected from theoretical considerations. In addition, *p*-phenylbenzoic acid and resinous matter are produced. Under similar conditions, *m*-xylene appears to yield benzoic acid, carbon dioxide, and a mixture of isomeric dimethyldiphenyls.

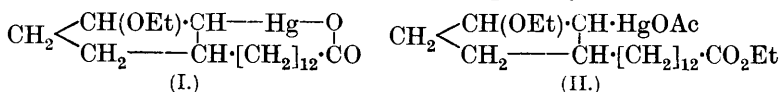
H. W.

**Syntheses by means of Organic Peroxides. III. Action of Benzoyl Peroxide on Benzene in the Presence of Aluminium and Iron Chlorides.** H. GELISSEN and P. H. HERMANS (*Ber.*, 1925, 58, [B], 479—481; cf. this vol., i, 379, and preceding abstract).—Addition of aluminium chloride or ferric chloride to a solution of benzoyl peroxide in hot benzene greatly decreases the production of resinous matter which occurs extensively in the absence of the catalyst, and appears to facilitate the formation of phenyl benzoate. With aluminium chloride, the main reaction leading to the production of benzoic acid and diphenyl, and further to the formation of diphenylbenzene, is still noticeable, but in the presence of ferric chloride diphenyl does not appear to be formed; on the other hand, the yield of benzoic acid is unexpectedly high, possibly owing to a direct "hydrolysis" of the peroxide by the liberated hydrogen chloride.

H. W.

**Synthesis of the Anhydride of Hydroxymercuri-ethoxychaulmoogric Acid and Ethyl Acetoxymmercuri-ethoxychaulmoograte.** A. L. DEAN, R. WRENSHALL, and G. FUJIMOTO (*J. Amer. Chem. Soc.*, 1925, 47, 403—407).—*Hydroxymercuri-ethoxy-*

*chaulmoogric anhydride*, (I), m. p. 112—113°, was obtained by adding chaulmoogric acid (1 mol.) to mercuric acetate (1 mol.) dissolved in a mixture of glacial acetic acid and absolute alcohol, at the ordinary temperature. A small quantity of an infusible



mercury compound was precipitated first, the anhydride separating on keeping the filtered reaction mixture at 0° for 3 months. *Ethyl acetoxymercuri-ethoxychaulmoograte*, (II), m. p. 67—68°, was obtained similarly from ethyl chaulmoograte, the product being isolated by pouring the filtered reaction mixture, which had been kept at 0° for 10 days, into water. F. G. W.

#### Action of Iodine on Desmotroposantonin : Artemisic Acid.

P. BERTOLO (*Atti R. Accad. Lincei*, 1925, [vi], 1, 127—130).—The action of iodine on desmotroposantonin in glacial acetic acid solution yields an acid identical, except for a lower melting point, in every way with artemisic acid (cf. A., 1923, i, 1013). T. H. P.

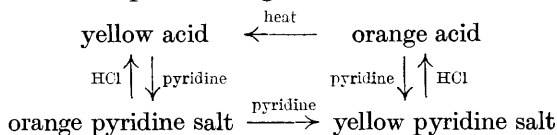
**Lactonic-Enolic Tautomerism of *o*-Hydroxydiphenylacetolactone.** A. LÖWENBEIN and W. FOLBERTH (*Ber.*, 1925, 58, [B], 610—612).—The existence of lactonic-enolic tautomerism of the

type  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CHPh} \\ \text{O} \end{array} > \text{CO} \rightleftharpoons \text{C}_6\text{H}_4 < \begin{array}{c} \text{CPh} \\ \text{O} \end{array} > \text{C} \cdot \text{OH}$ , assumed previously by Löwenbein and Simonis (A., 1924, i, 147), is established by the bromine titration method in ethyl-alcoholic solution, the validity of the process for the purpose being proved by the quantitative reduction of 2-hydroxy-5-methyldiphenylbromoacetolactone to 2-hydroxy-5-methyldiphenylacetolactone by hydriodic acid. *o*-Hydroxydiphenylacetolactone is in equilibrium with 3.54% of the enolic form, whereas this value is 4.92% and 3.20% in the cases of its 5- and 6-methyl derivatives and 1.58% and 1.50% for the 4'-methoxy-5-methyl and 2'-methoxy-5-methyl compounds. Phenylhydroxynaphthylacetolactone is enolised to the extent of 4.4%. H. W.

***o*-4-Bromo-*m*-toluoylbenzoic Acid.** G. HELLER and K. MÜLLER-BARDORFF (*Ber.*, 1925, 58, [B], 497—499).—The condensation of the three bromotoluenes with phthalic anhydride in the presence of aluminium chloride yields mainly the same acid, which has been considered to be *o*-4-bromo-*m*-toluoylbenzoic acid. The position of the methyl group has been established by the reduction of the corresponding anthraquinone derivative to 3-methyl-anthraquinone (Heller, A., 1912, i, 358). The position of the bromine atom is now established by oxidation of *o*-4-bromo-*m*-toluoylbenzoic acid by permanganate in alkaline solution to *o*-4-bromo-*m*-carboxybenzoylbenzoic acid, m. p. 196—197°, conversion of this acid by fuming sulphuric acid at 115° into 2-bromo-anthraquinone-3-carboxylic acid, m. p. 284°, and decarboxylation of the latter by treatment with zinc dust in alkaline solution and

subsequent sublimation of the product with formation of 2-bromo-anthraquinone.  
H. W.

**Border-line between Isomerism and Polymorphism. IV.**  
P. PFEIFFER, E. KALCKBRENNER, and H. BEHR (*J. pr. Chem.*, 1925, [ii], 109, 191—229; cf. A., 1918, i, 344).—The recognised differences between isomerism and polymorphism are discussed and attention is directed to certain compounds the behaviour of which appears to place them on the border-line between these phenomena. A number of these border compounds of the stilbene series is described. They occur in two differently coloured modifications, which in general are easily interconvertible, always give identical solutions, but show differences in the crystalline state, and according to ordinary definitions would be termed polymorphous. 2-Nitro-4'-methoxystilbene-4-carboxylic acid and its pyridine salt exist in two differently coloured forms which show reversible relationships according to the scheme,



Similarly, 2-nitro-4-benzamido-4'-methoxystilbene forms a yellow acetate which, when heated, gives the benzamido compound in an orange-coloured form, whilst the trichloroacetate is orange and gives a yellow modification of the benzamido compound on heating. These phenomena cannot be explained by the usual structural and stereochemical ideas. In all previously described compounds (*loc. cit.*) which show colour dimorphism, hydroxy or methoxy groups are present. The position of the auxochrome group is important, the *m*-methoxy group being always ineffective. Of the various derivatives of 2-nitro-4'-aminostilbene-4-carboxylic acid examined, only the methyl ester [(i) orange, (ii) Bordeaux-red leaves] and the ethyl ester [(i) brassy yellow leaves, (ii) violet needles] of the dimethylated amine showed colour dimorphism.

In the *o*-methoxy series, neither 2-nitro-2'-methoxystilbene-4-carboxylic acid (cf. Pfeiffer and Klinkert, A., 1917, i, 140), the nitrile, nor the ethyl ester showed dimorphism, but the alkali salts showed it in a marked degree; the *sodium* salt ( $3\text{H}_2\text{O}$ ) is greenish-yellow, becomes anhydrous at  $115^\circ$ , deep orange at  $140\text{--}200^\circ$ , retains this colour in dry air, but becomes yellow again in ordinary air with absorption of about 1 mol. of  $\text{H}_2\text{O}$ . The *potassium* salt ( $\text{H}_2\text{O}$ ) shows identical colour changes, but absorbs nearly  $2\text{H}_2\text{O}$  when kept.

The sodium and potassium salts of 2-nitro-3'-methoxystilbene-4-carboxylic acid, each containing not quite 1 mol. of  $\text{H}_2\text{O}$ , are orange-yellow, and scarcely change in colour at  $200^\circ$ . Colour dimorphism is much more frequent in the *p*- than in the *o*-methoxy series. Five different hydrates of *sodium* 2-nitro-4'-methoxystilbene-4-carboxylate (A., 1916, i, 24) have been prepared, viz., the *nonahydrate*, lustrous, bronze-brown scales; the *heptahydrate*,

greenish-yellow; the *pentahydrate*, lemon-yellow; the *dihydrate*, orange-yellow; and the *monohydrate*, canary-yellow. The anhydrous sodium salt below  $140^{\circ}$  is orange, at  $140$ — $200^{\circ}$  it becomes brown-orange. The potassium salt forms only the orange-coloured dihydrate. No colour dimorphism was shown by 2-nitro-2':3'-dimethoxystilbene-4-carboxylic acid, m. p.  $235^{\circ}$ , nor by any of the following derivatives: the *nitrile* (prepared by condensation of *o*-vanillin methyl ether with *o*-nitro-*p*-toluonitrile), m. p.  $152^{\circ}$ ; the *methyl ester*, m. p.  $112^{\circ}$ ; *sodium salt* ( $2\text{H}_2\text{O}$ ); *potassium salt* ( $\text{H}_2\text{O}$ ). The *op*-dimethoxy-acids and their derivatives sometimes resemble in their behaviour the compounds of the ortho and sometimes those of the para series.

2-Nitro-2':4'-dimethoxystilbene-4-carboxylic acid, m. p.  $252^{\circ}$ , orange-coloured needles, forms light yellow crystals containing 0.5 mol. of EtOH from alcohol. Two forms are obtained from hot acetic acid, a yellow form containing 1 mol. of acetic acid, and an orange-red form. The yellow form changes to red without appreciable alteration of its crystal form under various conditions. The *nitrile*, m. p.  $178^{\circ}$ , orange-coloured crystals (only one form), was prepared by condensing *o*-nitro-*p*-toluonitrile with 2:4-dimethoxybenzaldehyde. The *pyridine salt* with 1.5 mols. of pyridine occurs in a golden-yellow and an orange form. The *methyl ester*, m. p.  $130^{\circ}$ , orange-coloured, is best prepared by condensing methyl *o*-nitro-*p*-toluate, m. p.  $45^{\circ}$ , with 2:4-dimethoxybenzaldehyde. The *ethyl ester*, m. p. ca.  $100^{\circ}$ , forms golden-orange leaves; the *sodium salt* ( $\text{H}_2\text{O}$ ), canary-yellow leaves, becomes anhydrous at  $115^{\circ}$  without appreciable colour change, then orange-red at  $180$ — $200^{\circ}$ . The colour change is permanent in a closed vessel, but in the air 1 mol. of water is again taken up, and the salt becomes brownish- to golden-yellow. The *potassium salt* ( $\text{H}_2\text{O}$ ) behaves almost identically. 4-Nitro-2':4'-dimethoxystilbene-2-carboxylic acid, m. p.  $233$ — $235^{\circ}$ , forms brownish-orange needles; the *piperidide* (probably), m. p.  $265^{\circ}$ , was obtained as a by-product; the *nitrile*, m. p.  $161^{\circ}$ , reddish-orange needles, is obtained on heating *p*-nitro-*o*-toluonitrile with *op*-dimethoxybenzaldehyde. Neither the acid nor the nitrile showed colour dimorphism; the *methyl ester* has m. p.  $151^{\circ}$ . 2:4-Dinitro-2':4'-dimethoxystilbene, m. p.  $170^{\circ}$ , is obtained as orange to orange-brown crystals from *op*-dimethoxybenzaldehyde and *op*-dinitrotoluene at  $120^{\circ}$ . An attempt to prepare the red form of 2:4-dinitrostilbene (cf. Stoermer, A., 1922, i, 647) was unsuccessful. 2-Nitro-3':4'-dimethoxystilbene-4-carboxylic acid, m. p.  $240^{\circ}$ , was obtained in golden-yellow needles containing about 0.5 mol. of acetic acid; the anhydrous acid was obtained in an orange-red and a brown form, and the monohydrate in a golden-yellow and a brownish-yellow form. As explanation, a disguised form of colour dimorphism is suggested; it is pointed out that either this occurs or no dimorphism at all whenever a methoxy group occupies the meta position in the nitrostilbenes. The *nitrile*, m. p.  $177^{\circ}$ , the *methyl ester*, m. p.  $175^{\circ}$ , *ethyl ester*, m. p.  $158^{\circ}$ , and the *potassium salt* showed no appreciable colour change or change in weight on heating. 2-Nitro-4'-aminostilbene-

4-carboxylic acid, m. p. 260—263°, reddish-brown powder, is prepared from 2-nitro-4'-acetamido-4-cyanostilbene by the action of dry hydrogen chloride in methyl alcohol through the methyl ester and the ammonium salt, 1.5H<sub>2</sub>O, dark brownish-violet needles which dissolve in water to a blood-red solution. The nitrile, 2-nitro-4'-amino-4-cyanostilbene, m. p. 202°, Bordeaux-red leaves, yellow hydrochloride, forms an acetyl derivative, golden-yellow needles containing 1EtOH, m. p. 245°, prepared by condensation of *o*-nitro-*p*-toluonitrile with *p*-acetamidobenzaldehyde, and a benzoyl derivative, m. p. 242°, prepared by condensing *o*-nitro-*p*-toluonitrile with *p*-benzamidobenzaldehyde, m. p. 145°. The potassium salt, 2H<sub>2</sub>O, dark brownish-violet crystals, methyl ester, m. p. 161°, dark red needles, ethyl ester, m. p. 134°, dark red felted leaves, acetyl derivative, m. p. 275°, golden-yellow powder with 0.5 mol. of acetic acid, and benzoyl derivative, m. p. 297°, orange-coloured crystals, of 2-nitro-4'-aminostilbene-4-carboxylic acid are described, and the potassium salt, 1.5H<sub>2</sub>O, and methyl ester, m. p. 195°, of the benzamido-acid. Ethyl 2-nitro-4'-dimethylamino-stilbene-4-carboxylate, lustrous, brassy-yellow leaves, m. p. 128—129° from hot alcohol, changing to a brownish-orange powder on rubbing, gradually changes to violet needles, m. p. 129—130°, when left with the alcoholic mother-liquor. Methyl 2-nitro-4'-dimethylamino-4-carboxylate crystallises from hot methyl alcohol in Bordeaux-red leaves, m. p. ca. 134°, which in contact with the mother-liquor gradually become orange-coloured, m. p. 134.5°; both forms give orange-coloured solutions. A. C.

**Glutaconic Acids. XVIII. Three-carbon Tautomerism in the cycloPropane Series.** IV. F. R. GOSS, C. K. INGOLD, and J. F. THORPE (*J. Chem. Soc.*, 1925, **127**, 460—469).—The paper is largely polemical, criticising the experiments and conclusions of Feist (A., 1924, i, 511) and upholding the authors' original statements that there is only one form of cyclic glutaconic acid but three series of esters (T., 1923, **123**, 327, 3342; 1924, **125**, 1927). It is proved that the "labile" esters cannot have the

symmetrical structure  $\text{CHMe} \begin{smallmatrix} < \text{C} \cdot \text{CO}_2\text{R} \\ | \\ \text{C} \cdot \text{CO}_2\text{R} \end{smallmatrix}$ , since they, as well as the

parent acid and "normal" esters, show optical activity; 3-methyl- $\Delta^2$ -cyclopropene-1:2-dicarboxylic acid is resolved by means of quinine and brucine, and by digesting the silver salts of the *d*- and *l*-acids with ethyl iodide, the optically active "normal" esters are prepared, m. p. 55—56°, and may be recombined to give the racemic ester, m. p. 38—39°; on distillation, the active "normal" esters yield active "labile" esters. Partial hydrolysis of dimethyl 3-methyl- $\Delta^2$ -cyclopropene-1:2-dicarboxylate, and partial esterification of the acid give the same product, methyl hydrogen 3-methyl- $\Delta^2$ -cyclopropene 1:2-dicarboxylate, b. p. 169°/20 mm., m. p. 65°, instead of yielding isomeric acid esters of the types  $\text{CMe} \begin{smallmatrix} < \text{CH} \cdot \text{CO}_2\text{R} \\ | \\ \text{C} \cdot \text{CO}_2\text{H} \end{smallmatrix}$

and  $\text{CMe} \begin{smallmatrix} < \text{CH} \cdot \text{CO}_2\text{H} \\ | \\ \text{C} \cdot \text{CO}_2\text{R} \end{smallmatrix}$ ; similarly, the ethyl hydrogen ester, b. p.

174°/20 mm., m. p. 57°, is prepared by partial hydrolysis. One *methyl ethyl ester*, b. p. 130°/20 mm. (converted by bromine into *methyl ethyl 2 : 3-dibromo-3-methylcyclopropane-1 : 2-dicarboxylate*, b. p. 182°/20 mm.), is obtained, whether prepared by converting the methyl hydrogen ester into its silver salt and treating that with ethyl iodide, or whether prepared similarly from the ethyl hydrogen ester. The *cis*-structure of 3-methoxy-3-methylcyclopropane-1 : 2-dicarboxylic acid is proved, since boiling acetyl chloride yields the *anhydride*, m. p. 94°, from which the original acid is regenerated by treatment with water. The methoxyl group is oriented by boiling the acid with aqueous hydrogen chloride, when *lævulinic acid* is produced. F. M. H.

***p*-Orsellinic Acid.** A. WAGENHOFER (*Monatsh.*, 1925, 45, 223—229).—The investigations of Hemmelmayr (cf. A., 1913, i, 468) on the influence of substituents on the stability of the carboxyl group in substituted benzoic acids has been extended to methyl as substituent. *p*-Orsellinic acid (cf. Fischer and Hoesch, A., 1912, i, 859), on bromination in cooled ethyl ether (in acetic acid the product is a mixture), loses the carboxyl group and gives 2 : 4-*dibromo-orscinol*, m. p. 195—197°, which on methylation with methyl sulphate yields the known dimethyl ether, m. p. 161°. 2 : 4-Dibromo-orscinol is strongly acidic, and the following salts are described : *ammonium*,  $C_7H_5O_2Br_2NH_4$ ; *barium*,  $(C_7H_5O_2Br_2)_2Ba$ , light yellow needles; *barium*,  $C_7H_4O_2Br_2Ba$ , white. Methyl 3 : 5-dimethoxy-*p*-toluate, m. p. 87°, was prepared by the action of methyl sulphate on *p*-orsellinic acid; bromination of the cooled ethereal solution gives *methyl 2 : 6-dibromo-3 : 5-dimethoxy-p-toluate*, m. p. 82°, which on hydrolysis with potassium hydroxide loses the carbomethoxy group and gives 2 : 6-*dibromo-orscinol dimethyl ether*, m. p. 80°. Attempts to nitrate *p*-orsellinic acid resulted in the elimination of the carboxyl group, but the corresponding dimethoxy methyl ester yielded a *mononitro* compound,  $C_{11}H_{13}O_6N$ , m. p. 84°, brownish-red leaflets. A. C.

**Addition of Ethyl Malonate to Anils.** E. J. WAYNE and J. B. COHEN (*J. Chem. Soc.*, 1925, 127, 450—460).—The union of various anils with ethyl malonate, according to the equation  $CHR:NX + CH_2(CO_2Et)_2 = CHR(NHX) \cdot CH(CO_2Et)_2$ , is brought about in presence of piperidine and usually with the application of heat (*a*). The yields vary widely according to the substituent; when reaction does not occur, the anil may be recovered as picrate. The additive products are also prepared from aniline and the appropriate ethyl arylidenemalonate (*b*). Thus *ethyl β-anilinobenzylmalonate* may be prepared from benzylideneaniline and ethyl malonate, as also from aniline and ethyl benzylidenemalonate (or from benzaldehyde, aniline, and ethyl malonate). The following compounds have been made by both methods : *ethyl β-m-toluidinobenzylmalonate*, m. p. 91—92°; *hydrochloride*, m. p. 103—105° (from benzylidene-*m*-toluidine, m. p. 30—32°); *ethyl β-p-toluidinobenzylmalonate*, m. p. 80—82°; *ethyl β-2-naphthylaminobenzyl-*

malonate, m. p. 129—130°; ethyl  $\beta$ -anilino-*p*-tolylmalonate, m. p. 88—90° (from *p*-tolylideneaniline, m. p. 46·5—48°); ethyl  $\beta$ -*m*-nitro-anilino-benzylmalonate, m. p. given as 99—101° and 105—106°; ethyl  $\beta$ -*o*-carboxyanilino-benzylmalonate, m. p. 116—117·5°; ethyl  $\beta$ -*m*-carboxyanilino-benzylmalonate, m. p. 137—137·5°; ethyl  $\beta$ -*p*-carboxyanilino-benzylmalonate, m. p. 164—164·5°; ethyl  $\beta$ -*p*-bromoanilino-benzylmalonate, m. p. 84·5—85·5°; ethyl  $\beta$ -*p*-chloroanilino-benzylmalonate, m. p. 81—82·5°; ethyl  $\beta$ -anisidinobenzylmalonate, m. p. 97—99°; menthyl  $\beta$ -anilino-benzylmalonate, m. p. 200—201° (menthyl benzylidene-malonate, m. p. 94·5—95·5°). Salicylideneaniline and ethyl malonate give the anilide of coumarincarboxylic acid, m. p. 240—241·5°, and the *p*-toluidide of coumarincarboxylic acid, m. p. 220—222°, is obtained similarly. Methyl malonate behaves in the same way and the following are described: methyl  $\beta$ -anilino-benzylmalonate, m. p. 114—115°; methyl  $\beta$ -*m*-toluidinobenzylmalonate, m. p. 107—108·5°, and methyl  $\beta$ -*p*-toluidinobenzylmalonate, m. p. 120—121°. No reaction occurs between ethyl malonate and benzophenone, benzylidenemethylamine, benzylidene-2 : 4-xylydine, *p*-tolylidene-*p*-toluidine, benzylidene-*o*-nitroaniline, benzylidene-*p*-nitroaniline, *m*-nitrobenzylideneaniline, *o*-methoxybenzylideneaniline, *p*-methoxybenzylidene-*p*-toluidine (*picrate*, m. p. 178—180°), *p*-methoxybenzylidene- $\beta$ -naphthylamine (*picrate*, m. p. 185—186°), *p*-dimethylaminobenzylideneaniline, *p*-dimethylaminobenzylidene- $\beta$ -naphthylamine, m. p. 164—165°, benzylidene-*p*-aminodimethylaniline, benzylidene-*o*-toluidine [*picrate*, m. p. 203—205° (decomp.)], benzylidene- $\alpha$ -naphthylamine, or benzylidene-*o*-anisidine, nor between methyl malonate and benzylidene-*o*-toluidine. The following have, however, been prepared by method (b): ethyl  $\beta$ -*o*-toluidinobenzylmalonate, m. p. 67—68°; ethyl  $\beta$ - $\alpha$ -naphthylaminobenzylmalonate, m. p. 91·5—92°; ethyl  $\beta$ -*o*-anisidinobenzylmalonate, m. p. 68—68·5°. When method (b) is applied to *p*-aminodimethylaniline with ethyl benzylidenemalonate, the anil and ethyl malonate react in the cold, whilst ethyl *p*-dimethylaminobenzylidenemalonate and aniline behave similarly on heating, and this reaction is to some extent reversible; treatment of *p*-dimethylaminobenzylideneaniline and - $\beta$ -naphthylamine with ethyl malonate gives a little ethyl *p*-dimethylaminobenzylidenemalonate, m. p. 110—110·5° (also from *p*-dimethylaminobenzaldehyde and ethyl malonate). Benzylideneaniline forms no additive product with ethyl ethylmalonate or ethyl nitromalonate. From these data it is concluded that  $R'R''C:NR'''$  gives no additive compound with ethyl malonate when  $R'''$  is aliphatic, or when  $R'$ ,  $R''$ , and  $R'''$  are all aromatic, nor when  $R'$  is  $NHX$ ; the nitro group has an inhibiting action, but not the carboxyl group; only one *o*-substituted compound undergoes the addition; the accumulation of substituents diminishes the reactivity of anils towards ethyl malonate.

*p*-Dimethylaminobenzylidene-*p*-aminobenzoic acid, m. p. 261—262° (decomp.), and anisylidene-*p*-aminobenzoic acid, m. p. 194—195°, are described.

F. M. H.



**Radical Dissociation of Arylated Succinic Acid Derivatives.****I. Radical Dissociation of 2:2-Dihydroxytetraphenylsuccinodilactones [2:2'-Diketo-3:3'-diphenyl-3:3'-dicoumaranyls].** A. LÖWENBEIN [with W. FOLBERTH] (*Ber.*, 1925, 58, [B], 601—609; cf. Löwenbein and Simonis, A., 1924, i, 147).—

2:2'-Diketo-3:3'-diphenyl-5:5'-dimethyl-3:3'-dicoumaranyl,  

$$\text{O} \left\langle \begin{array}{c} \text{C}_6\text{H}_3\text{Me} \\ \text{CO} \end{array} \right\rangle \text{CPh} \cdot \text{CPh} \left\langle \begin{array}{c} \text{C}_6\text{H}_3\text{Me} \\ \text{CO} \end{array} \right\rangle \text{O}, \text{ m. p. } 200\text{--}203^\circ, \text{ is most}$$

advantageously prepared by the action of iodine on the sodium derivative of 2-hydroxy-3-phenyl-5-methylcoumarone. In cold solvents of high boiling point it yields colourless solutions, which become intensely blue when heated; dissociation into radicals is established by cryoscopic and ebullioscopic determinations of molecular weight, by the failure of the solutions to obey Beer's law, and by the absorption spectrum at different temperatures. Protracted ebullition of the solution causes spontaneous decomposition of the radicals even in an atmosphere of carbon dioxide. The compound is decomposed by methyl-alcoholic potassium hydroxide solution with production of 2-hydroxy-5-methyldiphenylacetic acid. The radical is somewhat insensitive towards gaseous oxygen, whereby it is slowly transformed into the peroxide,  $\text{C}_{30}\text{H}_{22}\text{O}_6$ , m. p.  $175\text{--}180^\circ$  (decomp.). It is readily converted by phenylhydrazine or hydrazobenzene, which are without action on the undissociated compound, into 2-hydroxy-3-phenyl-5-methylcoumarone. Quinol does not effect this change. The unusually turgid acceptance of oxygen and ready acceptance of hydrogen are explained by the hypothesis that the free valency is distributed between the carbonyl oxygen and the methine carbon atom as indicated by the formula  $\text{C}_6\text{H}_4 \left\langle \begin{array}{c} \text{CPh} \\ \text{O} \end{array} \right\rangle \text{C} \rightarrow \cdot$

The conception of the dilactones of this group as coumaranyl derivatives is strengthened by the observation that 2:2'-diketo-3:3'-diphenyl-5-methyl-3:3'-dicoumaranyl, m. p.  $163\text{--}165^\circ$ , is obtained from the sodium derivative of 2-hydroxy-3-phenyl-5-methylcoumarone and *o*-hydroxydiphenylbromoacetolactone or from the sodium compound of 2-hydroxy-3-phenylcoumarone and 2-hydroxy-5-methyldiphenylbromoacetolactone.

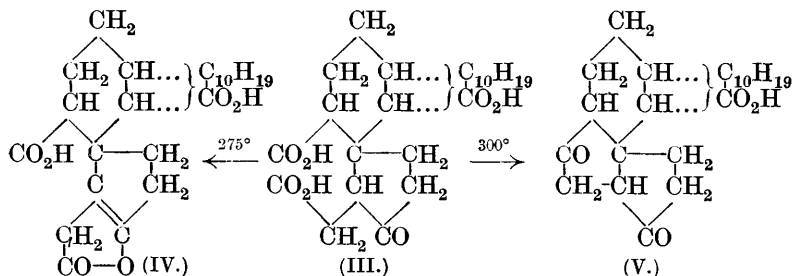
The following dicoumaranyl derivatives exhibit radical dissociation: 2:2'-dihydroxy-3:3'-diphenyl-4:4'-dimethyl-3:3'-dicoumaranyl, m. p. (indefinite)  $200^\circ$  (decomp.); 2:2'-dihydroxy-3:3'-diphenyl-3'':5'':3''':5'''-tetramethyl-3:3'-dicoumaranyl (m. p. about  $200^\circ$ ), from mandelonitrile and *as-m*-xylenol in the presence of 75% sulphuric acid; 2:2'-dihydroxy-4'':4'''-dimethoxy-3:3'-diphenyl-5:5'-dimethyl-3:3'-dicoumaranyl, m. p. about  $200^\circ$ ; 2:2'-dihydroxy-2'':2'''-dimethoxy-3:3'-diphenyl-5:5'-dimethyl-3:3'-dicoumaranyl, m. p.  $200^\circ$ .  
 H. W.

**Thermal Decomposition of  $\gamma$ - and  $\delta$ -Ketonic Acids and their Esters.** A. WINDAUS and A. BOHNE (*Annalen*, 1925, 442, 7—17).—The thermal decomposition of  $\gamma$ - and  $\delta$ -ketonic acids

containing cyclic ketonic groups is discussed in relation to Bredt's rule (cf. A., 1924, i, 643), and the failure of camphononic acid (I) to give a lactone (II) is attributed to the operation of this rule



that double bonds cannot exist in conjunction with the "bridge-heads" in bridged *cyclohexane* structures. The stability of the  $\delta$ -ketonic acid,  $\text{C}_{26}\text{H}_{44}\text{O}_3$  (A., 1917, i, 265), and the acid,  $\text{C}_{24}\text{H}_{40}\text{O}_3$ , obtained in the decomposition of cholesterol, are similarly explained, whilst, on the other hand, the conversion of pulegone-acetic acid into an unsaturated lactone (Vörlander, A., 1906, i, 362), and of prosolanellic acid (Wieland and Schulenberg, A., 1922, i, 346) and biloidanic acid (Wieland and Schlichtung, A., 1923, i, 41) into the corresponding pyro-acids, involves no contradiction of the rule. The authors postulate the following conditions for the formation by thermal decomposition of an unsaturated lactone from a ketonic acid containing the ketonic group in a *cyclohexane* ring: (1) the ketonic group must be in the  $\gamma$ - or  $\delta$ -position to the carboxyl group; (2) a hydrogen atom must be attached to the carbon atom adjacent to the ketonic group; (3) the carboxylic side-chain must be attached to the ring carbon atom adjacent to the ketonic group. If, however, the carbon atom carrying the carboxyl group in the side-chain is a member of a second ring, the mobility of this side-chain may be lessened and the formation of the lactone made more difficult. With ketonic di- and tri-carboxylic acids, the possibility of anhydride formation between the carboxylic groups introduces further complications. From a study of hyodeoxybilianic acid,  $\text{C}_{24}\text{H}_{36}\text{O}_7$ , m. p.  $242^\circ$ , an oxidation product of hyodeoxycholic acid, it is shown that the conditions can be varied so as to favour unsaturated lactone formation as against anhydride formation or *vice versa*. Thus at  $275^\circ$  in hydrogen, hyodeoxybilianic acid (III) loses only 1 mol. of water, yielding the unsaturated lactone (IV)



(*dimethyl* ester,  $\text{C}_{26}\text{H}_{38}\text{O}_6$ , m. p.  $123^\circ$ ), whilst at  $300^\circ$  by loss of 1 mol. of water and 1 mol. of carbon dioxide the cyclic *ketone* (V), m. p.  $182\text{--}183^\circ$  (*methyl* ester, m. p.  $105^\circ$ ), is produced. The esters

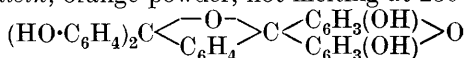
behave similarly; thus *trimethyl hydoxybilianate*,  $C_{27}H_{42}O_7$ , m. p. 129—130°, on distillation in a high vacuum loses 1 mol. of methyl alcohol and yields an unsaturated *lactone*, m. p. 109°, isomeric with the product obtained by methylation of the lactone (IV). This decomposition, however, only takes place in presence of potash glass; in Jena glass, the ester distils unchanged, but the addition of a little glass powder or of sodium ethoxide causes decomposition to take place. On the other hand, under the same conditions *trimethyl deoxybilianate*, m. p. 110°, *trimethyl isodeoxybilianate*, m. p. 136—137°, *trimethyl chenodeoxybilianate*, m. p. 92°, and *trimethyl bilianate* distil unchanged, and the authors conclude that the decomposition of such esters is governed by the three conditions indicated above. These relations are in agreement with the different structures assigned to hydoxybilianic acid and the isomeric acids. The method of thermal decomposition should be of great value in ascertaining the structure of the unknown deoxybilianic acids.

R. B.

### Condensation of Resorcinol and other Aromatic Hydroxy Compounds with some Acids, Esters, Lactones, and Lactams.

R. N. SEN and S. S. G. SIRCAR (*J. Indian Chem. Soc.*, 1925, **1**, 151—172).—The reactivity of the carbonyl group in various acids of the aliphatic, aromatic, and heterocyclic series, esters, lactones, and lactams in respect of condensation with resorcinol and other similar aromatic hydroxy compounds, with the formation of benzeins, fluoresceins, and rhodamine-like compounds is investigated. Generally, esters react with greater ease than the parent acid, and under suitable conditions both carbonyl groups of the anhydrides of dibasic acids can be made to react, either simultaneously or successively. One mol. of the acid, ester, lactone, or lactam is heated with 2 mols. of the hydroxy compound with powdered, anhydrous zinc chloride at 180—200° for 3—4 hours, generally in a current of dry hydrogen chloride. Salicylic acid and methyl salicylate with resorcinol yield *resorcinolsalicylein*, not melting at 260°; with pyrogallol, *pyrogallolsalicylein*, not melting at 250°. Gallic acid and resorcinol yield the *gallein*, dark red powder, not melting at 250°, *dibromo* derivative, not melting at 250°. Anthranilic acid and resorcinol yield *resorcinol-o-aminobenzein*, softening at 175—177°, *dibromo* derivative, decomp. 195°, *monopotassium* salt; anthranilic acid and *m*-diethylaminophenol yield *anthranilorhodamine*, a pink powder, softening from 230°. With stearic acid, resorcinol yields the *stearcin*, softening at 152°, and with pyromucic acid the *pyromucein*, not melting at 250°. Coumarin condenses with  $\alpha$ - and  $\beta$ -naphthols to yield the corresponding *coumareins*, dark brown powder, softening at 117°, and yellowish-brown powder, softening at 115°, respectively; with pyrogallol yielding *pyrogallolcoumarein*, not melting at 250°, and with diethylaminophenol to produce a *rhodamine*, softening at 156°. Phenolphthalein heated with resorcinol and zinc chloride in a current of dry hydrogen chloride at 180—200° yields only fluorescein, but when heated with an excess of resorcinol and a larger quantity of zinc chloride in a

current of dry hydrogen chloride at 220° for 5 hrs. it yields *phenol-resorcinolphthalein*, orange powder, not melting at 250°,



in which both of the carbonyl groups of the anhydride are acted on, the first with phenol and the second with resorcinol; it gives a *tetrabromo* derivative, orange powder, not melting at 250°, *dibenzoyl* derivative, m. p. 156—158°, and a *dipotassium* derivative which is doubly quinonoid in structure; *p*-cresolphthalein anhydride (cf. Drewson, A., 1882, 1098) reacts with resorcinol to yield the *resorcinol-p-cresolphthalein*, red powder, softening at 220°, whilst fluorescein similarly yields *resorcinolfluorescein*, decomp. 230°. Whilst phenol and isatin when heated with concentrated sulphuric acid at 120—130° for 6—7 hrs. yield the “phenolisatin” of Baeyer (A., 1886, 154), the β-carbonyl group reacting, an isomeric *phenolisatein*, greyish powder, softening at 285°, is produced by the condensing action of zinc chloride at 180—190°, the α-carbonyl group being attacked. Isatin condenses with resorcinol to yield *resorcinolisatein*, orange powder, not melting at 265°, *tetrabromo* derivative, decomp. 230°; with *m*-dimethylaminophenol to yield the *isatin-rhodamine*, softening at 242°; with pyrogallol to yield *pyrogallolisatein*, not melting at 250°, and with *p*-cresol giving *p-cresolisatein anhydride*, grey powder, not melting at 250°. All the compounds described, with the exception of those of which pyrogallol is the phenolic constituent, exhibit marked fluorescence and are dyes.

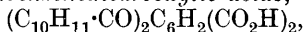
J. W. B.

**Dinaphthanthracene Series. VIII. Substituted Derivatives of Pyromellitic Acid.** E. PHILIPPI and R. SEKA [with W. BAUER] (*Monatsh.*, 1925, **45**, 266—271).—4 : 6-Diethyl-*m*-xylene on heating with bromine at 110° gives a small yield of 2 : 5-dibromo-4 : 6-diethyl-*m*-xylene, b. p. 150—170°/11 mm., which on heating with nitric acid at 220° yields dibromopyromellitic acid. With thionyl bromide, 2-bromo-4 : 6-diethyl-*m*-xylene, b. p. 141°/9 mm., is formed. Steric forces evidently play a part and hinder the introduction of a second bromine atom, as with 2 : 5-diethyl-*p*-xylene a dibromo compound is formed even in ice. The same monobromo compound is obtained by the action of bromine in acetic acid on 4 : 6-diethyl-*m*-xylene. Heating the monobromo compound at 170—190° with nitric acid (*d* 1.3) converts it into *bromopyromellitic acid*, C<sub>10</sub>H<sub>5</sub>O<sub>8</sub>Br, m. p. 240—265° (decomp.). The corresponding *anhydride*, m. p. 286° (uncorr.), is obtained by subliming the acid in a vacuum at 260—280°, or by allowing a solution of it in acetic anhydride to evaporate over potassium hydroxide in a vacuum. Condensation of bromopyromellitic anhydride with benzene by the Friedel and Crafts reaction gives a *bromodibenzoylbenzenedicarboxylic acid*, C<sub>22</sub>H<sub>13</sub>O<sub>6</sub>Br.2H<sub>2</sub>O, m. p. 140° (not sharp), which on long drying at 40° in a vacuum lost 1 mol. of water; with *p*-xylene a similar compound, C<sub>26</sub>H<sub>21</sub>O<sub>6</sub>Br.2H<sub>2</sub>O, m. p. 130—168°, was obtained. In neither case was it found possible to bring about closure of the ring with formation of a dinaphthanthracene derivative, although this takes

place readily with the corresponding non-brominated *p*-xylene derivative. A. C.

**Dinaphthanthracene Series. VII. Condensation of Pyromellitic Anhydride with Decalin and Tetralin ; Sulphonation of Dinaphthanthradiquinone.** E. PHILIPPI and R. ŠEKA [with K. FUNKE] (*Monatsh.*, 1925, **45**, 261—266; cf. A., 1923, i, 576, 577).—Decalin does not appear to form any condensation product with aluminium chloride, but when heated with pyromellitic anhydride in the presence of aluminium chloride gives a solid product, a small part of which is insoluble in ether or xylene. This insoluble compound, m. p. 286°, appears to be formed from 1 mol. of the anhydride and 2 mols. of partly dehydrogenated decalin. The portion (major) of the reaction product soluble in ether consists of 5-β-decahydronaphthoylbenzene-1 : 2 : 4-tricarboxylic acid, m. p. 224°, together with the corresponding lactone,  $C_{10}H_{16} \cdot C \cdot O \cdot CO \cdot C_6H_2(CO_2H)_2$ , m. p.

248°. On long drying in a vacuum at 110°, the lactone anhydride,  $C_{20}H_{18}O_5$ , m. p. 260° (not sharp), is obtained. The pyromellitic acid is assumed to have reacted with the β-position of the decalin, by analogy with Schroeter's observations (cf. A., 1921, i, 861). No conditions could be found under which closure of the ring takes place. The Friedel and Crafts reaction applied to tetralin and pyromellitic anhydride results in one of the possible isomeric ditetrahydronaphthoylbenzenedicarboxylic acids,



m. p. 240—242°, assuming reaction at the β-position of the benzenoid ring of the tetralin, the sharpness of the m. p. indicating a single isomeride. Closure of the ring did not take place on heating with fuming sulphuric acid or acetyl chloride (at 140—160°). The preparation of dinaphthanthradiquinonedisulphonic acid, greyish-green substance, unaltered up to 325°, is described. Its potassium, sodium, and calcium salts are very soluble, the barium and lead salts insoluble. A. C.

**Electrochemical Oxidation of Toluene to Benzaldehyde.** (A. MANN and P. M. PAULSON (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 31—42).—Yields of benzaldehyde amounting to 18 to 20% of the theoretical were obtained by Law and Perkin (*Trans. Faraday Soc.*, 1905, **1**, 251), by the electrochemical oxidation of toluene, using sulphuric acid as electrolyte with platinum electrodes and acetone as solvent. Sulphuric acid is now found unsuitable as electrolyte owing to the formation of large amounts of tarry condensation products, and acetone is unsuitable as solvent owing to its action as an anodic depolariser and the difficulty of finally separating it. The conditions for a maximum yield of benzaldehyde are 400 c.c. of 20% nitric acid, 50 c.c. of glacial acetic acid, 50 c.c. of toluene, 4.5—4.7 volts and anode current density 1.8—2 amps. per sq. dm. The solution, well agitated, is electrolysed for the theoretical number of ampère-hours at 8—10°, and a yield of 18—19% of the theoretical is obtained. C. S.

**Addition of Chloroform to Aldehydes.** J. W. HOWARD (*J. Amer. Chem. Soc.*, 1925, **47**, 455—456).—Phenyltrichloromethylcarbinol, b. p. 155—156°/150 mm.,  $d_{20}^{20}$  1.464,  $n_D^{25}$  1.5672, is obtained when powdered potassium hydroxide (4 g.) is added, over a period of 30 mins., with stirring, to a mixture of benzaldehyde (33 g.) and chloroform (60 g.), stirring being continued for another 90 mins. (cf. A., 1923, i, 309).

*Furyltrichloromethylcarbinol*, b. p. 115—118°/120 mm.,  $d_{20}^{20}$  1.452,  $n_D^{25}$  1.5346, obtained similarly from furfuraldehyde, darkens rapidly, even when protected from light. Similar compounds could not be isolated from aliphatic aldehydes (formic to valeric), nor from salicylaldehyde.

F. G. W.

**Valency. II. Decomposition of Organic Substances.** A. SCHÖNBERG (*Ber.*, 1925, **58**, [B], 580—586; cf. A., 1924, i, 520).—An attempt is made to express mathematically the relative tenacity with which two radicals are united to a given central atom, although it is pointed out that such expressions are valid only with respect to a definite reaction and under definite conditions. Reactions are considered which can be divided into “two-phase changes,” in which one molecule gives rise, through an intermediate “central compound,” to at least three fission products which differ amongst themselves; each central compound contains two different radicals united to the central atom. Polyphase changes are divided into those of the first order, in which all the migrating radicals of the central compound differ from one another, and those of the second order, in which at least two of the radicals attached to the central atom are identical. In the two types of change first described, the relative tenacity,  $H \frac{R_1}{R_2}$ , of two radicals,  $R_1$  and  $R_2$ , is given by the expression  $M_2/M_1$ , where  $M_2$  and  $M_1$  are the molecular quantities of the radicals  $R_2$  and  $R_1$  which have migrated within a given time. With polyphase changes of the second order, the expression is modified to  $M_2 n_1 / M_1 n_2$ , in which  $n_1$  and  $n_2$  is the number of the radicals,  $R_1$  and  $R_2$ , attached to the central atom.

[With R. ABELSDORFF, B. ANTONOFF, and H. KIRCHRATH.]—The behaviour of phenyl  $\beta$ -naphthyl ketone and phenyl  $\alpha$ -thienyl ketone towards sodamide and of diphenylbenzoylcarbinyl methyl ether towards alcoholic potassium hydroxide solution has been examined. *p*-Methylthiobenzamide, m. p. 189°, is described incidentally.

The data thus far obtained show that *p*-anisyl, *p*-dimethylaminophenyl, and  $\beta$ -naphthyl are more firmly united than phenyl, whereas *p*-chlorophenyl, *m*-chlorophenyl, *p*-bromophenyl, *m*-bromophenyl,  $\alpha$ -thienyl, triphenylmethyl, diphenylmethoxymethyl, and the group  $CPh_2(ONa)$  are less firmly attached.

H. W.

**Benzylbenzoin [Benzoylphenylbenzylcarbinol].** J. PASCUAL VILA and J. CEREZO (*Anal. Fis. Quím.*, 1925, **23**, 76—78).—It is now considered that the original formula assigned to benzylbenzoin (García Banus and Pascual Vila, A., 1922, i, 734) is correct and that it is not the benzyl ether of benzoin as suggested in a more recent communication (A., 1924, i, 1208). The preparation of benzyl-

benzoin by the action of benzyl chloride on the product of the reaction of benzoin with potassium amalgam is described.

G. W. R.

**Preparation of Aryl 4-Hydroxynaphthyl Ketones.** SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 212569).—Benzo-trichloride or other arylchloroform can be condensed with  $\alpha$ -naphthol to give an aryl 4-hydroxynaphthyl ketone, without formation of a triarylmethane dye, by carrying out the reaction, using 1 mol. of each of the reactants, in cold, concentrated sulphuric acid, or in a solvent such as nitrobenzene, in presence of a condensing agent such as zinc oxide or a phosphorus compound. E. H. R.

**Condensation of Aldehydes with Butylacetoacetic Ester [Ethyl  $\alpha$ -Acetylhexoate].** H. RYAN and M. J. SHANNON (*Proc. Roy. Irish Acad.*, 1924, **36**, [B], 322—328; cf. Ryan and Dunlea, A., 1915, i, 416; Ryan and Devine, A., 1916, i, 654).—The action of *n*-butyl iodide on ethyl sodioacetoacetate gave a 50% yield of ethyl  $\alpha$ -acetylhexoate,  $\text{COMe}\cdot\text{CH}(\text{C}_4\text{H}_9)\cdot\text{CO}_2\text{Et}$ , b. p. 225—226°. This ester was treated in alkaline solution with various aldehydes, the products in each case being a ketone from the ethereal extract and an acid from the acidified mother liquor. The condensation with piperonal yielded *piperonylidene*methyl amyl ketone,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}_4\text{H}_9$ , m. p. 75° (*oxime*, m. p. 126—127°; *phenylhydrazone*, m. p. 128—129°), and  $\alpha$ -*piperonylidene*-acetohectic acid, m. p. 184—185°. Similarly, the action with anisaldehyde yielded *p-methoxystyryl* amyl ketone, m. p. 60—61°, and *anisylidene*acetohectic acid, m. p. 171°. With benzaldehyde, the ester yielded *styryl* amyl ketone, m. p. 48° (*oxime*, m. p. 108—109°), and *benzylidene*acetohectic acid, m. p. 158—159°. Both piperonal and benzaldehyde condensed with methyl amyl ketone in presence of alcoholic hydrochloric acid, formed colourless, crystalline compounds, melting, respectively, at 237—239°, and 176—177°, derived from 3 mols. of the aldehyde to 1 mol. of the ketone in each case. B. W. A.

**Condensation of Aldehydes with Methyl Ethyl Ketone.** H. RYAN and P. J. CAHILL (*Proc. Roy. Irish Acad.*, 1924, **36**, [B], 334—339; cf. Ryan and Devine, A., 1916, i, 654).—In presence of alkali, methyl ethyl ketone condenses with piperonal to form *piperonylidene*methyl ethyl ketone, m. p. 101—102°, and with anisaldehyde to form *p-methoxystyryl* ethyl ketone, m. p. 53° (*dibromide*, m. p. 85°). Further condensation of anisaldehyde with *p-methoxystyryl* ethyl ketone yields 2:6-di-*p-methoxyphenyl*-3-methyltetrahydro-4-pyrone, m. p. 93—95°. In the presence of alcoholic hydrochloric acid, anisaldehyde reacts with methyl ethyl ketone, with *p-methoxystyryl* ethyl ketone, and with di-*p-methoxyphenyl*-methyltetrahydropyrone to form in each case the same substance,  $\text{C}_{28}\text{H}_{26}\text{O}_4$ , m. p. 158°. An analogous substance,  $\text{C}_{28}\text{H}_{22}\text{O}_6$ , m. p. 195°, is formed by the action of piperonal on *p-methoxystyryl* ethyl ketone. B. W. A.

**Phenyl Benzyl Diketone and some Derivatives.** T. MALKIN and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 369—377).—*o*-Methoxyacetophenone shows greater reactivity than phenyl propyl ketone when the two compete for salicylaldehyde. This fact, and others, are accounted for by considering the interaction of the electronic changes due to conjugation and the general polar effect. Four arylidene-*o*-methoxyacetophenones and the diketones formed by their hydrolysis are investigated.

Methoxyacetoneitrile is prepared in 70% yield by the action of formaldehyde on aqueous sodium cyanide, followed by treatment with methyl sulphate (cf. Polstorff and Meyer, A., 1912, i, 605). With benzaldehyde in presence of sodium hydroxide in aqueous-alcoholic solution, *o*-methoxyacetophenone yields *phenyl β-methoxystyryl ketone*, b. p. 202—204°/13 mm., m. p. 35°, which by addition of bromine to the ethereal solution forms *phenyl αβ-dibromo-α-methoxy-β-phenylethyl ketone*, m. p. 103°, which is unexpectedly stable, but converted by sodium hydroxide into a substance, m. p. 59°. By boiling a solution of phenyl β-methoxystyryl ketone in acetic and sulphuric acids, it is hydrolysed to phenyl benzyl diketone, m. p. 65° (cf. Dufraisse and Moureu, A., 1924, i, 405), which with *o*-phenylenediamine in alcoholic solution gives 2-*phenyl-3-benzylquinoxaline*, m. p. 97°. Similarly, *o*-methoxyacetophenone and anisaldehyde yield *phenyl β:p-dimethoxystyryl ketone*, b. p. 238—242°/14 mm., m. p. 75°, the acetic acid solution of which is hydrolysed by hydrogen bromide to *phenyl p-methoxybenzyl diketone*, m. p. 68° (which may be reconverted by the action of methyl sulphate on the alkaline solution); 2-*phenyl-3-p-methoxybenzylquinoxaline* has m. p. 119°. *ω:p*-Dimethoxyacetophenone and benzaldehyde give *p-methoxyphenyl β-methoxystyryl ketone*, b. p. 240—250°/33 mm., m. p. 74°, which yields *p-methoxyphenyl benzyl diketone*, m. p. 82°; 2-*p-methoxyphenyl-3-benzylquinoxaline*, m. p. 141°. *ω:p*-Dimethoxyacetophenone and anisaldehyde give *p-methoxyphenyl β:p-dimethoxystyryl ketone*, m. p. 72.5°, which is hydrolysed to *p-methoxyphenyl p-methoxybenzyl diketone*, m. p. 92°; 2-*p-methoxyphenyl-3-p-methoxybenzylquinoxaline*, m. p. 123°. In the derivatives of benzylideneacetophenone, a methoxy group in the *p*-position in the benzylidene nucleus is auxochromic, but in the acetophenone nucleus weakly bathochromic in character. On heating the sulphuric acid solutions, a change in colour occurs.

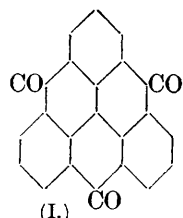
Phenyl benzyl diketone is reduced in alcoholic solution by hydrogen in presence of palladous chloride and gum arabic to *α-hydroxy-β-methoxy-αγ-diphenylpropane*, b. p. 197°/15 mm. By boiling the diketone in aqueous sodium hydroxide, it is converted, probably owing to migration of the benzyl group, into *α-benzylmandelic acid*, m. p. 164° (nearly quantitative yield); this may be oxidised to benzil, whilst bromine in presence of sodium carbonate gives a bromo compound (desyl bromide?), m. p. 54°, and distillation gives *α-phenylcinnamic acid* and stilbene (cf. Bogdanowska, A., 1892, 851). Similarly, from the other diketones are obtained *α-p-methoxybenzylmandelic acid*, m. p. 193°, *p-methoxy-α-benzyl-*



*mandelic acid*, m. p. 181°, and *p*:*p'*-*dimethoxy-α-benzylmandelic acid*, m. p. 170°. F. M. H.

**Triphenylmethane Compounds with Linked Benzene Nuclei. I. Trimethylenetriphenylmethane Triketone.** R. WEISS and J. KOREZYN (*Monatsh.*, 1925, **45**, 207—214).—Magnesium *o*-tolyl bromide in ether, on treatment with a hot suspension of phthalic anhydride in benzene, gives *di-o-tolylphthalide*,  $C_6H_4 \langle \frac{C(C_6H_4Me)_2}{CO} \rangle O$ , m. p. 128—131°, together with a small amount

of *o*-toluylbenzoic acid,  $CO_2H \cdot C_6H_4 \cdot CO \cdot C_6H_4Me$ , m. p. 127—130° (not sharp); *methyl o-toluylbenzoate* has m. p. 37—39°, b. p. 210—214°/12 mm. Reduction of the ditolylphthalide in alcohol with sodium amalgam gives *phenyldi-o-tolylmethane-o-carboxylic acid*,  $CO_2H \cdot C_6H_4 \cdot CH(C_6H_4Me)_2$ , m. p. 241·5—243°, in 70% yield (reduction with zinc in alcoholic sodium ethoxide solution gives a much poorer yield). Oxidation of the carboxylic acid by means of alkaline potassium permanganate gives *triphenylmethanetricarboxylic acid*,  $CH(C_6H_4 \cdot CO_2H)_3 \cdot H_2O$ , m. p. 303° (darkens), which on treatment with diazomethane yields a *trimethyl ester*,  $C_{25}H_{22}O_6$ , m. p. 170°. Concentrated sulphuric acid removes 3 mols. of



water from the tricarboxylic acid with threefold ring closure, giving *trimethylenetriphenylmethane triketone* (I), dark blue needles which do not melt at 450°, but sublime between 340° and 380°/12 mm., with slight decomposition. The action of thionyl chloride followed by heating with aluminium chloride also converts the tricarboxylic acid into the triketone. Substitution of ethyl phthalate for phthalic anhydride in the reaction with magnesium *o*-tolyl bromide produces 2-*o*-toluylphenyldi-*o*-tolylcarbinol,  $Me \cdot C_6H_4 \cdot CO \cdot C_6H_4 \cdot C(OH)(C_6H_4Me)_2$ . A. C.

**4-Acetamido-*o*-benzoquinone and some of its Derivatives.** F. KEHRMANN and E. HOEHN (*Helv. Chim. Acta*, 1925, **8**, 218—223).—4-Aminopyrocatechol, obtained by the action of hydrobromic acid on 4-aminoguaiacol (cf. A., 1898, i, 71, 72), yields a *triacetyl* derivative, m. p. 147°, hydrolysed by sodium hydroxide to 4-acetamidopyrocatechol, which is oxidised by sodium dichromate and sulphuric acid to 4-acetamido-*o*-benzoquinone, reddish-brown needles, decomposing at 170—180° without melting. The compound is rapidly decomposed by boiling water. It yields a reddish-brown *monoxime*, which is deposited from hot benzene in dark green, almost black, spear-shaped crystals. The reddish-brown modification is more readily soluble in cold sodium hydroxide than the green form. Dilute acids precipitate the reddish-brown modification from alkaline solutions. The green crystals pass into the reddish-brown form at 115—120°. The oximino group is shown to be in the para position to the acetamido group by reduction with stannous chloride and hydrochloric acid to 2-hydroxy-*p*-phenylenediamine.

4-Acetamido-*o*-benzoquinone condenses with *o*-phenylenediamine;

hydrolysis of the condensation product gives a poor yield of 2-aminophenazine. Similar condensations with *o*-aminophenol and *o*-aminodiphenylamine give indications of the formation of phenoxazine and *aposafranine*, respectively.

Oxidation of 4-aminoguaiacol by Willstätter's method gives an excellent yield of sulphur-yellow crystals of 2-methoxy-*p*-benzoquinoneimine, m. p. 95° (decomp.), very little different in colour from the corresponding methylbenzoquinoneimine.

4-Acetamidoguaiacol acetate, m. p. 152°, 4-benzamidoguaiacol, m. p. 166°, and 4-benzamidopyrocatechol, m. p. 169°, are also described.  
M. J.

**Dehydrogenation and Autoxidation and their Mutual Relationship.** W. MANCHOT and H. GALL (*Ber.*, 1925, 58, [B], 486—492).—The possibility of effecting catalytic dehydrogenation with the aid of spongy platinum completely free from oxygen is established by the rapid and quantitative conversion of anthraquinol in alcoholic or ethereal solution into anthraquinone in the presence of the catalyst; the latter is prepared by means of formaldehyde and potassium hydroxide at -10° and subsequently heated for 8 hours at 95° in a high vacuum in an atmosphere of nitrogen. In alkaline solution, anthraquinol and dihydroindigotin do not suffer dehydrogenation. The bearing of these observations on Wieland's theory of oxidation is discussed in detail, and the author is led to classify the modes of autoxidation as follows: (1) spongy platinum causes dehydrogenation in virtue of its affinity for hydrogen; the process does not occur in the absence of the catalyst, but is caused more or less readily by oxygen (*e.g.*, anthraquinol in neutral solution); (2) spongy platinum causes dehydrogenation of the oxidisable substance slowly if at all (*e.g.*, anthraquinol in alkaline solution); the effect is produced by oxygen and may be accelerated by platinum, which activates the oxygen; (3) spongy platinum, as true catalyst, accelerates the oxidation of the substance at the expense of the water (*e.g.*, chromous chloride); the process occurs more slowly in the absence of catalyst; (4) autoxidation of very slowly or apparently non-oxidisable substances can be effected by oxygen carriers, which may act catalytically to an unlimited extent or in a restricted manner, since they are themselves oxidised, probably with intermediate formation of a primary oxide peroxide which acts as effective carrier. H. W.

***o*-Nitroaldehydes of the Anthraquinone Series.** P. RUGGLI and E. BRUNNER (*Helv. Chim. Acta*, 1925, 8, 155—168).—Direct nitration of anthraquinone-2-aldehyde gives the 6-nitro derivative. To prevent nitration in this ring, 5:6:7:8-tetrachloroanthraquinone derivatives were used. 5:6:7:8-Tetrachloro-2-methylanthraquinone (Meister, Lucius, & Brüning, A., 1922, i, 179), on bromination in nitrobenzene solution, gives 5:6:7:8-tetrachloro-2-dibromomethylanthraquinone, m. p. 196—197°. Treatment with concentrated sulphuric acid converts this compound into 5:6:7:8-tetrachloroanthraquinone-2-aldehyde, a yellow, crystalline powder,

m. p. 182—183°; *phenylhydrazone*, violet-red needles, m. p. above 300°, *semicarbazone*, orange-yellow crystals, m. p. above 300°, *oxime*, yellow, crystalline powder, m. p. 234—235°, and *diacetyl* derivative, golden-yellow crystals, m. p. 172°. Attempts to nitrate the aldehyde gave only the carboxylic acid. Attempts to prepare a cinnamic acid analogue from the aldehyde, for subsequent nitration, were also unsuccessful.

5 : 6 : 7 : 8-Tetrachloro-1-nitro-2-methylanthraquinone (*loc. cit.*) yields, on bromination, 5 : 6 : 7 : 8-tetrachloro-1-nitro-2-dibromomethylanthraquinone, m. p. 246—248°, which with concentrated sulphuric acid, or preferably with silver acetate in glacial acetic acid, yields 5 : 6 : 7 : 8-tetrachloro-1-nitroanthraquinone-2-aldehyde, m. p. 265—268°, giving a *phenylhydrazone*, violet-red needles, m. p. above 300°, and a *diacetyl* derivative, yellow needles, melting with blackening at 250°. The aldehyde, like *o*-nitrobenzaldehyde, reacts with acetone and alkali, but the violet-black amorphous product, obtained in too small yield for further investigation, does not appear to be an anthraquinone-indigo.

1-Nitro-2-methylanthraquinone (A., 1924, i, 528) yields, on bromination, 1-nitro-2-dibromomethylanthraquinone, m. p. 242°, which with concentrated sulphuric acid gives a compound, reddish-violet needles, m. p. 228—230°, believed to be 1-nitrosoanthraquinone-2-carboxylic acid. Treatment of 1-nitro-2-dibromomethylanthraquinone with silver acetate and glacial acetic acid yields 1-nitroanthraquinone-2-aldehyde, yellow crystals, m. p. 228—230°, giving a *phenylhydrazone*, violet-red needles, m. p. above 300°, and a *diacetyl* derivative, m. p. 205°. With acetone and alkali, it yields a violet-black powder which does not appear to be an anthraquinone-indigo.

M. J.

**Derivatives of  $\beta$ -Methylanthraquinone. *Frangula Emodin*, *Emodic Acid*, and their Derivatives.** R. EDER and F. HAUSER (*Helv. Chim. Acta*, 1925, 8, 126—139; cf. A., 1924, i, 185).—The synthesis of *Frangula emodin* from 3 : 5-dinitrophthalic acid and *m*-cresol leaves it uncertain whether this substance is the 1 : 5 : 7- or 1 : 6 : 8-trihydroxy-3-methylanthraquinone. Oxidation to the carboxylic acid and elimination of the carboxyl group gives a trihydroxyanthraquinone identical with the compound obtained by oxidation of chrysophanic acid and replacement of the carboxyl group by hydroxyl (cf. A., 1911, i, 632). Emodin is therefore 1 : 6 : 8-trihydroxy-3-methylanthraquinone.

A series of emodic acid derivatives is described. Acetylation of emodin gives the triacetyl derivative oxidised by Fischer to emodic acid (cf. A., 1911, i, 886). By careful moderation of the oxidation conditions, *triacetylemodic acid*, m. p. 210—211°, can be isolated. Hydrolysis gives emodic acid, showing two modifications on crystallisation from 90% alcohol. Fischer's amorphous form, m. p. 350—355°, crystallises out first and is followed by short, compact, reddish-brown needles with the same m. p. Both modifications sublime in a vacuum without decomposition at 230—240°, yielding orange-red needles melting sharply at 360°. Attempts to prepare the acid

chloride were unsuccessful. Treatment with thionyl chloride gives a dark brown, amorphous substance, m. p. 150—175°, which is attacked with difficulty by boiling solutions of barium and calcium hydroxides, giving salts of emodic acid. The supposition that the compound is a lactone formed by elimination of water from the carboxyl group and the  $\beta$ -hydroxyl is supported by the fact that, when the latter is alkylated, an acid chloride is formed without difficulty. Oxidation of the *diacetyl* derivative, greenish-yellow needles, m. p. 190—191°, of the monomethyl ether of emodin obtained from chrysarobin (cf. following abstract) gives the *monomethyl ether of diacetylemodic acid*, greenish-yellow needles, m. p. 214—215°. Saponification gives *emodic acid monomethyl ether*, subliming in a vacuum without decomposition to reddish-brown needles, m. p. 300° (*pyridine* salt, yellow needles, decomp. 120°). Thionyl chloride reacts with this substance, giving the *monomethyl ether of emodic acid chloride*, orange needles, m. p. 205°, very slowly attacked by water, dilute acids, and alkalis; the corresponding *amide* has m. p. 292°. By treatment with sodium hypochlorite, the amide is converted into 3-amino-1:8-dihydroxy-6-methoxyanthraquinone, a dark violet, amorphous powder, carbonising at 450° without melting, never obtained quite pure because of its sparing solubility in organic solvents. Diazotisation and treatment with alcohol gives two products, 1:8-dihydroxy-6-methoxyanthraquinone, m. p. 178—180°, insoluble in alkali, yielding, on demethylation, 1:6:8-trihydroxyanthraquinone, identical with the product obtained by replacement of the methyl group of chrysophanic acid by hydroxyl; and 1:3:8-trihydroxy-6-methoxyanthraquinone, identical with the product obtained when the methyl group in the monomethyl ether of *Frangula* emodin is replaced by hydroxyl.

The following derivatives of emodic acid are also described: *ethyl* ester, reddish-brown, m. p. 252°; *isobutyl* ester, orange-red, m. p. 229°; *trimethyl ether*, yellow, m. p. 270°; *dipyridine* salt, orange, decomp. 120°; *tripotassium* salt, dark-violet, microcrystalline powder. M. J.

**Derivatives of  $\beta$ -Methylantraquinone. VI. Naturally-occurring Monomethyl Ether of *Frangula* Emodin.** R. EDER and F. HAUSER (*Helv. Chim. Acta*, 1925, 8, 140—145).—Collective evidence shows that, in anthraquinone rings, hydroxyl groups in the  $\beta$ -position are more acidic in character, more easily methylated, and more difficultly demethylated than these groups in the  $\alpha$ -position, and that only  $\beta$ -hydroxyl groups are available for alkali salt formation with alcoholic potassium acetate. The diminished acidity of the natural monomethyl ether of emodin suggests that the compound contains no free  $\beta$ -hydroxyl. It cannot be extracted from benzene solution by shaking with 5% sodium hydroxide solution, nor does it give a pyridine salt. Demethylation gives low yields of emodin. *Frangula* emodin, on treatment with alcoholic potassium acetate and subsequent methylation, yields a monomethyl ether identical with the natural product. The authors conclude that the methoxy group is in the  $\beta$ -position. M. J.

**Perylene and its Derivatives. VI.** A. ZINKE and F. HANSEL-MAYER (*Monatsh.*, 1925, **45**, 231—234; cf. Zinke and Dengg, *A.*, 1922, i, 132, 1013).—Dihydroxyperylene has been prepared in a pure state from 1:12-perylenequinone. The crude material obtained by heating  $\beta$ -dinaphthol with anhydrous aluminium chloride was dissolved in aqueous sodium hydroxide containing aluminium powder. The solution on oxidation by air gives a product which on heating with lead peroxide in benzene yields 1:12-perylenequinone, m. p.  $287^\circ$ , reddish-brown needles. The quinone gives a light yellow vat with intense yellowish-green fluorescence in which cotton is dyed a brilliant lemon-yellow. Hydrogen peroxide converts the colour into a light brownish-red. The alkaline perylenequinone vat with benzoyl chloride gives 1:12-dibenzoyloxyperylene, m. p.  $227^\circ$  (uncorr.). An acetic acid solution of 1:12-perylenequinone on treatment with zinc dust yields 1:12-dihydroxyperylene,  $C_{20}H_{12}O_2$ , yellow leaves, which dissolves in concentrated sulphuric acid to a blue solution and becomes brown (quinone) on adding oxidising agents. A. C.

**Camphor Series. IV.** S. KOMATSU and C. FUJIO (*Mem. Coll. Sci. Kyoto*, 1924, [A], **7**, 389—395).—The influence of various metallic chlorides and of alumina on the removal of hydrochloric acid from pinene hydrochloride and bornyl chloride is studied. The best yield of camphene is obtained using ferric chloride at temperatures up to  $100^\circ$ , or aluminium chloride or alumina at  $200^\circ$ . A hydrocarbon,  $C_{20}H_{32}$ , containing one ethylenic linking, b. p.  $208\text{--}210^\circ$ ,  $n_D^{25}$  1.5304,  $d_4^{25}$  0.9649, is obtained when the reaction is conducted under pressure. A liquid and a solid modification of camphene were obtained (but not in the pure state) by the removal of hydrochloric acid from pinene hydrochloride at different temperatures. L. F. H.

**Structural Relations between Pinenes and the Terpeneols or Limonenes Derived from them.** M. DÉLÉPINE (*Compt. rend.*, 1924, **179**, 980—982).—If the formula of  $\alpha$ -pinene is written in such a way that the double bond is to the right and the  $CMe_2$  group above the plane of the paper, the resulting terpeneol has the double bond to the left and the  $CMe_2OH$  group above the plane of the hexagon. This interpretation is based on the results obtained by Godlevsky (*A.*, 1899, i, 920) and by Barbier and Grignard (*A.*, 1908, i, 852; 1910, i, 555) and leads to a modification of the hypothesis that the tetramethylene ring is broken in the change from pinene to terpeneol. The suggestion as to the formation of an intermediate substance, methylnopinol (*A.*, 1924, i, 1088), is consistent with this view. H. J. E.

**Properties of some Ethereal Oils in Calabria.** F. LA FACE (*Riv. Ital. essenze e profumi*, **6**, 99—101; from *Chem. Zentr.*, 1924, ii, 2615—2616).—The bright yellow oil from *Timus vulgaris* has  $d_{15}^{15}$  0.903,  $[\alpha]_D^{15}$   $-2.18^\circ$ ,  $n_D^{20}$  1.4810, and contains 20.5% of phenols, of which thymol represents 95%. The yield varies from 0.117 to 0.173%, according to whether the plant is picked

in the early morning or the afternoon. The oil from *Mentha piperita*, yield 1.5%,  $d_{15}^{25}$  0.9192°,  $[\alpha]_D^{15}$   $-4^{\circ} 18'$ ,  $n_D^{20}$  1.4635, acid number, 1.16, ester number, 39.2, saponification value (acetylated oil), 142, contains 13.86% of esters, 41.29% of alcohols (30.37% free menthol), 9.3% of menthone. The bright yellow oil from *Mentha arvensis* var. *sativa*, Hort., yield 0.45%,  $d_{15}^{25}$  0.940,  $[\alpha]_D^{15}$   $-47^{\circ} 18'$ ,  $n_D^{20}$  1.4820, acid number 2.5, ester number 22.4, acetyl value 106.4, contains esters 7.92%, total alcohols, 41.42, free alcohols 24.88%. The pale yellow oil from *Coriandrum sativum* has  $d_{15}^{25}$  0.8810,  $[\alpha]_D^{15}$   $11^{\circ} 12'$ , acid number 1.4, ester number 11.2, saponification value of acetylated oil 201.6, and contains 61.6% of linalool.  
R. B.

**New Constituent in Oil of Juniper.** F. C. PALAZZO and E. ALINARI (*Atti I. Congr. Naz. Chim. pur. appl.*, 1923, 309—315; from *Chem. Zentr.*, 1924, ii, 1640).—From the terpene fraction of oil of juniper, the author isolated pinene and another compound as yet unidentified, of higher b. p. and lower d. G. W. R.

**Oil of [Jamaica] Pimenta Leaves.** M. KEMP (*Arch. Pharm.*, 1925, 263, 12—16).—This oil, derived from *Pimenta officinalis*,  $d_{19}^{20}$  1.062, is composed chiefly of eugenol (95.5% free, 1.1% combined). Besides this there are present caryophyllene, traces of aldehydes or ketones, and a mixture (0.45%) of a dibasic unsaturated acid,  $C_{10}H_{14}O_4$ , b. p. 70—73°/1.7 mm., and another unsaturated acid,  $C_{13}H_{14}O_4$ , m. p. 78° (crystallising from the former after the distillation).  
W. A. S.

**Constituents of some Indian Essential Oils. XIV. Essential Oil from the Seeds of *Zanthoxylum ovalifolium*.** J. L. SIMONSEN (*Indian Forest Rec.*, 1924, 11, 1—5).—The oil separated by steam distillation, amounting to about 0.3% of the seed and husk, consists chiefly of myrcene and safrole. Palmitic acid and combined lower fatty acids and a liquid phenol are present in small quantities.  
S. I. L.

**Constituents of some Indian Essential Oils. XV. Essential Oil from the Seeds of *Juniperus communis*.** J. L. SIMONSEN (*Indian Forest Rec.*, 1924, 11, 6—9).—The yield by steam distillation is 0.2%; the oil differs from normal juniper oil, and resembles oil of savin, containing about 50% of *d*-sabinene, but no  $\alpha$ -pinene.  
S. I. L.

**Constituents of some Indian Essential Oils. XVI. Rate of Oxidation of *d*- $\Delta^3$ -Carene and other Terpenes in the presence of Catalysts.** M. G. RAO (*Indian Forest Rec.*, 1924, 11, 197—206).—The addition of 0.001% of pyrogallol to readily-oxidised terpenes greatly delays the beginning of oxidation, although once started this proceeds very rapidly and the curves showing percentage of oxygen absorbed with time are very similar to those normally obtained.  
S. I. L.

**Travancore Essential Oils: Oil from the Leaves of *Lantana camara*.** II. K. L. MOUDGILL (*Perf. Essent. Oil Rec.*, 1925, 16, 9—10; cf. A., 1922, i, 754).—The hydrocarbon previously  
x\*

described, b. p. 253—255° (produced from the hydrocarbon originally present in the essential oil by isomerisation during distillation), oxidises when kept, giving a compound,  $C_{15}H_{26}O$ , m. p. 196—200°,  $\alpha_D^{30} +7.35^\circ$  in benzene, which is probably a resene. B. F.

**Constitution of the Caoutchouc Molecule.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1925, **44**, 229—238).—A criticism of the conclusions of Harries and Evers (A., 1922, i, 357) and of Boswell (*India-rubber J.*, 1922, **64**, 981) as to the molecular structure of caoutchouc. The author maintains the view put forward by himself (A., 1922, i, 45) and by Staudinger (A., 1922, i, 1043) that the molecule has a long open-chain structure. G. M. B.

**Oakwood Tannin. Preparation and Purification of Tannins. II.** K. FEIST and H. BESTEHORN (*Arch. Pharm.*, 1925, **263**, 16—31; cf. A., 1924, i, 1218).—The electro-osmotically purified tannin (*loc. cit.*) still contains reducing sugar; this, however, remains in solution when the tannin is precipitated by lead acetate, and the regenerated tannin then affords no reducing sugar when it is hydrolysed by hot dilute sulphuric acid. The action here is not solely hydrolysis; phlobaphen is formed, and ellagic acid and possibly gallic acid—but this is doubtful—are produced. When either the crude tannin or material partly purified through the potassium and lead salts is subjected to the action of *Aspergillus niger* until the mould ceases to grow, it affords ellagic acid (doubtful in the second case) and apparently simply a more homogeneous tannin. This resembles Vollbrecht's preparation (A., 1922, i, 1046). The product of both preparations afforded a methyl derivative of molecular weight 1210. Crude tannin cannot be purified or separated into its constituents by fractional crystallisation of the acetyl derivative, but the methyl derivative (*loc. cit.*), obtained by treating the tannin in acetone solution with diazomethane, is eventually isolated (from the crude tannin two other products are obtained in very small amount) by repeated solution in acetone and reprecipitation by water. The molecular weight of 1343 (*loc. cit.*) is a mean of four results, ranging from 1236 to 1462, of cryoscopic determinations in camphor solution. Analysis showed C 58.18%, H 5.28%.

An attempt to synthesise a tannin by oxidising ellagic acid in alkaline solution by means of a current of air gave inconclusive results.

*Tetracarbethoxyellagic acid*,  $C_{14}H_2O_4(O \cdot CO_2Et)_4$ , obtained by treating ellagic acid in alkaline solution with ethyl chloroformate, has m. p. 244°. W. A. S.

**Strophanthin. VI. Anhydrostrophanthidins and their Behaviour on Hydrogenation.** W. A. JACOBS and A. M. COLLINS (*J. Biol. Chem.*, 1925, **63**, 123—133; cf. A., 1924, i, 867 and 1331).—Dianhydrostrophanthidin, when treated with concentrated hydrochloric acid, gives *trianhydrostrophanthidin*,  $C_{23}H_{26}O_3$ , m. p. 135.5—137.5°,  $[\alpha]_D^{25} 98^\circ$ ; the substance was also obtained, in smaller yield, from monoanhydrostrophanthidin under similar conditions;

it does not form an oxime or a benzoate and therefore probably retains the oxidic structure of dianhydrostrophanthidin; on hydrogenation, it takes up 1 mol. of hydrogen only to give *dihydro-trianhydrostrophanthidin*,  $C_{23}H_{28}O_3$ , m. p. 132—133°,  $[\alpha]_D^{25}$  97°, which is also obtained by the action of hydrochloric acid on dihydrodianhydrostrophanthidin. The behaviour on hydrogenation indicates the probable existence of a benzenoid structure in the molecule of trianhydrostrophanthidin. Dianhydrostrophanthidin on hydrogenation takes up a maximum of 4 mols. of hydrogen with simultaneous loss of 1 mol. of water. After absorption of 3 mols. of hydrogen, there are obtained  $\alpha$ -*hexahydrotrianhydrostrophanthidin*,  $C_{23}H_{32}O_3$ , m. p. 183—187°,  $[\alpha]_D^{25}$  7°, and the  $\beta$ -isomeride, m. p. 224—227°,  $[\alpha]_D^{25}$  37°; after absorption of 4 mols. of hydrogen there are formed  $\alpha$ -*octahydrotrianhydrostrophanthidin*,  $C_{23}H_{34}O_3$ , m. p. 231—233°,  $[\alpha]_D^{25}$  49°, and the  $\beta$ -isomeride, m. p. 210—213°,  $[\alpha]_D^{25}$  67°; the same mixture, but with a preponderance of the  $\beta$ -isomeride, is obtained by the hydrogenation of dihydrodianhydrostrophanthidin. On treatment of strophanthidin with concentrated hydrochloric acid there is obtained no trace of trianhydrostrophanthidin, but a 25% yield of  $\psi$ -*strophanthidin*, which softens at 123—127°; this substance does not form an oxime or a phenylhydrazone, nor does it, like strophanthidin, isomerise in the presence of alkali. No acyl derivative could be crystallised.

C. R. H.

**Esters of Furfuryl Alcohol.** J. E. ZANETTI (*J. Amer. Chem. Soc.*, 1925, 47, 535—536).—*Furfuryl propionate*, b. p. 195—196°/764 mm., 59—60°/1 mm.,  $d^{20}$  1.1085, *butyrate*, b. p. 212—213°/764 mm., 69—70°/1 mm.,  $d^{20}$  1.0530, and *valerate*, b. p. 228—229°/764 mm., 82—83°/1 mm.,  $d^{20}$  1.0284, were prepared by heating furfuryl alcohol with the respective acid anhydrides at 130—150° for 2 hours. They are colourless, oily liquids with pleasant odours, which darken only slightly on long exposure to light. F. G. W.

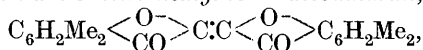
**Addition of Chloroform to Aldehydes.** J. W. HOWARD.—(See this vol., i, 557.)

**Oxindigo [3:3'-Diketo- $\Delta^{2:2'}$ -dicoumaran].** K. FRIES (*Annalen*, 1925, 442, 254—305; cf. A., 1914, i, 985).—The absence in oxindigo of the tinctorial properties of indigotin and thioindigotin is possibly due to the difficulty of reducing it to a compound analogous to indigo-white and re-oxidising the leuco compound in alkaline solution without rupturing the furan ring. Unsuccessful attempts have been made to stabilise the latter by introduction of substituents into the benzene nucleus.

**3:3'-Diketo-4:6:4':6'-tetramethyl- $\Delta^{2:2'}$ -dicoumaran and Other Indigoid Compounds from 4:6-Dimethylcoumaran-3-one.** [With K. BARTENS.]—4:6-Dimethylcoumaran-3-one is converted by *p*-nitrosodimethylaniline in alcoholic solution in the presence of sodium hydroxide into 4:6-dimethylcoumaran-3-one-2-*p*-dimethylaminoanil, m. p. 214°; 5-methylcoumaran-3-one-*p*-dimethylaminoanil, m. p. 173°, and 4:6-dimethylcoumaran-3-one-2-anil, m. p.



162°, are similarly prepared. The latter substance reacts with 4 : 6-dimethylcoumaran-3-one in the presence of boiling toluene to give 2-anilino-3 : 3'-diketo-4 : 6 : 4' : 6'-tetramethyl-2 : 2'-dicoumaran,  $C_6H_2Me_2 \begin{smallmatrix} O \\ \diagup \diagdown \\ CO \end{smallmatrix} C(NHPh) \cdot CH \begin{smallmatrix} O \\ \diagup \diagdown \\ CO \end{smallmatrix} C_6H_2Me_2$ , m. p. 214°, which is transformed by cold, concentrated sulphuric acid into 3 : 3'-diketo-4 : 6 : 4' : 6'-tetramethyl- $\Delta^{2:2'}$ -dicoumaran,



m. p. 280° after darkening at 265°; this is also obtained directly but in poor yield by the action of acetic anhydride and acetic acid on a mixture of 4 : 6-dimethylcoumaran-3-one-2-*p*-dimethylaminoanil and 4 : 6-dimethylcoumaranone. It is reduced by zinc dust and glacial acetic acid to 3 : 3'-diketo-4 : 6 : 4' : 6'-tetramethyl-2 : 2'-dicoumaran, m. p. 217° after softening at 210°, and is transformed by reductive acetylation into the corresponding O-diacetyl derivative, m. p. 235°, which could not be hydrolysed to the dihydroxy compound. 4 : 6-Dimethylcoumaran-2 : 3-dione, m. p. 145° (cf. Stollé and Knebel, A., 1921, i, 578), is readily prepared by the action of hydrochloric acid on 4 : 6-dimethylcoumaran-3-one-2-*p*-dimethylaminoanil suspended in acetic acid; it is slowly converted by 2*N*-sodium hydroxide into sodium 2-hydroxy-4 : 6-dimethylbenzoylformate, which immediately gives rise to the lactone when acidified. 4 : 6-Dimethylcoumaran-2 : 3-dione is transformed by an equivalent amount of aniline into 2-hydroxy-4 : 6-dimethylbenzoylformanilide, m. p. 127° (this is also obtained from 4 : 6-dimethylcoumaran-3-one-2-anil and cold, alcoholic sodium hydroxide), and by an excess of aniline into 2-hydroxy-4 : 6-dimethylbenzoylformanilanilide,  $C_{22}H_{20}O_2N_2$ , m. p. 197°, which is transformed by acetic anhydride into 4 : 6-dimethylcoumaran-2-one-3-anil, m. p. 150°. 4 : 6-Dimethylcoumaran-2 : 3-dione and *o*-phenylenediamine yield 2-hydroxy-3-*o*-hydroxy-*o* : *p*-dimethylphenylquinoxaline, m. p. 260° after softening at 253°, which passes at 280—290° into 4 : 6-dimethylcoumarophenazine, m. p. 206°. 3-Keto-4 : 6 : 4' : 6'-tetramethyl-2 : 3-dihydro-2 : 3'-dicoumaran, m. p. 151°, is converted by acetic anhydride and sodium acetate into the acetyl derivative of the corresponding enolic form, m. p. 114°. 3 : 2'-Diketo-4 : 6 : 4' : 6'-tetramethyl-2 : 3'-dicoumaran, yellow needles, m. p. 206° after softening at 202°, or orange-red prisms, m. p. 210° after softening at 205°, is prepared from dimethylcoumaranone and dimethylcoumarandione.

Di-*p*-tolyl succinate, m. p. 120°, is converted by aluminium chloride at 130° into  $\alpha\delta$ -diketo- $\alpha\delta$ -di-2'-hydroxy-*m*-tolylbutane, m. p. 187° (diacetate, m. p. 163°), which could not be brominated in the side-chain, but is converted by bromine in acetic acid solution into the nucleus-substituted compound,  $C_{18}H_{18}O_4Br_2$ , m. p. 232° (diacetate, m. p. 140°); if bromination is effected in acetic acid solution saturated with hydrogen bromide,  $\beta\gamma$ -dibromo- $\alpha\delta$ -diketo-di-2-hydroxy-*m*-tolylbutane, m. p. 183° (diacetate, m. p. 187°), is obtained. Di-*p*-tolyl dibromosuccinate, m. p. 167°, is converted by aluminium chloride into resinous products. Di-*m*-xylyl succinate,

m. p. 77°, is isomerised by aluminium chloride to  $\alpha\delta$ -diketo- $\alpha\delta$ -di-2-hydroxy-4 : 6-dimethylphenylbutane, m. p. 141°.

**4 : 5 : 4' : 5'-Dibenz- and 6 : 7 : 6' : 7'-Dibenz-oxindigo.** [With E. PUSCH.]—4 : 5-Benzcoumaran-3-one, m. p. 133°, is most readily prepared by treating naphthoxyacetic acid suspended in benzene successively with phosphorus pentachloride and aluminium chloride. It is converted by nitrosobenzene into 4 : 5-benzcoumaran-3-one-2-anil, m. p. 186°, and by aniline into 2-hydroxynaphthoylformanilide, m. p. 126° [prepared previously by Giua and De Francis (A., 1924, i, 1092), by whom it is erroneously designated 4 : 5-benzcoumaran-3-one-2-anil]. Bromine in the presence of glacial acetic acid converts it into 2-bromo-4 : 5-benzcoumaran-3-one, m. p. 150°, which is transformed by sodium nitrite in boiling, aqueous-alcoholic solution into the sodium salt of 2-acinitro-4 : 5-benzcoumaran-3-one, decomp. about 220°. The latter compound is transformed by boiling water into 3 : 3'-diketo-4 : 5 : 4' : 5'-dibenz- $\Delta^{2:2'}$ -dicoumaran (4 : 5 : 4' : 5'-dibenzoxindigo), m. p. 310° after darkening and softening at 290°; the stability of the furan ring in this substance is enhanced remarkably by the presence of the benzo group in the 4 : 5 position, but not to a sufficient extent to enable it to give a true vat. 2-Bromo-4 : 5-benzcoumaran-3-one and *o*-phenylenediamine give 3 : 2'-hydroxy- $\alpha$ -naphthylquinoxaline, m. p. 142° (benzoate, m. p. 156°). 2-Hydroxy-3- $\beta$ -hydroxy- $\alpha$ -naphthylquinoxaline, m. p. 287° (diacetate, m. p. 227°), prepared from 4 : 5-benzcoumaran-2 : 3-dione and *o*-phenylenediamine in glacial acetic acid solution, is converted when heated in a high vacuum into 4 : 5-benzcoumarophenazine,  $C_{10}H_6 \begin{array}{c} \diagup C:N \\ \diagdown O:C:N \end{array} C_6H_4$ , m. p. 218° [the compound described under this name by Giua and De Francis (*loc. cit.*) is 2-hydroxy-3- $\beta$ -hydroxy- $\alpha$ -naphthylquinoxaline]. 2 : 2'-Dibromo-4 : 5-benzcoumaran-3-one, m. p. 178°, does not react with sodium nitrite or *o*-phenylenediamine. 4 : 5-Benzcoumaran-3-one is converted by glacial acetic acid saturated with hydrogen chloride into 3-keto-4 : 5 : 4' : 5'-dibenz-2 : 3'-dicoumaran, m. p. 211°. Isatin and 4 : 5-benzcoumaran-3-one yield the compound,  $C_{20}H_{11}O_3N$ , m. p. about 340°.

6 : 7-Benzcoumaran-3-one is prepared according to the method of Lanz (*Diss.*, Bern, 1921); the preparation from pure 1-naphthoxyacetyl chloride or bromide, m. p. 150°, is not more advantageous. It is converted by nitrosobenzene into 6 : 7-benzcoumaran-3-one-2-anil, m. p. 169°, which with concentrated sulphuric acid yields 1-hydroxy-2-naphthoylformic acid, m. p. 151° (decomp.), which could not be dehydrated by phosphoric oxide and is converted by *o*-phenylenediamine into 2-hydroxy-3- $\alpha$ -hydroxy- $\beta$ -naphthylquinoxaline, m. p. 312°. 6 : 7-Benzcoumaran-3-one and 6 : 7-benzcoumaran-3-one-2-anil yield 2-anilino-3 : 3'-diketo-6 : 7 : 6' : 7'-dibenz-2 : 2'-dicoumaran, m. p. 173°, from which 3 : 3'-diketo-6 : 7 : 6' : 7'-dibenz- $\Delta^{2:2'}$ -dicoumaran (6 : 7 : 6' : 7'-dibenzoxindigo), m. p. 347° after darkening and softening, is obtained by the action of hydrogen chloride in the presence of glacial acetic acid. The stability of the furan ring in this compound is much less than in the corresponding 4 : 5-sub-

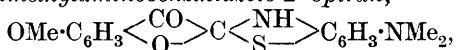
stance. 5-Bromo-6:7-benzcoumarandiol-2-anil, m. p. 204°, and 2:2:5-tribromo-6:7-benzcoumaran-3-one, m. p. 217°, are also described.

**Indigoid and other Compounds from 6-Methoxycoumaran-3-one.** [With K. SAFTIEN.]—6-Methoxycoumaran-3-one and *p*-nitrosodimethylaniline yield 6-methoxycoumaran-3-one-2-*p*-dimethylaminoanil, m. p. 156° after softening at 142°, which is transformed by concentrated sulphuric acid into *p*-aminodimethylaniline and 2-hydroxy-4-methoxybenzoylformic acid. 6-Methoxycoumaran-3-one-2-anil, m. p. 135° (or its dimethylamino derivative) is converted by 6-methoxycoumaran-3-one at 125° into 6:6'-dimethoxy-3:3'-diketo- $\Delta^{2:2'}\text{-dicoumaran}$  (6:6'-dimethoxyoxindigo), m. p. 310° after softening and darkening at 260°. 2-Oximino-6-methoxycoumaran-3-one, m. p. 180°, prepared from 6-methoxycoumaran-3-one and sodium nitrite in acetic acid solution, is transformed by fuming hydrochloric acid into 2-hydroxy-4-methoxybenzoylformic acid, m. p. 123°, which, when heated at 160°/1 mm., affords 6-methoxycoumaran-2:3-dione, m. p. 136°, and is transformed by *o*-phenylenediamine into 2-hydroxy-3-*o*-hydroxy-*p*-methoxyphenylquinoxaline, m. p. 312° after softening at 303°. 6:6'-Dimethoxy-2:3'-diketo- $\Delta^{2:3'}\text{-dicoumaran}$ , m. p. 250°, is prepared from 6-methoxycoumaran-3-one and 2-hydroxy-4-methoxybenzoylformic acid or 6-methoxycoumaran-3-one-2-*p*-dimethylaminoanil. 6:6'-Dimethoxy-3-keto-2:3-dihydro-2:3'-dicoumaran, m. p. 153° after darkening at 146°, is obtained by the condensation of 6-methoxycoumaran-3-one under the influence of acid or alkaline reagents; the compound is readily oxidised, and its formation in alkaline solution is accompanied by that of a substance,  $\text{C}_{36}\text{H}_{28}\text{O}_{11}$ , m. p. 156°, unless air is carefully excluded.

2-Hydroxy-4-methoxy- $\omega$ -chloroacetophenone is converted by bromine in the presence of chloroform into 5-bromo-2-hydroxy-4-methoxy- $\omega$ -chloroacetophenone, m. p. 194°. It is converted by boiling alcoholic sodium acetate solution into 5-bromo-6-methoxycoumaran-3-one, m. p. 186° (*m*-nitrobenzylidene derivative, m. p. 200°), which cannot be prepared advantageously by direct bromination of 6-methoxycoumaran-3-one. 2:5'-Dibromo-6-methoxycoumaran-3-one, m. p. 160° after darkening at 142°, prepared by the action of bromine on bromomethoxycoumaranone in the presence of glacial acetic acid and hydrogen bromide, is converted by *o*-phenylenediamine into 3-(5'-bromo-2'-hydroxy-4'-methoxyphenyl)quinoxaline, m. p. 240° (benzoyl derivative, m. p. 212°). 3-*o*-Hydroxyphenylquinoxaline, m. p. 189°, is prepared similarly from 2-bromocoumaran-3-one. The action of phenylhydrazine on dibromomethoxycoumaranone gives the osazone of 5-bromo-2-hydroxy-4-methoxyphenylglyoxal, m. p. 193°. 2:2:5-Tribromo-6-methoxycoumaran-3-one, m. p. 164°, is only slowly converted by *o*-phenylenediamine into the quinoxaline derivative just described, thus showing that the third bromine atom is located in the side ring and that the amine has a reducing action. 2:5:7-Trichloro-6-methoxycoumaran-3-one, m. p. 79°, is prepared by passing chlorine into 6-methoxycoumaran-3-one dissolved in glacial acetic acid in the

presence of sodium acetate; the position of the chlorine atoms is established by its conversion into 3-(3' : 5'-dichloro-2'-hydroxy-4'-methoxyphenyl)quinoxaline, m. p. 237°. 5-Bromo-6-methoxycoumaran-3-one-2-anil, m. p. 192°, is prepared from 5-bromo-6-methoxycoumaran-3-one and nitrosobenzene. The sodium salt of 5-bromo-2-acinitro-6-methoxycoumaran-3-one, decomp. 256°, is converted by boiling water into 5 : 5'-dibromo-6 : 6'-dimethoxy-3 : 3'-diketo- $\Delta^{2:2'}$ -dicoumaran, m. p. above 360° (decomp.). 5-Bromo-6-methoxycoumaran-3-one-2-anil is transformed by concentrated sulphuric acid into 5-bromo-2-hydroxy-4-methoxybenzoylformic acid, m. p. 155°, which with *o*-phenylenediamine yields 2-hydroxy-3-(5'-bromo-2'-hydroxy-4'-methoxyphenyl)quinoxaline, m. p. 360° (decomp.). 5 : 5'-Dibromo-6 : 6'-dimethoxy-2 : 3'-diketo- $\Delta^{2:3}$ -dicoumaran, m. p. 340°, is obtained by the condensation of bromomethoxybenzoylformic acid with bromomethoxycoumaranone, by protracted ebullition of a solution of 2 : 5-dibromo-6-methoxycoumaran-3-one in glacial acetic acid, and by the oxidation of 5 : 5'-dibromo-2'-hydroxy-6 : 6'-dimethoxy-3-keto- $\Delta^{2:3'}$ -dicoumaran, m. p. 295° after darkening at 190° (prepared from 2 : 5-dibromo-6-methoxycoumaran-3-one, 5-bromo-6-methoxycoumaran-3-one, and sodium acetate in boiling alcoholic solution; acetyl derivative, m. p. 210° after darkening at 180°; monophenylhydrazone, m. p. 178° after softening at 170°).

**Derivatives of 2-Coumaran-2-benzdihydrothiazolespiran.** [With K. SAFTIEN.]—The action of hydrogen sulphide on a boiling solution of 6-methoxycoumaran-3-one-2-*p*-dimethylaminoanil in benzene leads to the production of 2-*p*-dimethylanilino-6-methoxy-2-thiol-3-ketocoumaran,  $\text{OMe} \cdot \text{C}_6\text{H}_3 \langle \text{CO} \rangle \text{C}(\text{SH}) \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , m. p. 154° after darkening at 148°, which is oxidised to 6-methoxy-3-keto-2-coumaran-6'-dimethylaminobenzthiazole-2'-spiran,



m. p. 174° (acetyl derivative, m. p. 160°; sodium salt). The constitution of the latter compound is established by its decomposition with alcoholic potassium hydroxide into 2-hydroxy-4-methoxybenzoic acid and 2-amino-5-dimethylaminothiophenol. Similarly, 6-methoxycoumaran-3-one-2-*p*-aminoanil, m. p. 183° after softening at 170° (from 6-methoxycoumaran-3-one and *p*-nitrosoaniline), yields 2-*p*-aminoanilino-6-methoxy-2-thiol-3-ketocoumaran, m. p. 133° after softening at 115°; its oxidisability to a spiran could not be established with certainty. 2-Anilino-6-methoxy-2-thiol-3-ketocoumaran, m. p. 152°, and 2-anilino-2-thiol-3-ketocoumaran, m. p. 156°, do not appear to yield spirans, which thus seem to be formed only when the aniline residue contains a dimethylamino group in the para position (cf. Fries, A., 1914, i, 880). H. W.

**Synthesis of 2'-Chloroflavone and 2'-Chloroflavonol.** A. RÖTHLISBERGER (*Helv. Chim. Acta*, 1925, 8, 112—117; cf. A., 1921, i, 682).—The author continues the investigation of the influence of substituent groups on the decomposition of the

dibromides of *o*-hydroxyphenyl styryl ketones into flavones or benzylidenecoumaranones, respectively. *o*-Hydroxyphenyl *o*-chlorostyryl ketone, lemon-yellow, m. p. 102°, from *o*-chlorobenzaldehyde and *o*-hydroxyacetophenone, gives a *dibromide*, faintly yellow, m. p. 171°, and an *acetyl* derivative, yellow, softening at 49°, m. p. 52°. The *dibromide* of the latter is colourless, m. p. 92°. Treatment of either dibromide with alkali under varied conditions gives 2'-chloroflavone, colourless, m. p. 119°.

2'-Chloroflavonone, colourless, m. p. 103°, synthesised directly from *o*-chlorobenzaldehyde and *o*-hydroxyacetophenone by the method of Kostanecki, Lampe, and Tambor (A., 1904, i, 440), is readily converted into the yellow isonitroso derivative, m. p. (slow heating) 142° or (rapid heating) 158—159°. Subsequent hydrolysis yields colourless 2'-chloroflavanol, m. p. 178° (*acetyl* derivative, m. p. 143°).

β-Coumaranone, when condensed with *o*-chlorobenzaldehyde, gives 2'-chlorobenzylidenecoumaranone, yellow, m. p. 141°. The *dibromide*, colourless, m. p. 194° (decomp.), is converted by alcoholic potassium hydroxide into 2'-chloroflavanol. M. J.

**Ligulin, the Colouring Matter of Privet Berries.** E. PFAU (Arch. Pharm., 1925, 263, 50—51).—This colouring matter (from *Ligustrum vulgare*) used for improving the appearance of wine, is termed *ligulin*. It is extracted by water; the *hydrochloride* and *picrate* are described. The compound is considered to be akin to oenin. The berries contain no alkaloid or saponin. W. A. S.

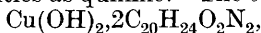
**Preparation of Dyes.** H. VOSWINCKEL (D.R.-P. 400391; from Chem. Zentr., 1924, ii, 2792—2793).—Acid dyes, showing pronounced green fluorescence in alkaline solution and dyeing direct yellow to brown shades on wool and silk, are obtained by melting aromatic sulphonic acids with polyhydric phenols, especially resorcinol, or aminophenols, especially alkylated *m*-aminophenols. The products from resorcinol and the sulphonic derivative of salicylic acid, *o*-, *m*-, and *p*-hydroxytoluic acids dye mordanted cotton and when boiled with sodium sulphide are converted into substantive cotton dyes. The dye obtained from resorcinol and sulphosalicylic acid at 140—160° gives brown shades on cotton after chroming.

R. B.

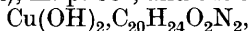
**Hydroferrocyanides and Hydroferricyanides of Alkaloids.** I. W. M. CUMMING and D. G. BROWN (J. Soc. Chem. Ind., 1925, 44, 110—115t).—The hydroferrocyanides and hydroferricyanides of various alkaloids (cf. Stephenson, "Microchemical Tests for Alkaloids," 1921; Cole, A., 1923, ii, 703) have been prepared in alcoholic, neutral, and acid solution by the general methods previously described (T., 1922, 121, 1287; 1923, 123, 2457; A., 1924, i, 778; this vol., i, 122). The *hydroferrocyanides* and *hydroferricyanides* of the following alkaloids are described: *cinchonine*, *quinine*, *phenazone*, *pyramidon*, *cocaine*, *narcotine*, *brucine*, and *strychnine*. A method for obtaining pure hydroferricyanic acid is given. L. F. H.

**apoQuinine.** S. FRÄNKEL and C. BUHLEA (*Ber.*, 1925, 58, [B], 559—563).—Quinine is converted by treatment with hydrochloric acid (*d* 1.125) during 7—8 hours at 140—145° mainly into apoquinine, m. p. 160°,  $[\alpha]_D^{25}$  —196.37° in ethyl alcohol (96%). The compound is converted by benzoyl chloride at 100° into apoquinine monobenzoate dihydrochloride, m. p. 187° (decomp.) after softening and darkening at 170°. apoQuinine can be obtained from anhydrous ether in microscopic crystals which are extraordinarily hygroscopic. It does not show the reactions of ketones. Small quantities of chlorinated and chlorine-free derivatives of quinine (which differ from apoquinine in their insolubility in potassium hydroxide solution) are produced during the action of hydrochloric acid on quinine. H. W.

**Compounds of Quinine and Copper.** F. ERBEN (*Ber.*, 1925, 58, [B], 468—470).—Complex compounds of quinine with cupric hydroxide are readily obtained by shaking a solution of the base in chloroform with copper hydroxide, free from acidic ions, dissolved in ammonia; the reaction is facilitated by the addition of a little sodium hydroxide. The ratio, alkaloid : copper, is variable as in the case of cuprammonium. Compounds containing 10, 8, 6, or 4 mols. of base to each mol. of copper hydroxide are pink and exhibit much the same solubilities as quinine. The compound,



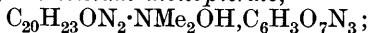
m. p. 192° or (hydrated), m. p. 88°, and the substance,



m. p. 220°, are described. The corresponding dihydrochlorides are yellow and yield yellow solutions in water. H. W.

**Aminoquinine.** S. FRÄNKEL, C. TRITT, M. MEHRER, and O. HERSCHMANN (*Ber.*, 1925, 58, [B], 544—554).—Attempts to introduce an amino group into the vinyl side-chain of quinine and its derivatives were unsuccessful. Hydroquinine chloride and ammonia yielded only quinine. Quinine chloride (A., 1923, i, 362) reacted to only a very limited extent with aqueous or alcoholic ammonia; a similar result was obtained with quinine dibromide and quinine tribromide. Quinine chloride was therefore heated with potassium phthalimide at 160—170°, whereby *phthalylamidoquinine*,  $\text{C}_{28}\text{H}_{27}\text{O}_3\text{N}_3 \cdot \text{H}_2\text{O}$ , m. p. 140°, was obtained (isolated as the *picrate*,  $\text{C}_{34}\text{H}_{30}\text{O}_{10}\text{N}_6$ , m. p. 145°, from the crude product of the reaction). Similarly, quinine chloride was converted by the sodium derivative of benzenesulphonamide at 160° in a vacuum into *benzenesulphonamidoquinine*, which was characterised as the *picrate*,  $\text{C}_{20}\text{H}_{23}\text{ON}_2 \cdot \text{NH} \cdot \text{SO}_2\text{Ph} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$ , decomp. 137°. Removal of the acyl groups from these compounds was exceptionally difficult, since the resulting aminoquinine was simultaneously demethylated and isomerised by the concentrated acids with production of a mixture of compounds; under certain conditions, *aminoquinine sulphate*,  $\text{C}_{20}\text{H}_{23}\text{ON}_2 \cdot \text{NH}_2 \cdot \text{H}_2\text{SO}_4$ , decomp. 227° (in a closed capillary), was obtained in small yield and was characterised further by conversion into the corresponding *picrate*,  $\text{C}_{20}\text{H}_{25}\text{ON}_3 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , m. p. 120°. Crude aminoquinine was converted by acetic anhydride

and sodium acetate into a substance which could not be caused to crystallise as free base or as sulphate; it was therefore precipitated with picric acid, whereby two *picrates*, m. p. 122—125° and 153°, respectively, were obtained which appeared to be diacetamidoquinine dipicrates,  $C_{20}H_{23}ON_2 \cdot NAc_2 \cdot 2C_6H_3O_7N_3$ . Treatment of the crude aminoquinine with methyl sulphate and sodium hydrogen carbonate gave a quaternary ammonium base which was isolated as *quininetrimethylammonium monopicrate*,

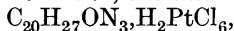


the product could not, however, be freed completely from a green dye which was formed during the reaction.

The difficulty of replacing the halogen atom of quinine chloride has led to the examination of other methods of obtaining aminated derivatives. Thus, quinotoxinephenylhydrazone was converted into the crystalline *dipicrate*,  $C_{26}H_{30}ON_4 \cdot 2C_6H_3O_7N_3$ , decomp. 130—137° (indefinite), from which potassium carbonate liberated only the amorphous phenylhydrazone (a crystalline *p-bromophenylhydrazone* was isolated). Reduction with sodium amalgam and acetic acid, sodium, and amyl or ethyl alcohol, or with zinc dust and glacial acetic acid did not lead to the desired aminoquinotoxine.

H. W.

**Aminoquinotoxine.** S. FRÄNKEL and N. DIAMANT (*Ber.*, 1925, **58**, [B], 554—559).—*Quinotoxineoxime*,  $C_{20}H_{25}O_2N_3$ , m. p. (indef.) 112—116°, is prepared as a yellow, amorphous powder which becomes resinified with unusual ease, by the interaction of quinotoxine oxalate and hydroxylamine hydrochloride in strongly alkaline, aqueous-alcoholic solution. It is only slowly attacked by sodium amalgam or sodium and ethyl alcohol, but is reduced by sodium and amyl alcohol in the presence of acetic acid to *aminoquinotoxine*, which could not be caused to crystallise and did not yield a crystalline hydrochloride, sulphate, tartrate, or oxalate. The *picrate*,  $C_{20}H_{27}ON_3 \cdot 2C_6H_3O_7N_3$ , m. p. 110°, the additive *compound* with cadmium chloride,  $C_{20}H_{27}ON_3 \cdot 3CdCl_2$ , decomp. 255—260° after softening at 210—220°, the *chloroplatinate*,



decomp. 295—305° after darkening at 250°, and the *benzoate*,  $C_{27}H_{31}O_2N_3 \cdot H_2O$ , m. p. 66°, are described.

H. W.

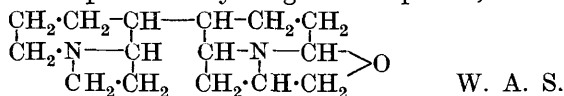
**Constitution of Physostigmine [Eserine].** E. SPÄTH and O. BRUNNER (*Ber.*, 1925, **58**, [B], 518—523).—Physostigmol is shown to be 5-hydroxy-1 : 3-dimethylindole by direct comparison of 5-methoxy-1 : 3-dimethyldehydroindole with hydrophysostigmol methyl ether, thus confirming the conclusion reached by Stedman (*A.*, 1924, i, 981) in a different manner.

*Acetone-p-methoxyphenylhydrazone*, m. p. 60°, is converted by treatment with anhydrous zinc chloride in a vacuum at 110° into 5-methoxy-2-methylindole, m. p. 85—86°, which is transformed by reduction with tin and hydrochloric acid and subsequent methylation into 5-methoxy-1 : 2-dimethyldehydroindole (*picrate*, m. p. 171—172°). By a similar series of reactions, *acetone-m-methoxyphenylhydrazone* is transformed successively into 6(?4)-methoxy-

2-methylindole, m. p. 102—103°, and 6(14)-methoxy-1 : 2-dimethyl-dihydroindole (*picrate*, m. p. 144—145°). Propaldehyde-*p*-methoxyphenylhydrazone is transformed into 5-methoxy-3-methylindole (cf. Blaikie and Perkin, A., 1924, i, 547) and 5-methoxy-1 : 3-dimethyl-dihydroindole, the *picrate* of which, m. p. 128—129°, is identical with that of hydrophysostigmol methyl ether. Methyl-*p*-anisidine, b. p. 111—113°/9 mm., is converted by nitrous acid and subsequent reduction of the nitroso compound into as-*p*-methoxyphenylmethylhydrazine, b. p. 135—139°/10 mm., which, when condensed with propaldehyde and subsequently heated with zinc chloride at 110°/vacuum gives 5-methoxy-1 : 3-dimethylindole, identical with physostigmol methyl ether. H. W.

**Constitution of Lupanine.** H. THOMS and K. BERGERHOFF (*Arch. Pharm.*, 1925, 263, 3—12).—This paper contains a survey of the literature of the lupin alkaloids. Lupanine, m. p. 44° (cf. Molander, A., 1921, i, 886), b. p. 215—220°/10 mm., *picrate*, m. p. 180°, when fused with potassium hydroxide, yields a base, (C<sub>7</sub>H<sub>9</sub>N)<sub>2</sub>, already described, and, in small amount, a hydrocarbon, C<sub>10</sub>H<sub>16</sub>, b. p. 120—135°/10 mm. Lupanine methiodide, m. p. 240—241°, affords a hydroxide which when distilled regenerates lupanine. This indicates that no methylimino group is present. When lupanine is treated with cyanogen bromide (von Braun's method), ring scission takes place, for the product is the compound C<sub>15</sub>H<sub>24</sub>ON<sub>2</sub>.BrCN, m. p. 122°. This substance, which is obtained only in meagre yield, is converted by the action of ammonia and hydrogen sulphide into the thiocarbamido derivative, m. p. 85° (+ alcohol of crystallisation) or 140° (after drying), and loses its cyanogen group when heated with concentrated hydrobromic acid, giving an oily product which forms an unstable chloroaurate, C<sub>15</sub>H<sub>24</sub>ON<sub>2</sub>.Br.HAuCl<sub>4</sub>, m. p. 147—150°. When lupanine is distilled with zinc dust, it yields two hydrocarbons, one (b. p. 118—125°/14 mm.) apparently identical with that from the potash fusion, and another, in very small amount, a solid, together with two bases, the first of which, C<sub>7</sub>H<sub>9</sub>N, has b. p. 150—151° and is apparently an ethylpyridine (*picrate*, m. p. 139—140°) and the second, b. p. 160—164°/14 mm., has the formula (C<sub>7</sub>H<sub>9</sub>N)<sub>2</sub>. The latter gives a mercuric chloride double salt (decomp. 91°) and appears to be identical with the basic product of the potash fusion.

On a basis of these results and the constitution of various analogues the annexed formula is provisionally assigned to lupanine,



W. A. S.

**Jaborandi Alkaloids. I. Pilocarpidine.** E. SPÄTH and E. KUNZ (*Ber.*, 1925, 58, [B], 513—518).—It is shown that pilocarpidine is demethylated pilocarpine of the constitution

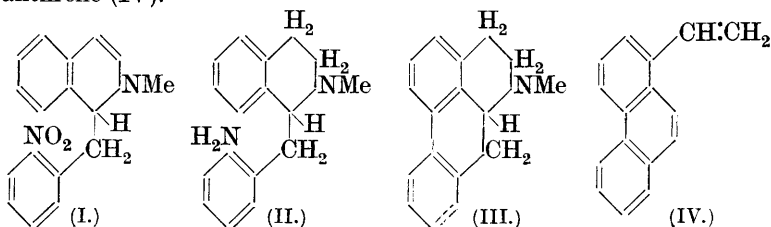


since it is converted by cold methyl iodide into pilocarpine (identified as the nitrate); further, the successive treatment of the



crude methylated pilocarpidine with methyl iodide and sodium picrate yields a *methopicrate*,  $C_{18}H_{21}O_9N_5$ , m. p. 142—143°, identical with that obtained from pilocarpine methiodide. The *methochloraurate*, m. p. 103—104°, and methochloroplatinate, m. p. about 220° when rapidly heated [Langenbeck (this vol., i, 151) gives m. p. 224—225°], from the two sources are identical. The possibility that pilocarpidine is stereochemically related to *isopilocarpine* and suffers conversion into a substance of the pilocarpine series during methylation is excluded, since the *isopilocarpidine* is converted by quaternary methylation and subsequent treatment with sodium picrate into *isopilocarpine methopicrate*, m. p. 119—120°; pilocarpidine is transformed into *isopilocarpidine (nitrate)*, m. p. 109—111° by treatment with alcoholic sodium ethoxide solution at the atmospheric temperature. The following salts are described incidentally: pilocarpidine chloraurate, m. p. 124—126°; *pilocarpidine 2:4:6-trinitro-m-tolylloxide*, m. p. 149—150°; *pilocarpine 2:4:6-trinitro-m-tolylloxide*, m. p. 188—189° after slight softening; pilocarpine chloraurate, m. p. 124—125° [Jowett (T., 1900, 77, 478) gives m. p. 117—130°]; *isopilocarpine chloraurate*, m. p. 159°. H. W.

**Synthesis of Aporphine.** J. GADAMER, M. OBERLIN, and A. SCHOELER (*Arch. Pharm.*, 1925, 263, 81—99; cf. A., 1924, i, 1227).—The  $\psi$ -basic form of *N*-methylisoquinolinium hydroxide is condensed with *o*-nitrotoluene in presence of sodium ethoxide giving 1-*o*-nitrobenzyl-2-methyl-1:2-dihydroisoquinoline (I); this on reduction gives 1-*o*-aminobenzyl-2-methyltetrahydroisoquinoline (II), which on diazotisation and treatment with copper powder yields aporphine (III). Proof of the structure of the latter is afforded by exhaustive methylation, when it gives 1-vinylphenanthrene (IV).



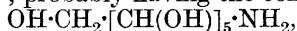
*o*-Nitrophenylaceto- $\beta$ -phenylethylamide gives, on heating with phosphoric oxide in xylene, an oily *base*, whilst on reduction with phenylhydrazine it gives *o*-aminophenylaceto- $\beta$ -phenylethylamide, m. p. 105° (uncorr.), white. 1-*o*-Nitrobenzyl-2-methyl-1:2-dihydroisoquinoline, m. p. 90° (uncorr.), reddish-brown, when reduced yields 1-*o*-aminobenzyl-2-methyltetrahydroisoquinoline hydrochloride, m. p. 247—250° (uncorr.), and chlorostannate. The hydrochloride, on treatment as above, yields *aporphine hydrochloride*, decomp. above 250°, from which are prepared the *hydriodide*, white, decomp. 260°, the *hydrobromide*, decomp. 230°, and the *nitrate*, decomp. 200—210°. Aporphine gives with Froehde's reagent a green, and

with Mandelin's reagent a bluish-red colour. On treatment with methyl sulphate and subsequently with sodium hydroxide, aporphine hydrochloride yields *aporphinemethine*, a viscous oil, which gives a solid *methiodide*. The latter is converted by potassium hydroxide into trimethylamine and 1-vinylphenanthrene (obtained in solution only), acid reduction of the latter leading to 1-ethylphenanthrene, and catalytic reduction to the isolation of a *picrate*, m. p. 170°. B. F.

**Electrolytic Reduction of Pyridine. Preparation of Piperidine.** C. MARIE and G. LEJEUNE (*J. Chim. physique*, 1925, 22, 59—61).—A 65% yield of piperidine may be obtained by electrolyzing at 30—40° a sulphuric acid solution of pyridine at a reduced lead cathode with a current density of 6 amp./dm.<sup>2</sup> Some tetrahydropyridine (dipiperidine) is simultaneously formed. F. G. T.

**Process of Nitration with the Aid of Nitrogen Oxides from Air or Ammonia. II.** A. SCHAARSCHMIDT, H. BALZERKIEWICZ, and J. GANTE.—(See i, 532.)

**Formation of the Pyrrole Ring by the Action of Ammonia on Carbohydrates.** A. SHMOOK (*Izvestia Petr. Selskochos. Akad. [Russ.]*, 1919, No. 1—4, 25—33).—The product obtained on heating dextrose, starch, or pentosans with ammonium salts (preferably oxalate) gives the pine-wood pyrrole reaction. Addition of zinc dust accelerates the process. Apparently furan, derived from ammonium mucate, then reacts with ammonia, so that the ammonia does not participate in ring closure, pyrrole being formed by the exchange of an oxygen atom for the imino group, as in the conversion of pyrone into the corresponding pyridine derivative. On passing dry ammonia into anhydrous alcoholic dextrose, a *substance*, m. p. 123°, probably having the composition



is obtained. In the presence of zinc oxide, or at a high temperature, some 5-methylglyoxaline is produced. The *product* (30%) obtained on refluxing dextrose with glycerol at 270—280°, ammonia being meanwhile passed through the liquid, is an oil of which the most stable fraction, possibly 2-methyl-5-aminomethylpyrrole, has b. p. 140—150°; it forms a *hydrochloride* and *chloroplatinate*. Its possible mode of formation is discussed. CHEMICAL ABSTRACTS.

**Synthesis of Xanthopyrrolecarboxylic Acid. Synthesis of the Acid Scission Products of Blood Pigment. III.** H. FISCHER and J. KLARER (*Annalen*, 1925, 442, 1—7).—The methods recently used in the synthesis of cryptopyrrolecarboxylic acid and phyllopyrrolecarboxylic acid (A., 1924, i, 543, 1233) have been applied to the synthesis of the xanthopyrrolecarboxylic acid described by Piloty and Dormann (A., 1913, i, 539; 1915, i, 451), and the structure originally assigned to this acid is thereby confirmed. Its presence in the scission products of blood pigment affords some support for Willstätter's assumption of a -C:C- bridge linking the four pyrrole rings in blood pigment.

Magnesium ethyl bromide on successive treatment in an atmo-

sphere of nitrogen with 4-methyl-2-ethylpyrrole and ethyl chloroformate gives in 88% yield *ethyl 4-methyl-2-ethylpyrrole-5-carboxylate*, m. p. 74°, which on treatment with hydrogen cyanide and hydrogen chloride in dry ether, and decomposition of the imide with water, is converted (yield 70%) into *5-carbethoxy-4-methyl-2-ethylpyrrole-3-aldehyde*, m. p. 98° (*oxime*, m. p. 202°, *rhodamine* condensation product, yellowish-brown needles, m. p. 208°, *azlactone* with hippuric acid, m. p. 227°). This aldehyde condenses with malonic acid in presence of piperidine to give the unstable *5-carbethoxy-4-methyl-2-ethylpyrrole-3-acrylic acid*, m. p. 240°, which when reduced with sodium amalgam affords *5-carbethoxy-4-methyl-2-ethylpyrrole-3-propionic acid*, m. p. 138°. From the latter acid, xanthopyrrole-carboxylic acid (4-methyl-2-ethylpyrrole-3-propionic acid), m. p. 109.5°, is obtained by heating with acetic and hydriodic acids at 100°. The free acid rapidly becomes red in air, owing to oxidation. Its alcoholic solution turns yellow, and shows the urobilin spectrum. With Ehrlich's reagent, the acid at first shows an intense red coloration and a band at 568.1 to 514, which gradually shifts and after 3 hrs. the characteristic bands of hæmatin, 662—629.3, 564.6—546, and a weaker band at 480 are produced. With cyanoacetic acid, the above aldehyde yields *5-carbethoxy-4-methyl-2-ethylpyrrole-3- $\alpha$ -cyanoacrylic acid*, bright yellow needles, m. p. 209°.

R. B.

**3-Cyanoindole.** N. I. GAVRILOV (*Isvestia Petr. Selskochos. Akad. [Russ.]*, 1919, No. 1—4, 14—25).—*o*-Aminobenzyl cyanide, sodium, and ammonium formate in ether give 3-cyanoindole, m. p. 178°, in 12.5% yield (cf. Majima, Shigematsu, and Rokkaku, A., 1924, i, 1235). Reduction of 3-cyanoindole with sodium and alcohol causes fission of the heterocyclic ring, producing *o*-aminoethylbenzene, together with 3-indolecarboxylic acid.

CHEMICAL ABSTRACTS.

### General Method of Preparation of Substituted Indoles.

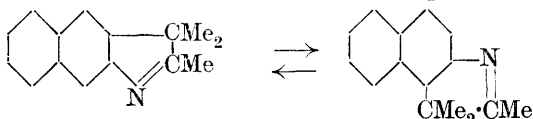
A. VERLEY and (MLLE.) J. BEDUWÉ (*Bull. Soc. chim.*, 1925, [iv], 37, 189—191).—The method for the preparation of  $\alpha$ -substituted indoles (cf. Verley, A., 1924, i, 1106) is exemplified by the preparation of  $\alpha$ -ethylindole, m. p. 43°, b. p. 142—143°/5 mm.,  $\alpha$ -propylindole, m. p. 34°, b. p. 147—148°/5 mm., and  $\alpha$ -isobutylindole, m. p. 42°, b. p. 149—150°/5 mm., by the action of sodamide at 250—260° on propiono-*o*-toluidide, m. p. 89.5°, butyro-*o*-toluidide, m. p. 75°, and valero-*o*-toluidide, m. p. 79°, respectively. The  $\alpha$ -alkylindoles have more ethereal and less unpleasant odours than those of the corresponding  $\beta$ -derivatives.

F. G. W.

**Constitution of Acridine.** K. VON AUWERS and R. KRAUL (*Ber.*, 1925, 58, [B], 543—544).—Spectrochemical comparison of acridine, *ms*-dihydroacridine, and certain of their derivatives and diphenylamine in the molten state or dissolved in quinoline shows that seven double linkings are present in the acridine molecule, as has been found previously for anthracene (A., 1920, i, 540). This

conception is in agreement with the relative basicity of acridine and its dihydro derivative. H. W.

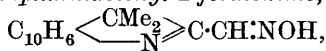
**2 : 3 : 3-Trimethyl- $\beta$ -naphthindolenine and the Formula of the Indolenines.** G. PLANCHER, U. COLACICCHI, and O. BARBIERI (*Gazzetta*, 1925, 55, 52—60).—Plancher (A., 1898, i, 536; 1899, i, 450) has shown that the 2-alkylindolenines,  $C_6H_4 \langle \text{CMe}_2 \rangle_N \gg CMe$ , react also as the isomeric 2-alkylideneindolines,  $C_6H_4 \langle \text{CMe}_2 \rangle_{NH} > C:CH_2$ , whereas Kanschegg (A., 1905, i, 924; 1906, i, 452; cf. also Zangerle, A., 1910, i, 430) gives exclusive preference to the alkylideneindoline formula. By condensing methyl isopropyl ketone with  $\beta$ -naphthylhydrazine in alcoholic solution in presence of zinc chloride, the authors have obtained 2 : 3 : 3-trimethyl- $\beta$ -naphthindolenine,



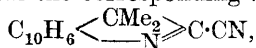
which (1) when reduced, takes up two atoms of hydrogen to form the corresponding 2 : 3 : 3-trimethylnaphthindoline; (2) when treated with benzoyl chloride according to the Schotten-Baumann method, gives a benzoyl derivative containing a molecule of benzoic acid more than the base and hence a molecule of water more than ordinary benzoyl derivatives, this being the behaviour of Reissert's tertiary quinoline bases; (3) reacts readily with nitrous acid giving, not a nitrosoamine, but, like other indolenines, an oxime having the  $\cdot CH:NOH$  in the 2-position and reacting with acetic anhydride to form a nitrile, which, in its turn, yields an amidoxime. Thus, 2 : 3 : 3-trimethyl- $\beta$ -naphthindolenine, which is found to be identical with Fischer and Steche's dimethyldihydronaphthaquinoline (A., 1887, 588; 1888, 298), behaves, in these reactions, in accordance with the indoleninic structure, this being confirmed also by its resistance to oxidation.

2 : 3 : 3-Trimethyl- $\beta$ -naphthindolenine, the hydriodide of which has m. p.  $232^\circ$  (Zangerle, *loc. cit.*, gave  $224$ — $225^\circ$ ), is accompanied, when prepared as described above, by a small quantity of a compound, m. p.  $145$ — $147^\circ$ , not yet investigated. 2 : 3 : 3-Trimethyl- $\beta$ -naphthindoline forms a hydriodide, m. p.  $264^\circ$ , and the benzoyl derivative,  $C_{15}H_{15}N, Ph \cdot CO_2H$ , m. p.  $175$ — $177^\circ$ ; Zangerle's supposed benzoyl compound of the ordinary type, m. p.  $114^\circ$ , was evidently impure.

3 : 3-Dimethyl- $\beta$ -naphthindolenyl-2-formoxime,



obtained when the above naphthindolenine is treated with nitrous acid, forms yellow silky needles, m. p.  $211$ — $212^\circ$ , and reacts with acetic anhydride to form the corresponding nitrile,

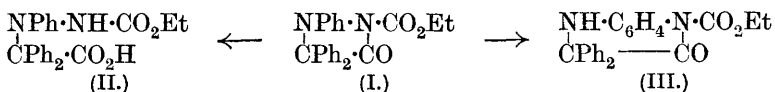


m. p. 130°. Treatment of this nitrile with hydroxylamine yields the *formamidoxime*,  $C_{10}H_6 \begin{smallmatrix} \text{CMe}_2 \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \gg C \cdot C(NH_2) : NOH$ , m. p. 182°.

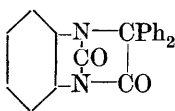
T. H. P.

**Additive Formation of Four-membered Rings. VI. Addition of Azo Compounds to Ethylenes and some Transformations of the Dimethylene-1 : 2-di-imine Ring.** C. K. INGOLD and S. D. WEAVER (*J. Chem. Soc.*, 1925, 127, 378—387).—Interaction of the  $\cdot N : N \cdot$  and  $: C : C :$  groupings, to form a four-membered ring, is favoured by employing ethylene derivatives with a large *gem*-grouping, whilst azo compounds possessing free residual affinity are chosen. Ethyl azodicarboxylate, b. p. 121—125°/16 mm., is obtained (together with ethyl hydrazotricarboxylate, b. p. 200—201°/23 mm.) by the action of ethyl chloroformate on hydrazine, followed by oxidation of the hydrazo-ester with nitric acid. Similarly, oxidation of the hydrazo-ester from ethyl chloroformate and phenylhydrazine, by means of permanganate, gives ethyl phenylazocarboxylate.

Ethyl phenylazocarboxylate combines with diphenylketen in light petroleum during 24 hrs., forming *ethyl 4-keto-2 : 3 : 3-triphenyldimethylene-1 : 2-di-imine-1-carboxylate* (I), m. p. 132—133° (yield 70%). This is converted by hot aqueous-alcoholic sodium hydroxide into  $\beta$ -phenyl- $\alpha$ -carbethoxyhydrazine- $\beta$ -diphenylacetic acid (II), m. p. 157—158°, to which this formula is assigned by analogy (cf. Staudinger, Klever, and Kober, A., 1910, i, 586), and II by acetic anhydride is reconverted into I. By boiling the alcoholic solution of I with hydrogen chloride it forms *ethyl 3-keto-2 : 2-diphenyltetrahydroquinoxaline-4-carboxylate* (III), by a transformation of the *o*-semidine type; for purification the alcoholic solution of



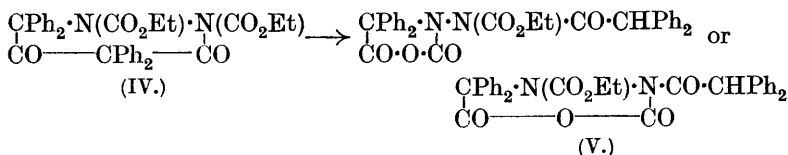
this product is boiled with sodium hydroxide, when a *substance*, m. p. 180—181° (a ketotriphenyloxadiazole?), is filtered off, whilst, from the acidified filtrate, chloroform extracts the quinoxaline, m. p. 168°; *monoacetyl* derivative, m. p. 190—191°. After heating I with phosphorus pentachloride in presence of phosphorus oxychloride, and then treating with water, alcohol extracts from the solid product *1 : 4-endoketo-2-keto-3 : 3-diphenyltetrahydroquinoxaline* (annexed formula), m. p. 335° (yield 6%), which is of interest because the space model lies in 3 planes; dilution of



the alcoholic solution with water yields a *dichloro* compound (2 : 2-dichloro-1 : 4-endoketo-3 : 3-diphenyltetrahydroquinoxaline?), m. p. 246° (decomp.); replacement of the phosphorus oxychloride by benzene leads to formation of a *monochloro* compound (3-chloro-2 : 2-diphenyl-1 : 2-dihydroquinoxaline?), m. p. 204°.

Ethyl azodicarboxylate and diphenylketen form *ethyl 3 : 5-diketo-4 : 4 : 6 : 6-tetraphenylhexahydropyridazine-1 : 2-dicarboxylate* (IV),

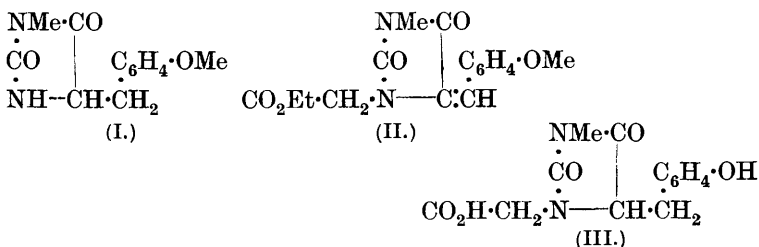
m. p. 129—131°, which in boiling alcoholic solution is hydrolysed by hydrogen chloride to *anhydro-α-diphenylacetyl-α(or β)-carboxy-β(or α)-carbethoxyhydrazine-β-diphenylacetic acid* (V), m. p. 155—156°. Ethyl azodicarboxylate and *as*-diphenylethylene give *ethyl 6:6-*



*diphenylhexahydro-1:2:3:4-tetrazine-1:2:3:4-tetracarboxylate*,  $\text{CPh}_2 \cdot \text{N}(\text{CO}_2\text{Et}) \cdot \text{N}(\text{CO}_2\text{Et}) \cdot \text{CH}_2 \cdot \text{N}(\text{CO}_2\text{Et}) \cdot \text{N}(\text{CO}_2\text{Et})$ , m. p. 164—166°. Ethyl azodicarboxylate and styrene give *ethyl 6-phenylhexahydro-1:2:3:4-tetrazine-1:2:3:4-tetracarboxylate*, m. p. 133—134°.

From benzylidene-*p*-nitrobenzylamine and diphenylketen is produced a *compound*, m. p. 133—134° (2-keto-3:3:4-triphenyl-1-*p*-nitrobenzyltrimethyleneimine?). F. M. H.

**Synthesis of the Polypeptide-Hydantoin: 1-Methyl-4-*p*-hydroxybenzylhydantoin-3-acetic Acid.** D. A. HAHN and A. G. RENFREW (*J. Amer. Chem. Soc.*, 1925, **47**, 147—163).—4-*Anisyl-1-methylhydantoin* (I), m. p. 116—118°, was prepared by reducing 1-methyl-4-anisylidenehydantoin (cf. Johnson and Nicolet, A., 1912, i, 585). *Ethyl 1-methyl-4-anisylidenehydantoin-3-acetate* (II), m. p.



107—108°, obtained by heating the sodium derivative of 1-methyl-4-anisylidenehydantoin with ethyl chloroacetate, affords, on hydrolysis with alkalis, 1-methyl-4-anisylidenehydantoin-3-acetic acid, m. p. 168—169° (*sodium salt*, m. p. 310°), whilst acid hydrolysis yields a mixture of the latter with an *isomeride*, m. p. 203—205°, from which an *ethyl ester*, m. p. 127—128°, isomeric with (II), was prepared. *Ethyl 4-anisyl-1-methylhydantoin-3-acetate*, m. p. 75·5—77°, was prepared analogously to (II) from (I) and also by the reduction of (II) with hydrogen in presence of palladium, in alcoholic solution. 1-Methyl-4-*p*-hydroxybenzylhydantoin-3-acetic acid (III), m. p. 167—167·5°, was obtained from either of the above 1-methyl-4-anisylidenehydantoin-3-acetic acids, or their ethyl esters, and also from ethyl 1-methyl-4-anisylhydantoin-3-acetate, in all cases by the action of hydriodic acid and red phosphorus at 130—140°.

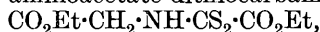
Hydrolysis of the *ethyl* ester, m. p. 145—146°, with barium hydroxide solution, afforded methylamine, carbon dioxide, and a solution from which a *barium hydrogen* salt  $[(+3\text{H}_2\text{O})$ , m. p. 110° with loss of water and subsequent resolidification, and m. p. 250—260° (decomp.)] of the acid  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ , was precipitated by acetic acid, or from which the normal *barium* salt, m. p. 280—290°, was obtained on concentration. The *ethyl* ester, m. p. 84—85.5°, was obtained from the above barium salts by treatment with alcohol and hydrogen chloride. F. G. W.

**Hydantoins. XLI. Synthesis of Hydantoins containing Phenolic Groups in the Glyoxaline Nucleus.** R. D. COGHILL and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1925, **47**, 184—193).—3-*p*-Methoxyphenyl-2-thiohydantoin, m. p. 214°, obtained by the action of ethyl aminoacetate on *p*-methoxyphenylcarbimide in alcohol in presence of an equivalent of potassium hydroxide, and heating the product with hydrochloric acid, yielded 3-*p*-methoxyphenylhydantoin (cf. Hill and Kelsey, A., 1922, i, 1141) when digested with aqueous chloroacetic acid, and this was demethylated by heating with hydrobromic acid in glacial acetic acid under pressure at 100°, with formation of 3-*p*-hydroxyphenylhydantoin, m. p. 267°. 3-*p*-Ethoxyphenyl-2-thiohydantoin, m. p. 197°, exists in a white (stable) and a yellow (labile) modification. The stable form is obtained analogously to the above corresponding methoxy derivative, the labile isomeride being obtained by using concentrated potassium hydroxide as the condensing agent, isolating the *potassium* salt of *p*-ethoxyphenylthiohydantoic acid, m. p. 128° (decomp.), which is the primary reaction product, and boiling this with hydrochloric acid. The unstable isomeride is converted into the stable modification by boiling in alcohol acidified with hydrochloric acid. 3-*p*-Ethoxyphenylhydantoin, m. p. 203°, could not be de-ethylated by heating with hydrobromic acid in acetic acid. 3-*p*-Nitrophenylthiohydantoin, yellow, m. p. 170—172° (decomp.), was also prepared. *p*-Methoxyphenylglycine has m. p. 146° (cf. Vater, A., 1884, 1144). *p*-Methoxyphenylcarbamide, m. p. 168°, obtained by the action of potassium cyanate on anisidine hydrochloride, does not condense with chloroacetic acid or chloroacetyl chloride at 100°. 1-*p*-Hydroxyphenylhydantoin, m. p. 280° (decomp.), was prepared by demethylating, as above, 1-*p*-methoxyphenylhydantoin (cf. Frerichs and Brenstedt, A., 1903, i, 16).  $\alpha$ -Amino-*p*-methoxyphenylacetic acid (cf. Tiemann and Köhler, A., 1882, 57) was converted, by the action of acetic anhydride and ammonium thiocyanate, into 1-acetyl-5-*p*-methoxyphenyl-2-thiohydantoin, m. p. 165°, from which 5-*p*-methoxyphenyl-2-thiohydantoin, m. p. 200—210° (decomp.), after turning red at 130°, was obtained by hydrolysis. When digested with aqueous chloroacetic acid, this thiohydantoin afforded 5-*p*-methoxyphenylhydantoin (cf. Clarke and Francis, T., 1911, **99**, 319), from which 5-*p*-hydroxyphenylhydantoin, m. p. 262°, was obtained on demethylation. By heating  $\alpha$ -amino-*p*-methoxyphenylacetic acid with *p*-methoxyphenylthiocarbimide at 140—160°, 1 : 3-di(*p*-methoxyphenyl)-2-thio-

*hydantoin*, m. p. 185°, was obtained, from which 1 : 3-*di*(*p*-methoxyphenyl)*hydantoin*, m. p. 157°, and 1 : 3-*di*(*p*-hydroxyphenyl)*hydantoin*, m. p. 242°, were prepared. 5 : 5-*Di*(*p*-hydroxyphenyl)*hydantoin*, m. p. not below 280°, was obtained from the corresponding dimethoxy derivative (cf. Biltz, A., 1909, i, 525). 3 : 5-*Di*(*p*-methoxyphenyl)-2-*thiohydantoin*, m. p. 193°, obtained by heating anisylthiocarbimide,  $\alpha$ -amino-*p*-methoxyphenylacetic acid, and sodium hydroxide in alcohol at 80°, 3 : 5-*di*(*p*-methoxyphenyl)-*hydantoin*, m. p. 170°, and 3 : 5-*di*(*p*-hydroxyphenyl)*hydantoin*, are described. F. G. W.

**Hydantoins. XLII. Method of Synthesising 1 : 5-Diaryl-hydantoins : 1 : 5-Di(*p*-hydroxyphenyl)*hydantoin*.** R. D. COGHILL (*J. Amer. Chem. Soc.*, 1925, 47, 216—221; cf. preceding abstract).—When *p*-anisidine is heated with the cyanohydrin of *p*-anisaldehyde, in alcoholic solution, *p*-anisylidene-*p*-anisidine, m. p. 146°, and *p*-methoxyphenylamino-*p*-methoxyphenylacetoneitrile,  $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}(\text{CN})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p. 90°, are obtained. The latter product is also obtained from the former by treatment with hydrocyanic acid (cf. Tiemann and Piest, A., 1883, 198). When treated with potassium cyanate in glacial acetic acid, the nitrile yields the *carbamide*,  $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{CO}\cdot\text{NH}_2)\cdot\text{CH}(\text{CN})\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , pale yellow, m. p. 131°, and this, when warmed with hydrochloric acid, is converted into 1 : 5-*di*(*p*-methoxyphenyl)*hydantoin*, m. p. 190°, from which 1 : 5-*di*(*p*-hydroxyphenyl)*hydantoin*, m. p. 160°, is obtained on demethylation. The *p*-hydroxyphenylhydantoins do not possess antiseptic properties comparable with those of phenol. F. G. W.

**Hydantoins. XLIII. Synthesis of the Polypeptide-Hydantoin : "Hydantoin-3-acetic Acid."** T. B. JOHNSON and A. G. RENFREW (*J. Amer. Chem. Soc.*, 1925, 47, 240—245).—When carbethoxy ethyl aminoacetate-dithiocarbamate,



obtained by the action of ethyl chloroformate on ethyl aminoacetate-dithiocarbamate, is distilled under diminished pressure, ethyl thiocarbimidoacetate (cf. Johnson and Ticknor, *Proc. Nat. Acad. Sci.*, 1917, 3, 303; Johnson and Hemingway, A., 1916, i, 635) is obtained, together with ethyl carbethoxyaminoacetate. *s*-Ethyl thiocarbamide-diacetate,  $\text{CS}(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$ , m. p. 85—87°, was obtained by the action of ethyl thiocarbimidoacetate on ethyl aminoacetate in dry ether. This was hydrolysed by 50% acetic acid to ethyl hydrogen thiocarbamide-diacetate, m. p. 96°. 2-*Thiohydantoin-3-acetic acid*, yellow, m. p. 210—212°, was obtained by the action of hydrochloric acid on either of the above thiocarbamides, and also by the action of ethyl thiocarbimidoacetate on glycine in alcoholic potassium hydroxide. When heated with chloroacetic acid, it yielded *hydantoin-3-acetic acid*, m. p. 190—191°. F. G. W.

**Hydantoins. XLIV. Pyvuril and Dipyrivic Triureide.** D. DAVIDSON (*J. Amer. Chem. Soc.*, 1925, 47, 255—259).—Pyvuril (5-methylallantoin, cf. Grimaux, A., 1877, 740) reacts with 1 mol.



of bromine in glacial acetic acid to form carbamide and bromopyruvic ureide (cf. Gabriel, A., 1906, i, 634) and with 2 mols. to form dibromopyruvic ureide, whilst excess of the halogen affords tribromopyruvic ureide (cf. Fischer, A., 1887, 918). Concentrated sulphuric acid converts pyvuril into dipyruric ureide (Gabriel, *loc. cit.*), whilst 5-methylhydantoin is obtained by the action of hydriodic acid. Dipyruric triureide gives the same products as pyvuril in the above reactions, and it is concluded that pyruvic monoureide (5-methylenehydantoin) is an intermediate in the decomposition of pyvuril and dipyruric triureide. F. G. W.

**Hydantoins. XLV. Dipyruric Ureide.** D. DAVIDSON and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1925, **47**, 561—567; cf. preceding abstract).—Dipyruric ureide is reduced by hydrogen in glacial acetic acid, in presence of platinum oxide, to hydrodipyruric ureide (cf. Gabriel, A., 1906, i, 634). It reacts with bromine in acetic acid to form bromodipyruric ureide, and with bromine water to form *bromomethenyl-5'-(5'-methyl)hydantoin-5-hydantoic acid*,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}(\text{CO}_2\text{H})\cdot\text{CBr}\cdot\text{CMe}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot 3\text{H}_2\text{O}$ , which becomes anhydrous on heating, and when treated with concentrated sulphuric acid, is converted into bromodipyruric ureide. The latter, when treated with bromine in aqueous solution, yields dibromodipyruric ureide. Nitric acid converts dipyruric ureide into nitropyruric ureide (cf. Grimaux, A., 1877, 740) and parabanic acid. F. G. W.

**Catalytic Hydrogenation with Hydrogen and Platinum.** E. WASER (*Helv. Chim. Acta*, 1925, **8**, 117—125).—Certain anomalies in catalytic reduction with hydrogen and platinum-black at the ordinary temperature are described. Benzoic acid in alcoholic solution gives a 30—40% yield of ethyl hexahydrobenzoate and a correspondingly reduced yield of the free acid, whereas reduction in butyl, *iso*amyl, and nonyl alcohols follows the normal course. Nitroantipyrine in glacial acetic acid yields *N*-acetamidoantipyrine, instead of the unsubstituted amino compound. On the other hand, with vanillylidenehippuric acid in alcoholic solution, a partial saponification occurs and ethyl benzoate is formed as well as the benzoyl derivative of vanillylidenealanine.

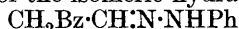
Three new catalytic reductions, following a normal course, are described: antipyrine in aqueous solution is slowly reduced to the dihydro compound at the ordinary temperature by use of platinum-black and hydrogen, although not with palladium and hydrogen (cf. this vol., i, 90). Benzamidocinnamic acid in alcoholic solution is reduced under similar conditions to benzoylphenylalanine. Cinnamyl alcohol gives  $\gamma$ -cyclohexylpropyl alcohol, b. p. 218—220°/730 mm. or 110—111°/11 mm.,  $d_4^{20}$  0.9259 (acetate, b. p. 232—233°/729 mm.,  $d_4^{20}$  0.9540, *phenylurethane*, m. p. 88°).

Sebacyl chloride,  $d_4^{20}$  1.1375,  $d_4^{20}$  1.1212, prepared by the action of thionyl chloride on the acid, is reduced in boiling xylene solution in a stream of hydrogen with a 2% palladium-calcium carbonate catalyst giving sebacic dialdehyde, polymerising spontaneously to

the termolecular compound. The unimolecular dialdehyde can be converted directly into the sodium hydrogen sulphite compound, and thence into the dioxime, small, colourless prisms, softening at  $138^{\circ}$ , m. p.  $142^{\circ}$  (cf. m. p.  $124$ — $127^{\circ}$ , Zetzsche and Enderlin, A., 1922, i, 431). M. J.

**Isomeric Relationships in the Pyrazole Series. II. 3(5)-Phenylpyrazole and its Derivatives.** K. VON AUWERS and W. SCHMIDT (*Ber.*, 1925, 58, [B], 528—543).—The preparation of 3- or 5-phenyl-1-alkylpyrazoles is described, whereas 1 : 5-dialkylpyrazoles (von Auwers and Broche, A., 1923, i, 151) do not appear capable of existence. The hypothesis that the mutual repulsion of electrochemically similar radicals is responsible for the non-existence of the dialkyl compounds does not, however, appear adequate.

Hydroxymethyleneacetophenone is readily prepared by the action of sodium on a mixture of acetophenone and ethyl formate dissolved in anhydrous benzene or ether. The corresponding *benzoate*,  $\text{CHBz}\cdot\text{CH}\cdot\text{OBz}$ , m. p.  $75$ — $75\cdot5^{\circ}$ , *carbethoxy* derivative, m. p.  $57$ — $59^{\circ}$ , and *ethyl ether*, b. p.  $162$ — $163^{\circ}/10$  mm., are described. Treatment of free hydroxymethyleneacetophenone with phenylhydrazine (cf. Claisen and Fischer, A., 1888, 680; Knorr and Duden, A., 1893, i, 230) yields a mixture of the isomeric hydrazones,



and  $\text{NHPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{CHO}$ , which lose water and pass into 1 : 5- and 1 : 3-diphenylpyrazole, respectively. 1 : 5-Diphenylpyrazole is most conveniently prepared by the action of boiling glacial acetic acid or alcoholic hydrogen chloride on *benzoylacetalddehydephenylhydrazone*, m. p.  $126^{\circ}$  (decomp.), obtained from hydroxymethyleneacetophenone and phenylhydrazine in ethereal solution. To obtain an initial material which would lead to the exclusive production of 1 : 3-diphenylpyrazole, phenylhydrazine has been caused to react with the benzoate, carbethoxy derivative, and ethyl ether of hydroxymethyleneacetophenone. In every case the action is attended by the elimination of the substituent in the hydroxymethylene group; the crude product, m. p.  $115$ — $120^{\circ}$ , after a single crystallisation from acetone, gives a *substance*,  $\text{C}_{15}\text{H}_{14}\text{ON}_2$ , m. p.  $162^{\circ}$  (*carbethoxy* derivative, m. p.  $156^{\circ}$ ), which does not dissolve in alkali hydroxide, give the reactions of an aldehyde, or yield aniline when reduced with sodium amalgam and acetic acid in alcoholic solution; the constitution  $\text{N} \leq \begin{array}{c} \text{CPh}\cdot\text{CH}_2 \\ \text{NPh}\cdot\text{CH}\cdot\text{OH} \end{array}$  is therefore

suggested for it, and it is considered to be produced by ring closure from the labile material, m. p.  $115$ — $120^{\circ}$ . 3(5)-Phenylpyrazole, prepared from hydroxymethyleneacetophenone, hydrazine sulphate, and sodium hydroxide solution, has m. p.  $79^{\circ}$ , b. p.  $177$ — $178^{\circ}/11$  mm.,  $313$ — $314^{\circ}/\text{atmos. pressure}$ ,  $d_4^{29\cdot3}$  1.0818,  $n_{\text{D}}^{20\cdot3}$  1.58890; it is converted by sodium nitrite and dilute sulphuric acid into 3(5)-phenylpyrazole nitrate, m. p.  $126^{\circ}$  (decomp.), which is also obtained from the base and dilute nitric acid. 3(5)-Phenyl-1-acetylpyrazole has b. p.  $157$ — $158^{\circ}/10$  mm., m. p.  $84$ — $85^{\circ}$ . 1 : 3-Diphenyl-

pyrazole, m. p. 84—85°, is converted by methyl iodide at 120° into the corresponding *methiodide*, m. p. 172°, which loses methyl iodide and re-forms 1 : 3-diphenylpyrazole when heated above its m. p. Similarly, 1 : 5-diphenylpyrazole *methiodide*, m. p. 207°, yields methyl iodide and 1 : 5-diphenylpyrazole, m. p. 55—56°.

3(5)-Phenylpyrazole is converted by methyl bromide at 100° into a mixture of bases from which aqueous hydrobromic acid allows the separation of a nearly homogeneous hydrobromide, this leading to the isolation of 3-phenyl-1-methylpyrazole, b. p. 145—146°/12 mm., m. p. 55—56°,  $d_4^{20}$  1.0232,  $n_{D16}^{103.7}$  1.56216 (picrate, m. p. 132—133°), identical with the product described by Knorr and Wenglein. The mixture of bases remaining in the hydrobromic acid solution can be separated readily by means of the picrates, whereby 5-phenyl-1-methylpyrazole, b. p. 127°/10 mm.,  $d_4^{15.8}$  1.0946,  $d_4^{20}$  1.090,  $n_{D16}^{15.8}$  1.58999 (picrate, m. p. 143—144°), is obtained. The solid base is the main product in the above reaction or when methylation is effected with methyl sulphate. Either phenylmethylpyrazole is converted by methyl iodide at 100° into 3-phenyl-1 : 2-dimethylpyrazolium iodide, m. p. 156—157°, which, when distilled under diminished pressure, gives 68% of 5-phenyl-1-methylpyrazole and 32% of 3-phenyl-1-methylpyrazole. The constitution of the phenylmethylpyrazoles is established by the synthesis of 5-phenyl-1-methylpyrazole by the condensation of  $\alpha$ -bromocinnamaldehyde with methylhydrazine and treatment of the brominated pyrazoline thus produced with sodium acetate. Further, the sodium salt of hydroxymethyleneacetophenone, methylhydrazine sulphate, and sodium acetate yield exclusively the compound  $\text{NHMe}\cdot\text{N}(\text{CH}_2\text{CHBz})_2$ , m. p. 138°, which is transformed by warm, glacial acetic acid or boiling, dilute, alcoholic hydrogen chloride into 5-phenyl-1-methylpyrazole. The same substance, m. p. 138°, is also formed from hydroxymethyleneacetophenone and methylhydrazine in ethereal solution, but is then accompanied by much oil, which yields a mixture of the 1 : 3- and 1 : 5-derivatives, the latter predominating; the hydroxymethyleneacetophenone in these circumstances reacts in each possible manner. The action of methylhydrazine on the benzoate of hydroxymethyleneacetophenone gives mainly 3-phenyl-1-methylpyrazole, but 5-phenyl-1-methylpyrazole is formed in small amount. The action of bromine on the phenylmethylpyrazoles in glacial acetic acid solution yields, respectively, 4-bromo-3-phenyl-1-methylpyrazole, b. p. 175—176°/12 mm.,  $d_4^{18.9}$  1.4707,  $d_4^{20}$  1.469,  $n_{D16}^{18.9}$  1.61711, and 4-bromo-5-phenyl-1-methylpyrazole, m. p. 53—54° or 65—66°,  $d_4^{56.6}$  1.4199,  $n_{D16}^{57.6}$  1.58790. 4-Bromo-3(5)-phenylpyrazole is converted by methyl sulphate into a mixture of the bromophenylmethylpyrazoles.

3(5)-Phenylpyrazole is converted by a large excess of ethyl bromide in the presence of alcoholic sodium ethoxide exclusively into 3-phenyl-1-ethylpyrazole, m. p. 36.5—37.5°, b. p. 152—153°/12 mm.,  $d_4^{11.6}$  1.0667,  $d_4^{20}$  1.059,  $n_{D16}^{11.6}$  1.58897 (picrate, m. p. 104—105°); the constitution of the base is deduced by comparison of its physical constants with those of 3-phenyl-1-methyl- and 5-phenyl-1-methylpyrazole.

H. W.

**8-Aminoquinoline and its Derivatives.** R. SEKA (*Monatsh.*, 1925, 45, 287—294).—8-Nitroquinoline, prepared by Knueppel's modification of Skraup's synthesis, was reduced to the amine in alcoholic solution by means of iron in presence of calcium chloride. Treated with hydrochloric acid, the colourless crystals first become yellow, then deep red, followed by a sudden change to a colourless powder, 8-aminoquinoline dihydrochloride, which dissolves in water to a yellow solution. The dihydrochloride, if dried in a vacuum at 90° for a long time, or immediately if mixed with 1 mol. of 8-aminoquinoline, yields the *monohydrochloride*, m. p. 208—209° (uncorr.), as a deep dark red mass, which sublimes at 100°. Diazotised 8-aminoquinoline gives with  $\beta$ -naphthol an *azo dye*,  $C_{19}H_{13}ON_3$ , m. p. 232° (decomp.), a dark red substance insoluble in water. Phenylcarbimide, when heated with 8-aminoquinoline, gives *s-phenyl-8-quinolylcarbamide*,  $C_9H_6N \cdot NH \cdot CO \cdot NHPh$ , m. p. 152° (uncorr.). Phenylthiocarbimide gives a similar substance (not described). *p*-Chloro-*o*-nitrobenzoic acid condenses with 8-aminoquinoline to form *o*-nitrophenyl-8-quinolylamine-*p*-carboxylic acid, m. p. 282° (uncorr.).

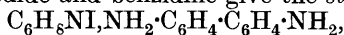
4-*o*-Nitroanilino-2 : 6-dimethylpyridine, m. p. 138.5°, yellow needles, is obtained in small yield by the condensation of 4-chloro-2 : 6-dimethylpyridine with *o*-nitroaniline. A. C.

**Preparation of Dyes Insoluble in Water.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 395917; from *Chem. Zentr.*, 1924, ii, 2790).—Diazo compounds which contain no sulphonic or carboxyl groups are coupled with the diacylacetyl derivatives of arylenediamines, alone or on a substrate, giving insoluble dyes, yellow to orange-brown in shade, fast to washing. The following acylacetylarylenediamines were obtained by heating the diamine with ethyl acetoacetate: *Diacetoacetyl-p-phenylenediamine*, m. p. 167° (decomp.); *diacetoacetyl-1 : 4-naphthylenediamine*, m. p. 197° (decomp.); *diacetoacetyl-1 : 5-naphthylenediamine*, m. p. 249—250° (decomp.); *diacetoacetyl-2 : 6-naphthylenediamine*, m. p. 203—204° (decomp.). R. B.

**New Group of Organic Molecular Compounds.** B. EMMERT and N. ROH (*Ber.*, 1925, 58, [B], 503—508).—4 : 4'-Dipyridylium dialkyl halides yield additive compounds with amines, phenols, or acetic acid when the components are brought together generally in more or less dilute alcoholic solution. They are usually decomposed by contact with solvents in which one component is considerably more soluble than the other, but appear to be present to some extent unchanged in solvents in which each component is freely soluble. The following *substances* are described, the figures indicating the number of mols. of amine united with 1 mol. of the salt: 4 : 4'-dipyridyl dibenzobromide with 4 aniline; 4 diphenylamine, m. p. 153°; 4 *p*-phenylenediamine, m. p. 163°; 2  $\beta$ -naphthylamine; 2 *o*-nitroaniline, m. p. 196—197°; 2 *p*-nitroaniline, m. p. 180—181°; 2  $\beta$ -naphthol, m. p. 188—189°; 1 quinol, m. p. 244°; 4 pyrocatechol, m. p. 153—155°; 2 acetic acid; 4 : 4'-dipyridyl dibenzochloride with 4 *p*-phenylenediamine, m. p. 166—167°; 1

quinol, m. p. 231—232° (a corresponding *dihydrate* is described); 4 pyrocatechol, m. p. 179—181°; 4 : 4'-dipyridyl dibenziodide with 4 *p*-phenylenediamine, m. p. 170—171°; 1 quinol, m. p. 217—218°; 4 : 4'-dipyridyl diphenyliodide with 4 aniline; 1 quinol; 4 : 4'-dipyridyl dimethiodide with 4(?) aniline; 4 *p*-phenylenediamine; 2 *p*-phenylenediamine; 1 quinol.

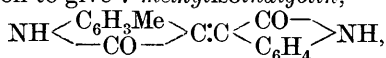
[With M. KOBERNE.]—Pyridinium salts show a rather less pronounced tendency to form molecular compounds. Thus, pyridinium methiodide and benzidine give the *substance*



m. p. 154°.

H. W.

**Derivatives of 7-Methylisatin.** A. WAHL and T. FAIVRET (*Compt. rend.*, 1925, **180**, 589—591).—7-Methylisatin, prepared by Sandmeyer's method (A., 1919, i, 318), condenses with oxindole in acetic acid solution to give 7-methylisoindigotin,

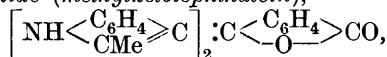


brown crystals reduced by zinc dust and acetic acid to the *leuco*-compound, m. p. 310—315°, soluble in alkalis. 7-Methylisoindigotin is sulphonated by warm concentrated sulphuric acid, yielding a *disulphonic acid* (sodium salt,  $\text{Na}_2\text{A}, 5\text{H}_2\text{O}$ ; potassium salt,  $\text{K}_2\text{A}, 3\text{H}_2\text{O}$ ; barium salt,  $\text{BaA}, 6\text{H}_2\text{O}$ ; silver salt,  $\text{Ag}_2\text{A}, \frac{1}{2}\text{H}_2\text{O}$ , described). On the other hand, when the condensation with oxindole occurs in alcohol in presence of piperidine a colourless substance, 7-methylisatan,  $\text{NH} \left\langle \begin{array}{c} \text{C}_6\text{H}_3\text{Me} \\ \text{CO} \end{array} \right\rangle \text{C}(\text{OH}) \cdot \text{CH} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CO} \end{array} \right\rangle \text{NH}$ ,

is produced, m. p. 259°, which loses water under the influence of heat or of sulphuric acid to give the *isoindigotin*. 7 : 7'-Dimethylisoindigotin is obtained in an impure condition by the action of warm alkalis on crude 7 : 7'-dimethyldisulphisatide, the product of the action of hydrogen sulphide on an alcoholic solution of 7-methylisatin. Sulphonation gives 7 : 7'-isoindigotindisulphonic acid (the salts,  $\text{Na}_2\text{A}, 6\text{H}_2\text{O}$ ,  $\text{K}_2\text{A}, 4\text{H}_2\text{O}$ ,  $\text{BaA}, 4\text{H}_2\text{O}$ ,  $\text{Ag}_2\text{A}, 5\text{H}_2\text{O}$ , are described). The chloride of 7-methylisatin reacts with oxindole in benzene solution to give 7-methylindirubin, brown needles with a coppery reflex.

G. M. B.

**Methylketole-yellow.** B. ODDO (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 236—238; cf. A., 1923, i, 709).—The action of phthalyl chloride on magnesium 2-methylindyl bromide yields : (1) *di-2-methylindylphthalide* (methylketolephthalein),



which forms bright red micro-crystals, m. p. 258° (decomp.), and when heated with alcoholic potassium hydroxide gives *potassium 2-methylindyl-2-methylindolenephylmethane-o-carboxylate*

(methylketole-yellow),  $\text{NH} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \right\rangle \text{C} : \text{C}(\text{C}_6\text{H}_4 \cdot \text{CO}_2\text{K}) : \text{C} \left\langle \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \right\rangle \text{N}$ ,

the corresponding free acid dyeing wool and silk red with violet reflexion, even in 0.001% solution; this coloration, which may be given also to cotton after mordanting, is stable to light, water, soap,

or free alkali or acid. (2) A compound, which is resistant towards fused potassium hydroxide and is possibly an isomeride of methylketolephthalein of the formula  $C_6H_4(CO \cdot C \leq \begin{smallmatrix} C_6H_4 \\ CMe \end{smallmatrix} > NH)_2$ , its formation being due to the presence of symmetrical chloride in the phthalyl chloride used.

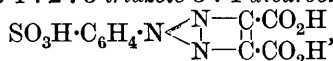
T. H. P.

**Preparation of 2:6-Diaminopyridine.** CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING), M. DOHRN, and H. HORSTERS (D.R.-P. 399902; from *Chem. Zentr.*, 1924, ii, 2788).—As a modification of D.R.-P. 398204 (this vol., i, 301) 2:6-diaminopyridines are obtained by decomposition of the reaction product of pyridine, sodamide, and high-boiling, mobile, and inert media, with water. Thus pyridine, sodamide, and cumene, heated first at 130—140°, and then at 180—190°, etc., yield 2:6-diaminopyridine, m. p. 121—122°, b. p. 148—150°/5 mm.

R. B.

**Synthesis of 1-*p*-Sulphophenyl-1:2:5-triazole-3:4-dicarboxylic Acid.** A. BERETTA (*Gazzetta*, 1925, 55, 63—66).—[With N. JACOB.]—2-*p*-Sulphophenyl-5-amino-6-methyl-1:3-benzotriazole (annexed formula), prepared by diazotising sulphanilic acid and coupling with *m*-tolylenediamine, and treating the *p*-sulphobenzeneazo-*m*-tolylenediamine thus obtained with ammoniacal copper sulphate, forms slender, green needles, infusible at 360°, and gives solutions in ammonia showing intense green fluorescence. The barium (+5H<sub>2</sub>O) and sodium salts are described.

1-*p*-Sulphophenyl-1:2:5-triazole-3:4-dicarboxylic acid,



prepared by oxidising the preceding compound by means of permanganate in alkaline solution, forms white needles, and its strontium salt, (C<sub>10</sub>H<sub>4</sub>O<sub>7</sub>N<sub>3</sub>)<sub>2</sub>Sr<sub>3</sub>·4H<sub>2</sub>O, white leaflets.

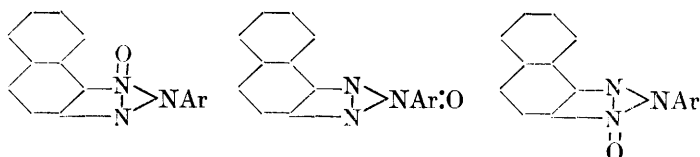
T. H. P.

**Destruction of the αβ-Naphthatriazole Nucleus.** G. CHARRIER and M. GALLOTTI (*Gazzetta*, 1925, 55, 7—11; cf. A., 1924, i, 329, 332; this vol., i, 76, 306).—Alkaline potassium permanganate oxidises 2-*p*-aminophenyl-αβ-naphthatriazole or, with better yield, its acetyl derivative to 5-carboxy-1:2:3-triazole-4-*o*-benzoic acid, which forms a monohydrate, m. p. 192° (decomp.), darkening from 160—170°; the barium salt (+4H<sub>2</sub>O) is described. When the acid is heated at 160—170°, it loses water and carbon dioxide, giving 4-phenyl-1:2:3-triazole-5-carboxylic acid (monohydrate, m. p. 205° decomp.; cf. Oliveri-Mandalà, A., 1910, i, 593). At 210—215°, this compound loses carbon dioxide, yielding 4-phenyl-1:2:3-triazole, m. p. 143—144° (cf. Oliveri-Mandalà, *loc. cit.*).

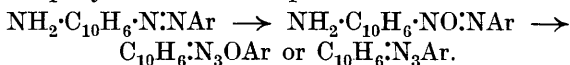
W. E. E.

**Oxidation of Arylazo-β-naphthylamines in Acetic Acid Solution by means of Hydrogen Peroxide.** G. CHARRIER and G. B. CRIPPA (*Gazzetta*, 1925, 55, 11—28; cf. A., 1923, i, 1140).—In the various cases examined, oxidation of *o*-aminoazo compounds

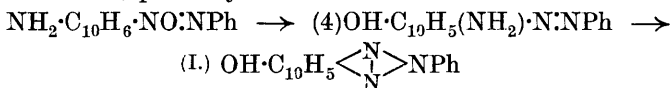
derived from  $\beta$ -naphthylamine in acetic acid solution by means of hydrogen peroxide gives rise to the formation, together with other compounds, of the oxide of the corresponding 2-aryl- $\alpha\beta$ -naphthatriazole, which has one of the three formulæ :



Reduction of 2-benzeneazo-1-nitronaphthalene and 1-benzeneazo-2-nitronaphthalene should yield compounds of the types of the first and third of the above oxides, but attempts to prepare such nitroazo derivatives by the action of nitrosobenzene on 1-nitro- $\beta$ -naphthylamine and 2-nitro- $\alpha$ -naphthylamine (cf. this vol., i, 21) proved unsuccessful. The above oxides are always accompanied by a proportion, varying with the temperature, of the naphthatriazole itself, the oxidation of these *o*-aminoazo compounds consisting principally of the two independent reactions :



It may be, however, that the naphthatriazoles are formed directly from the original aminoazo compounds and not from the azoxy-amino derivatives. Part of the latter remains unaltered and part undergoes Wallach's reaction, giving isomerides of the naphthatriazole oxides, probably in accordance with the scheme :



All the oxidations investigated give rise also to 2-nitro- $\alpha$ -naphthol, which is probably the result of diazo-scission of the azo group, followed by oxidation of the amino group successively to the hydroxylamino, nitroso, and nitro group. Another secondary reaction, observed in all instances, consists in oxidation of a considerable proportion of the 2-aryl- $\alpha\beta$ -naphthatriazole originally formed, with opening of one of the three nuclei of the tricyclic system and formation of 5-carboxy-2-aryl-2 : 1 : 3-triazole-4-benzoic acid.

[With V. TOIA and M. BIANCHESSI.]—The products obtained by oxidising 1-benzeneazo-2-aminonaphthalene in acetic acid solution by means of hydrogen peroxide are : 5-carboxy-2-phenyl-2 : 1 : 3-triazole-4-benzoic acid (this vol., i, 76), the sodium salt (+4H<sub>2</sub>O) of which has m. p. 325°; *N*-phenyl- $\alpha\beta$ -naphthatriazole oxide (cf. A., 1923, i, 1141); *N*-phenyl- $\alpha\beta$ -naphthatriazole; the compound (I) (see above), which forms colourless, prismatic needles, m. p. 196·5°, and is soluble in solutions of alkalis; 2-nitro-1-naphthol; the azoxy-amino derivative, NH<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·NO·NPh or NH<sub>2</sub>·C<sub>10</sub>H<sub>6</sub>·N·NPh·O, or a mixture of these, canary-yellow powder, m. p. about 206° (rapid heating); a *triazole* derivative, probably NPh·N·C<sub>10</sub>H<sub>6</sub>·N·N·C<sub>10</sub>H<sub>6</sub>·N·NPh,

which forms lustrous, deep garnet-red needles infusible at  $360^{\circ}$ , and dissolves in concentrated sulphuric acid to an intensely blue liquid. This trisazo compound is formed only when a large excess of hydrogen peroxide is used for the oxidation.

Similarly, oxidation of 1-*o*-tolueneazo-2-aminonaphthalene yields : 2-*o*-tolyl- $\alpha\beta$ -naphthatriazole oxide,  $C_{10}H_6 \cdot N_3O \cdot C_6H_4Me$ , colourless crystals, m. p.  $166.5^{\circ}$ , giving with concentrated sulphuric acid a deep yellow coloration changing to cherry-red on boiling; 2-*o*-tolyl- $\alpha\beta$ -naphthatriazole,  $C_{17}H_{13}N_3$ , m. p.  $96^{\circ}$ ; and 2-nitro- $\alpha$ -naphthol.

From 1-*p*-tolueneazo-2-aminonaphthalene were obtained : 2-*p*-tolyl- $\alpha\beta$ -naphthatriazole oxide,  $C_{17}H_{13}ON_3$ , colourless, m. p.  $147^{\circ}$ ; 2-*p*-tolyl- $\alpha\beta$ -naphthatriazole (cf. A., 1923, i, 1141); 1-*p*-tolyl-azoxy-2-aminonaphthalene,  $NH_2 \cdot C_{10}H_6 \cdot NO \cdot N \cdot C_6H_4Me$  or



m. p.  $208^{\circ}$ ; 5-carboxy-2-*p*-tolyl-2 : 1 : 3-triazole-4-benzoic acid,  $C_{17}H_{13}O_4N_3$ , m. p.  $233^{\circ}$ ; 4-hydroxy-2-*p*-tolyl- $\alpha\beta$ -naphthatriazole,  $OH \cdot C_{10}H_5 \cdot N_3 \cdot C_6H_4Me$ , m. p.  $274^{\circ}$ .

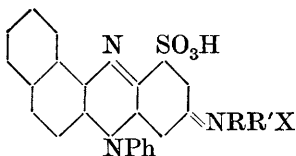
Oxidation of 1-*p*-bromobenzeneazo-2-aminonaphthalene gives : 2-*p*-bromophenyl- $\alpha\beta$ -naphthatriazole oxide,  $C_{16}H_{10}ON_3Br$ , m. p.  $205^{\circ}$ ; 2-*p*-bromophenyl- $\alpha\beta$ -naphthatriazole; 5-carboxy-2-*p*-bromophenyl-2 : 1 : 3-triazole-4-benzoic acid; 4-hydroxy-2-*p*-bromophenyl- $\alpha\beta$ -naphthatriazole,  $C_{16}H_{10}ON_3Br$ , m. p.  $245^{\circ}$ .

Oxidation of 1-*p*-chlorobenzeneazo-2-aminonaphthalene gives : 2-*p*-chlorophenyl- $\alpha\beta$ -naphthatriazole oxide, colourless, turning yellow in the light, m. p.  $200^{\circ}$ ; the triazole itself; and 5-carboxy-2-*p*-chlorophenyl-2 : 1 : 3-triazole-4-benzoic acid, m. p.  $264-265^{\circ}$ .

Oxidation of 2-phenyl- $\alpha\beta$ -naphthatriazole oxide by means of alkaline permanganate solution yields an acid,  $C_{16}H_{11}O_5N_3$ , m. p.  $234^{\circ}$ , probably 5-carboxy-2-phenyl-2 : 1 : 3-oxotriazole-4-benzoic acid.

T. H. P.

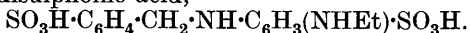
**Preparation of Safranine Dyes.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (Fr. Pat. 573368; from *Chem. Zentr.*, 1924, ii, 2505).—When isorosindulines with the annexed formula



(R, R' = dialkyl or arylalkyl; obtained by oxidising a mixture of an aryl- $\beta$ -naphthylamine with a tertiary aromatic amine containing a *p*-amino group and a 3-sulphonic acid group) are oxidised in presence of aromatic *p*-diamines or *p*-diaminesulphonic acids, fast safranine dyes result. Alternatively, the appropriate isorosinduline may be sulphonated. Thus, when a mixture of phenyl- $\beta$ -naphthylamine-*m*-sulphonic acid (obtained by boiling  $\beta$ -naphthol and metanilic acid with sodium hydrogen sulphite) and 2-amino-5-dimethylaminobenzenesulphonic acid is oxidised by dichromate and acetic acid there is formed an isorosindulinedisulphonic acid. The latter, when oxidised in a current of air in presence of *p*-phenylenediamine-2-sulphonic acid and sodium hydroxide and sulphite, gives a safranine dyeing blue shades on wool from an acid bath. Phenyl- $\beta$ -naphthylamine-*p*-sulphonic acid may be used in place of



the *m*-sulphonic acid, or the diethyl- in place of the dimethyl-amino compound. Another intermediate is 4-ethylaminobenzyl-aniline-3 : 4'-disulphonic acid,



Phenyl- $\beta$ -naphthylamine-6-sulphonic acid and 2-amino-5-diethylaminobenzenesulphonic acid similarly give rise to an *isorosinduline-disulphonic acid*. This, when oxidised in presence of 3-chloro-4-toluene-*p*-sulphonyl-*p*-phenylenediamine, followed by hydrolysis of the acyl group, affords a *safraninedisulphonic acid*, dyeing greenish-blue shades on wool.

R. B.

**Action of Catalysts on Oxidation of Uric Acid : Copper and Cuprous Urate.** L. PIAUX (*Compt. rend.*, 1924, 179, 901—903; cf. A., 1924, i, 430, 431).—Spongy metallic copper, in the proportion of from  $\frac{1}{40}$  to  $\frac{1}{5}$  atom per mol. of uric acid, acts as an oxidation catalyst. Rapid absorption of oxygen takes place and the solution turns pink, but the copper remains unattacked. The rate of oxidation is from  $1\frac{1}{2}$  to 3 times that of the non-catalysed reaction. After 40—80 mins., the rate of oxygen absorption decreases and the liquid turns grey, green, and, finally, blue. During this stage the copper is attacked and passes into solution. The products are oxonic acid and allantoin. Cuprous urate, possibly in virtue of its colloidal form, was found to be more active than the metal. With  $\frac{1}{450}$  atom of copper per mol. of acid, oxidation is twice as rapid as in the non-catalysed reaction and a 50% yield of oxonic acid is obtained, whilst when  $1/22.5$  atom is present oxidation is three times as rapid, the products being allantoin with some oxonic acid.

H. J. E.

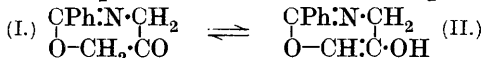
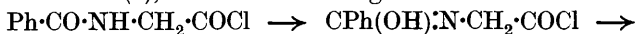
**Action of Free Oxygen on Uric Acid dissolved in Aqueous Potassium Hydroxide. Action of Catalysts.** L. PIAUX (*Bull. Soc. chim.*, 1925, [iv], 37, 311—326).—In continuance of previous work (A., 1924, i, 430, 431; this vol., i, 165 and preceding abstract), the rate of oxidation of uric acid in alkaline solution has been measured. The reaction is greatly accelerated by agitation and by heat; absorption of oxygen ceases after a few hours (cf. Biltz and Robl, A., 1920, i, 883). Potassium oxonate is the principal oxidation product. For oxidation to occur at least 2 mols. of potassium hydroxide must be present for each mol. of uric acid; thereafter the velocity of oxidation increases with increasing excess of alkali, the best yield of oxonate being obtained with 5 mols. of potassium hydroxide. The oxidation is accelerated by ferric hydroxide, manganous lactate, metallic copper, cuprous urate, and potassium manganitartrate (Job., A., 1911, i, 176). With manganous lactate, whilst the absorption of oxygen is accelerated, the total volume absorbed is diminished, being approximately 1 atom instead of 1.7 atoms per mol. of acid, and a yield of approximately 50% of allantoin is obtained. These results correspond with the two equations:  $\text{C}_5\text{H}_4\text{O}_3\text{N}_4 + \text{O} + \text{H}_2\text{O} = \text{C}_4\text{H}_6\text{O}_3\text{N}_4 + \text{CO}_2$ , and  $\text{C}_5\text{H}_4\text{O}_3\text{N}_4 + 2\text{O} + \text{H}_2\text{O} = \text{C}_4\text{H}_3\text{O}_4\text{N}_3 + \text{CO}_2 + \text{NH}_3$ , and the appearance of allantoin is regarded as due to the formation of an autoxidisable intermediate compound A (cf. More, A., 1924, i, 333), the production

of which, but not the autoxidation, is catalysed by manganese, copper, and cuprous urate. The formation of allantoin occurs to a slighter extent with copper or with cuprous urate than with manganese. These results are in agreement with the hypothesis advanced by Behrend (A., 1916, i, 164) and by Biltz (A., 1920, i, 884; 1921, i, 893). The *cuprammonium* salt of oxonic acid,  $C_4HO_4N_3Cu, 2NH_3$ , is described. R. B.

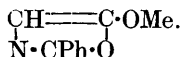
**Dyes derived from Phenanthraquinone. V. Phenanthraphenazinazines.** A. C. SIRCAR and P. C. DUTT (*J. Indian Chem. Soc.*, 1925, 1, 201—206; cf. T., 1922, 121, 1944; Watson and Dutt, T., 1921, 119, 1211).—Various phenanthraphenazinazines are prepared by condensing 2:3-diaminophenazine with phenanthraquinone and its derivatives. By the introduction of an additional chromophoric azine ring into the molecule, deeper (brownier) and fuller shades are obtained. By boiling equimolecular quantities of the appropriate quinone and 2:3-diaminophenazine in glacial acetic acid, the following compounds are obtained, which, with one exception, are all amorphous powders, not melting below  $290^\circ$ , insoluble in ordinary solvents, but soluble in pyridine: *phenanthraphenazinazine*, microscopic needles, 2:7-dinitrophenanthraphenazinazine, 4:5-dinitrophenanthraphenazinazine, 2-nitrophenanthraphenazinazine, 4-nitrophenanthraphenazinazine, 2-bromo- and 2:7-dibromo-phenanthraphenazinazine, dibromonitro- and bromodinitrophenanthraphenazinazine, 5-bromo-4-nitro- and bromo-2-nitrophenanthraphenazinazine, 2-aminophenanthraphenazinazine, 2:7-, 4:5-dihydroxy, 2-hydroxy-, and 4-hydroxy-phenanthraphenazinazine.

J. W. B.

**Amino-acids. Action of Diazomethane on Hippuryl Chloride.** P. KARRER and R. WIDMER (*Helv. Chim. Acta*, 1925, 8, 203—205).—Diazomethane in absolute ether solution reacts with an ethereal suspension of hippuryl chloride, giving in excellent yield a compound,  $C_{10}H_9O_2N$ , colourless prisms, m. p.  $91^\circ$ . The latter has a faintly acid reaction in water and, when titrated with phenolphthalein as indicator, requires only about 0.5 mol. of alkali. The end-point is not sharp. The tautomeric formula (II) is suggested in preference to (I), the reaction being indicated thus:



The completely dissimilar properties of compounds of the oxazole type eliminate from consideration the 5-ring formula,



As with other 1:3-oxazine derivatives, the smallest trace of mineral acid suffices to open the ring, giving, contrary to expectation, hippuric acid. Traces of formaldehyde account for the carbon atom which is lost. In spite of the loosening of the 5:6 ethylenic linking implied by this ring-opening, the authors consider that formula (II) most adequately explains the facts. M. J.

**Anhydrides of Acylamino-acids.** P. KARRER, E. MIYAMICHI, H. C. STORM, and R. WIDMER (*Helv. Chim. Acta*, 1925, 8, 205—211; cf. A., 1924, i, 1118).—Investigation of the influence of the substituting acyl group on the ease with which the esters of acylamino acids are converted into the corresponding oxazoles by the action of phosphorus pentoxide or pentachloride shows that the closing of the ring becomes increasingly difficult with rising mass of the acyl substituent. The *ethyl* ester of isovalerylglycine, b. p. 154°/11 mm., yields 5-ethoxy-2-isobutyloxazole, b. p. 96—97°/11 mm. The *ethyl* ester of *n*-hexoylglycine, b. p. 171°/11 mm., yields only a trace of oxazole, insufficient for isolation. The *ethyl* esters of *n*-octoylglycine, m. p. 32°, b. p. 189°/11 mm., *n*-dodecoylglycine, m. p. 62°, and palmitylglycine are unattacked. Three new oxazoles are described: 5-ethoxy-2:4-dimethyloxazole, b. p. 60°/12 mm. (*picrate*, m. p. 76°), from the *ethyl* ester of acetylalanine (m. p. 38—39°); 5-ethoxy-2-methyl-4-isopropyloxazole, b. p. 62°/11 mm. (*picrate*, m. p. 85°), from the *ethyl* ester of acetylvaline, b. p. 99°/2 mm., and 5-ethoxy-2-*n*-propyl-4-isobutyloxazole, b. p. 109—112°/11 mm., from the *ethyl* ester of butyryl-leucine, b. p. 126—127°/1 mm. The *ethyl* ester of *d*- $\alpha$ -methyl-*n*-butyryl-1-leucine, b. p. 132—133°/2 mm., yields the optically active 5-ethoxy-4-isopropyl-2-sec.-butyloxazole, b. p. 112°/10 mm. Hydrolysis with mineral acid yields an inactive leucine (cf. following abstract). M. J.

**Anhydrides of Amino-acid Derivatives.** C. GRANÄCHER (*Helv. Chim. Acta*, 1925, 8, 211—217).—Certain acylamino-acid esters of the type  $R\cdot CO\cdot NH\cdot CHR'\cdot CO_2Et$  contain an asymmetric carbon atom which loses its asymmetry when ring closure takes place, with formation of the oxazole. The asymmetry is restored when the ring is opened by hydrolysis with mineral acid. It was hoped that an optically active amino-acid might be obtained in this hydrolysis in the presence of a second asymmetric carbon atom in the substituent acyl group. Only inactive amino-acids have so far been obtained (cf. Karrer and others, preceding abstract).

5-Ethoxy-2- $\alpha\beta\gamma$ -tetramethylcyclopentyl-4-isobutyloxazole, b. p. 170—172°/12—14 mm., a thin oil without the characteristic weakly basic properties of the oxazoles, is obtained by the action of phosphoric oxide on the *ethyl* ester of *d*-campholyl-1-leucine, m. p. 66—67°. The oxazole is strongly dextrorotatory. It is not decomposed by alkali, but concentrated hydrochloric acid at 100° slowly converts it into inactive leucine and *d*-campholyl-leucine.

The following new compounds are described: *Ethyl* ester of chloroacetyl-leucine, b. p. 164—166°/15—18 mm. *Ethyl* ester of  $\alpha\beta$ -diphenylpropionylglycine, m. p. 78—79°. *Ethyl* ester of phthalylglycylglycine, m. p. 190—193°. Acetyl-leucinamide, m. p. 200—202°. Hippuric diethylamide, m. p. 80—81°. No corresponding oxazoles have yet been obtained. M. J.

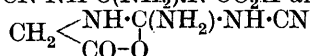
**Derivatives of Cyanamide.** E. FROMM [with H. BARRENSCHEEN, J. FRIEDER, L. PIRK, and R. KAPPELLER] (*Annalen*, 1925, 442, 130—149).—The observation that chlorinated compounds are formed by the interaction of epichlorohydrin and sodium cyanamide

has necessitated a revision of Fromm and Honold's conception (A., 1922, i, 529) of the course of the reaction of ethylene chlorohydrin and sodium cyanamide. The primary change is the hydrolysis of the disodium compound to monosodium cyanamide and sodium hydroxide; this is followed by conversion of ethylene chlorohydrin into ethylene oxide, which combines with the monosodium derivative to yield 2-amino-oxazoline,  $\begin{matrix} \text{CH}_2\cdot\text{O} \\ \text{CH}_2\cdot\text{N} \end{matrix} > \text{C}\cdot\text{NH}_2$

(Fromm and Honold's "cyanamidoethyl alcohol"), identical with the compound obtained by Gabriel (A., 1889, 848) from bromoethylamine hydrobromide and potassium cyanate. The "dibenzoyl derivatives of cyanamidoethyl alcohol" (*loc. cit.*) is shown to be 2-dibenzoylamido-oxazoline. 2-Hydroxyoxazoline benzoate, m. p. 168°, is prepared by the benzylation of the product of the action of nitrous acid on 2-amino-oxazoline. Contrary to the previous statement, 2-amino-oxazoline does not add ammonia, but the base reacts with ammonium chloride or its hydrochloride with ammonia to yield 2:2-diamino-oxazolidine,  $\text{CH}_2 < \begin{matrix} \text{O} \\ \text{CH} \end{matrix} \begin{matrix} \text{O} \\ \text{CH} \end{matrix} (\text{NH}_2)_2$  (Fromm and Honold's "guanidoethyl alcohol"). Methylamine hydrochloride and 2-amino-oxazoline yield 2-amino-2-methylamino-oxazolidine hydrochloride,  $\text{C}_4\text{H}_{12}\text{ON}_3\text{Cl}$ , which gives a tetrabenzoyl compound, m. p. 149°, and a *di-p-toluenesulphonyl* derivative, m. p. 185° after softening at 168°.

Epichlorohydrin or dichlorohydrin is transformed by the mono- or di-sodium derivative of cyanamide into 2-imino-5-chloromethyl-oxazolidine,  $\text{NH} < \begin{matrix} \text{C}(\text{NH})\cdot\text{O} \\ \text{CH}_2 - \text{CH} \end{matrix} \text{CH}_2\text{Cl}$ , m. p. 142° (hydrochloride; picrolonate, m. p. 213°; picrate, m. p. 193—194°; dibenzoyl derivative, m. p. 146—147°). The constitution of the compound is established by its conversion into 2-amino-5-tolylthiolmethyloxazoline, m. p. 148·5°, which is also prepared from 2-amino-5-bromomethyl-oxazoline. The base reacts with ammonium chloride in an unusually complicated manner, yielding (?) 2-amino-5-aminomethyliminazoline,  $\text{NH} < \begin{matrix} \text{CH}_2 - \text{CH} \\ \text{C}(\text{NH})\cdot\text{NH} \end{matrix} \text{CH}_2\cdot\text{NH}_2$ , isolated as the tetrabenzoate, m. p. 183·5°. 2-Amino-5-hydroxymethyloxazoline, prepared from glyceryl monochlorohydrin or glycide and sodium cyanamide, yields a tribenzoate, m. p. 130°.

The action of sodium cyanamide on chloroacetic acid or its esters yields initially cyanamidoacetic acid, but the additive power of this compound is so pronounced that it can be isolated only in small yield. The main product of the change is dicyanodiamidoacetic acid (cyanoguanidoacetic acid), decomp. 220—240°, which reacts in the forms  $\text{CN}\cdot\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{CO}_2\text{H}$  and



It yields a hydrochloride, m. p. 205°, sulphate, m. p. 188°, tetroxalate, m. p. 183°, picrate, m. p. 195°, chloroplatinate, decomp. 220—240°, phosphotungstate, phosphomolybdate, chloroacetate, m. p. 192°,

*phosphate*, m. p.  $196^{\circ}$ , *nitrate*, and *sodium salt*; the *tribenzoyl* derivative has m. p.  $202^{\circ}$  after decomposing at  $196^{\circ}$ . Cyanoguanidoacetic acid behaves as a primary amine towards nitrous acid, yielding (?) *cyanohydantoic acid*,  $\text{CN}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $260^{\circ}$ , which is also obtained by treating cyanoguanidoacetic acid with boiling, dilute acids. When heated with concentrated hydrochloric acid, cyanoguanidoacetic acid loses 2 mols. of ammonia, yielding, probably, hydantoic acid; it is converted by barium hydroxide into carbon dioxide, ammonia, and guanidoacetic acid, and by relatively short treatment with sodium hydroxide into carbon dioxide, ammonia, and glycine. *Cyanamidoacetic acid*, decomp.  $230\text{--}265^{\circ}$ , adds ammonium chloride with production of guanidoacetic acid hydrochloride, which is more readily prepared from glycine hydrochloride, sodium cyanamide, and hydrochloric acid. Small quantities of melidoacetic acid and hydantoin are also produced by the action of chloroacetic acid on sodium cyanamide.

Methylguanidine is readily prepared by the action of methylamine hydrochloride on sodium cyanamide in boiling aqueous solution; the *nitrate* is described. H. W.

**Action of Lead Monoxide on *oo'*-Dithioaniline. An Example of Simple Thiazine Formation.** H. H. HODGSON (*J. Soc. Dyers and Col.*, 1925, **41**, 99—102).—A vigorous reaction occurs when *oo'*-dithioaniline is boiled in aniline solution with litharge, and *oo'*-monothioaniline together with a smaller quantity of *op'*-monothioaniline is formed; aniline enters into the reaction product (cf. Hodgson and Dix, T., 1914, **105**, 952). When nitrobenzene, litharge, and *oo'*-dithioaniline are similarly heated at  $170\text{--}180^{\circ}$  for 6 hrs., the nitrobenzene acts as an oxidant with the production of a *base*, probably 5 : 7-di-*o*-aminophenylthiolphenthiazine. The latter yields an *acetyl* derivative, m. p. about  $102^{\circ}$  (softens at  $80^{\circ}$ ), and a *hydrochloride*, m. p.  $210\text{--}220^{\circ}$ . It may be benzoylated, and also diazotised and coupled with  $\beta$ -naphthol, thereby yielding a *red substance*, m. p. about  $230^{\circ}$ .

When the above reaction is carried out in nitrobenzene solution at  $200^{\circ}$ , further thiazine formation occurs and the product consists largely of a black tar. A. J. H.

**Preparation of Keto Derivatives of the Thiazine Series.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 402642; from *Chem. Zentr.*, 1924, ii, 2504—2505).—Keto derivatives of the thiazine series are obtained by the oxidation of 2'-amino-4-hydroxydiaryl sulphides, or by treating 2'-nitro-4-hydroxydiaryl sulphides with reducing agents and subsequent oxidation of the solution. Thus 4-hydroxy-2-nitrophenyl  $\alpha$ -naphthyl sulphide, from 2-chlorothioldinitrobenzene and  $\alpha$ -naphthol, with alkaline sodium hyposulphite and subsequent aëration of the solution, yields an oxidation *product*,  $\text{C}_{16}\text{H}_9\text{ONS}$ , lustrous red needles, m. p.  $174^{\circ}$ , dyeing brown shades on cotton (hyposulphite vat) and reddish-brown on wool. The *product* similarly obtained from 8-chloro- $\alpha$ -naphthol has m. p.  $199\text{--}200^{\circ}$ . R. B.

**Preparation of Polychrome Methylene-blue and Thiazine-red.** F. PROESCHER and A. P. KRUEGER (*J. Lab. Clin. Med.*, 1924, **10**, 153—159).—Polychrome methylene-blue is prepared by heating 100 c.c. of 1% methylene-blue solution with 20—30 mg. of sodium peroxide for 15 mins. at 100°, and subsequently neutralising with hydrochloric acid. Thiazine-red is prepared by heating 50 g. of methylene-blue in 200 c.c. of water with 5 g. of sodium peroxide at 75—80°, and drying the precipitate at 37° and then over calcium chloride.

CHEMICAL ABSTRACTS.

**Oxidation of Benzeneazophenol [*p*-Hydroxyazobenzene].** D. BIGIAMI and G. KINDT (*Gazzetta*, 1925, **55**, 83—86).—Oxidation of *p*-hydroxyazobenzene by means of peracetic acid (cf. Angeli, A., 1914, i, 882) yields, besides the two isomeric *p*-hydroxyazoxybenzenes, a small proportion of an orange-yellow compound,  $(C_{12}H_9O_2N_2)_2$  (?), m. p. 240° [acetyl derivative,  $(C_{14}H_{11}O_3N_2)_2$ , m. p. 140—150°; ethyl derivative  $(C_{14}H_{13}O_2N_2)_2$ , m. p. 218—222°], which is obtainable also from  $\alpha$ -*p*-hydroxyazoxybenzene, but not from the  $\beta$ -isomeride, by oxidation with various reagents. When reduced by means of stannous chloride and hydrochloric acid, it gives aniline and a readily oxidisable base,  $(C_6H_6ON)_2$ , which rapidly changes from colourless to violet-grey in the air and forms a benzoyl derivative, m. p. 250°. Reduction of the acetyl derivative, m. p. 140—150° (see above), in ethereal solution with aluminium amalgam yields a brick-red compound, m. p. 230° (decomp.), not identical with 5 : 5'-bisbenzeneazo-2 : 2'-diphenol (cf. Robertson and Brady, T., 1913, **103**, 1479).

T. H. P.

**Formation of Azoanilinesulphonic Acids.** W. LEWCOCK (*J. Soc. Chem. Ind.*, 1925, **44**, 152—155T).—4-Nitroaniline-3-sulphonic acid gave on treatment with sodium hypochlorite (5% available chlorine) *pp'*-dinitroazobenzene-*mm'*-disulphonic acid, which was reduced to *pp'*-diaminoazobenzene-*mm'*-disulphonic acid (*p*-azoanilinedisulphonic acid) by ammonium hydrosulphide (yield 50%) or by careful treatment with ferrous hydroxide (yield 80—90%). This disulphonic acid and the monosulphonic acid are also obtained by careful sulphonation of *pp'*-diaminoazobenzene. 2-Nitroaniline-4-sulphonic acid, 3-nitroaniline-4-sulphonic acid, 3-nitroaniline-6-sulphonic acid, and 4-nitroaniline-2-sulphonic acid were treated with sodium hypochlorite, but the corresponding diaminoazobenzenedisulphonic acids could not be isolated. When the five nitroanilinesulphonic acids were submitted to electrolytic reduction, only the 2-nitro-4-sulphonic acid gave the corresponding *oo'*-diaminoazobenzene-*mm'*-disulphonic acid in appreciable amount. *pp'*-Diaminoazobenzene and its monosulphonic acid gave trisazo dyes on coupling with phenol, whilst the disulphonic acid gave disazo dyes and trisazo dyes only with difficulty.

F. B.

**Some Benzeneazophenylpyrroles.** G. PLANCHER and E. GHIGI (*Gazzetta*, 1925, **55**, 49—51).—The compound described by Fischer and Hepp (A., 1886, 1042) as benzeneazo-1-phenylpyrrole, m. p. 117°, is actually 2-benzeneazo-5-phenylpyrrole, m. p. 116°

[Khotinsky and Soloweitschik (A., 1909, i, 616) gave m. p. 112°]. Hence it is probable that the compound used by the former authors in their preparation and obtained by the action of bromobenzene on the potassium derivative of pyrrole is mainly 2-phenylpyrrole. *Benzeneazo-1-phenylpyrrole*,  $C_{16}H_{13}N_3$ , forms orange-yellow crystals, m. p. 49—50°; *p-anisylideneazo-1-phenylpyrrole*,  $C_{17}H_{15}ON_3$ , slender, wood-yellow needles, m. p. 101°, and *p-anisylideneazo-2-phenylpyrrole*, green laminæ, m. p. 141°.

T. H. P.

**Monoazo Dyes.** FARBENFABRIKEN VORM. F. BAYER & CO., and R. STÜSSER (D.R.-P. 402869; from *Chem. Zentr.*, 1924, ii, 2502).—Diazotised nitroanilines or their derivatives are coupled with 4-chloro-5-nitro-*o*-acetoacetanilide, with or without the presence of substrate or on the fibre. 4-*Chloro-5-nitro-*o*-acetoacetanilide*, m. p. 126—127° (from 4-chloro-5-nitro-*o*-anisidine and ethyl acetoacetate), with diazotised *o*-nitroaniline gives a yellow dye. Similar dyes are obtained from 4-chloro- or 4-methyl-*o*-nitroaniline and 4-nitro-*o*-anisidine.

R. B.

**Monoazo Dyes.** FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Fr. Pat. 573603; from *Chem. Zentr.*, 1924, ii, 2502—2503).—Diazotised *m*-aminobenzaldehyde or its substitution derivatives, or compounds which yield *m*-aminobenzaldehyde, are coupled with pyrazolones or *N*-alkyl or aryl derivatives of 7-amino-1-naphthol-3-sulphonic acid, or acylaminonaphtholsulphonic acid, or  $\beta$ -naphthol-6 : 8-disulphonic acid or  $\alpha$ -naphthol-4 : 7-disulphonic and trisulphonic acids, yielding dyes which produce fast shades on wool. The dyes from *m*-aminobenzaldehyde and 7-anilino-1-naphthol-3-sulphonic acid, reddish-brown; from 8-acetamido-1-naphthol-3 : 6-disulphonic acid, bluish-red; from 6-acetamido-1-naphthol-3-sulphonic acid, reddish-yellow; from 8-acetamido-1-naphthol-3 : 5-disulphonic acid, red; from 6-*p*-aminobenzamido-1-naphthol-3-sulphonic acid, reddish-yellow; from  $\beta$ -naphthol-6 : 8-disulphonic acid, orange-yellow; from  $\alpha$ -naphthol-4 : 7-disulphonic acid, reddish-yellow; and from  $\beta$ -naphthol-3 : 6 : 8-trisulphonic acid, reddish-yellow, are described. If components such as *o*-hydroxycarboxylic acids or 1 : 5-dihydroxynaphthalene are used, the resulting dyes have mordant properties and can be chromed. Thus *m*-aminobenzaldehyde and *m*-hydroxytoluic acid, or salicylic acid or 1-*o*-hydroxy-*m*-carboxyphenyl-3-methyl-5-pyrazolone-*m'*-sulphonic acid yield dyes giving yellow shades on wool after chroming, whilst with resorcylic acid orange, and with 3-hydroxy- $\beta$ -naphthoic acid, red shades are produced. The shades are fast to light, milling, and potting. The *m*-aminobenzaldehyde can be replaced by 6-chloro-*m*-aminobenzaldehyde or benzaldehyde-*m*-sulphonic acid.

R. B.

**Azo Dyes.** CHEMISCHE FABRIK GREISHEIM-ELEKTRON and A. ZITSCHER (D.R.-P. 402868; from *Chem. Zentr.*, 1924, ii, 2503).—Diazo compounds are coupled with bis(3-hydroxy- $\beta$ -naphthoyl)-4 : 4'-diamino-3 : 3'-dialkyloxydiaryls alone or on a substrate, giving very fast brownish-red and brown dyes. *Bis*-3-

*hydroxy-β-naphthoyldianisidine*, pale yellow, has m. p. 348° (decomp.) and *bis-3-hydroxy-β-naphthoyldiphenetidine*, m. p. 346—348°. R. B.

**Preparation of Dyes Insoluble in Water.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 396519; from *Chem. Zentr.*, 1924, ii, 2791).—Blue pigment dyes, stable towards sodium peroxide bleach are obtained by coupling diazo compounds with anilides of 7-halogenated-3-hydroxy-β-naphthoic acids. These acids are obtained by adapting Franzen and Stäuble's method (A., 1922, i, 450) for 6-bromo-β-naphthol. *7-Bromo-3-hydroxy-β-naphthoic acid*, yellow plates, has m. p. 260—261°. The *anilide* has m. p. 273°, the *o-aniside*, m. p. 185—186°; the *p-aniside*, m. p. 290—292°; the *5-chloro-o-toluidide*, m. p. 257—258°; the *α-naphthalide*, m. p. 237—238°, and the *β-naphthalide*, m. p. 286—288°. R. B.

**Preparation of Brilliant Congo R ("Vital-red") and the Suitability of various Samples for Blood Volume Work.** S. PALKIN and H. M. EVANS (*J. Amer. Chem. Soc.*, 1925, 47, 429—434).—Pure tolidine is diazotised and coupled, below 5°, with one equivalent of amino-*R* salt, and the resulting "half-dye" precipitated by the addition of alcohol, and added to a solution of the sodium salt of Brönner acid. The precipitated Brönner acid is filtered off and the vital-red salted out. [Cf. B., 1925, 278.]

F. G. W.

**H. Finger's Investigations on the Preparation of "Cyanur-triazide."** E. OTT (*Z. angew. Chem.*, 1925, 38, 149—150).—Priority claim (cf. Ott and Ohse, A., 1921, i, 231). W. A. S.

**Hetero-ring Formations with Thiocarbohydrazide.** P. GUHA and S. DE (*J. Indian Chem. Soc.*, 1925, 1, 141—149).—A continuation of previous work (cf. A., 1924, i, 948). Two improved methods for the preparation of dithio-*p*-urazine are described: (1) by heating thiocarbohydrazide (1 mol.) and carbon disulphide (1 mol.) with water in a sealed tube at 130—140°, or hydrazine hydrate (1 mol.) and carbon disulphide (2 mols.) with water at 140—150°, the yield being almost theoretical; (2) by heating a mixture of hydrazine hydrate (1 mol.), alcoholic potassium hydroxide (1 mol.), and carbon disulphide (2 mols.) in a sealed tube at 100°. Dithio-*p*-urazine is converted by mercuric oxide into *p*-urazine. Potassium cyanate and thiocyanate, respectively, convert thiocarbohydrazide into *thiocarbohydrazidocarbonamide*, m. p. 230°, and *thiocarbohydrazidothiocarbonamide*, m. p. 218—219°. These compounds, with concentrated hydrochloric acid, afford 4-aminothiourazole (cf. Freund and Imgart, A., 1895, i, 400) and 4-aminodithiourazole (cf. Arndt and Bielich, A., 1923, i, 611), respectively. Phenylcarbimide, however, attacks both hydrazino groups, *thiocarbohydrazidodicarbonyldiphenylamide*, m. p. 216—217°, being formed. Whilst long heating of a mixture of hydrazine hydrate and thiocarbohydrazide yields 1-amino-5-thiol-2-hydrazino-1:3:4-triazole (Stolle and Bowles, A., 1908, i, 474), a mixture of

y\*\*



the hydrochlorides of these substances heated at 170—180° yields 5-thioketo-1 : 2 : 3 : 4-tetrahydroisotetrazole,  $\text{CS} \begin{smallmatrix} \text{NH} \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{NH} \end{smallmatrix}$ , a yellow, amorphous powder, m. p. 126—127°. Thiocarbonylhydrazide reacts in its  $\psi$ -form with chloroacetic acid, giving 2-hydrazino-5-keto-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazine,  $\text{NH}_2 \cdot \text{N} : \text{C} \begin{smallmatrix} \text{NH} \cdot \text{NH} \\ | \\ \text{S} - \text{CH}_2 \end{smallmatrix} \text{CO}$ , white plates, m. p. 220° (decomp.), whilst with glyoxal it forms a heptatetrazine compound,  $\text{SC} \begin{smallmatrix} \text{NH} \cdot \text{N} : \text{CH} \\ | \\ \text{NH} \cdot \text{N} : \text{CH} \end{smallmatrix}$ , m. p. 220° (decomp.) (benzylidene derivative, m. p. 149—150°).

J. W. B.

[Derivative of] **Phosphorus Chloronitride.** H. ROSSET (*Compt. rend.*, 1925, **180**, 750—751).—Diphenyl phosphorus nitride, prisms, m. p. 232°, is obtained by the interaction of magnesium phenyl bromide and phosphorus chloronitride ( $\text{PNCl}_2$ ) in toluene solution. Cryoscopic measurements indicate that it exists as the trimeride  $(\text{PNPh}_2)_3$ ; formula I or II is proposed.



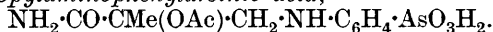
J. S. C.

### Action of Alkyl Chloroformates on Aminoarylsarsinic Acids.

C. S. HAMILTON and C. SLY (*J. Amer. Chem. Soc.*, 1925, **47**, 435—439).—The products listed below were obtained by adding the respective alkyl chloroformates, slowly, in slight excess, with stirring, to solutions of the appropriate aminoarylsarsinic acids in excess of *N*-sodium carbonate solution, the products being precipitated by rendering the reaction mixtures acid to Congo-red by means of concentrated hydrochloric acid. 4-Carbomethoxy-amino-, m. p. above 250°; 3-carbomethoxyamino-, m. p. 231° (decomp.); 3-carbomethoxyamino-4-methyl-, m. p. 191—193°; and 3-carbomethoxyamino-4-carbomethoxyhydroxy-phenylarsinic acid, m. p. 172—174°; 3 : 4-dicarbomethoxydiaminophenylarsinic acid, m. p. above 250°; 4-carbomethoxyamino-, m. p. above 250°; 3-carbomethoxyamino-, m. p. 180°; 3-carbomethoxyamino-4-methyl-, m. p. 181°; and 3-carbomethoxyamino-4-carbomethoxyhydroxy-phenylarsinic acid, m. p. 165°; 3 : 4-dicarbomethoxydiaminophenylarsinic acid, m. p. 187°; 4-carbo-*n*-propoxyamino-, m. p. above 250°; 3-carbo-*n*-propoxyamino-, m. p. 117°; 3-carbo-*n*-propoxyamino-4-methyl-, m. p. 150—151°; and 3-carbo-*n*-propoxyamino-4-carbo-*n*-propoxyhydroxy-phenylarsinic acid, m. p. 133—134°; 3 : 4-dicarbo-*n*-propoxydiaminophenylarsinic acid, m. p. 165—166°; 4-carboisopropoxyamino-, m. p. above 250°; 3-carboisopropoxyamino-, m. p. 144—145°; 3-carboisopropoxyamino-4-methyl-, m. p. 179°; and 3-carboisopropoxyamino-4-carboisopropoxyhydroxy-phenylarsinic acid, m. p. 154—155°; 3 : 4-dicarboisopropoxydiaminophenylarsinic acid, m. p. 177°; 4-carbo-*n*-butoxyamino-, m. p. above 250°; 3-carbo-*n*-butoxyamino-, m. p. 83—84°; 3-carbo-*n*-butoxyamino-4-methyl-, m. p. 143—144°; and 3-carbo-*n*-butoxyamino-4-carbo-*n*-butoxyhydroxy-phenylarsinic acid, m. p. 143°; 3 : 4-dicarbo-*n*-butoxydiamino-

*phenylarsinic acid*, m. p. 197—198°; 4-carboisobutoxyamino-, m. p. above 250°; 3-carboisobutoxyamino-, m. p. 142—143°; 4-methyl-3-carboisobutoxyamino-, m. p. 162°; and 3-carboisobutoxyamino-4-carboisobutoxyhydroxy-phenylarsinic acid, m. p. 142—143°; and 3:4-dicarboisobutoxydiaminophenylarsinic acid, m. p. 172°, are described.  
F. G. W.

**Preparation of *p*-β-Carbamido-β-acetoxy-*n*-propylamino-phenylarsinic Acid.** LES ÉTABLISSEMENTS POULENC FRÈRES (Fr. Pat. 543112; from *Chem. Zentr.*, 1924, ii, 1632).—β-Chloro-α-hydroxy-α-methylpropionic acid, when successively treated with acetyl chloride and thionyl chloride, affords β-chloro-α-acetoxy-α-methylpropionyl chloride, b. p. 95°/12 mm. The latter is converted by ammonia into β-chloro-α-acetoxy-α-methylpropionamide, m. p. 117°, which yields by interaction with sodium *p*-amino-phenylarsinate and subsequent acidification *p*-β-carbamido-β-acetoxy-*n*-propylaminophenylarsinic acid.

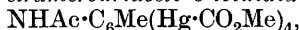


G. W. R.

**Mercuri-organic Compounds of 1-Phenylpyrrole.** G. PLANCHER and G. ROSSI (*Gazzetta*, 1925, 55, 61—63).—When treated with mercuric chloride in alcoholic solution, almost all pyrrole derivatives yield compounds having the properties of double salts, the mercury being, in part at least, readily eliminable (cf. Köttnitz, *J. pr. Chem.*, 1872, 6, 136). The action of mercuric acetate on 1-phenylpyrrole in alcoholic solution yields, according to the conditions, either (1) *dimercuri-1-phenylpyrrole acetate*,  $(\text{CH}_3 \cdot \text{CO}_2\text{Hg})_2\text{C}_4\text{H}_2\text{NPh}$ , m. p. 114°, or (2) *tetramercuri-1-phenylpyrrole acetate*,  $(\text{CH}_3 \cdot \text{CO}_2\text{Hg})_4\text{C}_4\text{NPh}$ , m. p. 229—230°. When treated with bromine, each of these compounds yields *dibromo-1-phenylpyrrole*,  $\text{C}_4\text{H}_2\text{NBr}_2\text{Ph}$ , m. p. 148°.

T. H. P.

**Colloidal Mercuri-organic Compounds.** G. ROSSI and C. BOCCHI (*Gazzetta*, 1925, 55, 93—96).—Like tri-, tetra-, and penta-mercuriacetanilide acetates (A., 1912, i, 931; 1914, i, 610; 1915, ii, 153; 1922, i, 605), mercuriaceto-*o*-toluidide acetates containing more than two mercury atoms in the nucleus are able to form colloidal aqueous solutions, the presence of acetic acid as stabilising electrolyte being necessary; dimercuriaceto-*o*-toluidide acetate (cf. Schrauth and Schoeller, A., 1912, i, 930) is apparently devoid of this property. *Tetramercuriaceto-*o*-toluidide acetate*,



forms an amorphous, gelatinous mass, giving a colourless powder. *Trimercuriaceto-*o*-toluidide acetate*,  $\text{NHAc} \cdot \text{C}_6\text{HMe}(\text{Hg} \cdot \text{CO}_2\text{Me})_3$  [Me: NHAc:  $(\text{Hg} \cdot \text{CO}_2\text{Me})_3$  = probably 1:2:3:5:6], forms a colourless, crystalline mass.

T. H. P.

**Green Colouring Matter, Related to Chlorophyll, from *Flores Primulae*.** A. VON LINGELSHEIM (*Arch. Pharm.*, 1925, 263, 121—122).—The yellow flowers of *Primula officinalis* and certain other *Primulaceae* (and yellow *Loteae*) become green on drying. The green substance may be completely extracted by warming the

flowers with water, and in solution the substance shows marked resemblance in many physical properties to chlorophyll, from which, however, it differs in its solubility in water and insolubility in alcohol or benzene. The development of the green substance is believed to be due to enzyme action, and light may not be an agent in its production. B. F.

**Evidence of a New Amino-acid in Proteins.** R. A. GORTNER and W. F. HOFFMAN (*J. Amer. Chem. Soc.*, 1925, 47, 580—584).—The amino-acids from 50 g. of teozein, a prolamine from *Euchlaena Mexicana*, Schrad., were precipitated with phosphotungstic acid by the method of Van Slyke (cf. A., 1911, ii, 944). The phosphotungstates were filtered off after keeping the mixture at 10° for 48 hrs., and no further precipitate formed in the filtrate during the next 72 hrs. The liquor was then partly frozen at -15° and re-melted at 0° several times. A syrup, which gradually crystallised, was precipitated and decomposed with barium hydroxide. After freeing the solution from inorganic reagents, evaporating to dryness, and crystallising from dilute alcohol, 1.4 g. of an amino-acid,  $C_4H_{11}O_3N$ , which still contained barium, was obtained. All the nitrogen of this acid is amino nitrogen. It showed slight levorotation in aqueous solution. The phenylcarbimide derivative,  $C_{11}H_{14}O_4N_2$ , m. p. 140°, is described. F. G. W.

**Evolution of Knowledge of the Chemical Structure of Protein Compounds.** A. BLANCHETIÈRE (*Bull. Soc. Chim. biol.*, 1925, 7, 218—330).—A lecture delivered before the Société de Chimie biologique on Nov. 18, 1924.

**Proteins. VII. Preparation of the Protein "Sericin" from Silk.** E. M. SHELTON and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1925, 47, 412—418).—Silk is heated with water in an autoclave under a pressure of 10 lb./in.<sup>2</sup>, and sericin is separated from the aqueous extract by precipitation with alcohol or ammonium sulphate. Only a portion of the product is soluble in water. [Cf. B., 1925, 279.] F. G. W.

**Solubility of Proteins.** S. P. L. SÖRENSEN (*J. Amer. Chem. Soc.*, 1925, 47, 457—469).—In the precipitation of egg-albumin from aqueous solution by adding ammonium sulphate, the concentration of the egg-albumin remaining in the mother-liquor is independent of the original concentration of the protein (cf. A., 1913, i, 1004) provided that the concentration of the ammonium sulphate is the same at the end of the precipitation as at the beginning, indicating that protein solutions follow the phase rule. This principle affords a criterion of purity of a protein, which should be soluble in the mother-liquor from which it is salted out to the same extent whatever its original concentration, provided always that salt and hydrogen-ion concentrations are kept constant. The data obtained by testing in this way a sample of pseudoglobulin from horse-serum, purified by repeated fractionation and dialysis, indicated that the sample was still not homogeneous, but associated with euglobin. The solubility relationships of these two proteins

can be explained by assuming the existence of a loose, dissociable compound between the two.

F. G. W.

**"Irregular Series" in the Precipitation of Albumin.**

A. W. THOMAS and E. R. NORRIS (*J. Amer. Chem. Soc.*, 1925, 47, 501—513).—The phenomena of the "first zone of precipitation" and the "tolerance zone" of the "irregular series" in the precipitation of proteins by heavy metal salt solutions are explained as follows: when a dilute solution of such a salt is added to a solution of a protein on the alkaline side of its isoelectric point, combination between the metal cation and the protein anion takes place, and a precipitate is formed if the resulting complex is insoluble. The heavy metal salt being hydrolysed meanwhile, further addition of it increases the acidity of the solution. As soon as this acidity passes the isoelectric point of the protein, the precipitate redissolves unless the anion of the added salt forms an insoluble complex with the protein cation.

In the precipitation of aqueous albumin solutions by zinc and thorium chlorides, a definite minimum concentration of heavy metal ion, depending on the solubility product of the precipitated complex, must be present before precipitation starts. The precipitate is soluble in solutions of  $p_H < 4.8$ . In solutions maintained, by means of sodium acetate-acetic acid buffers, at a  $p_H$  (7.2) greater than that of the isoelectric point, a smaller concentration of zinc chloride (0.003*M*) is necessary to cause precipitation, on account of the increased concentration of the protein anion, than that required (0.027*M*) at the isoelectric point, where the protein is least dissociated, whilst buffered solutions always require a higher concentration of zinc chloride than is necessary in unbuffered solutions (0.0008*M*) on account of the repression of the ionisation of the added zinc salt by the buffer salt.

The "second zone" of precipitation, in which the precipitate remains insoluble on dilution with water, even after the shortest time of contact with the heavy metal ion, is shown to be due to the denaturing of the protein by the heavy metal ion, and its rate increases with the temperature, hydrogen-ion concentration, and metal-ion concentration of the solution.

F. G. W.

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### Biochemistry.

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**Anaërobic Production of Carbon Dioxide by Muscle-cells in the Presence of Hydrogen Acceptors.** W. LIPSCHITZ and P. MEYER (*Pflüger's Archiv*, 205, 366—376; from *Chem. Zentr.*, 1924, ii, 2770).—Oxidation of the combustible material of muscle by hydrogen acceptors such as methylene-blue and nitroanthraquinone in the absence of oxygen results in formation of carbon dioxide. The dehydrogenation quotient, in contrast to earlier work with

dinitrobenzene as acceptor, is about 1, and is unchanged by poisoning the cells with hydrogen cyanide. The velocity of reduction is also only slightly affected. The absolute velocity of the process and the amount of carbon dioxide formed are approximately the same with methylene-blue and nitroanthraquinone, but the velocity is smaller than that of normal respiration. R. B.

**Oxygen-combining Capacity of Hæmoglobin Determined by the Ferricyanide Method.** S. MASUDA (*Biochem. Z.*, 1925, **156**, 21—34).—Using ammonia as hæmolytic agent in the Barcroft differential apparatus, the results obtained are too low, since part of the blood-oxygen combines with the ammonia. An error in the opposite sense is ascribed to the fact that the alkalinity of the blood mixture is often insufficient to prevent some carbon dioxide escaping with the oxygen. The accuracy of the method as a whole is called in question. J. P.

**Determination of Oxygen and Carbon Dioxide in Mixed Venous Human Blood.** C. S. BURWELL and G. C. ROBINSON (*J. Clin. Investigation*, 1924, **1**, 47—63).—The blood is equilibrated with a gaseous mixture in a tonometer, filled directly by a definite respiratory procedure. CHEMICAL ABSTRACTS.

**Gases in Fresh, Putrefied, and Frozen Blood.** C. KOHN-ABREST (*Compt. rend.*, 1924, **179**, 1171—1174).—Using the apparatus previously described (this vol., i, 451), the author has examined specimens of pig's blood of different degrees of freshness. Putrefaction appears to be correlated with the percentage of hydrogen sulphide produced, but no proportionality with the carbon dioxide was observed. Freezing inhibits putrefaction. H. J. E.

**Blood-corpuscles and the Alkali Reserve.** A. DESGREZ, H. BIERRY, and L. LESCŒUR (*Compt. rend.*, 1925, **180**, 705—711).—Carbon dioxide is removed completely from the blood by a current of air at 15°; it is removed quantitatively in this way from serum and plasma only after addition of acid. The conclusion that the corpuscles generate acid which liberates the carbon dioxide was confirmed by experiment, and it is shown that glycolysis is insufficient to account for the phenomenon. S. I. L.

**Chemical Parent of Blood Pigment and Chlorophyll.** L. MARCHLEWSKI (*Bull. Soc. chim.*, 1925, [iv], **37**, 340).—The author criticises the views of Maquenne (*ibid.*, 1924, **35**, 649) on the parent substance of blood pigment and chlorophyll. Existing knowledge does not allow of a decision whether coproporphyrin or another porphyrin represents the point of divergence in the syntheses of chlorophyll and blood pigment, but the author regards phylloporphyrin- $\alpha$  as the molecular skeleton which is as readily synthesised by the vegetable organism as by the animal (cf. Fischer and Hilger, A., 1924, i, 1130). R. B.

**Effect of High Fat Diets on Content of Uric Acid in Blood.** V. J. HARDING, K. D. ALLIN, B. A. EAGLES, and H. B. VAN WYCK (*J. Biol. Chem.*, 1925, **63**, 37—53).—Administration of a diet of

which the fat content is sufficiently high to produce a ketosis brings about an increase in the concentration of uric acid in the blood. This increase can be partly accounted for by decreased excretion consequent on decreased blood volume; the highest concentrations of uric acid were observed in the blood of those individuals who excreted the largest amounts of acetone.

C. R. H.

**Uric Acid Determinations in Blood.** F. M. R. BULMER, B. A. EAGLES, and G. HUNTER (*J. Biol. Chem.*, 1925, **63**, 17—35).—The direct application of the colorimetric reagent of Benedict (A., 1922, ii, 405) to the filtrate obtained after precipitation of the proteins of blood with tungstic acid gave higher results for uric acid than were obtained after preliminary precipitation of the uric acid by silver lactate in the case of various animals, and, usually, in the case of man. The interfering substance, which thus renders inaccurate the direct determination of uric acid in the blood filtrate, was found to be contained for the most part in the red corpuscles; it was proved not to be "combined uric acid."

C. R. H.

**Determination of Uric Acid by the Hopkins-Folin Method.** R. C. GARRY (*Biochem. J.*, 1924, **18**, 913—918).—Numerous precautions and conditions for obtaining consistent and accurate results are given.

S. S. Z.

**Modification of the Blood and Secretions by Ultra-filtration.** L. BLUM and L. DELAVILLE (*Compt. rend.*, 1925, **180**, 764—765).—The behaviour of the blood on ultra-filtration may be modified by physiological or pathological processes; sodium normally passing the ultra-filter may be partly retained, and calcium, normally retained, may pass through partly or completely, by modification of the colloids to which they are linked. The organic constituents of the body fluids such as uric acid and cholesterol suffer similar changes.

S. I. L.

**Modification of Bloor's Method for the Determination of Blood Phosphates.** K. L. MCCLUSKEY (*J. Lab. Clin. Med.*, 1924, **10**, 143—149).—The diluted blood is digested with nitric and sulphuric acids, the liquid diluted and neutralised to phenolphthalein, slightly acidified with sulphuric acid, and solutions of sodium sulphite and quinol are added. After dilution and addition of the ammonium molybdate reagent, the mixture is kept in a stoppered tube for 2—3 hours before colorimetric comparison with standards in a Kober colorimeter. The sum of the lipid and acid-soluble phosphoric acid of blood previously treated with either trichloroacetic acid or ammonium sulphate is practically equal to the total.

CHEMICAL ABSTRACTS.

**Relationship of the Blood-sugar to Glycogen.** H. PRINGSHEIM (*Biochem. Z.*, 1925, **156**, 109—117).—A theoretical review of the biochemical reactions of starch, glycogen, maltose, and the aldo- and keto-hexoses in which it is assumed that glycogen and amylopectin (from starch) are identical, and that the blood-sugar

is the so-called, supposedly reactive, " $\gamma$ " form to which a hexylene-oxidic structure is assigned. Such hexylene-oxidic glucose residues are also assumed to be present in glycogen and amylopectin. It is suggested that the difference in biochemical reactivity between galactose on the one hand and dextrose, mannose, and levulose on the other may depend on the amylenic-oxidic structure normally present in the former, and presumed to be absent from the latter sugars.

J. P.

**Adsorption of Cresol-red by Serum in Spectrophotometric Determination of  $p_H$ .** E. F. HIRSCH (*J. Biol. Chem.*, 1925, **63**, 55—59).—An attempt to apply the spectrophotometric method of Brode (A., 1924, ii, 346) and of Holmes (A., 1924, ii, 346) to the determination of the  $p_H$  of blood-serum or plasma showed that the amount of indicator necessary to give correct values was not necessarily the same as that required in a buffer solution, and, moreover, varied with the species; the variations were probably due to adsorption of indicator by some constituent of the serum.

C. R. H.

**New Chemical Anti-coagulants.** A. LUMIÈRE (*Compt. rend.*, 1925, **180**, 866—868).—Sodium mucate is as active an anti-coagulant as sodium citrate and is not toxic. The sodium salts of aconitic, ethanetetracarboxylic, sulphosalicylic, and phenoxypropanediol-carboxylic acids are less active anti-coagulating agents, but are also only one-tenth as toxic to guinea-pigs as is sodium citrate. Sodium  $\beta$ -naphtholdisulphonate and sodium  $\beta$ (?)-naphthylaminedisulphonate are very active as anti-coagulants, but are too toxic to be used. The sodium salts of phthalic, homophthalic, choleic, and malonic acids retard without preventing coagulation, whilst the sodium salts of succinic, camphoric, diphenylphosphoric, dicarballylic, quinic, malic, and uvitic acids have no anti-coagulating action.

No connexion can be traced between the anti-coagulating power of the sodium salts and the solubility of the corresponding calcium salts; it is suggested that the degree of ionisation of the calcium salt may be the deciding factor in preventing coagulation.

L. F. H.

**Representation of the Chemical Composition of Living Matter.** W. VERNADSKY (*Compt. rend.*, 1924, **179**, 1215—1217).—A general discussion of the methods of representing analytical results. The author points out that analyses of living matter should be represented, not as percentages by weight, but as atomic percentages, as is the case with geo-chemical analyses. Figures obtained by Volkmann (*Ber. Sachs. Ges. Wiss. Math. Phys.*, 1874, **26**, 202) and by Bruchard (*Compt. rend.*, 1897, **124**, 844) for an adult man, and by Ramdohr (*Arch. Pharm.*, 1856, **136**, 20) for the seed of *Lolium emulentum* are quoted and represented from the atomic point of view in support of the argument. H. J. E.

**Increased Imbibition by Colloids through Chemical Stimulants.** M. POPOV and K. SEISOV (*Biochem. Z.*, 1925, **156**, 97—108).—The action of various organic compounds and inorganic



salts in increasing the imbibition of water by gelatin is tabulated, and the results are correlated with the effects of similar substances in "regenerating" living plant and animal cells. J. P.

**Fractionation of Egg-yolk by Common Solvents.** M. A. RAKUSIN and G. PEKARSKAYA (*Z. Unters. Nahr. Genussm.*, 1925, 49, 39—41).—Successive extraction of dried egg-yolk with alcohol, water, acetic acid, and sodium hydroxide, showed the last extract to contain a protein unextracted by the former solvents. A. G. P.

**Formation of Ammonia in the Nervous System.** H. WINTERSTEIN and E. HIRSCHBERG (*Biochem. Z.*, 1925, 156, 138—149).—Isolated peripheral nerves of the frog give off small amounts of ammonia, which are markedly increased by electrical stimulation. The isolated spinal cord shows no evolution of ammonia in a gaseous atmosphere, but there is a slight loss of ammonia when it is kept in salt solution. Narcosis with 1% urethane inhibits the phenomenon, but after removal of the narcotic the ammonia produced is greater than the normal resting value. J. P.

**Reaction of Dry Proteins Applicable to Histochemistry.** M. ROMIEU (*Compt. rend.*, 1925, 180, 875—877).—On treatment with syrupy phosphoric acid and warming at 52° dried albumin, fresh white of egg, fibrin, casein, and keratin give a garnet-red coloration, changing to violet. Mucin, nuclein, and hæmoglobin give a very similar reaction. Gelatin does not give the reaction nor does tyrosine nor phenylalanine. Tryptophan gives a very intense reaction, and it is suggested that the presence in proteins of amino-acids of that type may cause the reaction. The mildness of the reagent makes it very suitable for histological work.

L. F. H.

**Colorimetric Determination of Tryptophan and its Separation from Indole and Skatole.** I. KRAUS.—(See ii, 448.)

**Calcium Chemistry of Teeth.** R. E. LIESEGANG (*Deut. zahnärzt. Woch.*, 1924, 27, 103—104; from *Chem. Zentr.*, 1924, ii, 1707).—The carbon dioxide and other acids produced by intracellular respiration prevent the deposition of calcium carbonate and calcium phosphate in the tissues. The connective-tissues in which the calcium salts of bone and teeth are deposited are relatively poor in cells. It is not necessary to postulate specific calcium fixers. The transparent zone in dental caries is the result of local hypermineralisation.

G. W. R.

**Biochemistry of Muscle Contraction.** W. E. GARNER (*Nature*, 1925, 115, 532—533).—If the anisotropy of alternate striæ of muscle fibre is due to the presence of oriented molecules of long chains of salts or esters of amino-acids, the contraction wave, which is associated with increase of hydrogen-ion concentration due to the production of lactic acid from glycogen, may cause liberation

of the amino-acids, with consequent alteration of the inclination of successive molecules to one another, shortening of the length of the zig-zag composed of a finite number of molecules, and the production of tension along the length of the fibre. A. A. E.

**Influence of the Intensity of Lactation on the Blood-sugar Concentration of Cows.** E. M. P. WIDMARK and O. CARLENS (*Biochem. Z.*, 1925, **156**, 454—459).—Non-lactating cows and heifers on normal diet have a blood-sugar concentration approximating to that of other normal animals, viz., 0.085%. In lactating cows and goats, the blood-sugar concentration is lower, the lowest value obtained being 0.040%, which in other animals would lead to hypoglycæmic symptoms. The blood-sugar concentration varies inversely as the intensity of lactation. A rich diet causes an increase in the concentration of blood-sugar of lactating cows. P. W. C.

**Action of Hydrogen Ions on the Clotting of Milk.** N. L. COSMOVICI (*Bull. Soc. Chim. biol.*, 1925, **7**, 124—152).—There is a definite  $p_H$  (5.36) at which the clotting of milk takes place, whether this occurs spontaneously or is brought about by direct addition of acid. The hydrogen-ion concentration also plays a direct part in clotting by rennin, since the minimum quantity of the enzyme necessary to cause clotting depends on the  $p_H$  value; and this is the case even with decalcified milk. When the calcium in milk is precipitated by means of an oxalate, the  $p_H$  value of the milk is increased, and, if the initial reaction is restored by addition of calcium chloride, the minimum quantity of rennet necessary to cause clotting is less than if the reaction is restored by addition of acid. When acid is added after the initial reaction has been re-established by calcium chloride, the minimum amount of enzyme required is further reduced. There is thus an additive action of calcium and hydrogen ions. Further, with a constant quantity of rennin, the smaller the amount of calcium chloride added to decalcified milk, the greater is the amount of acid required to bring about clotting, although the relationship is not a simple one. Hydrogen ions appear to play a double rôle, on the one hand acting directly as a precipitant of casein and reinforcing the action of the enzyme, and on the other, indirectly altering the equilibrium between the casein and the calcium ions in a direction unfavourable to precipitation. C. T. G.

**Rôle of Acidity in the Shrinkage of the Clot [in Milk].** N. L. COSMOVICI (*Bull. Soc. Chim. biol.*, 1925, **7**, 153—154).—By addition of different amounts and combinations of calcium chloride and acid to decalcified milk, it is shown that calcium ions determine the consistency of the clot and hydrogen ions the shrinkage and expulsion of whey. C. T. G.

**Electrical Conductivity of Disperse Systems. I. Cream.** H. FRICKE and S. MORSE (*Physical Rev.*, 1925, [ii], **25**, 361—367).

**Determination of Sugar in Urines containing Santonin.** G. PÉGURIER (*Ann. Chim. Analyt.*, 1925, [ii], 7, 66—67).—In using the Fehling reaction with urines of diabetics treated with santonin it is necessary to destroy the santonin acid produced by the sodium hydroxide, or no reduction of the sugar will take place. To do this, the hot liquid may be neutralised with glacial acetic acid added drop by drop until the appearance of the blue colour of the Fehling solution, after which reduction will proceed normally. D. G. H.

**Comparative Urea Determinations on Human and Animal Urines.** K. KIKUCHI (*Biochem. Z.*, 1925, 156, 35—39).—The xanthhydrol gravimetric, Folin, and urease methods give accurate and concordant results, the Henriques and Gamelthoft method gives low results, whilst the hypobromite method is rejected altogether. J. P.

**Micro-determination of Urea and Ammonium Salts.** J. GOLSE (*Bull. Soc. Chim. biol.*, 1925, 7, 167—172).—The method described by Pohorecka-Lelesz (this vol., ii, 76) and its application to biological fluids has already been referred to (cf. A., 1919, ii, 203). C. T. G.

**Urinary Elimination of isoQuinoline Alkaloids, in Particular of Hydrastine.** E. BAYLE and R. FABRE (*Compt. rend.*, 1925, 180, 605—607).—By methods previously described (A., 1924, i, 980), the amounts of hydrastine excreted in the urine after a dose of the alkaloid have been determined. The alkaloid appears to the greatest extent on the first day and cannot be detected after the fourth. Over the whole of this period some 3% of the total taken is excreted in the urine. G. M. B.

**Elimination of Amylase by the Kidneys.** AMBARD and VAUCHER (*Scalpel*, 1923, 76, 837—841; from *Chem. Zentr.*, 1924, ii, 2344; cf. Ambard and Wolf, *Compt. rend. Soc. Biol.*, 1924, 90, 786).—The elimination of amylase is neither by diffusion (ethyl alcohol, chloroform, acetone) nor by secretion (carbamide), but is of a particular type depending on the colloidal nature of the enzyme. The total amount of enzyme eliminated is unaffected even when the volume of urine excreted is appreciably increased; it is only slightly affected by variations in the amount present in the blood.

G. W. R.

**Plasma Lipoids in Experimental Anæmia.** W. R. BLOOR (*J. Biol. Chem.*, 1925, 63, 1—15).—In the blood of dogs suffering from anæmia as the result of profuse bleeding, the fatty acids were increased in total amount and showed a higher degree of unsaturation than in the normal animal, the differences being most marked in the lecithin and neutral fat fractions; there was also a smaller increase in the amount of unsaponifiable matter in the anæmic blood. C. R. H.

**Phosphorus, Calcium, and Alkaline Reserve of Blood Sera of Normal and Rachitic Chicks.** C. W. ACKERSON, M. J. BLISH, and F. E. MUSSEHL (*J. Biol. Chem.*, 1925, 63, 75—84).—There was found to be a definite reduction in the inorganic phos-

phorus and the calcium of the serum of rachitic chicks as compared with the normal; no change could be observed in the alkaline reserve; the onset of rickets in chicks fed on a diet lacking the anti-rachitic factor could not be prevented by the addition to the diet of an aqueous extract or the expressed juice of alfalfa (lucerne) (cf. Shipley, Kinney, and McCollum, A., 1924, i, 685). C. R. H.

**Metabolism in Avitaminosis.** G. SHINODA (*Pflüger's Archiv*, 1924, 203, 365—393; from *Chem. Zentr.*, 1924, ii, 1602).—The liver-tissue of dogs which have received a diet poor in vitamins shows a marked increase in cellular respiration, as measured by oxygen consumption, after addition of very small amounts of an extract of bran. The factor increasing respiration is thermo-stable. With a low vitamin diet the total nitrogen balance may be at first positive, then negative, and increase again before death. Lack of vitamins has the general effect of inhibiting respiration. Vitamins improve the utilisation of food. Residual nitrogen in the blood in avitaminosis is generally increased towards the end of the experimental period. In pigeons and dogs, nervous disturbances accompanied by characteristic hyperglycæmia occur. These disappear on administration of vitamin. In the occurrence of hyperglycæmia, disturbances of the central nervous system play a principal part. Sugar tolerance is depressed in avitaminosis only when starvation sets in. G. W. R.

**Cystinuria.** A. MAGNUS-LEVY (*Biochem. Z.*, 1925, 156, 150—160).—For determining cystine in urine, a modified Gaskell method is used in which the cystine precipitated by alcohol is filtered, redissolved in *N*-hydrochloric acid, and determined polarimetrically. Determinations must be made on fresh urine. The method was used to investigate a case of cystinuria, details of which are tabulated. J. P.

**Disturbances of Cystine Metabolism in Children.** G. O. E. LIGNAC (*Nederl. Tijdschr. Geneeskunde*, 1924, 68, I, 2987—2995; from *Chem. Zentr.*, 1924, ii, 1602—1603).—In two cases of children who had died from progressive atrophy, a crystalline deposit of cystine was found in the tissues. Before death, the urine contained serum-albumin, acetone, acetoacetic acid, pentoses, and lactose. It is considered that the formation of cystine did not occur *post mortem*. A possible explanation might be an inability of the liver to form taurine from cystine. G. W. R.

**Purine Metabolism in Diabetes insipidus.** E. LE BRETON and C. KAYSER (*Compt. rend.*, 1924, 179, 1218—1219).—The degree of polyuria is correlated with the quantity of purines other than uric acid which is excreted. The greater the polyuria, the smaller becomes the uric acid-hypoxanthine ratio (all purine-base nitrogen being calculated as hypoxanthine). In an extreme case, the ratio was less than unity. H. J. E.

**Detoxicating Function of the Liver. I. Coupling of Sulphuric Acid and of Glycuronic Acid in Liver Diseases.** M. HÄNDEL (*Z. ges. Exp. Med.*, 1924, 42, 172—193; from *Chem. Zentr.*, 1924, ii, 1706).—With normal and with diseased livers

administration of guaiacol resulted in increased output of ethereal sulphates, whilst administration of camphor resulted in an increased output of conjugated glycuronic acid. Some liver diseases are associated with diminution of the ability for guaiacol coupling, whilst camphor coupling generally remains normal. G. W. R.

**Neurosyphilis. II. Retention and Elimination of Silver with Special Reference to Silver Salvarsan and Silver Therapy.** C. N. MYERS and H. B. CORBITT (*Amer. J. Syphilis*, 1924, 8, 704—725).  
CHEMICAL ABSTRACTS.

**Neurosyphilis. III. Relative Arsenic Content of the Spinal Fluid, Brain, and Spinal Cord of Rabbits after Intravenous Injection of Silver Salvarsan.** L. H. CORNWALL and C. N. MYERS (*Amer. J. Syphilis*, 1924, 8, 726—733).  
CHEMICAL ABSTRACTS.

**Syphilis. XV. Excretion of Arsenic through the Kidney after Intravenous Administration of Salvarsan, Neosalvarsan, Silver Salvarsan, and Tryparsamide.** J. A. FORDYCE, I. ROSEN, and C. N. MYERS (*Amer. J. Syphilis*, 1924, 8, 619—703).  
CHEMICAL ABSTRACTS.

**Enzymes of Cerebro-spinal Fluid in Pathological Conditions.** S. DRAGANESCU and A. LISSIEVICI-DRAGANESCU (*Biochem. Z.*, 1925, 156, 460—470).—In a number of cases of different nervous diseases, the amounts of amylase, peroxydase, catalase, antitrypsin, and trypsin in cerebro-spinal fluid were determined. Amylase occurs simultaneously with leucocytes, but there is no strict parallel between the number of leucocytes and the amount of the enzyme. The appearance of peroxydase is related to the number of polynuclear cells. Catalase usually occurs along with peroxydase, but in a few cases it was present even in the absence of the latter, and must then be derived from nervous tissue. Antitrypsin is in general related to the existing quantity of protein. P. W. C.

**Quinhydrone Electrode for Clinical  $p_H$  Determinations.** R. SCHAEFFER and F. SCHMIDT (*Biochem. Z.*, 1925, 156, 63—79).—The ready applicability of the quinhydrone electrode for determining  $p_H$  in clinical investigations (*e.g.*, gastric contents, cerebro-spinal fluid, urine) is demonstrated, the results being in agreement with those obtained using the hydrogen cell and the indicator method. The use of both macro- and micro-electrodes is described. J. P.

**Synthesis and Degradation of Carbohydrates in the Organism. II.** A. GIGON and W. BRAUCH (*Helv. Chim. Acta*, 1925, 8, 97—106; cf. this vol., i, 192).—Analyses have been carried out on the blood of rabbits by the micro-combustion methods of Pregl as modified by Müller and Willenberg (*cf. A.*, 1919, ii, 297). The fluctuations in the total carbon content of the blood have been followed under various conditions, also the variations in the same when glucose is added to the food of fasting (24 hours or more after the last meal) and non-fasting (12 hours or less after the last meal) animals. The total nitrogen, the  $p_H$ , and the sugar in the blood

have also been determined under similar states of nutrition. With normal animals, the carbon content of the entire blood either immediately or some hours after eating is 9.0 to 10.5% and changes to 8.53 (minimum) to 9.32% (maximum) after 12—24 hours' fasting. The total nitrogen shows parallel variations for 2 days and then changes in the opposite direction to the carbon. The following conclusions have been drawn from the experiments. (1) The total carbon and nitrogen contents of the blood are subject to rapid and powerful fluctuations which find no expression in those of the urine. (2) A very definite line must be drawn between the fasting and non-fasting states in metabolism investigations of this kind. (3) A meal containing dextrose and the preceding fast can react for some days on the composition of the blood. (4) An intimate relation exists between the carbohydrate and protein metabolism in the blood. (5) The fluctuations of the carbon and nitrogen in the blood brought about by insulin poisoning show that the changes which take place have a deeper origin than merely in the variations of the sugar in the blood. A. C.

**Lactic Acid Metabolism in the Living Animal.** O. MEYERHOF and R. MEIER (*Pflüger's Archiv*, 1924, 204, 448—466; from *Chem. Zentr.*, 1924, ii, 1706).—The lactic acid exchange in the muscle of living frogs was compared with the consumption of oxygen under different conditions. During rest, 51 c.c. of oxygen per kg. body-weight are used, whilst 150 mg. of lactic acid are formed anaerobically. Of this, only 66.5 mg. can be oxidised by the oxygen, although the respiration of the muscle forms a little less than 50% of the total respiration. For the muscle the oxidation quotient (*i.e.*, the ratio of disappeared to oxidised lactic acid) is at least 6.4 during rest. The absolute anaerobic production of lactic acid in the muscles of the resting frog (intact or after removal of brain) is 0.037% per hour at 15°: the corresponding rate with isolated muscle is 0.010%. Administration of curare or novocaine, nerve section, or destruction of the spinal cord, result in a fall in lactic acid production, accompanying the disappearance of tonus, to a value approximately equal to that for isolated muscle (0.01—0.013%). The total respiration does not decrease, owing partly to the fact that the oxidation quotient of active muscle is greater than that of completely relaxed muscle. No explanation is forthcoming of the fact that an expected 10—15% depression of respiration does not take place. The oxidation quotient after recovery from fatigue (with accumulation of lactic acid) averages 4.5 at 15°. The quotient increases appreciably with temperature, presumably because it is the greater the more quickly lactic acid can disappear after fatigue. G. W. R.

**Function of Water-soluble Nutrients in the Metabolism of Aquatic Animals. IV. Significance of Carbamide in Modifying the Growth-promoting Effect of Dissolved Nutrients on Tadpoles.** J. KRŽENEČKÝ and J. PODHRADSKÝ (*Pflüger's Archiv*, 1924, 204, 471—476; from *Chem. Zentr.*, 1924, ii, 1706).—In experiments on tadpoles fed with formed food, carbamide added

to the solution which contained sucrose not only antagonised the effect of the latter in increasing growth, but actually resulted in an inhibition.  
G. W. R.

**Determination of Phosphoric Acid in Metabolic Investigations.** C. SCHMITT-KRAHMER (*Biochem. Z.*, 1925, 156, 40—50).—The Lorenz modification of the original Neumann method for determining phosphates in the presence of organic matter is given preference to other methods. Various crucibles suitable for filtering and drying the precipitated phosphomolybdate are described.  
J. P.

**Calcium Content of Organs of Cats treated with Calcium [Salts].** V. W. HEUBNER (*Biochem. Z.*, 1925, 156, 171—181).—Administration of calcium salts in toxic doses to cats produces increases of calcium in certain parts of the mid-brain and cerebellum, in tendons, and in arteries. The serum-calcium is increased by administration of calcium hexosephosphate, and a considerable portion of it cannot be precipitated by oxalate (cf. Jungmann and Samter, A., 1924, i, 452).  
J. P.

**Mechanism of Water Intoxication.** F. P. UNDERHILL and M. A. SALLICK (*J. Biol. Chem.*, 1925, 63, 61—69).—The administration by stomach tube of distilled water to dogs in quantities large enough to produce toxic effects causes a dilution of the blood and an increased urinary excretion of chlorides, phosphates, total acid, ammonia, and creatinine; the decrease in the chlorides of the blood is greater than can be accounted for by dilution of the blood; it is suggested that the toxic effects are due, in part at least, to depletion of the salt content of the tissues.  
C. R. H.

**Influence of Homologous Alcohols on Sugar Formation in the Liver of the Frog.** II. E. J. LESSER (*Biochem. Z.*, 1925, 156, 161—170).—The presence of ethyl, propyl, or butyl alcohol in 0.7% sodium chloride solution perfused through the isolated liver of the winter frog, increases the sugar output to 2—3 times its normal value.  
J. P.

**Pharmacological Effects on the Purine Metabolism of Men.**  
**I. Effect of Sympathico- and Vago-tropic Drugs.** K. HARPUEDER (*Z. ges. Exp. Med.*, 1924, 42, 1—14; from *Chem Zentr.*, 1924, ii, 1707).—Adrenaline increases slightly for a few hours the uric acid output of men receiving a diet low in purine, without, however, affecting the total daily output. Ergotamine depresses uric acid output appreciably, probably on account of retention of uric acid in the tissues. Atropine produces a slight depression, or, sometimes, no effect. Pilocarpine produces a slight increase. It is concluded that the sympathetic promotes uric acid excretion.  
G. W. R.

**Causes Modifying the Toxicity of Strophanthin.** L. TOCCO-TOCCO (*Arch. Farm. sper. Sci. aff.*, 1925, 39, 1—23).—In aqueous solution commercial strophanthin undergoes gradual change, with

modification of its activity. The seeds of *Strophanthus Kombé*, either fresh or as much as 12 years old, contain, in the endosperm and rind, substances capable of destroying the toxicity of a highly active strophanthin solution. Such substances, which are lacking in the embryo, are destroyed when heated at 100°. No relation exists between the toxicity of strophanthin and the reaction it gives with sulphuric acid.

T. H. P.

**Chemical and Pharmacodynamic Investigation of *Strophanthus letei*, Merrill.** A. H. WELLS and F. GARCIA (*Philippine J. Sci.*, 1925, 26, 9—20).—A saponin similar to *pseudostrophanthin* has been extracted from the bark of the roots (2.1%) and of the stems (0.9%) of *Strophanthus letei*, Merrill. The amorphous, brown powder isolated has m. p. 152° (decomp.), is readily soluble in water, giving a clear solution of low surface tension, reduces Fehling's solution, yields an acetyl and a nitro derivative, and does not give the strophanthin colour reactions. The extract slows the heart beat, increases both blood pressure and respiration, produces hæmolysis in 0.6% solution, and possesses a toxicity to the anæsthetised cat equal to one-twentieth of that of ouabain.

L. F. H.

**Germicidal Values of the Pure Constituents of Australian Essential Oils, Essential Oil Isolates, and Synthetics. II.** A. R. PENFOLD and R. GRANT (*J. Proc. Roy. Soc. N.S. Wales*, 1924, 58, 117—123; cf. A., 1924, i, 1329).—The Rideal-Walker coefficients of the above are tabulated, and range from 20 for menthol (natural and synthetic) to 1 for rhodinyl valerate.

B. F.

**Catalytic Properties of Bismuthoxyl.** A. MAUBERT, L. JALOUSTRE, P. LEMAY, and G. ANDREOLY (*Compt. rend.*, 1925, 180, 539—542; cf. Maubert and others, A., 1923, i, 723; 1924, i, 808).—Neutral sodium potassium tartrobismuthate precipitates catalase completely together with protein from liver extract. The catalase cannot be removed from the precipitate by dialysis or washing. The activity of the precipitate is retained after desiccation but is destroyed by heating at 100° for 5 mins.

J. W. B.

**Laccase. IV. Action of Sodium Chloride. Influence of the Reaction of the Medium.** P. FLEURY (*Bull. Soc. Chim. biol.*, 1925, 7, 188—194).—0.1N-Sodium chloride solution tends to inhibit the oxidation of guaiacol by laccase, the extent of inhibition depending on the reaction of the medium. In an acid medium ( $p_H$  4.5), the activity is reduced to one-tenth of the value when sodium chloride is absent, whereas in alkaline media ( $p_H$  7.6—9.0) the effect is very small. The optimum  $p_H$  is displaced in presence of 0.1N-sodium chloride from 6.7 to 7.1. The quantity of guaiacol fixed by the enzyme and the velocity of oxidation are influenced in opposite directions by the hydrogen-ion concentration; sodium chloride acts exclusively on the velocity of oxidation, the action increasing with increasing hydrogen-ion concentration.

C. T. G.



**Digestion of Carbohydrates and Proteins in Pigeons and Hens and the Penetration of Digestive Enzymes through Plant Cell Membranes.** E. MANGOLD (*Biochem. Z.*, 1925, 156, 3—14).—In the pigeon, digestion of starch (granules) is confined to the intestinal tract. In the hen, proteolytic digestion of the contents of the gluten cells of cereals and of plant cells generally takes place only in the intestine. J. P.

**Activation of Pancreatic Juice by Acidification.** M. LISBONNE (*Compt. rend.*, 1925, 180, 690—692).—The activation of pancreatic juice may be brought about by acidification to  $p_H$  4.5 to 5.5, when the maximum activity is produced in 11 hours at 45° or in several days at 0°. After neutralisation, the juice treated in this manner displays typical tryptic action. G. M. B.

**Phytochemical Reduction of  $\alpha\beta$ -Trichlorobutaldehyde to  $\alpha\beta$ -Trichlorobutanol.** L. ROSENFELD (*Biochem. Z.*, 1925, 156, 54—57).—Yeast in the presence of sucrose reduces inactive  $\alpha\beta$ -trichlorobutaldehyde to the corresponding alcohol,  $\alpha\beta$ -trichlorobutanol,  $[\alpha]_D^{18} + 2.5^\circ$  (cf. also Santomauro, this vol., i, 203; Sen, *ibid.*). J. P.

**Fermentation and Iron Salts.** P. HODEL and N. NEUENSCHWANDER (*Biochem. Z.*, 1925, 156, 118—123).—Ferric salts, more especially in concentrated solutions, inhibit the fermentation of dextrose and of pyruvic acid by yeast, whilst ferrous salts either are without action or slightly accelerate the initial stages of the fermentation. J. P.

**Peroxydases in Dried Seeds.** H. COUPIN (*Compt. rend.*, 1925, 180, 685—687).—Madelung's reagent, a solution of benzidine in dilute acetic acid, followed by hydrogen peroxide, is preferred to tincture of guaiacum as a test for vegetable peroxydases. Peroxydases are found to be present in abundance in most common dried seeds in the resting condition. G. M. B.

**Enzymic Hydrolysis of Monotropitin. Production of Primeverose.** M. BRIDEL (*Compt. rend.*, 1924, 179, 991—993; cf. A., 1924, i, 659).—Monotropitin in aqueous solution is readily hydrolysed by an enzyme present in a powder obtained from *Monotropa hypopitys*, L., the products being methyl salicylate and primeverose. H. J. E.

**Determination of the  $p_H$  "Spectrum" for Bacteria, and Application to *Bacillus coli*.** C. J. BLOK (*Pharm. Weekblad*, 1925, 62, 346—352).—The growth of a culture in a given medium during a constant time is measured by the degree of opalescence developed, solutions being diluted to a standard, and the degree of dilution required used as the basis of measurement of growth. A series of media of known hydrogen-ion concentrations was prepared, and the rate of growth of *Bacillus coli* obtained from various sources observed by this method, all conditions being kept constant. The maximum growth was always between  $p_H$  5 and  $p_H$  8, but varied with the different cultures. By exposure to a given  $p_H$  over a

period, the bacteria underwent selection. The optimum  $p_H$  for growth changed considerably for cultures grown on agar, but changed little for cultures in bouillon. S. I. L.

**Bacteriolytic Power of Colostrum and of Milk.** J. BORDET and M. BORDET (*Compt. rend.*, 1924, 179, 1109—1113).—One drop of colostrum, from which fats have been removed by centrifuging, added to 1—2 c.c. of an opaque suspension obtained from cultures of various organisms collected from the atmosphere results in the clearing of the liquid to an almost transparent condition. At 40°, the effect is visible in a few minutes. *Bacillus coli*, *B. typhosus*, and the cholera vibrio are not affected in this manner. Similar results are given by milk and by white of egg; heating at 60° diminishes without completely destroying this property in all three substances. H. J. E.

**Radiometric Investigation of the Germicidal Action of Ultra-violet Radiation.** W. W. COBLENTZ and H. R. FULTON (*U.S. Bur. Standards, Sci. Paper* 495; 1924, 19, 641—680; see also *ibid.*, Nos. 330 and 378).—Suspensions of *Bacillus coli* in sterile distilled water were atomised uniformly over the surface of hardened sterile beef-peptone agar in a Petri dish, and exposed to ultra-violet radiation from a quartz mercury arc lamp, the radiation being filtered through screens of mica, which is found to have a well-defined absorption band at about 260  $m\mu$ . Previous exposure of the agar had no effect, although with very high radiation intensities subsequent growth was inhibited. Germicidal action extends up to 365  $m\mu$ , decreasing with increasing wave-length; very prolonged exposure is required from 297 to 365  $m\mu$ . The lethal action of waves below 280  $m\mu$  is at least 10 times more rapid than that of waves beyond 305  $m\mu$ , in spite of the much lower intensity of the shorter waves. Intermittent exposure has the same effect as continuous exposure for the same time of radiation, *i.e.*, the action is cumulative. The energy between wave-lengths 170 and 280  $m\mu$  required to kill a bacterium is about  $19 \times 10^{-12}$  watt. S. I. L.

**Tuberculin.** J. H. MUELLER (*Proc. Nat. Acad. Sci.*, 1925, 11, 23—25).—A tuberculin fraction has been obtained, containing 1% of nitrogen, giving a specific ring precipitin test in dilutions up to 1—400,000 with immune serum, and yet without any ability to produce a skin reaction. The fraction contains carbohydrate and is comparable with yeast gum and the complex carbohydrates extracted from type II pneumococcus cultures. A second fraction has been obtained, giving a specific ring precipitin test in low dilutions only, but producing specific skin reactions in tuberculous animals. This fraction gives a strong biuret reaction in concentrated solution. J. S. C.

**Electrolytic Migrations in the Blood and Tissues caused by Adrenaline.** K. DRESEL and E. WOLLHEIM (*Pflüger's Archiv*, 205, 375—380; from *Chem. Zentr.*, 1924, ii, 2768).—Adrenaline causes calcium to pass from the body-fluids into the tissues; the behaviour of potassium is irregular. R. B.

**Preparation of Insulin.** D. A. SCOTT and C. H. BEST (*Ind. Eng. Chem.*, 1925, **17**, 238—240; cf. A., 1924, i, 108).—Full details of the revised large-scale method, including a description of the plant, are given. The essential features are: (i) extraction with (sulphuric) acid alcohol; (ii) precipitation of the partly neutralised, concentrated extract with ammonium sulphate; (iii) repeated fractional precipitation, from alcohol, at a carefully regulated acidity value, differing at each stage. W. A. S.

**Insulin.** A. RENSHAW (*J. Soc. Chem. Ind.*, 1925, **44**, 95—100r).—An account is given of the discovery, commercial preparation and purification, physiological effects, and standardisation of insulin. Incubation at 37° appears not to destroy the activity of insulin. L. F. H.

**Testing Insulin Preparations.** P. HÁRI (*Biochem. Z.*, 1925, **156**, 86—96).—The results obtained on administering 56 preparations of insulin to 138 rabbits are tabulated as regards the blood-sugar depressant action and the production of convulsions. The necessity for basing conclusions on a large series of observations is emphasised, and it is suggested that the frequent discrepancies are due to individual variations in the animals rather than to the presence in insulin of two components in varying amounts. J. P.

**Attempts to Identify Vitamin-A. Vitamin-A and Phytol.** M. JAVILLIER, P. BAUDE, and S. LEVY-LAJEUNESSE (*Compt. rend.*, 1924, **179**, 998—1000).—Vitamin-A is often associated in green leaves with chlorophyll, which yields phytol (in the unsaponifiable fraction) on hydrolysis. This substance was therefore examined to ascertain whether it possessed the properties of vitamin-A, with negative results. H. J. E.

**Relation of Sterols to Vitamin-A.** J. C. DRUMMOND, O. ROSENHEIM, and K. H. COWARD (*J. Soc. Chem. Ind.*, 1925, **44**, 123—124r).—Pure cholesterol, on irradiation by ultra-violet light, develops a yellow colour, has a lowered melting point, gives a new colour reaction, and produces, in rats fed on a diet deficient in vitamin-A, a resumption in growth. L. F. H.

**Vitamins. IV. Content of Vitamins-A and -B in Horse Flesh.** A. SCHEUNERT and C. HERMERSDÖRFER (*Biochem. Z.*, 1925, **156**, 58—62).—Horse flesh after being boiled for 2 hours contains vitamin-A but no vitamin-B. J. P.

**Presence of Vitamin-C in Livers of Chickens Fed on Scorbatic Diets.** C. W. CARRICK and S. M. HAUGE (*J. Biol. Chem.*, 1925, **63**, 115—122).—The addition of the liver of fowls which had been kept for several months on a diet lacking vitamin-C was able to protect guinea-pigs, fed on a similarly deficient diet, against scurvy; the fowls themselves showed no ill-effects from prolonged deprivation of vitamin-C. C. R. H.

**The "Bios" Question.** F. W. TANNER (*Chem. Reviews*, 1925, **1**, 397—472).

**Occurrence of Free Pentoses in Plants. Effect of Extraction of the Sugars with Ammoniacal Alcohol.** D. T. ENGLIS and C. HALE (*J. Amer. Chem. Soc.*, 1925, 47, 446—449).—When aqueous-alcoholic solutions of pure sucrose or invert-sugar are refluxed with ammonia for 18 hours, and concentrated under reduced pressure, appreciable quantities of apparent pentoses are indicated by the method of Krober and Tollens or by fermentation, but not sufficient to account for the total quantities reported in plant extracts. In absence of ammonia, the Krober-Tollens method still indicates traces of pentoses but the fermentation method does not (cf. Davis and Sawyer, A., 1915, ii, 72; Spoehr, A., 1921, ii, 714).  
F. G. W.

**Origin of Lævulosans in Plants.** H. COLIN (*Bull. Soc. Chim. biol.*, 1925, 7, 173—180).—Lævulosans are not primary products of assimilation. For example, the carbohydrates found in the leaves of plants such as the artichoke, which store inulin in their underground organs, are dextrorotatory and consist of sucrose and reducing sugars. No intermediate zone where the transformation to inulin takes place was discovered. In some plants, inulin may be found throughout the length of the stem, not only in the medullary ray tissue but in the wood and pith; in others, e.g., chicory, the aerial parts are practically free from inulin and contain dextro-rotatory reducing sugars, whereas the root contains abundance of inulin and reducing sugars are almost absent. Enzymes do not appear to play any part in the condensation of sugars to the state of lævulosans and the mechanism of the transformation is not known.  
C. T. G.

**Optical Properties of Sterol Plastids and of Phytosterol from Bulbs of *Lilium candidum*.** M. MIRANDE (*Compt. rend.*, 1924, 179, 986—989).—Normal sterol plastids from bulb scales of *Lilium candidum* exhibit negative birefringence. When the sterol plastids and the masses of sterol are aggregated in dry scales, a structure which possesses a series of fibrous layers, the birefringence is positive. The conclusion is drawn that liliosterol exists in two different chemical states.  
H. J. E.

**Effects of the Method of Desiccation on the Carbohydrates of Plant Tissue.** K. P. LINK (*J. Amer. Chem. Soc.*, 1925, 47, 470—476).—The changes in sugar content of leaves of barberry, maize, and sugar-beet, and ears of maize, when dried at various temperatures from 32° to 98°, were investigated. The results indicate that a drying temperature below 65° is not sufficient to check enzyme action, and that no one method of desiccation is applicable to all plant-tissues, some of which can only be dried successfully by means of alcohol. [Cf. B., 1925, 295.]  
F. G. W.

**Non-volatile Acids of the Blackberry.** E. K. NELSON (*J. Amer. Chem. Soc.*, 1925, 47, 568—572).—By the use of the ester-hydrazide method, traces of oxalic, succinic, and citric acids, with moderate amounts of *l*-malic acid, were identified in blackberry juice. The main ester fraction, b. p. 175—180°/10 mm., consisted

of *triethyl isocitrate* (cf. Fittig, A., 1890, 586); *hydrazide*, m. p. 178—179°, apparently identical with that of m. p. 181—182° obtained by Franzen and Keyssner (A., 1923, i, 1045) from bramble leaves. Hydrolysis of the ester gave *isocitric acid*, as a viscous, yellow syrup,  $[\alpha]_D = -13.9^\circ$ , which is converted into *lactoisocitric acid*, m. p. 146° after softening at 130°, when heated in a vacuum at 100°. *Barium* and *silver isocitrates* are described, and *aconitic acid* was obtained by heating the former at 300°. The *triethyl isocitrate*, obtained from different batches of fruit, was found in both dextro- and lævo-rotatory modifications. F. G. W.

**Chemical Examination of the Seeds of the "Bunya Bunya"** (*Araucaria Bidwilli*, Hooker). I. F. R. MORRISON (*J. Proc. Roy. Soc. N.S. Wales*, 1925, 58, 234—239).—The air-dried meal (kernel) has the following percentage composition: fat 2.6, dextrin 7.72, starch 66.49, crude fibre etc. 7.93, moisture 13.82, and ash 2.12. B. F.

**Application to *Laminaria flexicaulis* of the Combustion Method of Analysis.** J. LELIÈVRE and Y. MÉNAGER (*Compt. rend.*, 1925, 180, 536—538).—The observation (cf. Freundler, A., 1924, i, 354) that the iodine content of *Laminaria flexicaulis* is nearly doubled by the preservation of the specimen for several weeks is definitely established. A volatile compound of tin is formed during the combustion by the method previously described (cf. A., 1924, ii, 420). By comparison of the iodine content of the algæ with and without the stipo-frondal zone, and either heated at 120° or not, it is shown that the retention of the latter with the stipe causes the stabilisation of the very small quantity of iodine, the complete absence of volatile iodine in the heated specimens, and the formation of the maximum quantity of the volatile tin compound (cf. Freundler, *ibid.*, 811). J. W. B.

**A Protein of the Orange.** A. H. SMITH (*J. Biol. Chem.*, 1925, 63, 71—73).—From the chromatophore portion of orange pulp there was obtained a protein, insoluble in water, salt solution, or dilute acid but soluble in dilute alkali; it precipitates at  $p_H$  4.7; the material has not so far been obtained free from an accompanying carbohydrate. C. R. H.

**Changes in the Composition of *Rhinanthus Crista Galli*, L., *Melampyrum arvense*, L., and *M. pratense*, L. during a Year's Growth.** M. BRAECKE (*Bull. Soc. Chim. biol.*, 1925, 7, 155—166).—The three plants studied are annuals with a short growing season. They contain the glucoside aucubin, which is present throughout growth, attaining a maximum amount about the time of flowering and accumulating in the seed. Aucubin plays an important part as a reserve material and is utilised in the development of the young plant. C. T. G.

**Citrus Fruit Pectin.** H. D. POORE (*U.S. Dept. Agric. Bull.* 1323, 1—19).—The conditions for the extraction of pectin from

citrus fruit peels and residues to give the best yield and product have been studied. The pectin is most advantageously extracted by treatment of the finely-ground material with hot dilute solutions of citric acid (0.5%) and clarified by the use of kieselguhr. The bitter constituents cannot be removed by dialysis, as a large proportion of the pectin itself dialyses through the sac, but may be extracted by alcohol from the dried crude pectin or concentrated suspension. The chemical compositions of the pectins of the orange, lemon, and apple are very closely similar; all contain araban, galactan, about 67% of pectic acid, 11.2% of methoxyl, and have  $[\alpha]_D + 220^\circ$  approximately. The proportions of citric acid, pectin, and sucrose necessary to produce stable gels under standard conditions are interdependent, the lowest limits of concentration being citric acid 0.045%, pectin 0.20%, and sucrose 37%. [Cf. B., 1925, May 29.]  
L. F. H.

**Formation, Distribution, and Circulation of Inulin in the Stem of the Artichoke.** H. COLIN (*Compt. rend.*, 1924, 179, 1186—1188).—Inulin is distributed in all parts of the stem of *Helianthus tuberosus*. Determinations of the percentages present in outer layer, wood, and pith at different distances from the soil show that the inulin is conveyed in the interior rather than in the outer layer. Thus the annual decortication has little influence on the quantity present in the tubers. The formation of inulin from the hexoses supplied by the foliage takes place mainly in the pith and woody cells.  
H. J. E.

**Presence of Large Quantities of Free Maltose in the Fresh Tubers of *Umbilicus pendulinus*, DC.** M. BRIDEL (*Bull. Soc. Chim. biol.*, 1925, 7, 181—187).—Maltose has been extracted in considerable quantity from the fresh tubers of *Umbilicus pendulinus*, DC., and obtained in a pure crystalline condition. The yield was 40 g. of maltose per kg. of tubers.  
C. T. G.

**Chemical Constituents of *Matteuchia orientalis* (Hk.), Trev.** I. T. MUNESADA (*Ber. Ohara Inst. landw. Forsch.*, 1924, 4, 429—434).—The rhizomes and stipules of *Matteuchia orientalis* (Hk.), Trev., used as a drug by the Chinese, contain different substances from the male fern (cf. Boehr, A., 1898, i, 40; Kraft, A., 1904, i, 1039). By extraction of the dried rhizomes and stipules with acetone two new substances have been obtained. The first substance,  $C_{14}H_{14}O$ , to which the name *matteucinol* has been assigned, has m. p. 167—170°, saponification number 201, about 9% of methoxyl groups, decolorises bromine without yielding a crystalline compound, and is converted by concentrated sulphuric acid into a substance, containing no sulphur, with 74.9% C and 6.2% H, m. p. 194—197°. The other substance isolated from the acetone extract also has the composition  $C_{14}H_{14}O$ , with saponification number 479, m. p. 140—142°, is readily soluble in many organic solvents, and gives a brown coloration with sulphuric acid.  
L. F. H.

**Indole in the Flowers of Spanish Jasmine** [*Jasminum grandiflorum*, L.]. R. CERIGHELLI (*Compt. rend.*, 1924, 179, 1193—1195).—Indole is a normal constituent of the flowers of Spanish jasmine. It continues to be given off from plucked flowers, accumulating in a confined space to the extent of 5—6 mg. per 100 g. of material. H. J. E.

**Unstable Glucoside Complex obtained from Bark of *Rhamnus cathartica*.** L. M. BRIDEL and C. CHARAUX (*Compt. rend.*, 1925, 180, 857—860).—A glucoside complex has been extracted from the bark of *Rhamnus cathartica*. When dried this is a greenish-yellow, hygroscopic solid with 18.9% of the reducing power (Bertrand) of an equal weight of dextrose, soluble in water giving a brown, levorotatory solution, from which colourless needles slowly separate. These needles are insoluble in water and are composed of a glucoside (which it is proposed to call *rhamnucoside*), a compound of primeverose with a hydroxymethylanthraquinone constituent. The soluble glucosides comprise 79% of the extract and are hydrolysed by dilute sulphuric acid yielding dextrorotatory reducing sugars, which give pentose reactions. The soluble glucosides are also readily hydrolysed by the enzyme obtained from the seeds of the plant, and emodin and another hydroxymethylanthraquinone constituent (m. p. 234°), together with reducing sugars, have been isolated from the hydrolysis product. Primeverose ( $[\alpha]_D -3.6^\circ$ , and reducing power 64.4% of that of dextrose) was also isolated.

L. F. H.

**Pigments of the *Florideæ*.** G. RODIO (*Atti R. Accad. Lincei*, 1925, [vi], 1, 188—190).—Investigations on various *Florideæ* of the Gulf of Naples show that the red pigment, phycoerythrin, may be crystallised from its solutions in hexagonal prisms or tablets by addition of ammonium sulphate. It exhibits three absorption bands in the green, these occupying slightly different positions with different species. Phycocyanin accompanies phycoerythrin in a few forms and possesses analogous physical characters but exhibits only one or two bands, in the orange-red region. Contrary to common opinion, phycoerythrin appears to take part in photo-synthesis.

T. H. P.

**Occurrence of Quebrachitol and Sugar in *Hevea* Latex under various Conditions.** W. SPOON (*Archief Rubbercultuur Nederl.-Indië*, 1922, 6, 269—287; from *Chem. Zentr.*, 1924, ii, 2793).—The acetic acid serum of *Hevea* latex contains 0.99—1.91% of quebrachitol and 0.12—0.48% of sugar (as sucrose). From May to November the yield of latex from the tree was nearly constant but its rubber content was irregular. The density and dried residue of the serum vary together. At the end of the test the mineral matter appeared to increase, the quebrachitol to decrease. The greatest differences were observed in January and February at the fall of the seeds, the condition of the latex being thereafter improved.

R. B.

**Hydrogen-ion Concentration in the Latex of *Hevea braziliensis*.** W. BOBILIOFF (*Archief Rubbercultuur Nederl.-Indië*, 1924, 8, 609—624, 625; from *Chem. Zentr.*, 1924, ii, 2611).—The direct determination of the hydrogen-ion concentration gives inaccurate results, and the  $p_H$  values are best obtained by colorimetric method in the dialysate. At the commencement of spontaneous coagulation the change in  $p_H$  is only slight, at the end  $p_H$  4.8—5.6; with vinegar,  $p_H$  4.3—4.8, the alteration is also only slight initially. The  $p_H$  value for different trees fluctuates, mostly between 6.4 and 7.8. Glycerol is recommended as a stabiliser in the dialysis. R. B.

**Chemical Composition of the Latex of *Hevea*.** K. GORTER (*Archief Rubbercultuur Nederl.-Indië*, 1924, 1, 375—377; from *Chem. Zentr.*, 1924, ii, 1637).—The latex of 35-year-old *Hevea* trees contained the following constituents, expressed in grams per litre: Caoutchouc 370, dry matter in serum 29.1 including ash 5.3, protein 3.4, quebrachitol 14.5, sugar 2.5, unrecognised constituents 3.4. The hydrolytic products of protein resulting from bacterial action are of significance for the economic value of the caoutchouc. Thus, addition of 0.2% of leucine accelerates vulcanisation.

G. W. R.

**Influence of Hydrogen-ion Concentration of Soil on Formation and Composition of Peppermint Oil.** H. DEEL and (MME.) H. DEEL (*Bull. Soc. chim.*, 1925, [iv], 37, 453—455).—The influence of the reaction of the soil on the oil of the English and French varieties of peppermint grown on it has been studied. The hydrogen-ion concentration of the soil has very little effect on the percentage of oil in the plant, but it has a very decided effect on the weight of plants grown on a given area. The optimum  $p_H$  for English peppermint is about 5 and for the French variety about 7; at these optima the oils contain the largest proportion of free and total menthol.

L. F. H.

**Composition of Crude Gluten.** D. B. DILL (*Cereal Chem.*, 1925, 2, 1—11).—The carbohydrate present in gluten, which is shown to be mainly starch, may vary in amount from 5 to nearly 20%; it does not appear to affect gluten quality other than as an indifferent filler. The lipid content, determined by Hertwig's method (cf. *J. Assoc. Off. Agric. Chem.*, 1923, 7, 91), ranged from 5 to more than 10%; the ash also varied widely. In the case of a soft red winter wheat flour, 84.5% of the protein, 47.5% of the lipoids, 15.6% of the ash, and 20.4% of the total phosphoric acid present in the flour appeared in the gluten prepared from it. C. T. G.

**Wheat and Flour Studies. III. Amino-nitrogen Content of the Immature Wheat Kernel and the Effect of Freezing.** P. F. SHARP (*Cereal Chem.*, 1925, 2, 12—37).—Determinations of amino-nitrogen and protein in wheat grains, both fresh and dried, at various stages of growth lead to the conclusion that so far as a decrease in amino-nitrogen indicates protein synthesis, desiccation is not necessary for what is probably the first step in the synthesis;



amino-nitrogen decreased markedly in the threshed grain when there was no loss of moisture. The effect of freezing on the developing grain is to prevent the normal decrease of amino-nitrogen and tends to cause an increase.  
C. T. G.

**Soluble Material and Insoluble Tissues during the Development of Wheat. Influence of a Complete Mineral Fertiliser.** J. CHAUSSIN (*Compt. rend.*, 1924, **179**, 1195—1197).—To ascertain the effect of a complete mineral fertiliser on the composition of the soluble portion of the interior of wheat plants, specimens of leaves, stems, and ears were dried. The product was calcined, as also was the extract of the soluble portions. Examination of the relation between dry matter and ash leads to the conclusion that the constancy in the ratio between mineral matter and the dry extract of the soluble part of the leaf is a general property. The soluble portion of the stem has a greater mean molecular weight than that of other portions of the plant, the inference being that accumulation of reserves is accompanied by condensation reactions. As compared with unmanured wheat, addition of mineral fertilisers results in higher osmotic pressures in the plant.  
H. J. E.

**Alkaline Chlorosis of the Vine.** U. PRATOLONGO (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 319—322).—There is no causal connexion between high alkalinity of the soil or its tendency to produce chlorosis and the amount or state of division of the calcium carbonate which it contains.  
T. H. P.

**Volatile Fatty Acids formed by the Acid Fermentation of Foodstuffs. I. "Electrosilage" of Maize.** C. BRAHM (*Biochem. Z.*, 1925, **156**, 15—20).—Acetic, propionic, butyric, valeric,  $\alpha$ -methylbutyric, and hexoic acids are found in the liquid formed during the fermentation of maize in electrically heated silos. Formic acid is not present.  
J. P.

**Hexamethylenetetramine as a Nutrient for the Kidney Bean and for White Mustard (*Sinapis alba*).** E. NICOLAS and G. NICOLAS (*Compt. rend.*, 1925, **180**, 860—861).—Hexamethylenetetramine has a favourable influence on the dry weight of the plant, on the size of the roots, and on the leaves of the dwarf Hermitage kidney bean (cf. A., 1923, i, 77, 427; 1924, i, 128) and of white mustard.  
L. F. H.

**Influence of Phosphate Manuring on the Production of Vitamin-B in Plants.** C. HORNEMANN (*Z. Pflanz. Düng.*, 1925, **A**, **4**, 84—104).—Although phosphate manuring increased the yields of a number of crops the vitamin-B content per unit weight of crop remained unaltered.  
A. G. P.

**Measurement of the Nitrogen-fixing Capacity of Soils.** S. WINOGRADSKY (*Compt. rend.*, 1925, **180**, 711—716).—A weighed sample of the finely-divided soil is spread uniformly over the surface of a plate of purified silica gel previously impregnated with a solution of mannitol and the usual salts, to which chalk has been added, and the

plate is kept at 30° for 3 days; the number of colonies of *Azotobacter* found on the surface is then counted. After 8 days the surface is covered with a brown crust which undergoes no further change; the nitrogen content of the plate is then determined. The conditions best suited to ordinary soils are the presence of 2 g. of mannitol, addition of 1 g. of soil about the fineness of sand dried at 35–40°, and keeping at 30° for 10 days. S. I. L.

**Effect of Sulphur on Saline Soils.** A. A. KALUSHSKI and A. E. SSOLNIJEWA (*Ann. Inst. agron. Saratov*, 1923, 1, 141–159; from *Chem. Zentr.*, 1924, ii, 750; cf. this vol., i, 492).—In pot experiments with barley on an alkaline saline soil, a dressing of sulphur equivalent to 0.1% of the soil resulted in a ninefold increase in the yield of grain. A marked decrease in the alkalinity of the soil, as shown by the composition of its aqueous extract, was produced. The sulphur, after oxidation in the soil, appears principally as calcium sulphate. G. W. R.

**Interactions of Quicklime in the Soil.** F. SCHEFFER (*J. Landw.*, 1925, 72, 201–235).—The conversion of added calcium oxide into carbonate in neutral soils stored in the laboratory is not quantitative. A clay and a loam, both containing initially small amounts of carbonate but capable of liberating acid from acetate solutions, gave maximum carbonate formations of 76% and 47% of the theoretical amount respectively. These values were obtained after about 10 weeks; the carbonate content decreased subsequently. In a fairly pure sand, the conversion was more rapid and reached a maximum value of 83%. The addition of either sodium-, potassium-, or calcium-permutite or an acid permutite did not reduce the amount of carbonate formed in the sand. Treatment with hydrochloric acid was also without effect, but the addition of silica gel reduced the amount of carbonate formation. It is concluded that silica gel is one of the most important absorbents of calcium oxide and calcium carbonate in the soil. E. M. C.

**Soil Colloids.** W. O. ROBINSON and R. S. HOLMES (*U.S. Dept. Agric. Bull.* 1311, 1924, 1–41).—The colloidal material of soil is composed mainly of silica, alumina, ferric oxide, and water with smaller amounts of calcium, magnesium, potassium, sodium, phosphorus, manganese, sulphur, chlorine, and organic matter. Silica and alumina generally vary inversely, as also do silica and the sum of calcium, magnesium, potassium, and sodium oxides. The iron is present partly as yellow hydrated ferrous oxide and partly as a colourless silicate. Kaolinite and nontronite are not present. The colloidal matter consists of the products of the chemical weathering of soil-forming minerals, with small amounts of fine mineral fragments. CHEMICAL ABSTRACTS.

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## Organic Chemistry.

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**Chemical Change of some Gaseous Hydrocarbons by Radioactive Radiations.** W. MUND and W. KOCH (*Bull. Soc. chim. Belg.*, 1925, **34**, 119—126).—When methane is exposed in a differential manometer to radium emanation a very slight diminution of volume occurs. In the case of ethane, by freezing out the ethane after exposure it was shown that a considerable amount of gas, probably hydrogen or methane, had been formed; at the same time, minute drops of a highly refractive liquid formed on the walls of the vessel. This liquid was more rapidly formed in the case of ethylene, which is therefore considered to be an intermediate product in the decomposition of the ethane. With ethylene, a mist easily dispelled by an electric field was also formed. The contraction of acetylene was greater and more rapid than with the other gases. A dense cloud was formed, and a voluminous brownish-yellow, amorphous powder deposited in traces on the walls of the vessel; this powder was inflammable, but did not melt at 300°; it was not identified chemically. F. G. T.

**Platinum and Palladium Oxides as Catalysts in the Reduction of Organic Compounds. IX. Reduction of Olefines.** J. W. KERN, R. L. SHRINER, and R. ADAMS (*J. Amer. Chem. Soc.*, 1925, **47**, 1147—1158).—The efficiencies of platinum and palladium oxides, obtained by fusion of chloroplatinic acid and palladium chloride, respectively, with sodium nitrate, as catalysts for the hydrogenation of a number of olefines, under the standard conditions previously used (cf. A., 1924, i, 968), have been compared. These catalysts are generally more active than the corresponding colloidal metals, and palladium is less effective than platinum, in most cases, in the reduction of olefines. Olefines of the type  $\text{CHR}:\text{CH}_2$  are reduced most rapidly, those of the type  $\text{CRR}':\text{CH}_2$  slightly more slowly, further retardation being observed among olefines of the type  $\text{CHR}:\text{CHR}'$ , depending on the nature of the groups R and R'.  $\beta$ -Methyl- $\Delta^2$ -butylene is reduced much more rapidly than  $\alpha\alpha$ -diphenyl- $\Delta^2$ -propylene. Among conjugated olefines, mesityl oxide is much more rapidly reduced than phenyl styryl ketone, whilst reduction of  $\alpha\beta$ -unsaturated acids is generally slow, with a marked absence of regularity. Satisfactory reduction is only obtained with carefully purified materials. The presence of iron retards the reduction of pure products, but may accelerate that of impure materials. Oxygen has no reactivating effect on the catalyst in the reduction of olefines. It is concluded that the reduction of olefines takes place in all cases by  $\alpha:\beta$  addition.

F. G. W.

**Production of Ethylene for the Preparation of Ethylene Bromide from Alcohol by the Contact Process.** KESTING (*Z. angew. Chem.*, 1925, **38**, 362).—The usual method of making

ethylene for ethylene bromide by heating ethyl alcohol with concentrated sulphuric acid at 160—170° is not suitable for making large quantities of this gas. A considerable amount of ether is formed, some of the alcohol passes over unchanged, and a good deal of charring occurs. The yield of ethylene bromide is only 20—25%. The preparation of ethylene by the contact process gives much better results. Alcohol vapour is passed over pure powdered aluminium oxide heated at 260—270° in a combustion tube, and the evolved ethylene is absorbed by bromine in the usual way. The yield of ethylene bromide is 90%, and practically no side reactions occur. The process admits of the uninterrupted production of large amounts of ethylene. F. R.

**Diacetylene Hexabromide.** R. LESPIEAU and C. PREVOST (*Compt. rend.*, 1925, **180**, 1347—1349).—By the interaction of diacetylene and bromine in chloroform solution, the compound  $C_4H_2Br_6$ , m. p. 186·5°, is obtained. This is identical with the compound obtained by Noyes and Tucker (A., 1897, i, 261) from the product of the action of hydrochloric acid on copper acetylide, and by Willstätter and Bruce (A., 1907, i, 1018) by the bromination in the presence of iron powder of 1:2-dibromocyclobutane and 1:1:2:2-tetrabromocyclobutane. To the hexabromide Sabanéef attributed the constitution 1:1:2:3:3:4-hexabromocyclobutane, and Willstätter and Bruce the constitution 1:1:2:2:3:3-hexabromocyclobutane, since the compound appears to be fully saturated, as it does not absorb bromine. The present authors, however, ascribe this lack of bromine-absorbing power to a steric effect and, since the hexabromide, on treatment with zinc powder and alcohol, yields diacetylene, they consider it to be  $\alpha\alpha\beta\gamma\delta\delta$ -hexabromo- $\Delta^2$ -butylene. L. F. H.

### Reactivity of Atoms and Groups in Organic Compounds.

**I. Relative Reactivities of Hydroxyl-hydrogen Atoms in certain Alcohols.** J. A. NORRIS and A. A. ASHDOWN (*J. Amer. Chem. Soc.*, 1925, **47**, 837—846).—The relative values of the (second order) reaction constants for the reaction between *p*-nitrobenzoyl chloride and various alcohols in ether (1 mol. of each reactant in 1000 c.c. of solvent) at 25° are as follows: methyl, 100; ethyl, 45·7; propyl, 35·9; *n*-butyl, 40·2; isobutyl, 16·7; isopropyl, 5·4; *sec*.-butyl, 4·0; *tert*.-butyl, 1·46; benzyl, 9·3;  $\beta$ -phenylethyl, 21·6; and  $\gamma$ -phenylpropyl, 10·7. The reactivity of the hydroxyl-hydrogen in a homologous series appears to be an alternating function of the terminal group and the number of bonds between it and the reacting hydrogen atom. F. G. W.

**Dehydration of Alcohols over Alumina.** H. ADKINS and P. P. PERKINS (*J. Amer. Chem. Soc.*, 1925, **47**, 1163—1167).—The rates of dehydration of alcohols when passed over aluminium oxide at 280—440° increase in the following order: butyl, propyl, isobutyl, ethyl, isopropyl, and *sec*.-butyl alcohols, excess of alcohol being present in all cases. The rate of dehydration is a linear function of the temperature over the range investigated, and

increases more rapidly with rise in temperature in the case of the secondary alcohols. The relative reactivity is best defined as the temperature interval for a corresponding amount of reaction in the same time. Thus to obtain the same volume of olefine per hour from butyl as from ethyl alcohol, the temperature of the catalyst has to be  $19^{\circ}$  higher in the former case. The observation of Pease and Yung (A., 1924, i, 363) that ethyl ether and ethyl alcohol give the same volume of ethylene per hour when passed over aluminium oxide at  $400^{\circ}$  is confirmed, but butyl alcohol gives considerably more butylene than does butyl ether, indicating that the latter cannot be an intermediate in the formation of butylene from butyl alcohol, and that the above identity of rates of dehydration of ethyl alcohol and ethyl ether is fortuitous.

F. G. W.

**Preparation of Optically Active Primary Alcohols.** F. BECHERER.—(See i, 664.)

**Syntheses by Means of Organic Peroxides. V. Action of Benzoyl Peroxide on Alcohols.** H. GELISSEN and P. H. HERMANS.—(See i, 663.)

**Electro Reduction of Diacetone Alcohol.** R. R. READ and F. A. FLETCHER (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 127—131).—The reduction of diacetone alcohol, using lead electrodes in dilute sulphuric acid with low current density, proceeds with high efficiency, the products being  $\beta$ -methylpentane- $\beta\delta$ -diol and  $\beta$ -methylpentan- $\beta$ -ol. [Cf. B., 1925, 423.] N. H. H.

**Derivatives of Citronellol and their Optical Rotations.** H. RUPE and R. RINDERKNECHT.—(See i, 658.)

**Preparation of Primary Acetylenic Alcohols.** H. H. GUEST (*J. Amer. Chem. Soc.*, 1925, **47**, 860—863).—Acetylenic alcohols,  $\text{CR}_2\text{C}\cdot\text{CH}_2\cdot\text{OH}$ , are obtained in good yield by the action of gaseous formaldehyde on the magnesium bromide derivative of the corresponding acetylene in ethereal solution. The preparation of  $\Delta^{\beta}$ -octinen- $\alpha$ -ol and of phenylpropionic alcohol is described. The heptene, b. p.  $99\text{--}105^{\circ}$ , obtained by the action of sodamide on  $\alpha\alpha$ -dichloroheptane in toluene or xylene (Bourguet, A., 1923, i, 751, 1176), is a mixture (70—30%) of *n*- and *iso*-heptenes. Attention is directed to the pleasant odours of the above acetylenic alcohols (cf. Guest, A., 1923, i, 892). F. G. W.

**Further Syntheses with  $\beta\beta'$ -Dichlorodiethyl Ether.** L. H. CRETCHER, J. A. KOCH, and W. H. PITTENGER (*J. Amer. Chem. Soc.*, 1925, **47**, 1173—1177; cf. this vol., i, 228).—Better yields of substituted morpholines than were obtained previously are produced by heating 1 mol. of the above chloroether with 3 mols. of amine at  $200\text{--}215^{\circ}$ . *Di- $\beta$ -anilinoethyl ether*, m. p.  $115.5^{\circ}$ , is obtained as a by-product in the preparation of 4-phenylmorpholine. The following ethers were obtained by the action of sodium salts of the appropriate phenols on the dichloroether in alcoholic solution.  $\beta$ -Chloro- $\beta'$ -phenoxydiethyl ether, b. p.  $149^{\circ}$ ; *di- $\beta$ -phenoxydi-*

*ethyl ether*, m. p. 66°; *β-chloro-β'-phenylthioldiethyl ether*, b. p. 158°; *di-β-phenylthioldiethyl ether*, b. p. 257—258°; *di-β-naphthoxydiethyl ether*, m. p. 122°; and *di-α-naphthoxydiethyl ether*, m. p. 87°. Condensation of potassium phthalimide with the chloroether, at 125—140°, was catalysed by the addition of diethylamine. *β-Chloro-β'-phthalimidodiethyl ether*, m. p. 69°, and *di-β-phthalimidodiethyl ether*, m. p. 159° (cf. Gabriel, A., 1905, i, 862), are described. When distilled with solid sodium hydroxide, dichlorodiethyl ether yields *β-chloroethyl vinyl ether*, b. p. 109°,  $d_{15}^{25}$  1.0525, and 1:4-dioxane. The former is stable to alkalis, but yields acetaldehyde quantitatively when treated with dilute acids. F. G. W.

**Petroleum. I. Occurrence of Compounds of Sulphur in the Light Distillate from the Crude Oil of Maidan-i-Naftun.** C. F. BIRCH and W. S. G. P. NORRIS (*J. Chem. Soc.*, 1925, 127, 898—907).—By distillation of the "spent soda solution," used in refining the first 36% of the distillate from crude Persian petroleum, a mixture of sulphur compounds was obtained from which isopropyl and isobutyl mercaptans were separated and identified; there was evidence that ethyl and isoamyl mercaptans were also present. From the same source, diethyl, diisopropyl, and diisobutyl disulphides were isolated. B. W. A.

**Syntheses by Means of Organic Peroxides. VI. Action of Benzoyl Peroxide on Acetic Acid.** H. GELISSEN and P. H. HERMANS.—(See i, 664.)

**Preparation and Properties of Dichloroacetic Acid.** H. W. DOUGHTY and A. P. BLACK (*J. Amer. Chem. Soc.*, 1925, 47, 1091—1094; cf. A., 1922, i, 427).—Trichloroacetic acid (55 g.) is added to a solution of aniline (35 g.) in benzene (500 c.c.). The mixture is brought to the boiling point, the heating stopped, and copper powder (35 g.) added in 5-g. portions at about 5-min. intervals, with stirring, which is continued for about 10 mins. after the last addition of copper. Dry hydrogen chloride is then passed through the mixture, whereby cupric and cuprous chlorides and aniline hydrochloride are precipitated; hydrogen chloride is removed from the filtrate by means of a current of air. Aniline (35 g.) is then added, when aniline dichloroacetate separates as a crystalline precipitate, in a yield of 75%. If trichloroacetic acid is used instead of the aniline salt, the yield is reduced to 50%, whilst substitution of carbon tetrachloride for benzene completely inhibits the reaction. Free dichloroacetic acid is best obtained by the action of hydrogen chloride on a suspension of the aniline salt in benzene. It has b. p. 191—194.5°/760 mm. (decomp. with formation of acid chloride, carbonyl chloride, and tar), b. p. 95—96°/17 mm.,  $d_{20}^{20}$  1.5666—1.5694,  $n_D^{20}$  1.4659—1.4671. F. G. W.

**Labile Nature of the Halogen Atom in Organic Compounds. X. Action of Hydrazine Hydrate on the Halogen Derivatives of α-Nitro-fatty Acids.** A. K. MACBETH and D. TRAILL (*J. Chem. Soc.*, 1925, 127, 892—898; cf. T., 1922, 121, 892).—When the action of hydrazine hydrate is tested on various bromo- and chloro-

esters of similar structure, the superior reactivity of the bromine atoms with this reagent is evident. For example, *ethyl monochloronitroacetate*, b. p.  $77^{\circ}/8$  mm.,  $n_D$  1.4412 (*ammonio* derivative, m. p.  $114-115^{\circ}$ ), and *ethyl dichloronitroacetate*, b. p.  $72^{\circ}/8$  mm.,  $n_D$  1.4430, do not react with hydrazine hydrate, whereas *ethyl bromonitroacetate*, b. p.  $105^{\circ}/10$  mm.,  $n_D^{20}$  1.4798 (*ammonio* derivative, m. p.  $134^{\circ}$ ), and *ethyl dibromonitroacetate*, b. p.  $97.4^{\circ}/6$  mm.,  $n_D$  1.4985, are readily reduced by that reagent; furthermore, *ethyl chlorobromonitroacetate*, b. p.  $89^{\circ}/11$  mm.,  $n_D$  1.4663, reacts with removal of the bromine atom only. Similar results are obtained with *ethyl  $\alpha$ -chloronitropropionate*, b. p.  $80^{\circ}/9$  mm.,  $n_D$  1.4301, and *ethyl  $\alpha$ -bromonitropropionate*, b. p.  $88^{\circ}/20$  mm.,  $n_D$  1.4535 (*hydrazine* derivative, m. p.  $120^{\circ}$ ), and also with *ethyl  $\alpha$ -chloronitrobutyrate*, b. p.  $77-79^{\circ}/6$  mm.,  $n_D$  1.4338, and *ethyl  $\alpha$ -bromonitrobutyrate*, b. p.  $83-84^{\circ}/9$  mm.,  $n_D$  1.4990, in all of which the bromo compounds react with hydrazine hydrate and the chloro compounds do not. The effects are best explained on a polarity basis.

B. W. A.

**Catalytic Decomposition of Acid Chlorides.** A. MAILHE (*Compt. rend.*, 1925, **180**, 1111—1113).—When *isovaleryl* chloride vapour is passed over feebly active nickel at  $420^{\circ}$ , it decomposes into carbon monoxide, hydrogen chloride, and *isobutylene*, a small amount of which breaks up to propylene and the  $\text{CH}_2$  residue is hydrogenated to methane. Moreover, a little carbon is formed, *isobutyryl* chloride under similar conditions yields propylene, carbon monoxide, and hydrogen chloride. Propionyl chloride gives the same products except that ethylene is formed instead of propylene. Acetyl chloride at  $400^{\circ}$  decomposes smoothly. The gas contains 62% of carbon monoxide and 32% of hydrogen. Benzoyl chloride vapour decomposes normally at  $420^{\circ}$ . The gases evolved consist of 97% of carbon monoxide, 1% of carbon dioxide, 2% of hydrogen. The condensed liquid yields traces of benzene, 50% of chlorobenzene, 40% of unchanged benzoyl chloride, and benzil. Thus benzoyl chloride decomposes according to the scheme:  $\text{C}_6\text{H}_5\cdot\text{COCl} = \text{CO} + \text{C}_6\text{H}_5\text{Cl}$ , and apart from the formation of a little benzene, an accessory reaction occurs in which partial hydrogenation of the acid chloride results in the formation of benzil.

R. A. M.

**Isomerism of the Crotonic Acids.** A. GONZÁLEZ (*Anal. Fis. Quím.*, 1925, **23**, 100—112).—Tetrolic acid,  $\text{CMe}\cdot\text{C}\cdot\text{CO}_2\text{H}$ , on hydrogenation with nickel as catalyst behaves analogously to phenylpropionic acid, yielding principally *cis*-crotonic acid. Acids of the type  $\text{CR}\cdot\text{C}\cdot\text{CO}_2\text{H}$  thus behave in the same manner on hydrogenation whether the R is an alkyl or an aryl group. G. W. R.

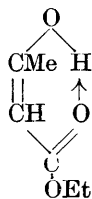
**Chemical Nature of Fats. I. Iodine Super-value of Fatty Oils and Unsaturated Fatty Acids.** B. M. MARGOSCHES, L. FRIEDMANN, and W. TSCHÖRNER (*Ber.*, 1925, **58**, [B], 794—797; cf. A., 1924, i, 828).—The absorption of iodine by olive, castor, and linseed oils and oleic, ricinoleic, and linoleic acids in aqueous alcoholic solution corresponds after 5 mins. with the Hübl iodine

value. The subsequent absorption of iodine corresponds exactly with the increase of hydrogen iodide. The action appears to follow the scheme:  $I_2 + H_2O = HI + HIO$ ;  $R' \cdot CH : CHR'' \xrightarrow{+HIO} R' \cdot CHI \cdot CH(OH) \cdot R'' \xrightarrow{+HIO} R' \cdot CHI \cdot CH(OH) \cdot CH(OH) \cdot R'' + HI$ . The final stage of the change appears to be greatly accelerated by the presence of hydroxy and esterified carboxy groups in the compound. The "iodine super-value" (iodine absorbed after 24 hrs.) has probably considerable diagnostic value; thus whereas the Hübl values for olive and castor oils are closely similar, the iodine supervalues are 119.7 and 162.2, respectively. H. W.

**Oxidation of Unsaturated Fatty Acids with Hydrogen Peroxide and Perbenzoic Acid.** K. H. BAUER and G. KUTSCHER (*Chem. Umschau*, 1925, 32, 57—64).—When linolenic acid in acetone solution is oxidised by hydrogen peroxide in presence of manganese or cobalt resinate and the product purified in the cold, a yellowish-green oil,  $C_{34}H_{58}O_8(CO_2H)_2$ , with a peroxide reaction, is obtained. The product is unstable and, on heating with water, is converted into a reddish-brown oil,  $C_{34}H_{58}O_6(CO_2H)_2$ , having no peroxide reaction. Oxidation of linolenic acid with perbenzoic acid gives a product with relatively more oxygen than that obtained with hydrogen peroxide, but in which the double bond has been saturated. Ethyl linolenate when oxidised by perbenzoic acid gives an oil,  $C_{20}H_{34}O_5$ , with a faint peroxide reaction. When the oil is extracted with hot water, the peroxidic oxygen is lost, but the material is apparently not otherwise changed. Although the carboxyl groups evidently play an important part in the condensation of the free acid, methylation of the product proves that both acid groups persist in the complex. Oleic acid in acetone with hydrogen peroxide gives a pale red oil which loses its peroxide reaction when treated with hot water. Ethyl oleate and hydrogen peroxide form an oil the active oxygen of which is lost on thrice treating with hot water. Oleic acid, oxidised with perbenzoic acid, forms a reddish-brown oil,  $(C_{18}H_{34}O_4)_x$ , with no peroxide reaction. Ethyl oleate with perbenzoic acid and subsequent extraction in the cold gives an oil,  $C_{20}H_{38}O_3$ , with a weak peroxide reaction which is lost on heating with water. [Cf. B., June 26th.]

A. COUSEN.

**Structure of the Enolic Forms of  $\beta$ -Keto-esters and  $\beta$ -Diketones.** N. V. SIDGWICK (*J. Chem. Soc.*, 1925, 127, 907—909).—The enolic forms of a large number of  $\beta$ -keto-esters and  $\beta$ -diketones show themselves, by their solubility relations, to be markedly less polar than the corresponding ketonic forms. A chelate ring structure, implicating the hydroxyl group, is therefore proposed in conformity with that already adopted in the case of certain ortho-substituted phenols (cf. A., 1924, i, 507). The enolic form of ethyl acetoacetate thus requires the annexed formula. Calculation on Baeyer's principles shows that this exceedingly stable type of ring is entirely without strain. M. J.





**Electrolytic Preparation of Succinic Acid.** J. F. NORRIS and E. O. CUMMINGS.—(See i, 668.)

**Halogenation of Fumaric and Maleic Acids. Walden Inversion.** E. M. TERRY and L. EICHELBERGER (*J. Amer. Chem. Soc.*, 1925, 47, 1067—1078).—Addition of chlorine to sodium maleate and fumarate in aqueous solution in presence of excess of sodium chloride (to depress formation of hypochlorous acid), yields sodium dichlorosuccinate and *isodichlorosuccinate*, respectively, whilst the similar addition of bromine yields mixtures, 78% of dibromosuccinate and 10% of *isodibromosuccinate* being obtained respectively in the two cases. Potassium and strontium salts afford the same results, which are also unaffected by variation of the bromide-ion concentration and the temperature of reaction. The authors postulate the formation of a primary additive product between the unsaturated acid and the entering molecule, in which rearrangement may take place as a result of the influence of electric charges on adjacent carbon atoms. The bearing of this postulate on the mechanism of the Walden inversion, which is often accompanied by the formation of an unsaturated compound, is pointed out.

Maleic anhydride is obtained in 99% yield by distilling a mixture of maleic acid with 70% of its weight of phosphoric oxide, under reduced pressure, at 100—110°.

F. G. W.

**Electrolysis of Salts of Alkyloxy-acids.** D. A. FAIRWEATHER (*Proc. Roy. Soc. Edinburgh*, 1924—1925, 45, 23—33).—The following compounds have been electrolysed, with a platinum crucible as cathode and a platinum spiral as anode: potassium ethyl ethoxymalonate, potassium ethyl diethoxysuccinate, potassium ethoxyacetate, and sodium amyloxyacetate. For the last, a mercury cathode was employed. The chief products were aldehydic, and it seems unlikely that this is due to oxidation. The results appear to confirm Hofer and Moest's explanation of the formation of formaldehyde in the electrolysis of sodium glycollate as due to the intermediate formation of  $\text{CH}_2(\text{OH})_2$  and subsequent removal of water. In the case of the alkyloxy compounds, alcohol is split off instead of water. A further objection to the oxidation theory is the formation of the readily oxidisable ethyl formylethoxyacetate as the chief product of electrolysis of potassium ethyl diethoxysuccinate.

The dissociation constant of ethoxymalonic acid at 25° is 0.71, and of *d*-diethoxysuccinic acid 0.097.

M. S. B.

**Optically Active Components of Chlorosulphoacetic Acid.** H. J. BACKER and W. G. BURGESS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, 28, 64).—The optically active components of chlorosulphoacetic acid have been obtained by "cold crystallisation" of the strychnine and cinchonine salts. Chlorosulphoacetic acid has  $[\alpha]_{589}^{20}$  39°,  $[\alpha]_{533}^{50}$  50°,  $[\alpha]_{494}^{62}$  62°, whereas the ammonium salt has  $[\alpha]_{589}^{20}$  20°,  $[\alpha]_{533}^{26}$  26°,  $[\alpha]_{494}^{34}$  34°. Racemisation of acid and salt occurs slowly at the ordinary temperature, and is greatly accelerated by traces of strong bases.

L. L. B.

**Optical Resolution of Bromosulphoacetic Acid.** H. J. BACKER and H. W. MOOK (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 65—66; cf. preceding abstract).—The method used for the chloro-acid has been applied to the resolution of bromosulphoacetic acid. Strychnine and brucine, respectively, proved to be the most suitable alkaloids for the preparation of the pure *d*- and *l*-acids. Bromosulphoacetic acid has  $[M]_{589} 31^\circ$ ,  $[M]_{560} 37^\circ$ ,  $[M]_{533} 42^\circ$ ,  $[M]_{510} 47^\circ$ ,  $[M]_{486} 56^\circ$ , and the normal ammonium salt has  $[M]_{589} 16^\circ$ ,  $[M]_{560} 18^\circ$ ,  $[M]_{533} 21^\circ$ ,  $[M]_{510} 24^\circ$ ,  $[M]_{486} 27^\circ$ . Racemisation of acid and salt takes place slowly at the ordinary temperature, and is greatly accelerated by traces of strong bases.

L. L. B.

**Determination of Formaldehyde.** E. SCHULEK.—(See ii, 606.)

**Condensation of Aldehydes to Esters by Alkoxides.** W. C. CHILD and H. ADKINS (*J. Amer. Chem. Soc.*, 1925, **47**, 798—807; cf. A., 1924, i, 139).—The rapidity of condensation of furfuraldehyde, benzaldehyde, butaldehyde, acetaldehyde, and heptaldehyde to the corresponding esters in presence of aluminium ethoxide is in the order named. Furfuraldehyde condenses much more slowly than benzaldehyde, whilst the condensations of acetaldehyde and heptaldehyde have almost identical velocities. The activity of the following catalysts is in the order named, in the case of the condensation of acetaldehyde to ethyl acetate: titanium ethoxide, aluminium ethoxide, aluminium isopropoxide, and aluminium butoxide, the last two being practically identical as catalysts, but both more effective than the ethoxide. The rate of condensation is very slightly influenced by variations in relative amount of aldehyde and catalyst, indicating that an aldehyde-catalyst complex is first formed rapidly and then decomposes slowly into ester and catalyst. The following solvents depress the rate of condensation in the order: carbon tetrachloride, heptane, chloroform, xylene, ether, and benzene, the last three being about the same in this respect. Aluminium, ferric, zinc, and mercuric chlorides react with aluminium ethoxide to form the respective double compounds:  $\text{AlCl}_3 \cdot 3\text{Al}(\text{OEt})_3$ ,  $\text{FeCl}_3 \cdot 3\text{Al}(\text{OEt})_3$ ,  $\text{ZnCl}_2 \cdot 2\text{Al}(\text{OEt})_3$ ,  $\text{HgCl}_2 \cdot 2\text{Al}(\text{OEt})_3$ . The latter are much more active catalysts for the ester condensation than is aluminium ethoxide, but if excess of ferric or aluminium chloride is present, ester formation is reduced owing to the formation of paraldehyde. Zinc chloride is the best promoter in ethereal solution, whilst ferric chloride is the most active if the solvent is a mixture of butyl alcohol and ether or of ethyl alcohol and xylene.

F. G. W.

**Isomerism of Vinylalkylcarbinols and Ethyl Alkyl Ketones.** R. DELABY and J. M. DUMOULIN (*Compt. rend.*, 1925, **180**, 1277—1279).—Unsuccessful attempts have been made to prepare vinyl alkyl ketones by the oxidation of vinylalkylcarbinols (cf. Delaby, A., 1923, i, 84). Although allyl alcohol is converted into acraldehyde

by passage with oxygen over reduced silver (A., 1921, i, 218), this treatment has no effect on the vinylalkylcarbinols at temperatures up to  $330^{\circ}$ , whilst at higher temperatures dehydration and decomposition take place. Similarly, mild oxidising agents, *e.g.*, lead peroxide in sulphuric acid solution, have no action on the unsaturated alcohols, whilst more vigorous oxidising agents, *e.g.*, chromic acid in acetic acid solution, destroy the compound completely. By catalytic dehydrogenation (cf. Sabatier and Senderens, A., 1905, i, 401; Bouveault, A., 1908, i, 117) in a vacuum by passage over reduced copper, allyl alcohol yields a mixture of propaldehyde and acraldehyde, the former predominating. No advantage attaches to conducting the reaction in a vacuum in the case of the vinylalkylcarbinols, so that the ordinary pressure was used. On passing over reduced copper or nickel at  $200$ – $300^{\circ}$ , vinyl-ethyl-, vinylpropyl-, and vinylbutyl-carbinols give a 51–73% yield of diethyl, ethyl propyl, and ethyl butyl ketones, respectively. By the use of nickel, a lower temperature can be used and a better yield is obtained.

L. F. H.

**Preparation of Acyclic  $\delta$ -Diketones.** E. E. BLAISE and M. MONTAGNE (*Compt. rend.*, 1925, **180**, 1345–1346).—Magnesium ethyl bromide reacts with glutarobisdiethylamide to give, not only nonane- $\gamma\gamma$ -dione (cf. A., 1921, i, 647), but also a mixture of ketones separable by crystallisation of their semicarbazones. The first ketone,  $\delta$ -ketoheptdiethylamide, b. p.  $163^{\circ}/14$  mm. (semicarbazone, m. p.  $126$ – $127^{\circ}$ ), on treatment with hydrobromic acid yields diethylamine and  $\delta$ -ketoheptioic acid (cf. Blaise and Maire, A., 1908, i, 392). The second ketone,  $\gamma$ -diethylamino- $\gamma$ -diethylnonan- $\eta$ -one, b. p.  $161^{\circ}/17$  mm. (semicarbazone, m. p.  $90^{\circ}$ , picrate, m. p.  $106$ – $107^{\circ}$ ), when treated with acetic anhydride, gives rise to acetdiethylamide and an unsaturated ketone.

L. F. H.

**Three-carbon System. IV. A Case of Retarded Mobility.** G. A. R. KON and R. P. LINSTAD (*J. Chem. Soc.*, 1925, **127**, 815–821).—The chlorides of  $\Delta^1$ -cyclohexenylacetic acid and cyclohexylideneacetic acid both give rise to the same cyclohexenylacetone, having the  $\beta\gamma$  structure, the  $\alpha\beta$  form changing to the more stable  $\beta\gamma$  without the aid of any reagent. The same mobility of the three-carbon system is found in the case of cyclopentenylacetone, which possesses the  $\beta\gamma$  structure, and although it reacts in the  $\alpha\beta$  form with ethyl sodiomalonate, it readily undergoes alkylation to  $\alpha$ -ethyl- $\Delta^1$ -cyclopentenylacetone, b. p.  $84$ – $86^{\circ}/14$  mm. (semicarbazone, m. p.  $167^{\circ}$ ). A contrast is found in the case of the ketones produced from  $\beta\beta$ -diethylacrylic acid and  $\beta$ -ethyl- $\Delta^2$ -pentenoic acid, respectively. These are  $\delta$ -ethyl- $\Delta^{\gamma}$ -hexen- $\beta$ -one (the  $\alpha\beta$  form), b. p.  $164^{\circ}/770$  mm.,  $d_4^{17.9}$  0.85633,  $n_D^{17.9}$  1.45223 (semicarbazone, m. p.  $159^{\circ}$ ), and  $\delta$ -ethyl- $\Delta^{\delta}$ -hexen- $\beta$ -one (the  $\beta\gamma$  form), b. p.  $163$ – $164^{\circ}/756$  mm.,  $d_4^{19.6}$  0.85883,  $n_D^{19.6}$  1.44301 (semicarbazone, m. p.  $144$ – $145^{\circ}$ ; cf. this vol., i, 506). The two are quite distinct and non-tautomeric under the conditions of synthesis, but in the presence of sodium ethoxide both condense equally readily with ethyl sodiomalonate to form an ester which hydrolyses to 3:5-diketo-1:1-diethylcyclohexane

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(*diethylhydihydroresorcinol*), m. p. 113°. Dilute sulphuric acid converts the  $\alpha\beta$  form quantitatively into the more stable  $\beta\gamma$  form.

B. W. A.

**cycloTelluropentanediones Containing Aliphatic and Aromatic Substituents.** G. T. MORGAN and C. J. A. TAYLOR (*J. Chem. Soc.*, 1925, 127, 797—806; cf. A., 1924, i, 1044).—Dipropionylmethane condenses with tellurium tetrachloride, forming 2 : 6-dimethylcyclostelluripentane-3 : 5-dione-1 : 1-dichloride, which on reduction yields 2 : 6-dimethylcyclostelluropentane-3 : 5-dione which, under the name of tellurium dipropionylmethane, was already known as a powerful germicide. The diketonic structure of this substance is shown by the production of its *dioxime*, decomp. 168—170°. The monoenolic form of dipropionylmethane being present in the above condensation, some tellurium *O*-ethylpropionylmethane trichloride is formed, but with  $\gamma$ -methylpropionylmethane, b. p. 92°/10 mm. (copper compound, m. p. 172—173°), this tendency is inhibited, and 2 : 4 : 6-trimethylcyclostelluripentane-3 : 5-dione 1 : 1-dichloride (darkens at 180°) is the sole product, giving on reduction 2 : 4 : 6-trimethylcyclostelluropentane-3 : 5-dione, m. p. 135° (decomp.); *dioxime*, decomp. 170°. Similar condensations with  $\gamma$ -benzylacetylacetone, b. p. 150°/3 mm., and with  $\gamma\gamma$ -dibenzylacetylacetone, m. p. 111—112° (copper compound, m. p. 176°; sodium compound, m. p. 101°), yield telluridichlorides, decomp. 180° and m. p. 189—190° (decomp.), which form on reduction 4-benzylcyclostelluropentane-3 : 5-dione, m. p. 153° (decomp.) (*dioxime*, decomp. 168—170°), and 4 : 4-dibenzylcyclostelluropentane-3 : 5-dione, m. p. 128° after softening at 123°, respectively. On attempting to condense tellurium tetrachloride with diisobutrylmethane, b. p. 75—77°/7 mm. (copper compound, m. p. 113—114°), only a small quantity of tellurium *O*-ethyl-diisobutrylmethane trichloride,  $\text{CHMe}_2\cdot\text{C}(\text{OEt})\cdot\text{CH}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{TeCl}_3$ , m. p. 87—89°, is obtained, whereas condensation with *n*-octoylacetone and with *n*-nonoylacetone readily yields, respectively, 2-*n*-hexylcyclostelluripentane-3 : 5-dione 1 : 1-dichloride, m. p. 80°, which on reduction gives 2-*n*-hexylcyclostelluropentane-3 : 5-dione, m. p. 74—75°, and 2-*n*-heptylcyclostelluripentane-3 : 5-dione 1 : 1-dichloride, m. p. 89°, which on reduction gives 2-*n*-heptylcyclostelluropentane-3 : 5-dione, m. p. 89°. Thus terminal branched chains inhibit cyclic linking where long normal chains do not. Another product of the last-named condensation is tellurium *n*-nonoylacetone trichloride, m. p. 114—115°.

B. W. A.

**Compounds of Sugars with Sulphuric Acid.** I. H. OHLE and W. BOURJAN (*Ber.*, 1925, 58, [B], 721—723).—The compound, m. p. 143°, obtained by the action of acetobromoglucose on silver sulphate in the presence of pyridine (cf. Ohle, A., 1922, i, 987) is found to contain nitrogen and is regarded as *tetra-acetyldextrose-1-pyridinium tetra-acetyldextrose- $\zeta$ -sulphate*. It can also be prepared from silver tetra-acetyldextrose- $\zeta$ -sulphate and acetobromoglucose in pyridine solution.

H. W.

**Structure of Phenylhydrazones of Dextrose.** M. FRÉRE-JACQUE (*Compt. rend.*, 1925, **180**, 1210—1212).—It is shown that the isomeric phenylhydrazones of dextrose (Fischer, A., 1887, i, 567; Skraup, A., 1889, i, 1130; Behrend and Lohr, A., 1908, i, 765) are not derivatives of  $\alpha$ - and  $\beta$ -dextrose, respectively (Simon and Bénard, A., 1901, i, 257), but are dynamic isomerides derived from  $\alpha$ -dextrose, one having, it is suggested, the oxidic ring structure and the other being a true phenylhydrazone (cf. Hofmann, A., 1909, i, 519; Behrend and Reinsberg, A., 1911, i, 83). The evidence for this view is that on hydrolysis with oxalic acid both phenylhydrazones yield a solution of dextrose of which the rotation falls on making alkaline, and therefore contains  $\alpha$ -dextrose. Alkali hydroxide increases the rate of mutarotation of dextrose, but greatly decreases the rate of mutarotation of the phenylhydrazones.

L. F. H.

**Derivatives of Maltose and Dextrose.** K. FREUDENBERG, H. VON HOCHSTETTER, and H. ENGELS (*Ber.*, 1925, **58**, [B], 666—671).—The compound obtained previously by Freudenberg and Ivers (A., 1922, i, 524) by the action of a saturated solution of hydrogen chloride in anhydrous ether on octa-acetylmaltose dissolved in benzene is shown to be *hepta-acetylchloromaltose* containing about 4% of hepta-acetylmaltose. It is stable in the absence of moisture, by which it is converted readily into the known hepta-acetylmaltose. It is transformed by methyl alcohol in the presence of pyridine into a crystalline *hepta-acetylmethylmaltoside*, m. p. 163—164°,  $[\alpha]_{578} +101.6^\circ$ , in *s*-tetrachloroethane, which, when treated with ammonia, yields a syrupy *methylmaltoside*,  $[\alpha]_{578} +117.12^\circ$  in aqueous solution, from which the hepta-acetate is re-formed by the cautious action of acetic anhydride and pyridine. It is suggested that these compounds are of the  $\gamma$ -glucosidic type. *Hepta-acetylmethylmaltoside*, m. p. 142—143°, yields similarly a non-crystalline *ethylmaltoside*. Hepta-acetylchloromaltose and silver acetate appear to give a new *octa-acetylmaltose*.

Dextrose diisopropylidene ether is converted by successive treatment with sodium and ether (cf. Freudenberg and Hixon, A., 1923, i, 1179) and benzyl bromide into  *$\gamma$ -benzyl dextrose diisopropylidene ether*, b. p. 165—169°/0.2—0.5 mm.,  $[\alpha]_{578} -26.9^\circ$  in ethyl alcohol, which is hydrolysed by dilute sulphuric acid to  *$\gamma$ -benzyl dextrose*, m. p. 127—128°,  $[\alpha]_{578} +29.1^\circ$  in aqueous solution (*osazone*, m. p. 149—150°).  *$\gamma$ -Allyl dextrose diisopropylidene ether*, b. p. 133°/2 mm.,  $[\alpha]_{578} -21.01^\circ$  in *s*-tetrachloroethane, and  *$\gamma$ -allyl dextrose*, m. p. 131°,  $[\alpha]_{578} +37.15^\circ$  in aqueous solution (*osazone*, m. p. 145°), are prepared similarly.

H. W.

**Mutarotation. V. Solution Volume and Refraction Constants of Lævulose.** C. N. RIIBER and V. ESP [with E. BERNER] (*Ber.*, 1925, **58**, [B], 737—746; cf. A., 1924, ii, 806; this vol., i, 8).—The increase in volume of an aqueous solution of lævulose which is undergoing mutarotation is about six times as great as that observed with  $\alpha$ -dextrose. Whereas the refractive index increases gradually with dextrose, it falls with lævulose in

such a manner that the refraction constant,  $m(n-1)/d$ , remains almost unchanged. The mutarotation of lævulose is accompanied by the absorption of about eight times the amount of heat evolved during the mutarotation of dextrose. The velocity constant of the conversion of  $\beta$ -lævulose into the equilibrium mixture is 0.0839, 0.0862, 0.0850, and 0.0824 at 20°, according to the dilatometric, interferometric, calorimetric, and polarimetric methods; greater concordance cannot be expected, since the change occurs so rapidly (half-period  $3\frac{1}{2}$  mins.) that it is considerably advanced before measurements can be made. Attempts to isolate crystalline  $\alpha$ -lævulose in the homogeneous condition were unsuccessful; the proportion of  $\alpha$ - to  $\beta$ -lævulose in the product obtained by cautiously melting and rapidly cooling the  $\beta$ -compound is greater than that in the equilibrium mixture in aqueous solution. The equilibrium between the  $\alpha$ - and  $\beta$ -forms is established slowly in the solid product, the half-period being about 5 days at 20°. H. W.

**Relations between Rotatory Power and Structure in the Sugar Group. IX. Rotation of the  $\alpha$ -Form of Methylgentobioside.** C. S. HUDSON (*J. Amer. Chem. Soc.*, 1925, **47**, 872—873).—The rotation of  $\alpha$ -methylgentobioside (cf. Helferich and Becker, this vol., i, 9) is in good agreement with that predicted by Hudson and Johnson (cf. A., 1917, i, 446). F. G. W.

**Hydrolytic Products of Fermentation of Rhamnicoside : Primeverose and Rhamnicogenol.** M. BRIDEL and C. CHARAUX (*Compt. rend.*, 1925, **180**, 1219—1222).—On hydrolysis with acids or boiling water, rhamnicoside (cf. this vol., i, 621) yields primeverose and a compound insoluble in water. The same products have been obtained by the action of the enzyme obtained from plants containing rhamnicoside; the fermentation proceeds rapidly, despite the insolubility of both the enzyme and the substrate, probably due to the formation of a loose compound which forms an emulsion. The insoluble compound, *rhamnicogenol*,  $C_{15}H_{12}O_6$ , m. p. 193°, has a green fluorescence in solution, is unstable in most solvents, gives a pink coloration with aqueous sodium hydroxide, and an emerald-green colour with ferric chloride, and, it is suggested, is a pentahydroxymethylanthranol. The hydrolysis of rhamnicoside is represented by the equation  $C_{26}H_{30}O_{15} + H_2O = C_{11}H_{20}O_{10} + C_{15}H_{12}O_6$ . L. F. H.

**Mechanism of the Action of Amylases. Constitution of Starch.** R. KUHN (*Annalen*, 1925, **443**, 1—71).—The relationship of activity to hydrogen-ion concentration in the action of malt amylase on potato starch and on the dextrins remaining after saccharification of 75% of the starch indicates that the change is not noticeably dependent on the nature of the substrate, but that the affinity of the amylase towards the dextrins produced becomes continuously less. Whereas a definite amount of enzyme in solutions of starch of increasing concentrations produces within wide limits equal quantities of sugar in equal intervals of time, the amounts produced by the action of amylase on solutions of the

"residual substances" increase regularly with increasing concentration of the latter. The position of the limit of saccharification is governed by the presence of one or more of the constituents of malt which either pass more slowly than the amylase into solution or are formed during the maceration of the fermented barley (cf. Pringsheim and Beiser, A., 1924, i, 106, 1142). The "autoexcitation" of malt extract (cf. Maquenne, A., 1906, ii, 623) is due to the presence of these substances and may therefore be attributed to an increase of the affinity of diastase towards dextrins of low molecular weight; the simultaneous production of acid is solely responsible for the initial velocity of saccharification of starch, but has no influence on the quantitative production of maltose. The assumption of the presence of two enzymes of differing stability (*e.g.*, amylase and dextrinase) does not appear to be necessary. For the conversion of amylose into crystalline maltose in 96% yield it is usually sufficient to shake kiln malt with water in the presence of toluene for 4–6 hrs. and to allow the extract, after dialysis, to react with the polysaccharide at  $p_H$  4–5.

The possibility is established of obtaining from yeast suitable maltase-free activators for the hydrolysis of the "residual substances" of starch in the presence of malt amylase (cf. Pringsheim and Fuchs, A., 1924, i, 965; Holmbergh, A., 1924, i, 799).

In the saccharification of starch by malt extract at a high temperature (cf. Brown and Heron, J., 1879, 35, 596), the diminution of optical activity is completely parallel with the increase of reducing power, but this parallelism is lost when enzymic hydrolysis occurs rapidly in the cold (cf. Brown and Morris, T., 1885, 47, 527). If the ultimate content of maltose of solutions obtained by the action of maltase-free amylase solutions from green and kiln malt on soluble starch or amylose is determined by the reducing power and this value is applied to the ascending portion of the time-optical rotation graph, it is found that the curve is coincident with that given by the mutarotation of an equally concentrated solution of crystalline maltose at the same temperature and hydrogen-ion concentration; it follows, therefore, that the whole of the maltose is formed by the action of malt amylase on starch as the  $\beta$ -variety,  $[\alpha]_D^{20} + 112^\circ$ . The assumption that this form of the disaccharide exists preformed in the molecule of amylose and amylopectin appears to receive confirmation from the observation that the hydrolysis of Lintner starch and amylose is restricted to a greater extent by  $\beta$ -maltose than by the equilibrium mixture of the  $\alpha$ - and  $\beta$ -forms. The steric relationship of malt amylase to the  $\beta$ -sugar is not, however, universal, since malt extracts have been isolated which show less or no differences in the restrictive powers of  $\beta$ - and  $\alpha\beta$ -maltose. The phenomena just described considered in conjunction with the quantitative transformability of amylose into maltose by purified emulsin render it possible that  $\alpha$ - and  $\beta$ -linkings between the dextrose residues occur in regular sequence in the carbohydrates of starch. The partly  $\beta$ -glucosidic nature is supported by the production of lævoglucozan by the dry distillation of starch (Pictet and Sarasin, A., 1918, i, 59), since this compound

can be derived from  $\beta$ - but not from  $\alpha$ -dextrose (Karrer, A., 1920, i, 370). The presence of butylene-oxide dextrose residues cannot, however, be regarded as placed beyond doubt (see below). Taka-diastase, on the other hand, appears to attack the  $\alpha$ -linkings of polysaccharides. The maltose formed by rapid saccharification in cold solution exhibits marked decreasing mutarotation; the partial restriction of the enzyme by maltose is mainly, if not entirely, due to  $\alpha$ -maltose. Pancreas amylase resembles taka-diastase in yielding a decreasing mutarotatory maltose; the mutarotation graphs indicate the initial production of a disaccharide having  $[\alpha]_D^{20} +158^\circ \pm 5^\circ$ , which agrees within the possible limits of experimental error with the value,  $[\alpha]_D^{20} +160^\circ$ , calculated for  $\alpha$ -maltose by Hudson and Yanovsky (A., 1917, i, 445). A difference in the restrictive action of  $\alpha$ - and  $\beta$ -maltose could not be established, but this is not surprising, since the equilibrium between the two forms of the disaccharide is established with unusual rapidity at the optimal hydrogen-ion concentration for the action of pancreas amylase. It appears, therefore, that the amylases are divisible into  $\alpha$ - and  $\beta$ -groups in accordance with the variety of maltose initially produced; it is considered improbable that the differences in the direction of mutarotation can be caused by a Walden inversion.

Somewhat unexpectedly, the final product of the hydrolysis of starch is found to be independent of the nature of the amylase used. Since during rapid saccharification by pancreas amylase the initial fall in optical activity of the solution is followed by a sudden rise and then by the slow fall which is attributed to the mutarotation of  $\alpha$ -maltose, it is assumed that the dextrose residues which acquire reducing power in the presence of  $\beta$ -amylases do not contain the butylene-oxide ring. The phenomena of mutarotation therefore receive the following explanation. If the  $\beta$ -linkings are loosened (*e.g.*, by malt diastase) isomerisation with production of the butylene-oxide ring such as is present in maltose occurs in the reducing dextrose residue of the primary disaccharide, and has no influence on the mode of union of the two dextrose residues. If, however, the  $\alpha$ -glucosidic linkings are first affected by enzymic hydrolysis, ring extension or closure must occur in the non-reducing sugar residue. This change directly affects the spatial orientation of the second dextrose residue which is also attached to the  $\alpha$ -carbon atom. In addition to the closure of the oxygen bridge in the  $\alpha$ -position, a transition of the  $\beta$ -linking into the  $\alpha$ -linking of a new maltose molecule occurs which finds its expression in an immediate increase of the optical activity.

The observations made during the saccharification of glycogen by pancreas amylase are so similar to those observed with starch that the theoretical considerations deduced with regard to the constitution of the latter are probably applicable also to glycogen.

A critical review of the literature leads the author to the conclusion that neither the polyamyloses nor the hexosans can be regarded with certainty as the fundamental units of the starch molecule, since each class of compound has the characteristics of starch to only a limited extent. Pringsheim's recent extension of



the two-enzyme theory of the amylases ("Die Polysaccharide," 1923, p. 141) by the conception of an amylobiase which causes depolymerisation of the starch molecule to the non-reducing hexosans (A., 1924, i, 1170), does not appear to be necessary, and the quantitative conversion of trihexosan into maltose by the amylases (*loc. cit.*) is more readily explained by the assumption of inter- and intra-glucosidic isomerisations than by the hypothesis of the elimination of a dextrose group as a radical which subsequently unites with a second similar radical to yield maltose.

H. W.

**Effect of Heat on Cellulose.** J. W. BAIN and G. F. KAY (*Univ. Toronto, Sch. Eng. Res. Bull.*, 1925, 5, 119—122; cf. Karrer, A., 1920, i, 370; Pictet and Sarasin, A., 1918, i, 59).—Cotton wool, when heated to incipient decomposition, yields a small quantity of a dextrorotatory substance which reduces Fehling's solution and yields a phenylosazone with the melting point of dextrophenylosazone. A reducing substance, probably a sugar, is formed also when cotton wool is heated to 190—200° with water in an autoclave.

T. H. P.

**Constitution of Cellulose.** R. O. HERZOG (*Cellulosechemie*, 1925, 6, 39—40).—Assuming that, according to the Röntgen spectrogram, the elementary unit of cellulose comprises four  $C_6$  residues, these may be united in various ways: (1) The cellulose consists of interminable chains of  $C_6$  components arranged so that each set of four occupies a position of crystallographic symmetry relatively to the other sets, with or without chemical bonds of valency uniting components in the different sets. (2) The cellulose consists of an anhydride of a single  $C_6$  residue, four of these anhydride units in a cell, the cells being symmetrically arranged, but neither the components nor the cells being necessarily united by chemical bonds. (3) The cellulose consists of an anhydride of a disaccharide, two in a cell, other conditions being as defined under case (2). Then, if the cellulose molecule is  $(C_6H_{10}O_5)_n$ ,  $n$  may be 1 (case 2), 2 (cases 2 and 3), 4 (cases 2 and 3), or indefinitely large (case 1), but  $n$  cannot be 3, 5, or any larger odd number.

J. F. B.

**Röntgen-spectrographic Phenomena in the Swelling of Cellulose in various Alkali Hydroxide Solutions.** J. R. KATZ (*Cellulosechemie*, 1925, 6, 35—37).—When cellulose swells in a solution of an alkali hydroxide the characteristic interference stripes in the Röntgen spectrum of cellulose gradually disappear as the concentration of the alkali is increased and new equatorial bands appear. The concentration at which the most characteristic cellulose stripes totally disappear and the new bands acquire their full development coincides with the concentration at which the formation of a chemical compound, alkali-cellulose, is indicated by the flat portion of the absorption curve by Vieweg's method. This change in the Röntgen spectrogram is identical for the hydroxides of lithium, sodium, and potassium at concentrations corre-

sponding with the combination of equimolecular proportions. Hence the new band characterises hydrated cellulose rather than any specific alkali-cellulose compound. When the alkali-cellulose is decomposed by washing, the original interference stripes of cellulose reappear, but the new band characteristic of hydrated cellulose persists in the regenerated product. Further, in this modified product the size of the mesh or network of the elementary units in the Röntgen spectrogram is distinctly enlarged, this distension amounting in some cases to 4% or more. On re-treating the hydrated cellulose with solutions of alkali hydroxide, the intensity of the characteristic cellulose spectrum begins to diminish at a lower concentration than in the case of the original cellulose, showing that hydrated cellulose is more susceptible to attack.

J. F. B.

**Röntgen-spectrographic Observations.** J. R. KATZ (*Cellulosechemie*, 1925, 6, 37—39).—The Röntgen-spectrographic diagram of cellulose reveals elementary units which correspond with dimensions not greater than four  $C_6$  residues. In order to reconcile this relatively small dimension of the cellulose molecule with the ideas existing previously as to the highly polymerised condition of cellulose, Fringsheim's view may be considered, according to which the four  $C_6$  residues are held together by primary valencies, whilst several of such molecules are united by secondary valencies to form associated or polymerised aggregates. In support of this, it may be postulated that the size of the mesh of the network of elementary units or molecules is smaller, *i.e.*, the units are more compactly associated the more powerful the action of the secondary valencies, and the stronger these forces the larger is the polymerised or associated aggregate. It has now been observed that after mercerisation or hydration the network of elementary units in the Röntgen spectrogram is distinctly enlarged and this distension may amount to 4% or more. Distension of the network is particularly marked in various artificial silks and the degree of distension is subject to variations with different specimens of similar "silk." The measurement of the size of the network may therefore indicate the degree of "depolymerisation" according to the older nomenclature, *i.e.*, distension of the spacing of the elementary units may indicate a weakening of the secondary affinities and a diminution of the number of the associated molecules.

J. F. B.

**Röntgen Diagram of Hydrated Cellulose and its Behaviour in Reversion Treatments.** J. R. KATZ and H. MARK (*Z. Elektrochem.*, 1925, 31, 105—112; cf. preceding abstracts).—No appreciable change can be detected in the Röntgen diagram when ramie fibre is swollen with saline hydrating agents or with sulphuric or hydrochloric acid. The new interference stripes described (*loc. cit.*) as characteristic of mercerised cellulose are produced equally by the various alkali hydroxides, "cuprammonium" solution, and by nitric acid. In the process of mercerisation and washing, the fibre passes through a plastic stage, and if it is stretched and dried

at this stage the physico-chemical phenomena accompanying hydration are partly reversed, in that the increased absorption capacity for water and dissolved substances is diminished; at the same time, the parallel orientation of the crystallites is increased. Treatments which have the object of reversing or decreasing the degree of hydration, such as prolonged stoving or digestion under pressure or boiling with alcohol, may reduce the absorptive capacity, but have no effect on the characteristic mercerisation bands of the Röntgen spectrum. From these observations it follows that these mercerisation bands are the irreversible result of the action of certain hydrating agents, but not of others, hence it is probable that these bands are not characteristic of the difference between ordinary cellulose and hydrated cellulose. Rather it appears that they indicate some chemical isomeric change in the substance of the cellulose, for instance, the transposition of an oxygen bridge or the opening up of a new hydroxyl group under the specific action of certain reagents. A less probable alternative is that they represent the crystallisation or the appearance of optical reflexion activity in some ordinarily amorphous component of the cellulose structure; for instance, the substance in which the crystallites are embedded.

J. F. B.

**Cellulose. XIII. K. HESS. Acetolysis of Cellulose. I.** W. WELTZEL and R. SINGER (*Annalen*, 1925, **443**, 71—112).—The action of acetic anhydride in the presence of sulphuric acid on cellulose leads to the production of cellulose acetate, cellulose acetate *A*, cello-dextrin acetates which are divisible into a number of groups in accordance with their solubility or insolubility in alcohol and ether, cellobiose octa-acetate, and dextrose penta-acetate. Slow separation of the cello-dextrin acetates from very dilute alcoholic solution permits the isolation of a crystalline material which is identified as celloisobiose acetate. The approximately straight graph showing the relationship between molecular weight and specific rotation of the various fractions of the cello-dextrin acetates indicates that the latter are mixtures of few substances, and its approximation to the straight line between cellulose acetate *A* and celloisobiose acetate points to the conclusion that only these two substances are present.

The action of acetic anhydride containing about 10% of sulphuric acid on cellulose at the atmospheric temperature gives cellobiose octa-acetate, cello-dextrin acetates, and monose derivatives soluble in water in about equal amount. Cellulose triacetate yields the same products when subjected to acetolytic degradation, but the yield of cellobiose octa-acetate is very much less. To account for the yield of cellobiose from acetyl-free cellulose, it is therefore necessary to assume a second mode for its production, namely, through non- or partly-acetylated celloisobiose. Contrary to the usual hypothesis, therefore, the main change is primarily in the direction of sulpholysis, not acetolysis. This appears to be quite probable in view of the extremely slow acetylation of free cellulose, and is confirmed by Madsen's observation (*Diss.*, Hannover, 1917)

that the highest yields of cellobiose are furnished when acetic anhydride is used without addition of acetic acid only in the presence of relatively large quantities of sulphuric acid (15—20%); similar high concentrations of sulphuric acid are also used by Freudenberg (A., 1921, i, 401) at the atmospheric temperature. During acetolysis, a certain amount of cellulose acetate remains mixed with the celloextrin acetates. According to Freudenberg (*loc. cit.*), the acetylation of free cellobiose in the acetolysis mixture is complete within 2—3 hrs.; in this period, the sulpholytic action is slight in comparison with the acetylating change. The loss of cellobiose due to sulpholytic change must therefore be regarded as taking place during contact with the mixture subsequent to acetylation. According to Freudenberg's data, about half of the substances soluble in water are derived from cellobiose octa-acetate; the remainder must be assumed to be formed from celloisobiose acetate; the loss of cellobiose acetate amounts to at least 25%. According to Ost (A., 1906, i, 560) dextrose is produced mainly as the tetra-acetate by the action of acetylating mixtures containing 10% of sulphuric acid; the yield of 33% obtained in the author's experiments is therefore that of the tetra-acetate, whereas that of the penta-acetate is somewhat higher than that recorded. Since celloisobiose octa-acetate is not convertible into cellobiose octa-acetate, it is possible that the conversion of cellulose into dextrose occurs through celloisobiose; the scheme proposed previously (A., 1924, i, 142) cannot, however, be excluded completely. A change in the conditions of the reaction (variation of acid concentration, temperature, etc.) brings about displacements of the relative rates of the reactions, thus leading to higher or lower yields of cellobiose (cf. Ost, A., 1913, i, 446).

It is considered that for the present cellobiose and its constitution are less important for the investigation of cellulose than is the elucidation of the structure of celloisobiose. The irreversible transformation of celloisobiose into cellobiose indicates that in all probability labile isomerides of the sugars or their anhydrides are the units of cellulose.

H. W.

**Cellulose Acetonitrate.** K. ATSUKI (*J. Fac. Eng. Tokyo*, 1925, 15, 309—316).—Cellulose acetonitrates of varying composition were obtained by adding 100 g. of cellulose nitrate (11·13% N), in small quantities and with constant agitation and cooling, to a mixture of 400 g. of glacial acetic acid, 400 g. of acetic anhydride, and 0—17·5 g. of sulphuric acid. After 2 hrs. the resulting viscous solution was poured into a large quantity of cold 2% sodium carbonate solution. With increasing proportions of sulphuric acid in the acetylating bath, the precipitated product varied in character from a hard, corneous mass, difficult to wash or stabilise by boiling, to a voluminous powder. The extent of acetylation, *i.e.*, replacement of nitro groups by acetyl groups, increases with increase in the sulphuric acid content of the acetylation bath, and with an optimum proportion of sulphuric acid the unnitrated hydroxyl groups in the cellulose nitrate molecule become attacked and

acetylated. An excess of condensing agent, however, reduces the total number of acid radicals, probably owing to its hydrolytic action. Cellulose acetonitrate burns quietly, showing no sign of explosion, but on being heated for several hours at 50° acetic and nitrous fumes are evolved in considerable quantity. Its viscosity (in acetone solution) is much lower than that of the corresponding cellulose nitrate and its solubility in alcoholic camphor is negligibly small.

D. J. N.

**Tendering of Cotton Fabric by Acids.** H. F. COWARD, F. C. WOOD, and F. L. BARRETT (*J. Text. Inst.*, 1923, **14**, T 520—528).—The tendering of cotton when left in contact with acids, usually ascribed to the formation of “hydrocellulose,” has been studied by means of strength tests and also by measuring the viscosity of solutions of the material in ammoniacal copper oxide solution, the latter being the more sensitive indicator. In aqueous solutions, the tendering is roughly parallel to the hydrogen-ion concentration at constant temperature, and is a function of temperature. Solutions of hydrogen chloride in ether, alcohol, and benzene are much more destructive than aqueous solutions of the same concentration at the same temperature, but the dry gas itself only reacts very slowly with dry cotton at the ordinary temperature.

J. C. W.

**Unsaturated Aldehydes and their Relation to  $\alpha$ -Lignin.** E. HÄGGLUND (*Cellulosechemie*, 1925, **6**, 29—35).—According to Klason,  $\alpha$ -lignin reacts with sulphurous acid in virtue of the presence of an acraldehyde or similar unsaturated aldehydic residue. Studies with acraldehyde and crotonaldehyde have shown analogous reactions, but it is concluded that the sulphonic acid group attaches itself to the  $\beta$ -carbon atom and not to the  $\alpha$ , in relation to the aldehyde group. With the  $\beta$ -sulphonic acids of the unsaturated aldehydes, naphthylamine compounds have been prepared exactly similar to those with lignosulphonic acid from sulphite wood liquor. It is shown that in the presence of an excess of acid these  $\beta$ -sulphonic acids of aldehydes yield, with aromatic amines, anils of the free sulphonic acid, one amino group combining with the aldehyde. In neutral solutions, 2 mols. of the amine react, one forming the anil and the other the normal naphthylamine salt of the sulphonic acid. Cinnamaldehyde in the presence of hydrochloric acid undergoes condensation of the aldol type and the resulting aldol forms an anil with naphthylamine. It is probable that under certain conditions  $\alpha$ -lignosulphonic acid also tends to form associated molecules by aldol condensation.

J. F. B.

**Determination of Lignin.** H. SCHWALBE (*Papier-Fabr.*, 1925, **23**, 174—177).—The determination of lignin as a residue after complete saccharification of the cellulose by strong mineral acids is greatly facilitated by moistening the material with hydrochloric acid, *d* 1.07, and then adding 72% sulphuric acid. The evolution of hydrogen chloride thus produced opens up the material so that the cellulose is rapidly dissolved by the sulphuric acid without the

objectionable gelatinisation which takes place when the latter is used alone. Rise of temperature is to be avoided and rapid filtration is ensured by not keeping the product of the reaction too long before collecting the residue. Results are generally substantially lower than by the older methods. The material should be previously freed from fat and resin. [Cf. *B.*, 1925, 395.] J. F. B.

**Resolution of Coal by Oxidation.** W. FRANCIS and R. V. WHEELER (*Trans. Amer. Inst. Min. Mech. Eng.*, 1925, No. 1430—1).—A more detailed account of work already abstracted (this vol., i, 373). C. J. S.

**Preparation of Diacetoneamine.** P. R. HAESELER (*J. Amer. Chem. Soc.*, 1925, 47, 1195—1196).—Mesityl oxide (200 g.) and 27% aqueous ammonia (280 c.c.) are mixed and cooled. The liquid is homogeneous after stirring for 3 hrs., and is then kept for 3 days at the ordinary temperature. Excess of ammonia is removed by means of a current of air, the solution mixed with an equal volume of absolute alcohol, and the diluted mixture titrated with oxalic acid, using litmus as an outside indicator. It is then added, with stirring and cooling, to the calculated amount of oxalic acid, dissolved in alcohol (4 litres). This mixture is heated at 70°, with stirring, filtered hot, and the diacetoneamine hydrogen oxalate is allowed to crystallise, the residue being once more extracted with boiling alcohol. After separation of the crystals, a further crop is obtained by evaporating the mother-liquor at 70°. The yield is 310 g. (68%), m. p. 126—127°, the only impurity being 1—2% of ammonium hydrogen oxalate. F. G. W.

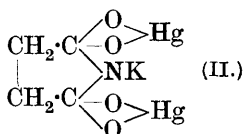
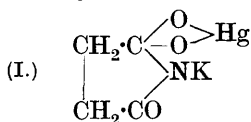
**Heavy-metal Salts of Disubstituted Dithiocarbamic Acids.** G. S. WHITBY and G. L. MATHESON (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 111—114).—Amines are converted into dithiocarbamates by causing them to react with carbon disulphide in the presence of a suitable base. The heavy-metal dithiocarbamates are conveniently obtained by precipitating aqueous solutions of the corresponding potassium or ammonium salts with solutions of the heavy-metal acetates, followed by recrystallisation from some organic solvent. Zinc, cadmium, and nickel pentamethylenedithiocarbamate (m. p. 232°, 257°, 295·5°), diethyldithiocarbamate [m. p. 180°, 251° (decomp.), 236°], dipropyldithiocarbamate (m. p. 114°, 160·5°, 135·5°), phenylmethyldithiocarbamate [m. p. 254°, 295° (decomp.), about 300° (decomp.)], phenylethyldithiocarbamate (m. p. 208°, 281°, 271°), and phenylisoamyldithiocarbamate (m. p. 247°, 222°, 196°) are described. Aqueous solutions of ammonium phenylethyldithiocarbamate give precipitates with salts of lead, aluminium, mercury, tin, copper, manganese, silver, bismuth, and cobalt. Magnesium and the alkaline-earth metals give no precipitate. J. S. C.

**Two Forms of Nitroguanidine.** T. L. DAVIS, A. A. ASHDOWN, and H. R. COUCH (*J. Amer. Chem. Soc.*, 1925, 47, 1063—1066).— $\alpha$ -Nitroguanidine is obtained when guanidine nitrate is dissolved in concentrated sulphuric acid and the solution poured into water.

It forms long needles,  $n_a$  1.518,  $n_\beta$  > 1.668,  $n_\gamma$  > 1.768, double refraction 0.250.  $\beta$ -Nitroguanidine. is produced, with varying proportions of the  $\alpha$  form, by nitration of the mixture of guanidine and ammonium sulphates obtained by the hydrolysis of dicyanodiamide with sulphuric acid. It forms fern-like clusters of elongated plates,  $n_a$  1.525,  $n_\gamma$  1.710, double refraction 0.185. Both forms have m. p.  $232^\circ$  (decomp.), and the same molecular weight in aqueous solution. They crystallise unchanged from water, and can be separated by fractional crystallisation from this solvent. They yield identical nitrates and hydrochlorides, from which only the  $\alpha$  form is regenerated on crystallisation from water. Dilution of a solution of either form in concentrated sulphuric acid affords only the  $\alpha$  form.

F. G. W.

**Mercury Derivatives of some Imides.** E. LYONS (*J. Amer. Chem. Soc.*, 1925, **47**, 830—833).—When succinimide, dissolved in cold aqueous potassium hydroxide solution, is treated with mercuric acetate solution (about 1 mol. per mol. of succinimide) and the mixture poured into alcohol, the yellow *potassium* salt (I) of a monomercury succinimide derivative is obtained (cf. Dessaignes,



*Annalen*, 1852, **82**, 234; Menshutkin, *ibid.*, 1871, **162**, 171; Landsberg, A., 1883, 475). This is soluble in water, and yields, when treated as above with another equivalent of mercuric acetate and potassium hydroxide, the greenish-yellow *dimercury* derivative (II). Analogous water-soluble mono- and di-mercury compounds were obtained similarly from phthalimide (white and orange, respectively), whilst "saccharin" afforded mono- (white), di- (white), and tri-mercury (greenish-yellow) derivatives. The mercury atoms of the above compounds are less firmly held than those of true organomercury derivatives.

F. G. W.

**Synthesis of Sodium Cyanide from Sodium Sulphate or Sodium Chloride.** R. HARA and H. MIURA (*Tech. Repts. Tohoku Univ.*, 1925, **4**, 191—211).—Sodium cyanide has been produced in good yield by heating at  $1000^\circ$  in an electric furnace a mixture of sodium sulphate, barium carbonate, and carbon, together with iron powder as catalyst, in a slow stream of nitrogen. 85.5% of the sodium sulphate was converted into cyanide and 4.6% into cyanamide when the reacting substances were used in the proportions of 10 mols. of nitrogen, 1 mol. of sodium sulphate, 1.2 mols. of barium carbonate, 10 mols. of carbon, and 0.5 mol. of iron. When 2 mols. of sodium chloride were substituted for the sulphate, the yield was 72.3% of cyanide and 5% of cyanamide. Smaller yields were obtained when calcium or strontium carbonates or calcium oxide were used in place of barium carbonate.

C. J. S.

**Aliphatic Hydroxyphosphinic Acids. I.  $\alpha$ -Carboxy- $\alpha$ -hydroxyethylphosphinic Acid.** A. BERNTON (*Ber.*, 1925, 58, [B], 661—663; cf. Conant, A., 1918, i, 74; 1920, i, 454; 1921, i, 69; 1923, i, 69, 186, 498).—Pyruvic acid is converted by successive treatment at the atmospheric temperature with phosphorus trichloride and glacial acetic acid into  $\alpha$ -carboxy- $\alpha$ -hydroxyethylphosphinic acid,  $\text{CO}_2\text{H}\cdot\text{CMe}(\text{OH})\cdot\text{PO}(\text{OH})_2$ , m. p. 165—170° (decomp.), which can be titrated sharply as a tribasic acid in the presence of thymolphthalein. The manganese salt ( $+3\text{H}_2\text{O}$ ), tri-aniline salt, m. p. 213°, di-*p*-toluidine salt, m. p. 211°, and tri-phenylhydrazine salt, m. p. 184°, are described. H. W.

**Reduction of Nitro Compounds by Calcium Hydride.** J. F. DURAND and S. HOUGHTON (*Compt. rend.*, 1925, 180, 1034—1036).—Calcium hydride reacts with nitromethane (2 mols.) with liberation of hydrogen (2 mols.) and formation of the calcium salt of the nitro compound. Nitrobenzene is reduced by calcium hydride with formation of nitrosobenzene and finally of azoxybenzene. G. M. B.

**Alternating Effect in Carbon Chains. I. Directive Influence of the Nitroso Group in Aromatic Substitution.** C. K. INGOLD (*J. Chem. Soc.*, 1925, 127, 513—518).—The hypothesis of the alternating strengths of chemical affinity (Flürscheim) has been set counter to that of alternating polarities (Fry, Lapworth, Robinson, and others) by an examination of the products formed on introducing substituents into nitrosobenzene, this substance having been chosen on account of its freedom from the complicating presence of hydrogen and other possible "key-atoms." Bromination was carried out by mixing carbon disulphide solutions of nitrosobenzene and bromine at  $-5^\circ$ , and removing the solvent and hydrogen bromide as rapidly as possible. The product was mainly *p*-bromonitrosobenzene (yields up to 40%), together with *p*-bromonitrobenzene, *pp'*-dibromoazoxybenzene, *p*-bromoazobenzene, and azobenzene. Chlorination of nitrosobenzene resulted in the corresponding chloro compounds, but more nitrosobenzene remained unaltered. Nitric acid (100%) converts nitrosobenzene completely into nitrobenzene at  $0^\circ$ . On adding freshly-prepared crystalline nitrogen pentoxide to a carbon tetrachloride solution of nitrosobenzene containing phosphorus pentoxide in a freezing mixture, *p*-nitronitrosobenzene is formed and can be separated from the nitrobenzene by steam distillation. No meta-isomerides could be detected in any of the substitutions (cf. Bamberger, Büsdorf, and Sand, A., 1898, i, 521; Ingold and Weaver, A., 1924, i, 1116). The results are considered to be distinctly favourable to the view that directive effects in aromatic substitution are dependent on an alternation of quantity rather than of electropolar quality of chemical affinity. A. C.

**Decomposition of [2 : 4 : 6]-Trinitrotoluene by the Action of Sunlight.** C. KRAUZ and O. TUREK (*Z. ges. Schiess- u. Sprengstoffw.*, 1925, 20, 49—58).—2 : 4 : 6-Trinitrotoluene is readily



decomposed on exposure to sunlight. The m. p. falls from  $81.4^{\circ}$  to  $73.5^{\circ}$ , and the product contains picric and trinitrobenzoic acids. Both these acids and their salts increase the sensitiveness of trinitrotoluene to shock. The influence of the two acids is almost exactly similar, but this is not the case with their corresponding salts. The following *trinitrobenzoates* are described: *mercurous*, *mercuric*, *lead*, *copper* ( $+2\text{H}_2\text{O}$ ), *iron*,  $[\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{CO}_2]_2\text{FeOH}$ , *nickel* ( $+2\text{H}_2\text{O}$ ), *aluminium*,  $[\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{CO}_2]_2\text{AlOH}$ , *manganese*, *zinc*, *magnesium* ( $+ \text{H}_2\text{O}$ ), *barium*, *calcium*, *sodium* ( $+3\text{H}_2\text{O}$ ), and *potassium*.  
R. B.

**Chemical Action of Light on the Polynitrotoluenes.** G. SCHULTZ and K. L. GANGULY (*Ber.*, 1925, **58**, [B], 702—708).—The action of light on 2 : 4 : 6-trinitrotoluene in an atmosphere of oxygen, hydrogen, or nitrogen or in a vacuum leads to the production of two tautomeric substances,  $\text{C}_7\text{H}_5\text{O}_6\text{N}_3$ , neither of which melts below  $280^{\circ}$ , which are considered to be *2-nitro-6-nitroso-5-hydroxymethyl-p-benzoquinone-4-oxime* and *2-nitro-4-nitroso-5-hydroxymethyl-o-benzoquinone-2-oxime*, respectively. When treated with acetic anhydride and anhydrous potassium acetate, either substance gives *4-nitro-2 : 6-dinitroso-3-acetoxybenzyl acetate*. The elucidation of the constitution of the tautomerides is based on the established migratory tendency of the oxygen atoms of the nitro group in *o*-nitro aromatic compounds. The primary product of the change is regarded therefore as *4-nitro-2 : 6-dinitrosobenzyl alcohol* [this is probably the compound isolated (m. p.  $108\text{—}111^{\circ}$ ) when a solution of 2 : 4 : 6-trinitrotoluene in acetone is exposed to light], which is then converted into the unstable *4-nitro-2 : 6-dinitrosodihydroxymethylbenzene* and thence by migration of a hydroxy group into the quinone oximes. The assumption that only the 2- and 6-nitro groups are concerned in the change is supported by the observation that 2 : 6-dinitrotoluene is converted by exposure to light into a yellow substance, probably *2 : 6-dinitroso-4-hydroxybenzyl alcohol* and a dark yellow compound, whereas *p*-nitrotoluene is completely unchanged. The presence of a nitro group in the *para* position appears actually to retard the change, since 2 : 4-dinitrotoluene is almost stable to light. 2 : 4 : 6-Trinitrosobenzyl alcohol dissolved in benzene and 2 : 4 : 6-trinitrosobenzyl bromide in the solid state or in benzene solution are sensitive to light.  
H. W.

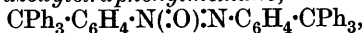
**Halogenation of 2 : 4 : 6-Trinitrotoluene.** K. L. GANGULY (*Ber.*, 1925, **58**, [B], 708—712).—Attempts to chlorinate 2 : 4 : 6-trinitrotoluene by the action of gaseous chlorine on the compound dissolved in carbon tetrachloride or on the liquid substance in the presence of iodine, ferric chloride, or aluminium chloride were unsuccessful; nitration of 2 : 4-dinitrosobenzyl chloride does not appear to yield 2 : 4 : 6-trinitrosobenzyl chloride. The action of phosphorus pentachloride and iodine (whereby the effective agent is iodine trichloride) on 2 : 4 : 6-trinitrotoluene in a sealed tube at  $150\text{—}160^{\circ}$  gives a mixture of 2 : 4 : 6-trinitrosobenzotrichloride, b. p.  $156\text{—}157^{\circ}/2\text{ mm.}$ , 2 : 4 : 6-trinitrosobenzyl chloride, m. p.  $85^{\circ}$  (more readily prepared by the action of phosphorus pentachloride on

2:4:6-trinitrobenzyl alcohol in the presence of chloroform), pentachlorobenzyl chloride, m. p. 103°, 2:3:4-trichloro-6-nitrobenzyl chloride, m. p. 122°, unchanged 2:4:6-trinitrotoluene, and a liquid containing probably 2:4:6-trinitrobenzylidene chloride and more highly chlorinated compounds; the main products are 2:4:6-trinitrobenzotrichloride and pentachlorobenzyl chloride. The primary action consists in the successive replacement of the hydrogen atoms of the methyl group by chlorine; halogenation of the nucleus is due to the initial elimination of nitrous acid and entry of the chlorine atoms in the two positions thus rendered vacant. 2:4:6-Trinitrobenzyl bromide, m. p. 65° (cf. Reich, Wetter, and Widmer, A., 1912, i, 958), is prepared in 70% yield by heating 2:4:6-trinitrotoluene with bromine in the presence of magnesium carbonate at 150–160°; it is transformed by boiling water into 2:4:6-trinitrobenzyl alcohol in 82% yield. H. W.

**Alkylation by Esters of Toluene-*p*-sulphonic Acid.** C. FINZI (*Annali Chim. Appl.*, 1925, **15**, 41–50).—Ethyl toluene-*p*-sulphonate forms an excellent agent for the ethylation of phenols, aromatic amines, and carboxylic acids, the reaction being effected in aqueous solution with phenols or acids soluble in alkaline solution, and in absence of solvent with the amines. The ester may be readily prepared by Izmailski and Razorenov's method (A., 1923, i, 770). In the ethylation of phenol to phenetole, *p*-cresol to *p*-tolyl ethyl ether, resorcinol and quinol to their diethyl ethers, guaiacol to its ethyl ether, brilliant-yellow to chrysophenine, aniline to ethylaniline, *o*- and *m*-toluidines to ethyl-*o*- and -*m*-toluidines, benzoic and salicylic acids to their ethyl esters, anthranilic to ethylanthranilic acid, and *p*-aminobenzoic to *p*-ethylamino-benzoic acid, yields of 70–85% are obtainable. T. H. P.

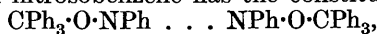
**Mechanism of Substitution Reactions in the Aromatic Nucleus. II.** E. DE B. BARNETT, J. W. COOK, and M. A. MATTHEWS (*Rec. trav. chim.*, 1925, **44**, 217–223; cf. this vol., i, 123).—The behaviour of anthracene dibromide with a number of reagents is described, and the conclusion is reached that the substance has the *trans* configuration but is readily converted into the *cis* isomeride. Dimethylaniline yields 9-dimethylaminophenyl-anthracene, m. p. 258°, and 9:10-tetramethyldiaminodiphenyl-9:10-dihydroanthracene, m. p. 265°. Diethylamine gives no condensation product, but anthracene and 9-bromoanthracene are produced. With piperidine, 9-piperidinoanthracene (N-anthranyl-piperidine), m. p. 147°, is obtained. Primary and secondary aromatic amines give the corresponding compounds, C<sub>14</sub>H<sub>9</sub>NHAr and C<sub>14</sub>H<sub>9</sub>NRAr (A., 1909, i, 655), identical with the substances previously incorrectly described as dihydroanthracene derivatives (T., 1921, **119**, 901). The action of ammonia in chloroform solution, potassium hydroxide, or sodium hydrosulphide in alcohol and sulphur dioxide in acetic acid produced varying quantities of anthracene or 9-bromoanthracene. Cold ethyl alcohol yields dianthrone and anthranilyl ethyl ether. G. M. B.

**Constitution of Nitroso Compounds.** S. GOLDSCHMIDT and F. CHRISTMANN (*Annalen*, 1925, **442**, 246—253).—Hexaphenylethane combines readily with nitrosobenzene in the presence of benzene, yielding *azoxytetraphenylmethane*,

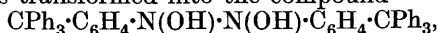


decomp. 333—336°, which obstinately retains solvent of crystallisation and is analysed as its compound with  $1\text{C}_6\text{H}_5\text{Cl}$ . It is reduced by zinc dust and glacial acetic acid to *hydroxylaminotetraphenylmethane*,  $\text{CPh}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{OH} \cdot 1.5\text{C}_6\text{H}_6$ , m. p. 218—219°. Azoxytetraphenylmethane is also obtained by the oxidation of *p*-aminotetraphenylmethane with Caro's acid, and the compound thus prepared is similarly reduced to hydroxylaminotetraphenylmethane, so that its constitution may be regarded as established. It is, however, unusual that the final stage in the reduction of an azoxy compound should be a hydroxylamino derivative. Attempts to reduce the latter to the amino compound or to oxidise it to the azoxy derivative were, however, unsuccessful, but it is converted by nitrous fumes into *nitrosohydroxylaminotetraphenylmethane*,  $\text{CPh}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{NO}) \cdot \text{OH} \cdot 1.5\text{CHCl}_3$ , which is reduced by zinc dust and acetic acid to aminotetraphenylmethane.

It appears probable that the primary product of the action of triphenylmethyl on nitrosobenzene has the constitution



which becomes transformed into the compound

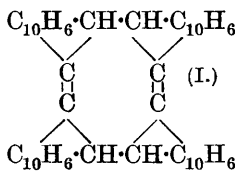


from which the azoxy derivative is formed by loss of water. This transformation is certainly incomplete, since a freely soluble compound is also produced which could not be isolated, but yields triphenylcarbinol as one of the products of its hydrolysis.

The chemical and physical analogy between nitrosobenzene and radicals containing univalent oxygen and bivalent nitrogen is so great that tautomerism,  $\text{C}_6\text{H}_5 \cdot \text{N} \cdot \text{O} \rightleftharpoons \text{C}_6\text{H}_5 \cdot \text{N} = \text{O}$ , must be assumed for the free compound unless it be considered that the double bond between nitrogen and oxygen is in such an unbalanced condition that it differs but little from the bonds of oxygen and nitrogen in their radicals.

H. W.

**Fluorocyclene.** K. DZIEWOŃSKI and J. SUSZKO (*Ber.*, 1925, **58**, [B], 723—732; cf. A., 1914, i, 826; 1918, i, 296).—An improved method for the preparation of fluorocyclene (I), whereby the production of decacyclene is largely avoided, consists in heating acenaphthene with lead peroxide in a sealed tube at 170°, opening the somewhat cooled tube to permit the escape of steam, and subsequently heating the closed tube at 200—220°. When suspended in cold chloroform it readily absorbs bromine (4 mols.) without evolution of hydrogen bromide; after some time or immediately on warming, hydrogen bromide is freely evolved and (mainly)  $\alpha\alpha'$ -dibromodehydrofluorocyclene [ $\alpha\alpha'$ -dibromotetranaphthylencyclo-octatetraene],  $\text{C}_{48}\text{H}_{22}\text{Br}_2$ , m. p. 390—394°, separates (the constitution



of the substance is established by its oxidation to 5-bromonaphthalene-1 : 8-dicarboxylic anhydride, m. p. 211—212°. It is suggested that the primary change is the addition of bromine (2 mols.) to the cyclooctadiene ring, followed by the loss of hydrogen bromide (4 mols.) with production of the cyclooctatetraene ring; the halogen then substitutes in the naphthalene nucleus. If fluorocyclene is treated with a considerable excess of bromine in boiling chloroform in the presence of iron, it yields tetrabromofluorocyclene,  $C_{48}H_{26}Br_4$ , m. p. 360—365°, in which two of the bromine atoms are attached to naphthalene nuclei and the other two are joined to the cyclooctane ring as shown by the evolution of bromine and production of 5-bromonaphthalene-1 : 8-dicarboxylic anhydride when the compound is oxidised. Both bromo derivatives are non-fluorescent, presumably owing to the impossibility of atomic oscillation within the molecule.

Fluorocyclene is converted by nitric acid ( $d$  1.5) in the presence of glacial acetic acid at the atmospheric temperature mainly into the strongly fluorescent  $\alpha\alpha'$ -dinitrofluorocyclene, decomp. above 360°, in which the position of the nitro groups is established by the oxidative production of 5-nitronaphthalene-1 : 8-dicarboxylic acid; in addition, tetranitrofluorocyclene, decomp. above 330°, is produced in small amount. Dibromotetranitrodehydrofluorocyclene, which does not melt below 440°, is obtained in a similar manner.

Fluorocyclene is energetically attacked by cold sulphuric acid (20%  $SO_3$ ), sulphonation and oxidation occurring with production of dihydroxyfluorocyclenetetrasulphonic acid,  $C_{48}H_{22}(OH)_2(SO_3H)_4$ ; the corresponding lead and barium salts are described. Similarly, dibromodehydrofluorocyclene is transformed into dibromodihydroxydehydrofluorocyclenetetrasulphonic acid; the barium salt was prepared.

H. W.

**Triphenylmethane Dyes.** W. DILTHEY (*J. pr. Chem.*, 1925, [ii], 109, 273—323; cf. A., 1920, i, 324).—This is an elaborate résumé of recent investigations into the relationship between colour and constitution, with particular reference to these dyes. Pfeiffer's suggestion (A., 1911, i, 789) that their chromogen is triphenylmethyl itself is rejected, as also is the older explanation in terms of the quinonoid theory. The triphenylmethane dyes are salts, and their chromogen must be a salt. This chromogen can therefore be no other than a salt-like (ionised) isomeride of, e.g., triphenylmethyl chloride. This supposition is not entirely novel (cf. Kehrman, A., 1918, i, 312), but its expression in terms of the only satisfactory theory, that of Werner, has hitherto remained incomplete (cf., however, Madelung, A., 1922, ii, 344; Brand, this vol., i, 397). The reason for this is as follows. Although, e.g., triphenylmethyl chloride dissolves in phenol, and in strong sulphuric acid, to give a coloured solution, and combines with metallic chlorides to give what are undoubtedly double salts, yet that any triarylmethyl halide (colourless) can change into a triarylmethyl halide (salt-like in nature, and coloured), by a simple alteration in affinity, expressible in Werner's fashion thus

$\text{CPh}_3\text{Cl} \rightleftharpoons [\text{CPh}_3]\text{Cl}$ , has not been clearly demonstrated. This actually takes place, as the following observations show, and the true nature of the chromogen in the triphenylmethane dyes is thus evident.

Similar considerations are applied to other classes of dyes and coloured compounds, and the sudden development of colour in organic compounds is attributed to one or more of the following, emphasis being laid on the importance of recognising the difference between ionisable and non-ionisable combination: (i) presence of "crossed double bonds"; (ii) "unsaturatedness," true or co-ordinative; (iii) simultaneous presence of oxidised and reduced "stages," as in the quinhydrones; (iv) "heteropolar" condition, as in the above carbonium compounds and in molecular compounds.

That the true chromogen of the triphenylmethane dyes is the triphenylmethyl salt is indicated when the solution of, e.g., parafuchsin in concentrated sulphuric acid is compared with that of triphenylcarbinol in the same solvent. The two solutions have almost the same colour; the auxochrome groups, therefore, have a negligible bathochromic effect, and Kehrman's hypothesis (*loc. cit.*) is unnecessary. But this solution of triphenylcarbinol in concentrated sulphuric acid, although commonly supposed to contain a true salt, does not necessarily contain a simple salt, but more probably an acid one (cf. Pfeiffer, "Organische Molekülverbindungen," 1922, 135). Of other known compounds none contains a radical of precisely the properties necessary for a decisive test. *Phenyl-p-anisyl- $\alpha$ -naphthylmethyl chloride* is, however, well adapted to this purpose. This substance, prepared from phenyl *p*-anisyl ketone and magnesium  $\alpha$ -naphthyl bromide, has m. p.  $171^\circ$ . It forms a colourless solution with benzene, ether, and light petroleum, but gives a red solution with sulphuric acid, phenol, tetrachloroethane, formic acid, acetic acid, and acetic anhydride, even in the cold. These coloured solutions (in the "indifferent" solvents) are decolorised when either ether etc. or sodium acetate is added, and the corresponding carbinol (see below) does not form coloured solutions (except in sulphuric acid). Cryoscopic determinations of the molecular weight of the chloride in acetic acid gave results indicating that dissociation had taken place. When the solution of the compound in benzene is boiled, hydrogen chloride is slowly evolved (see below). *Phenyl-p-anisyl- $\alpha$ -naphthylmethyl bromide* has m. p.  $140^\circ$  and resembles the chloride; its reddish-yellow solution in cold chlorobenzene becomes yellower on heating. The corresponding *carbinol* has m. p.  $92\text{--}94^\circ$  (+0.5 mol. pyridine, cf. below). *Phenyl-p-anisyl- $\alpha$ -naphthylmethane*, m. p.  $112^\circ$ , gives no colour with concentrated sulphuric acid.

It is evident from the above that the colour is simply that of the carbonium chloride, and that in concentrated sulphuric acid there is no acid salt formation, because the colour here is the same as in acetic acid. Phenyldiphenyl- $\alpha$ -naphthylmethyl chloride (Schmidlin, A., 1913, i, 33) behaves similarly, but in acetic acid colour develops only when the solution is heated, and in 100% sulphuric acid the dark violet colour gradually becomes red and

shows green "dichroism," indicating that an acid salt is formed. Moreover, with this compound it is very evident that it is solely the formation of the simple carbonium salt that is the cause of the colour, for solutions in hot acetic acid, cold acetic acid and phenol (mixture), molten phenol, or of the carbinol in sulphuric or trichloroacetic acids, all show the same absorption bands, viz., a strong band at  $\lambda$  495, and a weak band at  $\lambda$  595 (or at  $\lambda$  620 in molten phenol or molten trichloroacetic acid). This carbinol gives a coloured solution when warmed, also with chloroacetic, salicylic, formic, glycollic, mandelic, and succinic acids, but not with benzoic or weaker acids.

The presence of the oxygen atom in the above anisyl derivatives may cause abnormalities, and to eliminate this possibility *phenyl-p-tolyl- $\alpha$ -naphthylmethyl chloride*, m. p. 142°, was investigated. This again exhibits the remarkable colour phenomenon. The colourless cold solution in such solvents as acetic anhydride or chlorobenzene becomes violet when heated, and loses its colour again when cooled. It gives a green-red dichroic solution with concentrated sulphuric acid. The heating and cooling of the solution in chlorobenzene, with simultaneous gain and loss of colour, can be frequently repeated, but hydrogen chloride is gradually evolved, and eventually the solution becomes permanently yellow (see below). The corresponding *bromide* has m. p. 140°; the *carbinol* has m. p. 87—89° (+1 mol. of pyridine); the *methane* has m. p. 133°.

The evolution of hydrogen chloride, referred to above, has no direct connexion with the development of colour. It is due to decomposition. Thus, *diphenyl- $\alpha$ -naphthylmethyl chloride* (Schlenk, A., 1913, i, 34) also gives a coloured solution in, e.g., hot chlorobenzene. Here, however, the experiment cannot be repeated many times, as hydrogen chloride is rapidly evolved. The yellow solution obtained now contains phenylchrysofluorene (Ullmann and Mourawiew-Winogradoff, A., 1905, i, 642). The formation of this compound and the evolution of hydrochloric acid run parallel to one another. If air is passed into the reacting solution, scarcely any phenylchrysofluorene is formed, but hydrogen chloride is still evolved. This indicates that the second hydrogen atom, transference of which is necessary for chrysofluorene formation, is oxidised, and demonstrates that the evolution of hydrogen chloride is not directly connected with the "ionisation" of the carbonium chloride. When ammonia is passed into a hot solution of *diphenyl- $\alpha$ -naphthylmethyl chloride* *diphenyl- $\alpha$ -naphthylmethylamine*, m. p. 168—169°, is formed (yield 75%). This compound gives no coloured solutions, except with sulphuric acid, but there the solution is that of the carbinol, for the amino group is displaced. The *hydrochloride*, *hydrobromide*, and *picrate* [m. p. 250—251° (decomp.)] are described. *Diphenyl- $\alpha$ -naphthylmethyl bromide*, m. p. 164—167°, is more stable than its chloro analogue, and the colour changes in its solutions are more marked. *Phenyl-p-xylyl- $\alpha$ -naphthylmethyl chloride*, m. p. 133°, resembles its analogues. When the solution in, e.g., chlorobenzene is heated, it becomes green, then brown; hydrogen chloride is evolved, and *p-xylylchrysofluorene*, m. p. 215°, is formed.

formed. *Phenyl-m-xylyl- $\alpha$ -naphthylmethyl chloride* has m. p. 132—133°. *p-Tolyl diphenyl ketone*, prepared from diphenyl, toluoyl chloride, and aluminium chloride, has m. p. 129° (*oxime*, m. p. 188°), and with magnesium  $\alpha$ -naphthyl bromide affords *p-tolyldiphenyl- $\alpha$ -naphthylmethyl chloride*, m. p. 184° (decomp.). This also gives a colourless solution in cold chlorobenzene, which becomes blue on heating. Other similar compounds are *di-p-tolyl- $\alpha$ -naphthylmethyl chloride*, m. p. 163°, *phenyl-p-bromophenyl- $\alpha$ -naphthylmethyl chloride*, m. p. 180° (prepared from bromobenzene, it being proved that substitution in this Friedel-Crafts reaction takes place in the para position), and *phenyldiphenyl- $\alpha$ -naphthylmethyl bromide*, m. p. 177°. The carbinol or chloride corresponding with the last of these decomposes, like its analogues, and so affords *diphenyl-chrysofluorene*, m. p. 275—276°. When these chlorotriarylmethanes are boiled with alcohols, the ethers of the carbinols are formed: *diphenyl- $\alpha$ -naphthylmethyl methyl ether* has m. p. 140—141°, and the corresponding *ethyl ether* has m. p. 128°. *Phenyl-p-tolyl- $\alpha$ -naphthylmethyl methyl ether*, m. p. 120—121°, *phenyl-m-xylyl- $\alpha$ -naphthylmethyl methyl ether*, m. p. 121—122°, *p-tolyldiphenyl- $\alpha$ -naphthylmethyl methyl ether*, m. p. 186°, *di-p-tolyl- $\alpha$ -naphthylmethyl methyl ether*, m. p. 141—142°, and *phenyldiphenyl- $\alpha$ -naphthylmethyl methyl ether*, m. p. 187°, are similarly obtained. All these substances dissolve in strong sulphuric acid, the corresponding carbinol being regenerated. The chlorotriarylmethanes also react with *m*-nitroaniline, yielding "anilides"; the *anilide* of diphenyl- $\alpha$ -naphthylcarbinol has m. p. 173—175°, and that of phenyl-*p*-tolyl- $\alpha$ -naphthylcarbinol, m. p. 147—148°. Phenyldiphenyl- $\alpha$ -naphthylcarbinol forms various additive compounds (cf. Schmidlin, *loc. cit.*). When it is prepared by interaction of the chloride with pyridine, the product is a stable compound with 0.5 mol. of pyridine, m. p. 126—128°. With acetic acid, the compound,  $C_{29}H_{22}O, C_2H_4O_2$ , m. p. 98—160° (decomp.), is obtained, and with trichloroacetic acid a compound,  $4C_{29}H_{22}O, CCl_3 \cdot CO_2H$ , m. p. 115—120°. A similar compound (m. p. 96—98°) with  $\frac{1}{2}$  or  $\frac{1}{4}$  molecular proportion of water is also formed.

W. A. S.

**Additive Compounds of 3:5-Dibromo-*o*-toluidine with Metallic Salts.** R. M. HANN and G. C. SPENCER (*J. Washington Acad. Sci.*, 1925, 15, 163—165).—Various metallic halides combine with 3:5-dibromo-*o*-toluidine in concentrated alcoholic solution to form crystalline additive compounds containing 2 mols. of base to 1 mol. of salt. *Mercuric 3:5-dibromo-*o*-toluidine chloride* forms colourless needles becoming red in air, m. p. 120°, after a colour-change at 80°; the corresponding compounds with *zinc chloride* (m. p. 211°, colour change 200°), *cadmium bromide* (m. p. >225°), and *cadmium chloride* (m. p. >200°) were prepared and analysed. The presence of the metals did not vitiate the nitrogen determinations carried out in the usual way.

B. W. A.

**[Mechanism of the Catalytic Reduction of Oximes.]** W. GULEWITSCH (*Ber.*, 1925, 58, [B], 798; cf. A., 1924, i, 1285).—A reply to Rosenmund and Jordan (this vol., i, 245). H. W.

**Antimonyl Tartrates of some Organic Bases.** W. G. CHRISTIANSEN and A. J. NORTON (*J. Amer. Chem. Soc.*, 1925, **47**, 876—881).—The following amine antimonyl tartrates were prepared by double decomposition of the amine sulphate and barium antimonyl tartrate in aqueous solution: *benzylamine* ( $+ \frac{1}{2} \text{H}_2\text{O}$ ), *phenylhydrazine*, *p-aminoacetophenone* ( $\text{H}_2\text{O}$ ), *aniline-m-carboxylic acid* ( $+ \text{H}_2\text{O}$ , loses 0.5 mol. of water at  $110^\circ$ ), *p-aminoacetanilide* ( $+ \text{H}_2\text{O}$ ), *benzidine* ( $+ 3\text{H}_2\text{O}$ ), and *hexamethylenetetramine antimonyl tartrates*. s-p : p'-*Diaminodiphenylthiocarbamide antimonyl tartrate* ( $4\text{H}_2\text{O}$ ) was obtained by adding the base to a cold, freshly-prepared solution of antimonyl tartaric acid, made by adding sulphuric acid to a cooled solution of the barium salt. It sinters at  $295\text{--}300^\circ$ , but does not melt at  $310^\circ$ . *isoPropyl* and *n-butyl* antimonyl tartrates were prepared by the action of silver antimonyl tartrate on the respective alkyl iodides. The above antimonyl derivatives are no better trypanocides than the potassium salt. When s-p : p'-diaminodiphenylthiocarbamide is boiled in aqueous solution, it decomposes with formation of di-p-phenylenedithiocarbamide (cf. Bolser and Hartshorn, A., 1924, i, 317). s-p : p'-*Diaminodiphenylthiocarbamide dihydrochloride* is described. F. G. W.

**$\alpha$ -Halides of Indane.** C. COURTOT and A. DONDELINGER (*Compt. rend.*, 1924, **179**, 1168—1171; cf. Weissgerber and Brehme, A., 1911, i, 623).—Indene, cooled to  $0^\circ$  or below, absorbs hydrogen bromide or iodide with quantitative formation of the  $\alpha$ -halogen derivative of indane, but these compounds are decomposed on distillation, yielding hydrogen halide and indene or polymerides of indene. Both bromide and iodide react with 2 mols. of *o*-toluidine, yielding *o*-tolylindanylamine. H. J. E.

**Reduction of Aromatic Nitro Derivatives by Means of Sulphides.** V. VESELY and L. K. CHUDOŽILOV (*Chem. Listy*, 1925, **19**, 123—127).—Selective reduction by means of alkali sulphides may be applied to the mixture of 5- and 6-nitrotetralins obtained by the mononitration of tetralin, to mixtures of  $\alpha$ - and  $\beta$ -nitronaphthalenes, and to the 2- and 4-nitro-*m*-xylenes resulting from the mononitration of *m*-xylene. [Cf. B., 1925, 393.]

D. G. H.

**Derivatives of 1-Naphthylamine-8-sulphonic Acid.** C. FINZI (*Annali Chim. Appl.*, 1925, **15**, 50—54).—1-o : p-Dinitrophenylaminonaphthalene-8-sulphonic acid,



prepared from 1-naphthylamine-8-sulphonic acid and 1-chloro-2 : 4-dinitrobenzene in presence of sodium carbonate, forms yellow crystals, m. p. (frothing)  $179^\circ$ , and its sodium salt, tufts of red, prismatic crystals, m. p.  $257^\circ$ . 1-p-Toluenesulphonamidonaphthalene-8-sulphonic acid, from p-toluenesulphonyl chloride and sodium 1-naphthylamine-8-sulphonate in presence of sodium carbonate, fails to melt at  $300^\circ$ ; its sodium salt was prepared. Like the preceding acid, it does not react with diazo compounds.

Reduction of 1-o : p-dinitrophenylaminonaphthalene-8-sulphonic



acid (1) by means of sodium sulphide yields 1-*o*-nitro-*p*-aminophenylaminonaphthalene-8-sulphonic acid,  $C_{16}H_{13}O_5N_3S$ , pale yellow (orange-red sodium salt), or (2) by means of tin and hydrochloric acid yields 1-*o* : *p*-diaminophenylaminonaphthalene-8-sulphonic acid (dihydrochloride, dibenzoyl derivative, m. p. 235°; diazo compound).  
T. H. P.

**Nitration with Nitrates. II.** J. B. MENKE (*Rec. trav. chim.*, 1925, **44**, 269—270; cf. this vol., i, 386).—Nitration by means of nitrates of heavy metals and glacial acetic acid can be effected without oxidation up to 100°, but the mixtures are not so powerful as those with acetic anhydride. Phenol is completely nitrated to pure *o*-nitrophenol in 20 mins. at 26° by a mixture of cupric nitrate and acetic acid.  
S. I. L.

***m*-Bromophenols. VI.** M. KOHN and M. WEISSBERG (*Monatsh.*, 1925, **45**, 295—303).—The orientation of the 4 : 6-dibromo-*o*-cresol, m. p. 98—101° (Kohn and Jawetz, this vol., i, 135), is confirmed by its ready nitration to give 4 : 6-dibromo-3 : 5-dinitro-*o*-cresol, yellow crystals, m. p. 135°. Tetrabromo-*p*-cresol is converted by benzene and aluminium chloride into 2 : 6-dibromo-*p*-cresol, m. p. 97°, b. p. 280—286°, the two vacant positions ortho to the hydroxyl group being confirmed by its nitration to give 2 : 6-dibromo-3 : 5-dinitro-*p*-cresol, yellow crystals, m. p. 152°. The dibromo-*p*-cresol is readily brominated in glacial acetic acid solution to yield 2 : 3 : 6-tribromo-*p*-cresol, m. p. 84° (methyl ether, m. p. 115°, b. p. 320°), distinct from the known 2 : 3 : 5-tribromo compound. Tetrabromo-*m*-cresol, m. p. 196°, prepared in a way similar to that used for pentabromophenol (this vol., i, 133), gives, on treatment with benzene and aluminium chloride, 5-bromo-*m*-cresol, m. p. 54°, b. p. 255° (picryl derivative, m. p. 130°), converted by formaldehyde in the presence of aqueous sodium hydroxide into 6-bromo-4-hydroxy-2-methylbenzyl alcohol, m. p. 154°. Although Auwers thought that halogenated phenols usually failed to give this Lederer and Manasse reaction, it is found to occur in other cases, 3 : 5-dibromophenol giving 2 : 6-dibromo-*p*-hydroxybenzyl alcohol, m. p. 180°, and 2 : 6-dibromo-*p*-cresol giving 2 : 6-dibromo-3 : 5-dihydroxymethyl-*p*-cresol, m. p. 235°.  
G. M. B.

**Nitro Derivatives of Diphenyl Ethylene Ether.** C. DOSIOS and T. TSATSAS (*Compt. rend.*, 1925, **180**, 1275—1277).—Diphenyl ethylene ether has not previously been directly nitrated, but the isomeric dinitro derivatives have been obtained (cf. Weddige, A., 1880, 316) by the action of ethylene dibromide on the alkali salts of the corresponding nitrophenols. Sodium 2 : 4-dinitrophenoxide does not react with ethylene dibromide, but the disodium salt of glycol reacts with fused chloro-2 : 4-dinitrobenzene with deflagration, the reaction proceeding smoothly if the disodium salt of glycol is added in small portions. The yellow 2 : 4 : 2' : 4'-tetranitrodiphenyl ethylene ether thus obtained has m. p. 215.2° (corr.). The same product is obtained by nitration of diphenyl ethylene ether at -10° with fuming nitric acid. By reduction of the tetranitro

compound with stannous chloride, 2 : 4 : 2' : 4'-tetraminodiphenyl ethylene ether is produced, a colourless compound which becomes brown when exposed to air, and couples with diazotised aniline, giving an orange coloration.

L. F. H.

**C-Alkylation (Nucleus Alkylation) of Phenols.** L. CLAISEN [with F. KREMERS, F. ROTH, and E. TIETZE] (*Annalen*, 1925, **442**, 210—245).—A detailed account of work previously abstracted in part (A., 1923, i, 1094). The formation of *O*- or *C*-alkyl derivatives by the action of alkyl halides on the sodium or potassium derivatives of monohydric phenols depends on the solvent employed, the *C*-derivatives preponderating in non-dissociating media, whereas *O*-compounds are produced in dissociating solvents. Further, the tendency towards the production of *C*-derivatives increases with increasing mobility of the halogen atom of the halide. The following compounds do not appear to have been described previously: phenyl  $\alpha$ -methyl- $\Delta^{\beta}$ -butenyl ether, b. p. 96—98°/13 mm.,  $d_{15}^{15}$  0.9510; *o*- $\alpha$ -methyl- $\Delta^{\beta}$ -butenylphenol, b. p. 245°/750 mm., 118—119°/12 mm.,  $d_{15}^{15}$  0.993, which yields a phenylcarbamate,  $C_{18}H_{19}ON_2$ , m. p. 107—109°, and is converted by glacial acetic acid and hydrogen bromide into 3-methyl-2-ethylcoumaran or 2 : 4-dimethylchroman, b. p. 225—226°/753 mm.; phenylcarbamate of 2- $\alpha$ -methyl- $\Delta^{\beta}$ -butenyl-*p*-cresol, m. p. 96.5—98.5°; 2 : 6-di- $\alpha$ -methyl- $\Delta^{\beta}$ -butenyl-*p*-cresol, b. p. 171—173°/15 mm.; 3 : 5-dimethyl-2-ethylcoumaran (or 2 : 4 : 6-trimethylchroman), b. p. 243.5—244.5°/atmos. pressure, 118—120°/15 mm.; 3 : 5-dimethyl-2-ethyl-7- $\alpha$ -methyl- $\Delta^{\beta}$ -butenylcoumaran (or 2 : 4 : 6-trimethyl-8- $\alpha$ -methyl- $\Delta^{\beta}$ -butenylchroman), b. p. 294—296°/atmos. pressure, 163—165°/15 mm.; phenyl cinnamyl ether, m. p. 66—66.5°, b. p. 190°/13 mm.; *p*-tolyl cinnamyl ether, m. p. 78—79°; phenyl  $\gamma$ -phenylpropyl ether, b. p. 171—173°/11 mm., m. p. 27.5—28.5°; *o*-benzyl-*p*-cresol, b. p. 180—182°/12 mm. (phenylcarbamate, m. p. 144.5—145°); 2 : 6-dibenzyl-*p*-cresol, b. p. 250—252°/12 mm.

H. W.

**Constitution of Disulphoxides.** H. GILMAN, L. E. SMITH, and H. H. PARKER (*J. Amer. Chem. Soc.*, 1925, **47**, 851—860).—When di-*p*-tolyl disulphoxide is added to 1.5—2.5 equivalents of magnesium benzyl chloride in ether, and the mixture refluxed for an hour before hydrolysis, *p*-tolyl benzyl sulfoxide and *p*-toluenesulphonic acid are obtained. If equivalent quantities of the reactants are employed, and the mixture is hydrolysed without being boiled, the products are *p*-tolyl benzyl sulfoxide, *p*-toluenesulphinic acid, and *p*-tolyl benzyl sulphide. The sulfoxide is probably derived from the sulphinic acid and the Grignard reagent, as when the magnesium benzyl chloride (1 equivalent) is added to the boiling ethereal solution of the disulphoxide the sole products are *p*-tolyl benzyl sulphide and *p*-toluenesulphinic acid. Reactions between di-*p*-tolyl disulphoxide and magnesium phenyl bromide, magnesium *p*-tolyl bromide, and magnesium methyl iodide afforded, similarly, sulphides containing the radical attached to the magnesium atom and the *p*-tolyl group, and either *p*-toluenesulphinic or -sulphonic acid, the former when the ethereal layer of the hydrolysed

reaction mixture is extracted with dilute alkali, the latter when it is steam-distilled. The formation of the above products is in agreement with either the anhydride ( $R\cdot SO\cdot O\cdot SR$ ) or thiosulphonic ester ( $R\cdot SO_2\cdot SR$ ) structure for the disulphoxides. The disulphoxide structure ( $R\cdot SO\cdot SO\cdot R$ ) would require reduction of an intermediately formed sulphoxide by the Grignard reagent to explain the formation of the sulphide, whilst *p*-tolyl benzyl sulphoxide is not reduced by magnesium benzyl chloride in boiling ethereal solution. When *p*-toluenesulphonyl chloride is treated with *p*-thiocresol or *n*-butyl mercaptan and potassium hydroxide in dry ether at  $0^\circ$ , di-*p*-tolyl disulphide, or *di-n-butyl disulphide*, b. p.  $110-113^\circ/15$  mm.,  $n_D^{25}$  1.494;  $d_4^{20}$  0.930, respectively, is obtained, apparently according to the scheme (1)  $Me\cdot C_6H_4\cdot SO_2Cl + RSK \rightarrow Me\cdot C_6H_4\cdot SO_2SR + KCl + H_2O$ ; (2)  $Me\cdot C_6H_4\cdot SO_2SR + RSK \rightarrow Me\cdot C_6H_4\cdot SO_2K + RS\cdot SR$ . This scheme, which formulates the disulphoxide as a thiosulphonic ester in equation (2), is supported by the smooth formation of di-*p*-tolyl disulphide from di-*p*-tolyl disulphoxide, thiocresol, and potassium hydroxide in dry ether at  $0^\circ$ . Further, phenyl *p*-toluenesulphonate, when treated with magnesium *p*-thiotolyl iodide,  $Me\cdot C_6H_4S\cdot MgI$ , gives di-*p*-tolyl disulphide instead of the expected *p*-tolyl *p*-toluenesulphonate. As di-*p*-tolyl disulphoxide also affords di-*p*-tolyl disulphide when treated with magnesium *p*-thiotolyl iodide, it is concluded that the thiosulphonate is formed intermediately and is identical with the disulphoxide. The oxidation of the disulphoxide to the disulphone with hydrogen peroxide in acetic anhydride is explained on the thiosulphonic ester or the disulphoxide structure, but the latter has been shown (Gibson and Smiles, A., 1924, i, 275) to be untenable.

F. G. W.

[**Valency Problem of Sulphur.**] W. STEINKOPF (*Ber.*, 1925, 58, [B], 785).—A reply to Lecher (this vol., i, 390). H. W.

**Thermochemical Study of the Sodium Derivatives of cycloHexanol.** G. CAUQUIL (*Compt. rend.*, 1925, 180, 1207—1210).—On warming excess of cyclohexanol with sodium, the compound  $C_6H_{11}\cdot ONa, 5C_6H_{11}\cdot OH$  is obtained, and this on heating in a current of hydrogen yields sodium cyclohexanoxide, a white powder. Sodium hydroxide in aqueous solution, however, does not react with cyclohexanol at the ordinary temperature and the sodium derivative is completely dissociated in aqueous solution, as are the sodium derivatives of the simple open-chain alcohols. From this fact and the measured heat of fusion of cyclohexanol and heat of solution of sodium cyclohexanoxide, the following equation is deduced:  $C_6H_{11}\cdot OH(\text{solid}) + Na(\text{solid}) = H(\text{gas}) + C_6H_{11}\cdot ONa(\text{solid}) + 31.99$  cal. The heat of reaction is greater than that of acyclic secondary alcohols and as great as that of open-chain primary alcohols and is, as in the case of phenol, 2 cal. in excess of that required by Forcrand's theory (A., 1900, ii, 527, 528) for aliphatic alcohols. L. F. H.

**Alternating Effect in Carbon Chains. II. Directing Influence of the  $\alpha$ -Methoxyvinyl Group in Aromatic Substitution.** C. K. INGOLD and E. H. INGOLD (*J. Chem. Soc.*, 1925, 127, 870—875).—When the nitroso group is selected as the

directive substituent (cf. this vol., i, 646), complicating factors are introduced in that two competing negative key-atoms are present and the group is attached to the benzene ring by an atom containing a "lone-pair" of electrons. The selection of the  $\alpha$ -methoxyvinyl group eliminates these factors, retaining the condition that opposite forecasts as to its directive effect shall flow from the simple application of the principles of alternating affinity and induced polarity. The almost exclusive ortho-para nitration of  $\alpha$ -methoxystyrene is in accordance with the hypothesis of alternating affinity-demand. M. J.

### Derivatives of Citronellol and their Optical Rotations.

H. RUPE and R. RINDERKNECHT (*Helv. Chim. Acta*, 1925, 8, 169—178; cf. A., 1924, i, 709).—Bromination of citronellol by means of phosphorus tribromide usually gives a product containing phosphorus tribromide which is very difficult to separate. *Citronellyl bromide*,  $\text{CH}_3\text{CMe}[\text{CH}_2]_3\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , b. p.  $102\cdot5$ — $103^\circ/10$  mm.,  $d_4^{20}$  1.0923,  $[\alpha]_D^{20}$   $-5\cdot218^\circ$ , is obtained pure in 70—75% yield under the special conditions described. Added to activated magnesium in ether solution, the bromide reacts with benzaldehyde to form *phenylcitronellylcarbinol*,  $\text{C}_{10}\text{H}_{19}\cdot\text{CHPh}\cdot\text{OH}$ , b. p.  $186$ — $190^\circ/10$  mm., together with a small amount of dicitronellyl,  $\text{C}_{20}\text{H}_{38}$ . *Phenylcitronellylamine* (*citronellylaniline*),  $\text{C}_{16}\text{H}_{25}\text{N}$ , b. p.  $178^\circ/10$  mm.;  $92^\circ/0\cdot05$ — $0\cdot1$  mm.,  $d_4^{20}$  0.0196,  $[\alpha]_D^{20}$   $2\cdot021^\circ$ , which becomes coloured in the air, is obtained on heating the bromide with aniline at  $100^\circ$ ; the *hydrochloride*, m. p.  $78$ — $79^\circ$ , contains more than 1 mol. but less than 2 mols. of hydrogen chloride; the *chloroplatinate*,  $\text{C}_{32}\text{H}_{52}\text{N}_2\text{Cl}_6\text{Pt}$ , forms pale greenish-yellow needles which blacken on keeping. The *acetyl* derivative of phenylcitronellylamine, a pleasant-smelling oil, has b. p.  $198^\circ/13$  mm., and the *benzoyl* derivative, b. p.  $242$ — $244^\circ$ . The *nitrosoamine*,  $\text{C}_{10}\text{H}_{19}\cdot\text{NPh}\cdot\text{NO}$ , a reddish-yellow oil, cannot be distilled at 10 mm. without decomposition. *as-Phenylcitronellylhydrazine*,  $\text{C}_{10}\text{H}_{19}\cdot\text{NPh}\cdot\text{NH}_2$ , b. p.  $186^\circ/10$  mm.,  $110^\circ/0\cdot05$ — $0\cdot01$  mm.,  $d_4^{20}$  0.9352,  $[\alpha]_D^{20}$   $3\cdot507^\circ$ , a colourless oil which darkens in the air, is obtained on treating a cooled acetic acid solution of the amine with sodium nitrite followed by reduction with zinc powder; it is purified by forming the *citrate*,  $\text{C}_{22}\text{H}_{34}\text{O}_7\text{N}_2$ , m. p.  $129\cdot5^\circ$ . The hydrazine is strongly reducing, and reacts with aldehydes and ketones, but no solid hydrazones could be obtained. With methyl ethyl ketone the *hydrazone*,  $\text{C}_{10}\text{H}_{19}\cdot\text{NPh}\cdot\text{N}\cdot\text{CMeEt}$ , b. p.  $187^\circ/10$  mm., is obtained as a light yellow oil which rapidly darkens. *Benzaldehydephenylcitronellylhydrazone*,  $\text{C}_{23}\text{H}_{30}\text{N}_2$ , b. p.  $250^\circ/10$  mm., is accompanied by a small amount of a crystalline compound, m. p.  $161$ — $162^\circ$ , probably an isomeride. *p-Tolylcitronellylamine*,  $\text{C}_{17}\text{H}_{27}\text{N}$ , has b. p.  $186^\circ/10$  mm.; it forms the *hydrazine*,  $\text{C}_{17}\text{H}_{28}\text{N}_2$ , b. p.  $193\cdot5^\circ/10$  mm. (*citrate*, m. p.  $134\cdot5^\circ$ ), which, like the corresponding phenyl compound, gives no solid hydrazones and only that from benzaldehyde can be distilled without decomposition. A. C.

**Molecular Transpositions. Preparation and Dehydration of some  $\beta\beta$ -Diarylethyl and Diarylalkylethyl Alcohols.** P. RAMART and (MILLE.) AMAGAT (*Compt. rend.*, 1924, 179, 899—901).—The

method of alkylating esters of diphenylacetic acid (Ramart, A., 1924, i, 286) is applied to derivatives of phenyl-*p*-tolylacetic acid; the reaction is general, but the yields are smaller than in the previous case. Reduction of these esters by means of sodium and alcohol gives the corresponding primary alcohols.  $\beta$ -Phenyl- $\beta$ -*p*-tolylethyl alcohol is transformed on dehydration into *s*-phenyl-*p*-tolylethylene, and in the case of  $\beta\beta$ -diphenylethyl alcohol a phenyl group undergoes similar change of position (cf. Hepp, A., 1874, 368). Similarly,  $\beta\beta$ -diphenylpropyl alcohol is converted into methylstilbene (cf. Korolev, *J. Russ. Phys. Chem. Soc.*, 1918, 50, 77). The following are described: *benzyl phenyl-p-tolylacetate*, b. p.  $252^{\circ}/12$  mm.; *benzyl phenyl-p-tolylbenzylacetate*, m. p.  $83-84^{\circ}$ , b. p.  $265^{\circ}/5$  mm.; *phenyl-p-tolylbenzylacetic acid*, m. p.  $145-146^{\circ}$ ; *benzyl  $\alpha$ -phenyl-p-tolylpropionate*, b. p.  $254^{\circ}/12$  mm.;  *$\alpha$ -phenyl-p-tolylpropionic acid*, m. p.  $128^{\circ}$ ;  *$\beta$ -phenyl- $\beta$ -p-tolylethyl alcohol*, m. p.  $45-46^{\circ}$ , b. p.  $194^{\circ}/12$  mm.;  *$\beta\beta$ -triphenylpropyl alcohol*, m. p.  $79^{\circ}$ , b. p.  $232-235^{\circ}/14$  mm. H. J. E.

**Synthesis of Glycols from Atrolactic Acid.** R. ROGER (*J. Chem. Soc.*, 1925, 127, 518—523; cf. McKenzie, T., 1904, 85, 1249; 1906, 89, 365; McKenzie and Wren, T., 1906, 89, 688; McKenzie and Müller, T., 1909, 95, 544).—Magnesium methyl iodide reacts with ethyl atrolactinate under the usual conditions to give only small amounts of the pinacol (cf. McKenzie and Müller, *loc. cit.*) but at  $100^{\circ}$  under the conditions described it forms  $\beta$ -phenyl- $\gamma$ -methylbutylene  $\beta\gamma$ -glycol,  $\text{OH}\cdot\text{CPhMe}\cdot\text{CMe}_2\text{OH}$ , m. p.  $83.5-84.5^{\circ}$  in 37% yield. A poor yield of the same glycol is obtained by the action of magnesium methyl iodide on ethyl benzoylformate, and the yield is not improved by using anisole as the Grignard medium.

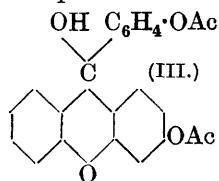
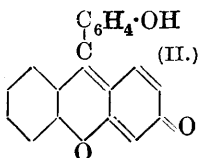
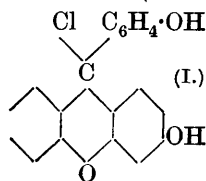
The results of Meerwein (A., 1920, i, 2) on the action of Grignard reagents on ethyl glycolate and on ethyl oxalate and those of Bouvet (A., 1915, i, 766) are discussed. It is pointed out that the selective action of Grignard reagents may depend on the practical conditions employed (cf. Hepworth, T., 1919, 115, 1203), but that in some cases there is a total inability of the carbethoxy group to react completely. This selective action may be accounted for in two ways. First, the two reactions: (a) ester  $\rightarrow$  hydroxy ester, (b) hydroxy ester  $\rightarrow$  pinacol, possess very different velocities, the second stage being the slower. Secondly, spatial effects lead to a complex which is not prone to attack by the reagent (cf. McKenzie and Wren, T., 1908, 93, 312; 1910, 97, 473). The activity of ethyl atrolactinate appears to fall between the extremes of those of the differently substituted glycollic acids, from ethyl dimethylglycolate which contains two groups of moderate saturation capacity (Meerwein and Tiffeneau) and reacts with most Grignard reagents, to ethyl diethylglycolate which reacts only partly with a group of low saturation capacity such as ethyl, giving the hydroxy-ketone. Magnesium ethyl bromide gave only meagre yields of a glycol under the conditions employed above with magnesium methyl bromide, but on heating 1 mol. of ethyl atrolactinate with 12 mols. of magnesium ethyl bromide for 20—25 hrs. a 65%

yield of  $\beta$ -phenyl- $\gamma$ -ethylamylene  $\beta$ - $\gamma$ -glycol,  $\text{OH}\cdot\text{CPhMe}\cdot\text{CEt}_2\cdot\text{OH}$ , m. p. 70—71°, camphoraceous odour with sulphuric acid ( $d$  1.55), is obtained. With magnesium phenyl bromide, a good yield of  $\alpha\beta$ -triphenylpropylene  $\alpha\beta$ -glycol,  $\text{OH}\cdot\text{CPhMe}\cdot\text{CPh}_2\cdot\text{OH}$ , m. p. 76—77°, was obtained after heating for 9 hrs. The same glycol was also obtained in good yields by (1) the action of magnesium methyl iodide (6 mols.) on phenylbenzoin and (2) the action of magnesium phenyl bromide (4 mols.) on methylbenzoin. A. C.

### Condensation of Carbon Tetrachloride and Phenol : Aurin.

M. GOMBERG and H. R. SNOW (*J. Amer. Chem. Soc.*, 1925, 47, 198—211).—When phenol (330 g.) and carbon tetrachloride (154 g.) are heated at 135° for 18 hrs. under a reflux condenser with zinc chloride (50 g.), aurin (90—94 g.) is obtained, together with *p*-hydroxyphenylfluorone (25 g.), 2 : 4' : 4''-trihydroxytriphenylcarbinol (15 g.), leuco-aurin (20 g.), *p*-hydroxyphenylxanthene (7 g.), small amounts of ketones, and a trace of phenyl carbonate.

The primary reaction is the formation of diphenoxydichloromethane (cf. Gomberg and Jickling, A., 1916, i, 29). If water is present, this is hydrolysed to phenyl carbonate, and the latter can be prepared in 50% yield, calculated on the phenol used, by replacing the necessary proportion of zinc chloride by zinc oxide in the above condensation. In absence of water, rearrangement takes place under the influence of the hydrogen chloride produced, 4 : 4'-dihydroxybenzophenone chloride, with a small proportion of the 2 : 4'-isomeride, being formed. Hydrolysis at this stage affords a good method for the preparation of 4 : 4'-dihydroxybenzophenone. Continued reaction next results in the condensation of the above keto chlorides with phenol, with formation of 4 : 4' : 4''-, 2 : 2' : 4''-, and 2 : 4' : 4''-trihydroxytriphenylmethyl chlorides. Aurin results by elimination of hydrogen chloride from the first of these. The second forms, in part, an isomeride of aurin, and in part, by loss of hydrogen, the compound (I), which then loses hydrogen chloride with formation of *p*-hydroxyphenylfluorone (II), orange-red, m. p. 285—295° (decomp.) (cf. Baeyer, A., 1907, i, 757), whilst the last affords, on hydrolysis, the corresponding carbinol, which was identified by conversion into 2 : 4' : 4''-trimethoxytriphenylmethane, m. p. 113—114°, identical with that obtained by the Grignard reaction from *o*-iodoanisole and 4 : 4'-dimethoxybenzophenone. The hydrogen, liberated as above, gives rise to the presence, in the final product, of leuco-aurin, and *p*-hydroxyphenylxanthene, m. p. 148—150° (decomp.). *p*-Acetoxyphenylfluorone, m. p. 204—205°,



and *p*-acetoxyphenyl-3-acetoxyxanthidrol (III), m. p. 138—140°, were obtained by acetylating *p*-hydroxyphenylfluorone. *p*-Methoxy-

*phenylfluorone*, orange, m. p. 206—208°, and *p-methoxyphenyl-3-methoxyxanthinol*, m. p. 112—114°, obtained by methylation of *p*-hydroxyphenylfluorone, and by Grignard syntheses from *p*-iodoanisole and 3-hydroxyxanthone (cf. Baeyer, A., 1910, i, 249; Ullmann and Denzler, A., 1907, i, 142) and 3-methoxyxanthone (cf. Gomberg and West, A., 1913, i, 72), respectively, are described. *p*-Methoxyphenylfluorone is demethylated when heated with aluminium chloride in antimony trichloride. *p*-Hydroxyphenylfluorone is oxidised, when warmed with sodium hydroxide solution, to 2 : 4'-dihydroxybenzophenone.

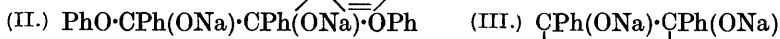
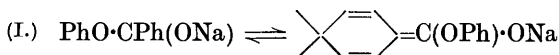
Aurin forms compounds with the following solvents : acetic acid and benzene,  $2\text{C}_{19}\text{H}_{14}\text{O}_3 \cdot 2\text{C}_2\text{H}_4\text{O}_2 \cdot \text{C}_6\text{H}_6$ ; acetic acid and water,  $\text{C}_{19}\text{H}_{14}\text{O}_3 \cdot 1\frac{1}{2}\text{C}_2\text{H}_4\text{O}_2 \cdot \text{H}_2\text{O}$ ; acetone (+1.5 mols.); methyl ethyl ketone (+1 mol.); and ether (+1 mol.). Aurin hydrochloride crystallises with alcohol (1 mol.) (cf. Dale and Schorlemmer, *J. Chem. Soc.*, 1879, 35, 154), acetic acid (2 mols.), or water (2 mols.). When aurin is precipitated, at 60—70°, by hydrochloric acid from its solution in sodium hydroxide, 4 : 4' : 4''-trihydroxytriphenylcarbinol monohydrate can be obtained as purple crystals which gradually lose 2 mols. of water. Triacetylaurin, m. p. 172—173°, is obtained without by-products (cf. Herzig, A., 1896, i, 486) by acetylating aurin. *Tri-p-acetoxytriphenylmethyl chloride* ( $+\text{C}_6\text{H}_5$ ), m. p. 168—174° (decomp.), obtained by the action of acetyl chloride on triacetylaurin in benzene, loses acetyl chloride when heated, with formation of diacetylaurin. When treated with molecular silver in bromobenzene solution in presence of oxygen, the above chloromethane yields *tri-p-acetoxytriphenylmethyl peroxide*, m. p. 184—185°. *Tribenzoylaurin*, m. p. 190—191°, forms compounds with the following solvents : benzene (1.5 mols.); acetic acid, alcohol, carbon tetrachloride, acetone (1 mol.); methyl ethyl ketone, methyl propyl ketone (0.5 mol.). *Tri-p-benzoxoytriphenylmethyl chloride* ( $+\text{C}_6\text{H}_5$ ), m. p. 172—174° after losing benzene, and *tri-p-benzoxoytriphenylmethyl peroxide* ( $+\text{CHCl}_3$ ), m. p. 218° after losing chloroform at 100°, are described. Aurin is oxidised to 4 : 4'-dihydroxybenzophenone when air is drawn through its cold solution in sodium hydroxide. [Cf. B., 1925, 309.] F. G. W.

### Rearrangement of Diphenyl-*p*-tolylacethydroxamic Acid.

C. D. HURD and H. J. BROWNSTEIN (*J. Amer. Chem. Soc.*, 1925, 47, 174—178).—*Diphenyl-p-tolylacethydroxamic acid*, m. p. 146.5° (acetyl derivative, m. p. 135°), was prepared by the action of hydroxylamine on diphenyl-*p*-tolylacetyl chloride (cf. Bistrzycki and Landtewing, A., 1908, i, 270). When the acetyl derivative is treated with alcoholic potassium or sodium hydroxide, the corresponding metallic salts are obtained only in an impure condition, and in small yield, the bulk of the material undergoing a Lossen rearrangement with formation of *diphenyl-p-tolylmethylurethane*, m. p. 116—118° after softening at 114°, and *diphenyl-p-tolylmethylcarbamide*, the latter being identified by its conversion, when heated with aniline, into  $\alpha$ -phenyl- $\beta$ -diphenyl-*p*-tolylmethylcarbamide.

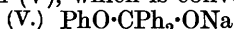
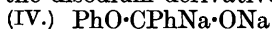
F. G. W.

**Reaction between Metallic Sodium and Aromatic Aldehydes, Ketones, and Esters. II. Esters.** F. F. BLICKE (*J. Amer. Chem. Soc.*, 1925, **47**, 229—239; cf. this vol., i, 37).—When phenyl benzoate is treated with 1 mol. of sodium in absolute ether, with exclusion of air, the metal dissolves and an intense brown-red solution is obtained which contains the tervalent carbon compound (I) in equilibrium with its dimeride (II). The latter separates as a flocculent precipitate and passes spontaneously into benzil and



sodium phenoxide (cf. Scheibler and Voss, A., 1920, i, 366). The benzil reacts with some of the sodium (cf. Beckmann and Paul, A., 1892, 169) with formation of the tervalent carbon compound (III), which then tautomerises into the disodium salt of stilbenediol. Addition of water to the reaction mixture and acidification affords phenol, a trace of benzoic acid, benzil, phenyl benzoate, and benzoin, the latter arising from the stilbenediol by rearrangement.

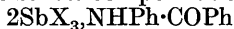
When 2 mols. of sodium are applied per mol. of ester in a mixture of ether and benzene, phenol is obtained in amount almost equal to that which would be derived by complete elimination of sodium phenoxide from the ester-sodium compound, together with traces of benzoic acid and benzoin. If bromobenzene is present, it reacts with the disodium derivative (IV) to form (V), which is converted



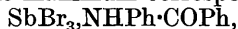
into benzophenone by loss of sodium phenoxide. The ketone then forms the disodium derivative,  $\text{CPh}_2\text{Na}(\text{ONa})$ , which reacts with bromobenzene to yield the sodium salt of triphenylcarbinol (cf. Acree, A., 1903, i, 724; Frey, A., 1896, i, 99). *Phenyl hexahydrobenzoate*, b. p. 160—163°/15 mm., and ethyl hexahydrobenzoate yield, when treated with 1 mol. of sodium, phenol and ethyl alcohol respectively, with other products; benzyl benzoate affords benzyl alcohol and a high-boiling liquid; phenyl  $\alpha$ -naphthoate affords phenol and, apparently, the naphthalene analogue of benzoin.

F. G. W.

**Reactivity of Antimony Halides with certain Aromatic Compounds. II.** E. VANSTONE [with W. G. MESSENGER] (*J. Chem. Soc.*, 1925, **127**, 550—552; cf. T., 1914, **105**, 1491).—The behaviour of compounds of the type  $\text{Ph} \cdot \alpha \cdot \beta \cdot \text{Ph}$  (Vanstone, *loc. cit.*) has been investigated. Benzanilide forms mixtures with antimony halides which are dark red when liquid and reddish-brown when solid. Curves connecting the melting points of the mixtures with the percentages of the constituents consist of four branches and show that in each system two stable compounds are formed:



and  $\text{SbX}_3 \cdot \text{NHPH} \cdot \text{COPh}$ . For the trichloride, the respective m. p. at the maxima are 99° and 112°. The system containing the tribromide has only one maximum corresponding with





m. p.  $116^{\circ}$ ; the compound with  $2\text{SbBr}_3$  is unstable and decomposes below its m. p. In general, the reactivity of benzanilide towards antimony halides is closely allied to that of toluene. Benzyl-aniline differs from the other similar aromatic compounds investigated in its reduced activity towards antimony halides. The mixtures (both liquid and solid) are dark green, and only one stable compound,  $\text{CH}_2\text{Ph}\cdot\text{NHPh}\cdot\text{SbCl}_3[\text{SbBr}_3]$ , is formed.

A. C.

**Bromonovocaine.** J. FREJKA and J. VITHA (*Pub. Fac. Sci. Univ. Masaryk*, 1925, No. 48, 1—22).—2-Bromo-*p*-aminobenzoic acid reacts with ethylene chlorohydrin to give  $\beta$ -chloroethyl 2-bromo-*p*-aminobenzoate, m. p.  $123$ — $124^{\circ}$ , which on treatment with diethylamine gives  $\beta$ -diethylaminoethyl 2-bromo-*p*-aminobenzoate, m. p.  $130$ — $131^{\circ}$  (hydrochloride, m. p.  $172$ — $173^{\circ}$ ), the base of bromonovocaine. The following new substances are described: the silver salt, m. p.  $234^{\circ}$ , the lead salt, and the ethyl ester, m. p.  $125^{\circ}$ , of 2-bromo-*p*-aminobenzoic acid; 2-bromo-*p*-nitrobenzoyl chloride, m. p.  $132$ — $133^{\circ}$ ;  $\beta$ -chloroethyl 2-bromo-*p*-nitrobenzoate, m. p.  $59$ — $60^{\circ}$ ; ethylene di-2-bromo-*p*-nitrobenzoate, m. p.  $134$ — $135^{\circ}$ ; 3:3'-dibromoazobenzene-4:4'-dicarboxylic acid, m. p. above  $300^{\circ}$  (formed on reduction of 2-bromo-*p*-nitrobenzoic acid with zinc and alkali, the corresponding hydrazine first formed being oxidised with air), its silver salt, and its glycol ester.

B. F.

**Syntheses by Means of Organic Peroxides. IV. Action of Benzoyl Peroxide on Diphenyl.** H. GELISSEN and P. H. HERMANS (*Ber.*, 1925, 58, [B], 764—765).—The action of benzoyl peroxide on molten diphenyl leads to the formation of benzene in addition to 1:4-diphenylbenzene and bisdiphenyl reported previously (this vol., i, 379), thus indicating the production of benzoic esters. The yield of polyphenylenes can be increased by moderating the temperature of the reaction, which should be maintained below  $95^{\circ}$ .

H. W.

**Syntheses by Means of Organic Peroxides. V. Action of Benzoyl Peroxide on Alcohols.** H. GELISSEN and P. H. HERMANS (*Ber.*, 1925, 58, [B], 765—770; cf. this vol., i, 379).—The action of benzoyl peroxide on isobutyl alcohol occurs mainly according to the scheme  $(\text{PhCO}\cdot\text{O})_2 + \text{C}_4\text{H}_9\text{O}\cdot\text{H} \rightarrow \text{PhCO}\cdot\text{O}\cdot\text{OC}_4\text{H}_9 + \text{C}_6\text{H}_6 + \text{CO}_2$  and  $\text{Ph}\cdot\text{CO}_2\text{H} + \text{Ph}\cdot\text{O}\cdot\text{C}_4\text{H}_9 + \text{CO}_2$ . *iso*Butyl perbenzoate is not found as such among the products, its place being taken by a mixture of *o*- and *p*-isobutoxybenzoic acids and small amounts of *isobutyl* salicylate. Benzene is produced in quantity. In contrast to the observations made with hydrocarbons, the second reaction occurs to only a very limited extent; the formation of phenol when the neutral and unsaponifiable portions of the reaction products are treated with aluminium chloride probably indicates the original presence of its *isobutyl* ether. The observation that noticeably less carbon dioxide is evolved in the reaction with alcohols than with hydrocarbons indicates that the action  $(\text{PhCO}\cdot\text{O})_2 + \text{R}\cdot\text{OH} \rightarrow \text{PhCO}\cdot\text{O}\cdot\text{OH} + \text{Ph}\cdot\text{CO}_2\text{R}$  also occurs; this

is supported by the isolation of *isobutaldehyde* (formed by the action of the per-acid on excess of *isobutyl alcohol*) and *isobutyl benzoate* in much greater quantity than could be formed by the action of the alcohol on benzoic acid produced in the change. The isolation of *p*-phenylbenzoic acid from benzoyl peroxide and toluene, *isobutyl alcohol*, or acetic acid indicates that it is formed by the decomposition of the peroxide itself. Benzoyl peroxide and boiling absolute ethyl alcohol yield carbon dioxide, acetaldehyde, benzene, and ethyl benzoate. The peroxide reacts very slowly if at all with boiling methyl alcohol.

H. W.

**Syntheses by Means of Organic Peroxides. VI. Action of Benzoyl Peroxide on Acetic Acid.** H. GELISSEN and P. H. HERMANS (*Ber.*, 1925, 58, [B], 770—772; cf. this vol., i, 545).—When heated over boiling water, benzoyl peroxide and glacial acetic acid give much resinous matter, carbon dioxide, benzene, phenyl acetate, benzoic and acetylsalicylic acids; *p*-phenylbenzoic acid is also produced (cf. preceding abstract).

H. W.

**Ethyl Anisylidene-*p*-aminocinnamate.** G. FRIEDEL (*Compt. rend.*, 1925, 180, 892—895; cf. A., 1923, ii, 223).—Feldtkeller and Walter's conclusions as to the existence of four crystalline liquid phases of ethyl anisylidene-*p*-aminocinnamate (*Z. Kryst.*, 1924, 60, 349) are unjustifiable. When the substance is heated, melting occurs at 107°, when a smectic and a nematic phase co-exist in equilibrium. When 114° is reached, the former has disappeared, and at 133° the nematic phase passes into an amorphous form. On cooling, the nematic phase reappears at 133° and the smectic at 114°, but, owing to supercooling, crystallisation does not occur at 107°; at 98°, all the nematic form has disappeared. The temperatures 98° and 114° are not definite transformation points, comparable with those of a pure substance, but depend on the composition of the mixture.

F. M. H.

**Preparation of Optically Active Primary Alcohols.** F. BECHERER (*Helv. Chim. Acta*, 1925, 8, 184—195).—It was thought that the introduction of the phenyl group into citronellol might increase its optical rotation. Phenylacetonitrile on treatment with sodamide in absolute ether yields a sodio derivative (in benzene the yield is much reduced by the formation of resinous products), which reacts with citronellyl bromide with formation of *phenylcitronellylacetonitrile*,  $C_{10}H_{19}CHPhCN$ , b. p. 191—192°/10 mm. in 93% yield. On hydrolysis by means of potassium methoxide, this gives *phenylcitronellylacetic acid*,  $C_{18}H_{25}O_2$ , b. p. 145—147°/0.01 mm.,  $d_4^{20}$  0.9823,  $[\alpha]_D^{20}$  6.98°; *methyl ester*, b. p. 190—191°/9 mm., 104°/0.01 mm.; *ethyl ester*, b. p. 192—193°/9 mm. Attempts to reduce these esters to primary alcohols by the method of Bouveault and Blanc resulted only in the formation of resinous products. Dihydrocitronellol on bromination by means of phosphorus tribromide gave *dihydrocitronellyl bromide*, b. p. 96°, unaccompanied by any phosphorus additive product (cf. this vol., i, 658), in almost

quantitative yield. Ethyl 1-hydroxy-3-methylcyclohexylacetate,  $\text{CH}_2\left\langle\begin{smallmatrix}\text{CH}_2-\text{CH}_2 \\ \text{CHMe}\cdot\text{CH}_2\end{smallmatrix}\right\rangle\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p. 126—128°/10 mm., was prepared from 3-methylcyclohexanone and ethyl bromoacetate, by a modification of Wallach's method, in 84% yield. Heating it with formic acid converts it into 3-methylcyclohexylidene-1-acetic acid,  $\text{C}_7\text{H}_{12}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , b. p. 143—145°/12 mm., and ethyl 3-methylcyclohexylidene-1-acetate, b. p. 107—108°/12 mm. The latter on reduction by Bouveault and Blanc's method gives a rather poor yield of 3-methylcyclohexylethyl alcohol, b. p. 99—102°/12 mm., having an odour like that of guaiacol. Ethyl 3-methylcyclohexylidene-1-acetate on reduction with hydrogen in the presence of nickel gives ethyl 3-methylcyclohexylacetate,  $\text{C}_7\text{H}_{13}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p. 104·5°/12 mm.; reduction of this substance with sodium ethoxide gives a very small yield of alcohol. 3-Methylcyclohexanone reacts with ethyl  $\alpha$ -bromopropionate and zinc to form ethyl 1-hydroxy- $\alpha$ -3-methylcyclohexylpropionate,  $\text{C}_7\text{H}_{12}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{Et}$ , b. p. 128—129°/12 mm. (86% yield), an oil with a strong odour of mint, which, when heated with formic acid, yields ethyl  $\alpha$ -3-methylcyclohexylidenepropionate,  $\text{C}_7\text{H}_{12}\cdot\text{CMe}\cdot\text{CO}_2\text{Et}$ , together with the free acid, b. p. 146—148°/12 mm. The ester on reduction gives a small yield of  $\beta$ -3-methylcyclohexylpropyl alcohol, b. p. 104—105°/12 mm. The reduction of the hydroxy ester or the hydrolysis of ethyl  $\alpha$ -1-hydroxy-3-methylcyclohexylpropionate yields  $\alpha$ -1-hydroxy-3-methylcyclohexylpropionic acid, b. p. 175°/12 mm., and a compound, b. p. 80°/vac.

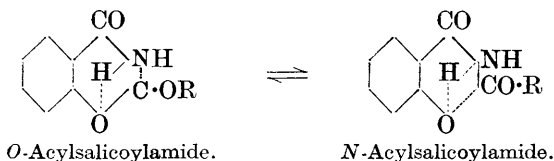
Tetrahydrocarvone on treatment with ethyl bromoacetate and zinc gives ethyl 1-hydroxy-2-methyl-5-isopropylcyclohexylacetate, b. p. 150—151°/12 mm., as main product, with much resinous matter. Heating with formic acid or aluminium phosphate caused no dehydration, but boiling with phosphoric acid gave ethyl 2-methyl-5-isopropylcyclohexylidene-1-acetate,  $\text{C}_{10}\text{H}_{18}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , b. p. 140—142°/12 mm., together with unaltered hydroxy ester and resinous matter. Reduction of this ester gave impure 2-methyl-5-isopropylcyclohexylethyl alcohol, b. p. 120—130°. The non-volatile residue was sodium 2-methyl-5-isopropylcyclohexylideneacetate. Ethyl  $\alpha$ -1-hydroxy-2-methyl-5-isopropylcyclohexylpropionate, b. p. 155—156°/12 mm., was obtained from tetrahydrocarvone and ethyl bromopropionate and zinc, together with much resinous and non-distillable products. On heating with phosphoric acid, it forms ethyl  $\alpha$ -2-methyl-5-isopropylcyclohexylidenepropionate, b. p. 141—142°/12 mm., a mobile oil with a pleasant, aromatic odour. Reduction of the unsaturated ester by Bouveault and Blanc's method gave a 12% yield of  $\beta$ -2-methyl-5-isopropylcyclohexylpropyl alcohol, b. p. 127—131°/12 mm., having the unpleasant phenol-like odour characteristic of other homologues of this series. The greater part of the ester was hydrolysed to  $\alpha$ -2-methyl-5-isopropylcyclohexylidenepropionic acid, b. p. 173—175°/12 mm. A. C.

**Hydrogenation of Diphenyl-*o*-carboxylic Acid.** J. RANEDO and A. LÉON (*Anal. Fis. Quím.*, 1925, 23, 113—117).—By the

hydrogenation of diphenyl-*o*-carboxylic acid two isomeric *acids* having the empirical formula  $C_{13}H_{22}O_2$  are obtained. The first, obtained by catalytic hydrogenation in the presence of platinum-black, has m. p.  $89^\circ$ . The other, obtained by partial reduction with sodium and amyl alcohol and subsequent catalytic hydrogenation, has m. p.  $69^\circ$ . The ammonium and calcium salts of the first acid are much less soluble in water than those of the second.

G. W. R.

**Reciprocal Changes of the Isomeric *O*- and *N*-Acylsalicylamides, and the Constitution of Acylsalicylimide Salts.** R. ANSCHÜTZ, H. ASCHENBERG, H. KUCKERTZ, F. KRONE, K. RIEPENKRÖGER, and C. ZERBE (*Annalen*, 1925, **442**, 18–46; cf. A., 1924, i, 18).—The interconversion of *O*- and *N*-acylsalicylamides may be due to the formation of secondary linkings which change in either direction to full valency linkings under the influence of light, heat, electricity, or chemical reaction :



(cf. McConnan and Titherley, T., 1906, **89**, 1318). For such intramolecular changes and also for the formation of salts of the *N*-acyl compounds, the presence of a free hydroxyl group in the ortho position to carboxyl is essential. Since di-*p*-hydroxybenzimidide,  $(HO\cdot C_6H_4\cdot CO)_2NH$ , forms no ammonium salt, the formula previously proposed for the silver salt of *N*-benzoylsalicylamide (Einhorn and Schupp, A., 1905, i, 778) and the ammonium salt of disalicylimide (Anschütz, A., 1920, i, 48) are insufficient. Since salicylanilide, which contains an ortho phenolic hydroxyl group, also forms no ammonium salt, some further condition is necessary for the formation of such coloured salts. A study of the hydrolysis of *o*-methoxydibenzimidide and similar compounds leads to the conclusion that in the hydrolysis of the methyl ethers of *N*-benzoylsalicylamides and disalicylimides the amide group remains in combination with the stronger acid radical.

The observation of McConnan (T., 1907, **91**, 198) that *o*-2-hydroxybenzoyloxybenzamide melts at  $157^\circ$ , resolidifying and melting again at  $200^\circ$ , could not be confirmed, and this substance on heating for 5 mins. at  $150^\circ$  is completely converted into the isomeric disalicylamide without melting. The isomeric change is complete in 1 hr. at  $140^\circ$ , but does not take place at  $130^\circ$ . Similarly, 4-benzoyloxy-*m*-toluamide and *O*-*m*-hydroxytoluoyl-*m*-hydroxytoluamide (cf. A., 1924, i, 1072) are converted completely into the corresponding imides without melting, whilst *o*-acetoxybenzamide, 4-acetoxy-*m*-toluamide, *m*-acetoxy-*p*-toluamide, 2-acetoxy-*m*-toluamide, *o*-benzoyloxybenzamide, and *o*-2-methoxybenzoyloxybenzamide are partly converted into the imide without melting, the observed m. p.

varying accordingly with the rate of heating. 4-Hydroxy-*m*-toluoylacetamide has m. p. 151—151·5°; 3-hydroxy-*p*-toluoylacetamide, m. p. 148—148·5°; 2-hydroxy-*m*-toluoylacetamide, m. p. 134—134·5°; benzoyl-4-hydroxy-*m*-toluamide, m. p. 206—207° (decomp.), and 2-*o*-methoxybenzoyloxybenzamide, m. p. 189—190°.

[With H. KUCKERTZ.]—In many cases, the conversion of the *N*-acyl into the isomeric *O*-acyl amides is incomplete, and the four *N*-acetyl amides described above are quite unchanged on boiling with acetic acid. This is because the temperature of the boiling acetic acid is above the stability limit previously found for the *O*-acyl compound; consequently the conversion of *N*-acyl into *O*-acyl amides can only take place when this temperature limit for the *O*-acyl derivative lies above the boiling point of the acetic acid. Thus *O*-acetoxybenzamide (stability limit 100°) on boiling with toluene is converted into salicylacetamide.

[With K. RIEPENKRÖGER and H. KUCKERTZ.]—*o*-Monomethyl-disalicylimide in chloroform solution on treatment with ammonia and then with methyl-alcoholic silver nitrate gives a silver salt,  $C_{15}H_{12}O_4NaAg + C_{15}H_{13}O_4N$ , which with methyl iodide in benzene yields *di*-*o*-methoxybenzimidide, m. p. 113—114°, hydrolysed by sodium hydroxide to *o*-methoxybenzoic acid.

[With H. H. ASCHENBERG.]—4-Methoxy-*m*-toluoyl chloride has b. p. 148°/20 mm.; 3-methoxy-*p*-toluoyl chloride, b. p. 149—151°/14 mm.; 2-methoxy-*m*-toluoyl chloride, b. p. 116°/12 mm. Methyl 4-methoxy-*m*-toluate has b. p. 128—130°/14 mm.; methyl 3-methoxy-*p*-toluate, b. p. 137—139°/14 mm., and methyl 2-methoxy-*m*-toluate, b. p. 114—116°/14 mm. *N*-Benzoyl-4-hydroxy-*m*-toluamide, m. p. 206—207° (decomp.), obtained by the action of benzoyl chloride on *p*-hydroxytoluamide in pyridine, gives in methyl-alcoholic solution a sulphur-yellow silver salt,  $C_{15}H_{12}O_3NaAg$ . *N*-Benzoyl-4-methoxy-*m*-toluamide, m. p. 160·5—161°, with sodium hydroxide, yields benzoic acid and 4-methoxy-*m*-toluamide, m. p. 166°. *N*-Benzoyl-3-hydroxy-*p*-toluamide has m. p. 169·5° (sulphur-yellow silver salt); the *O*-methyl derivative, m. p. 129°, is similarly decomposed into 3-methoxy-*p*-toluamide and benzoic acid. *N*-Benzoyl-2-hydroxy-*m*-toluamide has m. p. 147·5—148° (silver salt, sulphur-yellow) and its *O*-methyl derivative, yellow, m. p. 83°, on hydrolysis similarly yields 2-methoxy-*m*-toluamide and benzoic acid. 4-Hydroxy-4'-methoxydi-*m*-toluimide, m. p. 193—194°, on hydrolysis with sodium hydroxide yields 4-hydroxy-*m*-toluamide and 4-methoxy-*m*-toluic acid. 3-Hydroxy-3'-methoxydi-*p*-toluimide, m. p. 196—197°, and 2-hydroxy-2'-methoxydi-*m*-toluimide, m. p. 93°, are decomposed similarly on hydrolysis.

[With C. ZERBE.]—*p*-Hydroxybenzoyl chloride (Kopetschni and Karczag, A., 1914, i, 180) with *p*-toluidine in chloroform yields *p*-hydroxybenzoyl-*p*-toluidide, m. p. 203—204°. *Di*-*p*-hydroxybenzimidide, m. p. 215°, obtained by the action of hydrogen chloride on the molten amide at 190°, does not form salts. *p*-Acetoxybenzoyl chloride, b. p. 144°/12 mm., in ethereal solution with ammonia yields the amide, m. p. 179·5°; the anilide has m. p. 160—161° and the *p*-toluidide, m. p. 174—175°. *Di*-*p*-acetoxybenzimidide,

sintering at  $165^{\circ}$ , has m. p.  $174^{\circ}$ . 4-*p*-Acetoxybenzoyloxybenzoyl chloride (acetoxy-*p*-diplosal chloride),  $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{COCl}$ , m. p.  $114\text{--}115^{\circ}$ , is obtained by the action of phosphorus pentachloride on the corresponding acid in chloroform. The *ethyl* ester has m. p.  $94\text{--}95^{\circ}$ ; the *amide*, m. p.  $201\text{--}202^{\circ}$ ; the *anilide*, m. p.  $197\text{--}198^{\circ}$ ; the *p*-toluidide, m. p.  $212\text{--}213^{\circ}$  (decomp.).

[With F. KRONE.]—*m*-Hydroxybenzoyl chloride has b. p.  $110\text{--}113^{\circ}/0.5$  mm.; the methyl ester, b. p.  $178^{\circ}/17$  mm.; the ethyl ester, b. p.  $180^{\circ}/17$  mm.; the *p*-toluidide, m. p.  $163^{\circ}$ . *m*-Acetoxybenzoyl chloride, obtained by the action of phosphorus pentachloride on the acid, has b. p.  $155^{\circ}/16$  mm.; the methyl ester, m. p.  $29^{\circ}$ , b. p.  $156^{\circ}/17$  mm.; the *amide*, m. p.  $140^{\circ}$ ; the *anilide*, m. p.  $127^{\circ}$ , and the *p*-toluidide, m. p.  $119^{\circ}$ , are described. With phosphoryl chloride *m*-hydroxybenzoic acid gives only small quantities of *m*-diplosal (cf. Fischer and Freudenberg, A., 1910, i, 265); better yields were obtained by the action of ammonia in acetone on 3-*m*-acetoxybenzoyloxybenzoic acid (acetyl-*m*-diplosal), m. p.  $148^{\circ}$ , obtained by the action of *m*-acetoxybenzoyl chloride on *m*-hydroxybenzoic acid. The acid chloride has m. p.  $63^{\circ}$ , b. p.  $190\text{--}200^{\circ}/0.5$  mm.; the corresponding *amide*, m. p.  $138^{\circ}$ , *anilide*, m. p.  $133^{\circ}$ , and *p*-toluidide, m. p.  $148^{\circ}$ , are described. 3-*m*-Hydroxybenzoyloxybenzoic acid (*m*-diplosal), m. p.  $199^{\circ}$ , is converted by thionyl chloride into the *chloride*, from which the corresponding *amide*, m. p.  $178^{\circ}$ , *anilide*, m. p.  $205^{\circ}$ , and *p*-toluidide, m. p.  $234^{\circ}$ , were prepared.

R. B.

### Electrolytic Preparation of *p*-Phenylenediamine, Amino-salicylic Acid, Succinic Acid, and Hydrocinnamic Acid.

J. F. NORRIS and E. O. CUMMINGS (*Ind. Eng. Chem.*, 1925, **17**, 305—307).—In the electrolytic reduction of *p*-nitroaniline, the cathode may be of carbon and the anode of lead. The cell is divided by a porous diaphragm. The cathode solution is 15% hydrochloric acid containing the *p*-nitroaniline to be reduced; the anode solution is 5% sulphuric acid. Electrolysis is carried out at  $75^{\circ}$  with a cathode current density of  $11.2$  amp./dm.<sup>2</sup> The yield of isolated *p*-phenylenediamine hydrochloride is then 91.5% of theory, and the current efficiency 84%. When titanium tetrachloride is added to the cathode solution, the yield is 94.7% and the current efficiency 92.5%.

Benzeneazosalicylic acid is not readily reduced electrolytically in either acid or alkaline solution. It is easily reduced by titanous chloride in the cold and the solution of the latter may be regenerated electrolytically. In this way, aminosalicylic acid is not lost in the mother-liquor and the yield in repeated experiments is 94%.

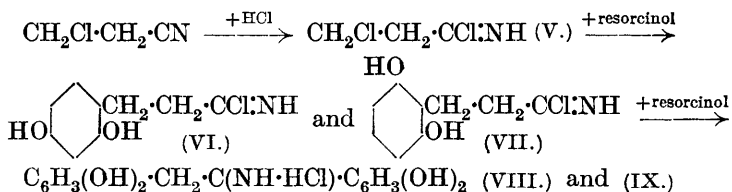
Fumaric acid is reduced electrolytically as follows. The cell, which need not have a diaphragm, contains dilute sulphuric acid with the fumaric acid in solution. The electrodes are both of lead. Reduction is carried out at  $84^{\circ}$  with a cathode current density of  $6.5$  amp./dm.<sup>2</sup> The yield of succinic acid (isolated) is 85.2% of theory. The current efficiency is 77%. Maleic acid is similarly

reduced, but a diaphragm is here necessary. The yield is 90.5% and the current efficiency is 82%.

Cinnamic acid is reduced in presence of an excess of sodium hydroxide, using lead electrodes. The cathode solution, contained in a porous vessel, is stirred rapidly during the electrolysis, because some of the sodium cinnamate is in suspension. The current density is 5.7 amp./dm.<sup>2</sup> and the temperature 60°. The yield is 91% and the current efficiency is 83%. W. A. S.

**Constitution of Abietic Acid.** J. FREJKA and F. BALÁŠ (*Pub. Fac. Sci. Univ. Masaryk*, 1923, (29), 1—12).—On oxidising abietic acid (from American colophony, type I) there are formed isobutyric acid and an amorphous, monobasic ketonic acid, C<sub>10</sub>H<sub>16</sub>O<sub>3</sub>, m. p. 89—90°, perhaps identical with Mach's acid (cf. A., 1895, i, 384). It is thought to be 2-ethyl-1-propylcyclopropane-1-glyoxylic acid or a similar substance. It yields an oxime, C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>.NOH, m. p. 127°, and silver, lead, and barium salts. B. F.

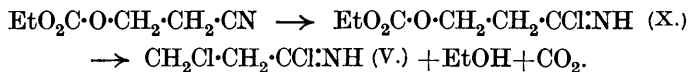
**Condensation of β-Chloro- and β-Ethylcarbonato-propionitriles with Resorcinol.** E. CHAPMAN and H. STEPHEN (*J. Chem. Soc.*, 1925, 127, 885—892; cf. Langley and Adams, A., 1922, i, 1153).—β-Chloropropionitrile does not react normally with resorcinol in presence of hydrogen chloride (cf. Hoesch, A., 1915, i, 820). With equimolecular quantities of the reactants, the main product, β-2 : 4-dihydroxyphenylpropionic acid (I) (*lactone*, 7-hydroxy-3 : 4-dihydrocoumarin, m. p. 133—134°; *acetyl-lactone*, m. p. 111—111.5°) is accompanied by β-2 : 6-dihydroxyphenylpropionic acid (II), m. p. 174—176° (decomp.), resolidifying at 178° and melting again at 224—225° (*lactone*, 5-hydroxy-3 : 4-dihydrocoumarin, m. p. 224—225°). With excess of resorcinol (4 mols.), 2 : 4-dihydroxyphenyl β-2 : 6-dihydroxyphenylethyl ketone (III), m. p. 228—229°, and 2 : 4-dihydroxyphenyl β-2 : 4-dihydroxyphenylethyl ketone (IV), m. p. 186° (*phenylhydrazone*, m. p. 214—215°), are also obtained. The course of the reaction is shown by the scheme :



The iminochlorides (VI) and (VII), on hydrolysis, give the acids (I) and (II); the ketimine hydrochlorides (VIII) and (IX), resulting from reaction of (VI) and (VII) with excess of resorcinol, give the ketones (III) and (IV).

β-Ethylcarbonatopropionitrile, obtained by the action of ethyl chloroformate on a pyridine solution of ethylene cyanohydrin, heavy, colourless oil, b. p. 127—128°/15 mm., 206°/760 mm., condenses with an equimolecular proportion of resorcinol to give the

same four compounds. Hydrogen chloride reacts with the nitrile thus :



The alcohol formed is shared between the iminochlorides (X) and (V), giving a mixture of the hydrochlorides of  $\beta$ -ethylcarbonatopropioimino ethyl ether,  $\text{EtO}_2\text{C}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{HCl}$ , and  $\beta$ -chloropropioimino ethyl ether,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{C}(\text{OEt})\cdot\text{NH}\cdot\text{HCl}$ . Hydrolysis gives *ethyl  $\beta$ -ethylcarbonatopropionate*, colourless liquid, b. p.  $230^\circ$ , and ethyl  $\beta$ -chloropropionate. These esters can be isolated in the reaction with resorcinol. Their formation diminishes the concentration of  $\beta$ -chloropropioiminochloride (V) and the consequent excess of resorcinol gives all four products obtained with  $\beta$ -chloropropionitrile.

M. J.

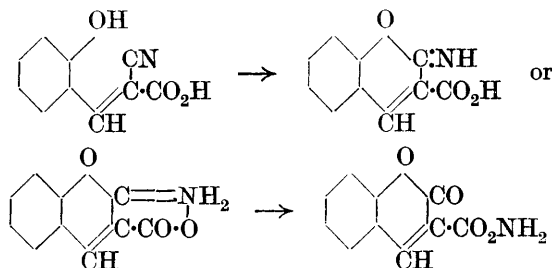
**Artificial "Saccharin" Substances. Synthesis of Diphenyl-4:4'-dicarboxy-3:3'-sulphimide (Diphenyl-4:3:4':3'-dicarboxylicsulphinide).** L. HARDING (*J. Soc. Chem. Ind.*, 1925, **44**, 138—140T).—*p*-Ditolyl was sulphonated and the product treated with ammonia. The resulting *pp'*-dimethyldiphenyl-3:3'-disulphonamide, m. p. about  $300^\circ$ , was oxidised in alkaline solution and the sodium salt of the di-imide recrystallised many times. *Diphenyl-4:3:4':3'-dicarboxylicsulphinide* was difficult to purify. Although this substance is constituted of two "saccharin" molecules fused in the para position, it is tasteless like the monoimide, diphenyl-4:4'-dicarboxamide-2:2'-disulphimide.

F. B.

**Syntheses of Substituted Succinic Acids containing Aromatic Residues.** W. BAKER and A. LAPWORTH (*J. Chem. Soc.*, 1925, **127**, 560—567; cf. Lapworth and McRae, T., 1922, **121**, 1699; Lapworth and Higginbotham, T., 1922, **121**, 49).—Various arylidenecyanoacetic acids have been esterified by boiling with alcoholic anhydrous hydrogen chloride (yields all above 90%). The esters combine more readily with alkali cyanide than the free acids (cf. Higginbotham and Lapworth, *loc. cit.*). Ethyl cyanophenylacrylate, on heating with sodium cyanide in alcohol, yields a product which on treatment with hydrochloric acid gives ethyl  $\alpha\beta$ -dicyano- $\beta$ -phenylpropionate, m. p.  $64^\circ$  (cf. Higson and Thorpe, T., 1906, **89**, 1471). This on boiling with concentrated hydrochloric acid is hydrolysed to phenylsuccinic acid, m. p.  $165^\circ$ , yield 95%. The influence which the  $\alpha$ -cyano group exerts on the reactivity of the double bond is pointed out; in the case of ethyl cinnamate, the yield is only 20% (cf. Higginbotham and Lapworth, *loc. cit.*). Vanillylidenecyanoacetic acid in the same way gives *vanillylsuccinic acid*,  $\text{C}_{11}\text{H}_{12}\text{O}_6$ , m. p.  $175$ — $176^\circ$ , in 45% yield, the smallness of which is due to the extreme solubility of the acid in water. Solutions of the acid in alkali show various colour phenomena due to oxidation. The *carbethoxy* derivative has m. p.



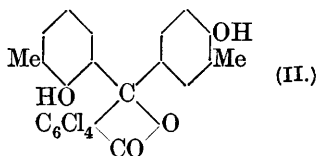
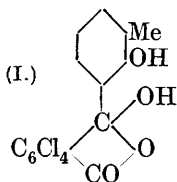
197—198°. *Acetovanillylsuccinic anhydride*, m. p. 112—113°, is formed on boiling vanillylsuccinic acid with acetyl chloride. The oily dicyano compound obtained by treating ethyl cyanoanisylacrylate with sodium cyanide could not be hydrolysed as in the above cases without forming tarry products, but in ethereal solution hydrogen chloride caused the separation of the imino-ether hydrochloride, orange crystals. After 48 hours, prolonged boiling with concentrated hydrochloric acid gave *anisylsuccinic acid*, m. p. 194—195°, in 70% yield. *Anisylsuccinic anhydride* has m. p. 90.5°. Piperonylsuccinic acid (Lapworth and McRae, *loc. cit.*), prepared as above, was obtained in poor yield; *piperonylsuccinic anhydride* has m. p. 96°. Salicylideneacyanoacetic acid could not be esterified by boiling the alcoholic solution with hydrogen chloride, instead, a bulky white solid separated and then gradually dissolved, leaving a precipitate of ammonium chloride, whilst the solution on keeping deposited ethyl coumarin-3-carboxylate, m. p. 94° (cf. Haarmann and Reimer, D.R.-P. 189252; Bechert, A., 1894, i, 488). Bechert's explanation of the formation of coumarin is shown to be untenable in view of the great stability of the nitrile group. The authors explain the change by the scheme :



The cyano group condenses with the *o*-hydroxyl group, forming an imino compound (the white insoluble substance) which is decomposed by water with formation of a solution of ammonium coumarin-3-carboxylate. On acidification coumarin-3-carboxylic acid,  $\text{C}_{10}\text{H}_6\text{O}_4$ , m. p. 187—188°, is precipitated. The configuration of salicylideneacyanoacetic acid, which does not form a lactone, is that of the *trans* acid. The apparent easy hydrolysis of the nitrile group in this acid (cf. Clarke and Francis, A., 1911, i, 205), according to the above scheme, is not that of the nitrile, but that of the imino group formed by its condensation with the *o*-hydroxyl group. A. C.

**Isomerism of the Diphenylsuccinic Acids.** A. MADINA-VEITIA and I. RIBAS (*Anal. Fis. Quím.*, 1925, 23, 96—99, 138—147).—Catalytic hydrogenation of diphenylmaleic acid yields principally (70%) *s*-diphenylsuccinic acid, which is optically inactive by internal compensation. From a study of the salts of  $\alpha$ -diphenylsuccinic acid, it is concluded that the carboxyl groups are in the *cis* position. G. W. R.

***o*-Cresoltetrachlorophthalein, some of its Derivatives, and *iso-o*-Cresoltetrachlorophthalein.** W. R. ORNDORFF and M. S. PATEL (*J. Amer. Chem. Soc.*, 1925, **47**, 863—867).—In the condensation of *o*-cresol with tetrachlorophthalic anhydride to form *o*-cresoltetrachlorophthalein, fuming sulphuric acid (15%) can be used advantageously instead of stannic chloride (cf. Arnold, A., 1924, i, 403). *Dibenzoyl-o-cresoltetrachlorophthalein* has m. p. 198—200°. *Dibromo-o-cresoltetrachlorophthalein*, m. p. 270—271°, is obtained by brominating *o*-cresoltetrachlorophthalein in alcohol. It becomes blue at  $p_H$  7.2—7.6, forms a light blue *silver* salt, and a dark blue *diammonium* salt which loses ammonia at 80°. The *diacetate*, m. p. 237—239°, *dibenzoate*, m. p. 176—178°, *dimethyl ether*, m. p. 245—247°, and *diethyl ether*, m. p. 172—175° (decomp.), are described. *Dinitro-o-cresoltetrachlorophthalein*, yellow, m. p. 232—234°, obtained by nitrating *o*-cresoltetrachlorophthalein in acetic acid, is yellow in alkaline solution, and yields a *triammonium* salt which loses ammonia on keeping. The *diacetate* (+H<sub>2</sub>O) has m. p. 140° with loss of water, the anhydrous compound having m. p. 206—208°. By the condensation of *o*-cresol with 2'-hydroxy-*m*-toluoyl-3 : 4 : 5 : 6-tetrachloro-2-benzoic acid (I), m. p. 217—220°



(cf. Ullmann and Schmidt, A., 1920, i, 53), by means of stannic chloride, *iso-o-cresoltetrachlorophthalein* (II), m. p. 261—263° (decomp.), was obtained. It turns blue at  $p_H$  9.2—9.6. F. G. W.

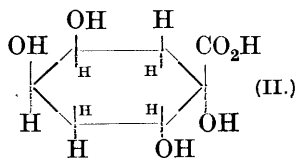
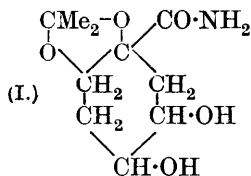
**Derivatives of Acenaphthene.** F. R. LORRIMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 211—216).—When *o*-(4-acenaphthoyl)-benzoic acid (cf. Graebe, A., 1903, i, 408) is warmed with acetic anhydride, an *acetyl* derivative, m. p. 131—132°, is obtained, which decomposes at 165° with formation of a *product*, m. p. above 300°, identical with that obtained by prolonged action of acetic anhydride on the above acid.

*Phenyl-4-acenaphthylphthalide*, m. p. 216—217°, is prepared by the successive action of benzene and acenaphthene on phthalic anhydride in presence of aluminium chloride (cf. Rubidge and Qua, A., 1914, i, 539). It yields, on oxidation with dichromate in acetic acid, *phenyl-1'-naphthylphthalide-4' : 5'-dicarboxylic acid*, the *anhydride* of which has m. p. 291°. This gives, on reduction, *diphenyl-1'-naphthylmethane-2 : 4' : 5'-tricarboxylic acid*, the *anhydride* of which has m. p. 206°, and from which, by distillation with excess of barium hydroxide, diphenyl- $\alpha$ -naphthylmethane was obtained. *Diphenyl-4'-acenaphthylmethane-2-carboxylic acid*, m. p. 220° (*methyl ester*, m. p. 135—136°), is obtained from the above phenyl-4-acenaphthylphthalide by reduction with zinc and

alcoholic potassium hydroxide. When the *barium* salt is reduced by the method of Scholl and Neovius (A., 1911, i, 452), *diphenyl-4-acenaphthylmethane*, m. p. 176°, is obtained, and this, on oxidation, affords *diphenyl-1'-naphthylcarbinol-4':5'-dicarboxylic acid*, the *anhydride* of which has m. p. 209°. *Phenyl-1'-naphthylphthalide-4:4':5'-tricarboxylic acid (anhydride)*, m. p. 245°, *phenyl-p-tolyl-4'-acenaphthylmethane-2-carboxylic acid*, m. p. 210° (*methyl ester*, m. p. 147°), and *phenyl-p-tolyl-4-acenaphthylmethane*, m. p. 209°, obtained analogously, are described. *o*-(4-Acenaphthoyl)benzoic acid yields *4-acenaphthylphthalide*, m. p. 206°, on reduction with zinc and ammonia, and *phenyl-4'-acenaphthylmethane-2-carboxylic acid*, m. p. 215—216°, by the method of Scholl and Neovius. The barium salt of the latter acid afforded *phenyl-4-acenaphthylmethane*, m. p. 111—112°, on distillation, and this was oxidised to *4-benzoylnaphthalic acid* (Graebe, *loc. cit.*).

4-(*o*-Carboxybenzoyl)naphthalic acid was reduced to the corresponding benzyl derivative, m. p. 266°. *Methyl*, m. p. 73—74°, and *ethyl*, m. p. 84—85°, *4-acenaphthoates* were prepared. F. G. W.

**Constitution and Configuration of Quinic Acid.** P. KARRER, R. WIDMER, and P. RISO (*Helv. Chim. Acta*, 1925, 8, 195—202; cf. Erwig and Königs, A., 1889, 991; Emde, A., 1918, i, 265).—Quinic acid is either 1:3:4:6-, 1:3:4:5-, or 1:2:3:4-tetrahydroxycyclohexane-1-carboxylic acid, the position of one hydroxy group being uncertain. Methyl tetramethylquinat prepared according to Herzig and Ortony (cf. A., 1920, i, 878), on keeping with ammonia at the ordinary temperature, gives *tetramethylquinamide*, C<sub>11</sub>H<sub>21</sub>O<sub>5</sub>N, m. p. 115—116°, which on treatment with bromine and potassium hydroxide yields small amounts of the quinol mono- and di-methyl ethers. The formation of the dimethyl ether would appear to exclude the 1:3:4:5- and 1:2:3:4-isomerides, since in the Hofmann degradation the  $\alpha$ -methoxy acid amide group is decomposed. The presence of two pairs of vicinal hydroxy groups is confirmed by the fact that quinamide reacts with acetone containing 1% of hydrogen chloride to form *diisopropylidenequinamide*, m. p. 155°,  $[\alpha]_D^{25}$  -27.1°. *iso*Propylidenequinide (cf. Fischer, A., 1921, i, 419) on treatment with cold ammonia yields *isopropylidenequinamide*, m. p. 141°,  $[\alpha]_D^{25}$  -50.92°. Since further condensation



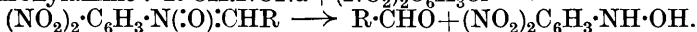
with acetone takes place with formation of the *diisopropylidenequinamide* (above), the formula (I.) is indicated. It is concluded that the Erwig and Königs formula (*loc. cit.*) is the correct one, that the hydroxyl groups are in the positions 1:3:4:6. Evidence is given which shows the 1:6-hydroxyl groups to be in

the *cis* position on one side of the plane of the ring and the 3:4-hydroxyl groups also in the *cis* position on the other side of the plane (cf. Böeseken, A., 1920, i, 837), giving the configuration (II). The conductivity of boric acid solutions is reduced by the addition of monoacetone quinamide (cf. Böeseken, *loc. cit.*).

A. C.

**Constitution of Grignard's Magnesium Compounds. II.**  
J. MEISENHEIMER.—(See i, 527.)

**Isomerism of the Oximes. XXI. Action of Picryl Chloride and of Chloro-2:4-dinitrobenzene on Aldoximes.**  
O. L. BRADY and L. KLEIN (*J. Chem. Soc.*, 1925, 127, 844—852; cf. A., 1924, i, 741).—Picryl chloride reacts readily in alcoholic solution with the sodium salts of substituted benzantialdoximes, yielding trinitrophenyl derivatives to which the *syn* configuration is assigned, since they are hydrolysed by concentrated hydrochloric acid to picric acid and the carboxylic acid through the nitrile, or by alkalis to picric acid and the nitrile:  $R\cdot CH:N\cdot O\cdot C_6H_2(NO_2)_3 \rightarrow (NO_2)_3C_6H_2\cdot OH + R\cdot CN \rightarrow R\cdot CO_2H$ . No derivatives could be obtained from the sodium salts of *o*- and *p*-hydroxybenzantialdoximes. The reaction was studied in the case of the sodium salts of the following *syn*-oximes: benzaldoxime, *p*-methoxybenzaldoxime, cinnamaldoxime, and heptaldoxime. In each case, a mixture of the corresponding aldehyde and nitrile was obtained. Further investigation of the mechanism of the reaction of chloro-2:4-dinitrobenzene on the sodium salts of the *syn*-aldoximes suggests that an *N*-dinitrophenyl derivative is first formed and is immediately hydrolysed to the aldehyde and  $\beta$ -dinitrophenylhydroxylamine:  $R\cdot CH:NONa + (NO_2)_2C_6H_3Cl \rightarrow$



The method of decomposition of the latter is not clear, since the final product, sodium dinitrophenoxide, is accompanied by no trace of hydroxylamine.

Fusion of equimolecular quantities of chloro-2:4-dinitrobenzene and either *syn*- or *anti*-cinnamaldoxime gives the same additive compound, m. p. 69·6°, decomposed by rapid treatment with dilute sodium hydroxide into chlorodinitrobenzene and cinnamantialdoxime. The sodium salts of the corresponding *anti*-aldoximes yielded picryl derivatives of the following: benzsynaldoxime, m. p. 181—182° (decomp.); *o*-methoxybenzsynaldoxime, m. p. 153—154°; *p*-methoxybenzsynaldoxime, m. p. 142—143°; 3:4-methylenedioxybenzsynaldoxime, m. p. 152°; *o*-nitrobenzsynaldoxime, m. p. 157—158°; *m*-nitrobenzsynaldoxime, m. p. 169°; *p*-nitrobenzsynaldoxime, m. p. 168°; *p*-dimethylaminobenzsynaldoxime, decomp. 130°; cinnamsynaldoxime, m. p. 164—165°. 4-Hydroxy-3-methoxybenzantialdoxime gave picryl-4-picryloxy-3-methoxybenzsynaldoxime, m. p. 178—179°. Each of these compounds decomposes at the m. p.

M. J.

**Bromo Derivatives of *m*-Hydroxybenzaldehyde.** H. H. HODGSON and H. G. BEARD (*J. Chem. Soc.*, 1925, 127, 875—881; cf. Pschorr, A., 1912, i, 775; Krause, A., 1899, i, 281).—Tribromination

of *m*-hydroxybenzaldehyde in aqueous solution at 50° is sufficiently quantitative to be suitable for its determination. Regulated bromination to the 6-mono-, 4:6-di-, and 2:4:6-tri-bromo derivatives can be carried out in chloroform or carbon tetrachloride. The 2-, 4-, and 6-monobromo isomerides are obtained from the corresponding 2-, 4-, and 6-nitro-3-hydroxybenzaldehydes. The last gives a very bad yield of bromo derivative, because of formation from the amino compound during reduction of a red, amorphous substance corresponding with the formula  $\text{HO}\cdot\text{C}_6\text{H}_3\text{<}\begin{smallmatrix}\text{CH} \\ \text{N} \end{smallmatrix}$ . An

attempt to introduce bromine into the *p*-nitrophenylhydrazone of 4-amino-3-hydroxybenzaldehyde by the Sandmeyer reaction gave *p*-nitrophenylazoimide.

2-Bromo-3-hydroxybenzaldehyde, m. p. 141—142° (oxime, m. p. 148°; *p*-nitrophenylhydrazone, red, m. p. 241°), gives a methoxy derivative, m. p. 45—46° (oxime, m. p. 148°; *p*-nitrophenylhydrazone, yellow, m. p. 206—208°). 4-Bromo-3-hydroxybenzaldehyde, m. p. 131·5° (oxime, m. p. 173—174°; *p*-nitrophenylhydrazone, m. p. 210—212°, decomp. above 220°), gives a methoxy derivative, m. p. 74° (oxime, m. p. 94·5°; *p*-nitrophenylhydrazone, m. p. 246°; 4-bromo-3-methoxybenzoic acid, m. p. 219—220°). 6-Bromo-3-hydroxybenzaldehyde (oxime, m. p. 157°, pale yellow sodium salt; *p*-nitrophenylhydrazone, m. p. 240—243°) gives a methoxy derivative (oxime, m. p. 117°; *p*-nitrophenylhydrazone, m. p. 225°). 4:6-Dibromo-3-hydroxybenzaldehyde, m. p. 139° [oxime, m. p. 243°; *p*-nitrophenylhydrazone, m. p. 259—260° (decomp.)], gives a methoxy derivative, m. p. 110°. 4:6-Dibromo-3-methoxybenzoic acid has m. p. 202—203°. 2:4:6-Tribromo-3-hydroxybenzaldehyde gives a *p*-nitrophenylhydrazone, m. p. 229—230° (decomp.). 2-Nitro-3-hydroxybenzaldehyde gives a dark red silver salt, which is decomposed by boiling water; oxime, m. p. 172·5°, red sodium salt; and *p*-nitrophenylhydrazone, m. p. 240—250° (decomp.). 4-Nitro-3-hydroxybenzaldehyde gives a brick-red silver salt, stable in hot water; oxime, m. p. 164°, brilliant red sodium salt; *p*-nitrophenylhydrazone, m. p. 265—266°; and methoxy derivative (*p*-nitrophenylhydrazone, m. p. 236—238°). 6-Nitro-3-hydroxybenzaldehyde gives a brownish-yellow silver salt, decomposed by boiling water; oxime, m. p. 178—179°, yellow sodium salt; and *p*-nitrophenylhydrazone, decomp. 250°, m. p. above 300°. M. J.

**Substitution in Resorcinol Derivatives. I. Nitration of Derivatives of  $\beta$ -Resorcylaldehyde.** M. G. S. RAO, C. SRIKANTIA, and M. S. IYENGAR (*J. Chem. Soc.*, 1925, **127**, 556—560).—Nitration of 2-hydroxy-4-methoxybenzaldehyde in glacial acetic acid at 10—15° gives a 75—80% yield of 5-nitro-2-hydroxy-4-methoxybenzaldehyde, m. p. 168—169°; the oxime, yellow, has m. p. 215—216°, the phenylhydrazone, orange, has m. p. 197—198°. Oxidation of the nitro-aldehyde with permanganate or nitration of *p*-methoxysalicylic acid (cf. Perkin, T., 1902, **81**, 1056) gives 5-nitro-2-hydroxy-4-methoxybenzoic acid, m. p. 228° (decomp.), which when heated with water at 160—170° is almost quantitatively

converted into 4-nitroresorcinol 3-methyl ether, m. p.  $143^{\circ}$  (Weselsky and Benedikt, *Monatsh.*, 1880, **1**, 887, give m. p.  $144^{\circ}$ ). The nitro group in the nitro-acid, and consequently in the nitro-aldehyde, is therefore in position 5. It was not found possible to confirm this by treating 5-nitro- $\beta$ -resorcylic acid with methyl iodide or sulphate, as methylation did not take place. Methyl *p*-methoxysalicylate, m. p.  $49^{\circ}$  (prepared by the action of methyl sulphate on  $\beta$ -resorcylic acid), on treatment with nitric acid (*d* 1.42) in acetic acid gives methyl 5-nitro-2-hydroxy-4-methoxybenzoate, m. p.  $137$ — $138^{\circ}$ . This nitro ester on hydrolysis with potassium ethoxide gives 5-nitro-2-hydroxy-4-methoxybenzoic acid. 2 : 4-Dimethoxybenzaldehyde (from methyl sulphate, sodium hydroxide, and 2-hydroxy-4-methoxybenzaldehyde) on nitration gives 5-nitro-2 : 4-dimethoxybenzaldehyde, m. p.  $188$ — $189^{\circ}$ , in 75—80% yield. Methylation of 5-nitro-2-hydroxy-4-methoxybenzaldehyde with methyl iodide and silver oxide gives the same compound with m. p. one degree higher; the *oxime* has m. p.  $184$ — $185^{\circ}$  and the *hydrazone*, m. p.  $169$ — $170^{\circ}$ . 4-Methoxy-2-ethoxybenzaldehyde, m. p.  $65$ — $66^{\circ}$ , is obtained by treating a chloroform solution of 2-hydroxy-4-methoxybenzaldehyde with ethyl iodide and silver oxide. The *oxime* has m. p.  $95$ — $96^{\circ}$ , the *hydrazone*, m. p.  $110$ — $111^{\circ}$ . Nitration of the aldehyde or ethylation of 5-nitro-2-hydroxy-4-methoxybenzaldehyde gives 5-nitro-4-methoxy-2-ethoxybenzaldehyde, m. p.  $138$ — $139^{\circ}$ ; *oxime*, m. p.  $185$ — $186^{\circ}$ , *hydrazone*, m. p.  $185$ — $186^{\circ}$ . The nitro compounds obtained by alkylating nitro-phenolic aldehydes by Purdie's method are usually yellow and melt a degree higher than those (red or brown) obtained by direct nitration of the dialkyl-aldehydes. The position [5] of the nitro group is in accord with the results of other workers (cf. Gattermann, A., 1908, i, 28; Perkin, T., 1902, **81**, 1056; Bauer, A., 1915, i, 606). The authors are unable to decide whether the 3-isomeride is also formed. 2-Hydroxy-4-methoxybenzaldehyde, unlike its isomeride vanillin, is affected by moisture. Halogen acids (except hydrofluoric) convert it into dark red solids. That produced by hydrochloric acid contains methoxy groups but no halogen, and gives an acetyl derivative and a crimson bromo derivative. 2 : 4-Dimethoxy- and 4-methoxy-2-ethoxy-benzaldehyde dissolve more readily in concentrated hydrochloric acid, and from the solutions violet and crimson amorphous solids are deposited. The nitro-phenolic aldehydes and their ethers do not give these coloured solids. 2-Hydroxy-4-methoxybenzaldehyde may be used to detect indole in cultures and gives similar but more delicate and less transient colorations than vanillin. Vanillylidenenitromethane (prepared by dissolving vanillin in absolute alcohol and adding the calculated quantity of nitromethane) may be used as an indicator for colorimetric measurements within the two ranges  $p_H$  7—8.5 and  $p_H$  10—11.5. A rough determination gave  $p_H$  2—6, pale yellow;  $p_H$  7, pale pink;  $p_H$  8—10, pink;  $p_H$  11, pale pink;  $p_H$  12, colourless. It is sensitive to carbonic acid, but gives sharp results with ammonia and mineral acids.

A. C.

**Acid Character of Ketoximes : Addendum.** P. PFEIFFER (*J. pr. Chem.*, 1925, [ii], 109, 376).—Explanatory, in reply to Marckwald. The work in question (this vol., i, 270) was approached from the practical and not from the physical side. The solution-acidity is defined as the number of mols. of acid dissolved by 100 mols. of *N*-potassium hydroxide. R. B.

**Organo-metallic Compounds of Aluminium. II. Action of Ketones.** P. LEONE and A. BRAICOVIC (*Atti R. Accad. Lincei*, 1924, [v], 33, 567—569; cf. this vol., i, 529).—The interaction between a ketone and an aluminium alkyl (or aryl) iodide results in the formation of either an unsaturated ketone or a benzenoid hydrocarbon. Thus, when treated with aluminium ethyl (or isoamyl) iodide, acetone yields mesityl oxide, whilst acetophenone yields triphenylbenzene. T. H. P.

**Transformations of 5-Tetralone [1-Keto-1:2:3:4-tetrahydronaphthalene].** G. SCHROETER [with F. ZADEK and J. HOFFMANN] (*Ber.*, 1925, 58, [B], 713—721; cf. Schroeter, A., 1922, i, 1036).—1-Keto-1:2:3:4-tetrahydronaphthalene is smoothly converted by zinc and ethyl bromoacetate in the presence of benzene into *ethyl 1-hydroxy-1:2:3:4-tetrahydronaphthyl-1-acetate*, b. p. 145—150°/0.3 mm. (*1-hydroxy-1:2:3:4-tetrahydronaphthyl-1-acetic acid*, its lead salt, and *1-hydroxy-1:2:3:4-tetrahydronaphthyl-1-acetylhydrazide*, m. p. 97—99°, are described). Condensation proceeds less smoothly if magnesium is substituted for zinc and leads also to the production of *1:1'-dihydroxydi-1:1'-tetrahydrodinaphthyl*, m. p. 189—190°, which readily loses water with formation of *1:1'-bisdihydronaphthyl*, m. p. 139—140° (corresponding *dibromide*, m. p. 100° (decomp.)). The oily *1-hydroxy-1:2:3:4-tetrahydronaphthyl-1-acetic acid* when preserved in a desiccator, or its ester when treated with formic acid or phosphoric oxide in the presence of benzene, loses water, yielding a mixture of *tetrahydronaphthyl-1-acetic acid*,  $C_{10}H_{10} \cdot CH \cdot CO_2H$ , m. p. 90—92°, and *3:4-dihydronaphthyl-1-acetic acid*, m. p. 105—106°, with a small amount of an isomeric acid, m. p. 163—164°. The dihydronaphthylacetic acid, m. p. 100°, described by von Braun (A., 1923, i, 108) appears to be a mixture of the acids of m. p. 90—92° and 105—106°. Tetrahydronaphthyl-1-acetic acid appears to be converted into *3:4-dihydronaphthyl-1-acetic acid* when its alcoholic solution is exposed to light. *Ethyl tetrahydronaphthyl-1-acetate*, b. p. 145°/0.5 mm.,  $d_4^{20}$  1.078, is prepared by the action of ethyl iodide on the silver salt of the acid. Treatment of tetrahydronaphthyl-1-acetic acid or *3:4-dihydronaphthyl-1-acetic acid* with ethyl alcohol and sulphuric acid yields *ethyl 3:4-dihydronaphthyl-1-acetate*, b. p. 172°/14 mm., 176°/16 mm.,  $d_4^{20}$  1.0828. Catalytic reduction of the esters of the mixed, unsaturated acids gives slightly impure *ethyl tetrahydronaphthyl-1-acetate*, b. p. 160—164°/1.5 mm.,  $d_4^{20}$  1.0595, from which *tetrahydronaphthyl-1-acetic acid*, b. p. 192°/13 mm., is obtained by hydrolysis and is purified by means of the copper salt. The unsaturated acids quantitatively

evolve carbon dioxide when boiled with dilute sulphuric acid. Tetrahydronaphthylene-1-acetic acid yields homogeneous 1-methylene-1 : 2 : 3 : 4-tetrahydronaphthalene, b. p.  $103^{\circ}/14$  mm.,  $d_4^{20}$  0.9836, which is converted by ozone in the presence of chloroform and subsequent decomposition of the vitreous ozonide with water into formaldehyde and 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene. 3 : 4-Dihydronaphthyl-1-acetic acid affords 1-methyl-3 : 4-dihydronaphthalene, b. p.  $107^{\circ}/14$  mm.,  $d_4^{20}$  0.9901, which is converted by ozone into  $\beta$ -o-acetylphenylpropaldehyde (identified as the *disemicarbazone*, m. p.  $232^{\circ}$ ). The action of warm formic acid on 1-methyl-ac-tetrahydro- $\alpha$ -naphthol yields exclusively 1-methyl-3 : 4-dihydronaphthalene, whereas according to von Auwers (this vol., i, 241) 1-methylene-1 : 2 : 3 : 4-tetrahydronaphthalene is produced simultaneously when the cold reagent is used.

H. W.

**Beckmann Rearrangement. II.** A. LACHMANN (*J. Amer. Chem. Soc.*, 1925, 47, 260—265).—As the formation of benzophenone-oxime is a reversible reaction, hydrolysis of the oxime being brought about by hydrochloric acid, it follows that when the oxime hydrochloride is heated in water, only a small concentration of the salt is present at any instant. Consequently, products of the Beckmann rearrangement, which takes place through the salt (cf. A., 1924, i, 861), will appear only slowly. At  $100$ — $150^{\circ}$ , 1—2 days are necessary for the rearrangement to take place, and as benzaniline is hydrolysed under these conditions, the final products are aniline and benzoic acid. Phenol is obtained as a by-product, derived from the aniline by nitrous acid from some decomposition of the hydroxylamine.

F. G. W.

**Asymmetric Nitrogen Atom. LIII. Activation Problem in the Case of Quaternary Ammonium Bases with a Double Linking at the Nitrogen Atom.** E. WEDEKIND (*Annalen*, 1925, 442, 119—129).—In the hope that it might be possible to activate the nitrogen atom in a compound of the type,  $N(A)BCD$ , the double linking between nitrogen and carbon not being present in a ring, benzophenonephenylimine methiodide,  $CPh_2:NMePh \cdot I$ , was treated with silver *d*-camphorsulphonate, whereby, owing to hydrolysis, *methylaniline d-camphorsulphonate*,  $[M]_D +50.46^{\circ}$  in water, was obtained. The case in which the double linking is placed between two nitrogen atoms in a ring was examined by converting triphenyltetrazolium bromide,  $CPh \begin{smallmatrix} N^+NPh \\ | \\ N^-NPh \end{smallmatrix} Br$ , into the corresponding *d-camphorsulphonate*, m. p. (indefinite)  $187^{\circ}$ , and *d-bromocamphorsulphonate*, the molecular rotations of which did not differ appreciably from those of the acidic ions; the regenerated bromides were optically inactive.

A further effort to establish the presence of an asymmetric centre was made by attempting to isolate two stereoisomeric salts,  $N^+ \dots C^-$  and  $N^- \dots C^-$ , by the addition of an optically active alkyl halide to a tertiary base with a double linking between carbon and nitrogen. The quaternary salt, m. p.  $164$ — $166^{\circ}$  (decomp.),



obtained from *isoquinoline* and *l*-menthyl iodoacetate appeared, however, to be homogeneous; this was also the case with the corresponding *chloride*, decomp. 147—150°, and *nitrate*, m. p. 178°. Attempts to separate the *d*-camphorsulphonate, m. p. 151—152°, into different components were unsuccessful. Similar negative results were obtained with the additive compound, m. p. 203—206°, from *isoquinoline* and *l*-bornyl iodoacetate and with the corresponding *nitrate*, m. p. 116—118°, and *d*-camphorsulphonate, m. p. 119—121°. The conclusion is reached that there is no evidence of the presence of an asymmetric centre in quaternary ammonium salts containing a doubly-linked nitrogen atom and that the latter becomes asymmetric only when all its valencies are attached to different groups.

H. W.

**Comparison of Migratory Tendencies of Hydrogen and some Acyclic Radicals.** J. LÉVY and R. LAGRAVE (*Compt. rend.*, 1925, **180**, 1032—1034).—The conversion of substances of the type  $\text{CRR}'(\text{OH})\cdot\text{CH}(\text{OH})\text{Me}$  into the ketones  $\text{CHRR}'\cdot\text{CO}\cdot\text{Me}$  (A., 1906, i, 581, 724; 1907, i, 130; 1910, i, 316) appeared to indicate preferential migration of hydrogen as compared with the methyl group, but the evidence is not conclusive since the change might have taken place through the dehydration product  $\text{CRR}'\cdot\text{C}(\text{OH})\text{Me}$ . To remove this uncertainty, isomeric change in

the substituted ethylene oxides,  $\begin{matrix} \text{CPh}_2 \\ | \\ \text{CHR} \end{matrix} > \text{O}$ , has been studied. By

oxidation of the corresponding olefines with perbenzoic acid are obtained  $\alpha\alpha$ -diphenyl- $\alpha$ -propyleneoxide, b. p. 178—180°/21 mm., m. p. 34°, and  $\alpha\alpha$ -diphenyl- $\alpha$ -butylene oxide,  $\begin{matrix} \text{CPh}_2 \\ | \\ \text{CHEt} \end{matrix} > \text{O}$ , b. p. 170—

175°/18 mm. The former yields on distillation at atmospheric pressure  $\alpha$ -phenylbenzyl methyl ketone (*semicarbazone*, m. p. 165—166°), whereas the latter yields a mixture of  $\alpha$ -phenylbenzyl ethyl ketone (*semicarbazone*, m. p. 194—195°) and  $\alpha\alpha$ -diphenylbutaldehyde,  $\text{CEtPh}_2\cdot\text{CHO}$  (*semicarbazone*, m. p. 175—176°), the ketone predominating. Migration of the hydrogen atom therefore occurs exclusively in preference to that of a methyl group and preponderates over the migration of an ethyl group.

G. M. B.

**Migrational Tendencies of Organic Radicals. II. Comparison of *p*-Anisyl and Phenyl Groups.** M. TIFFENEAU and A. OREKHOV (*Bull. Soc. chim.*, 1925, [iv], **37**, 430—439).—In the pinacolic and semipinacolic transpositions the migratory power of the *p*-anisyl group is, in every case studied, greater than that of the phenyl group. *s*-*p*-Dimethoxybenzpinacone, on dehydration with sulphuric acid or acetyl chloride, yields exclusively phenyl  $\alpha\alpha$ -di-*p*-anisylbenzyl ketone, the constitution of which is determined by (a) its hydrolysis to phenyldi-*p*-anisylmethane and benzoic acid, and (b) its reduction by means of the Grignard reagent to  $\alpha\beta$ -diphenyl- $\beta\beta$ -di-*p*-anisylethyl alcohol. *p*-Methoxybenzophenone and di-*p*-methoxybenzophenone, on reduction by zinc in acetic acid solution, give directly the transposed pinacolins and

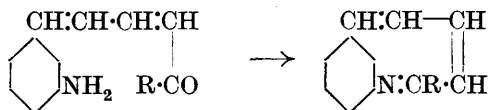
not the intermediate pinacones; this behaviour appears characteristic of the *p*-anisyl group.

On treatment with silver nitrate,  $\alpha\alpha$ -phenyl-*p*-anisylethylene iodohydrin gives exclusively *p*-methoxydeoxybenzoin by the migration of the *p*-anisyl group. The action of magnesium phenyl bromide on di-*p*-methoxybenzil in ethereal solution yields *s*-di-*p*-methoxybenzypinacone, m. p. 170—171°, which, on warming with 50% sulphuric acid or acetyl chloride, gives phenyl  $\alpha$ -di-*p*-anisylbenzyl ketone, m. p. 125—126°. By reduction of the pinacolin with magnesium ethyl bromide,  $\alpha\beta$ -diphenyl- $\beta\beta$ -di-*p*-anisylethyl alcohol is obtained.

On reduction by zinc powder in acetic acid, *p*-methoxybenzophenone also gives the above ketone, and di-*p*-methoxybenzophenone yields tetra-*p*-methoxybenzypinacolin, pale yellow crystals, m. p. 136—137°, which, on hydrolysis with alcoholic potassium hydroxide, yields tri-*p*-anisylmethane and anisic acid.

The iodohydrin of  $\alpha\alpha$ -phenyl-*p*-anisylethylene, prepared by treating the hydrocarbon with iodine in the presence of mercuric oxide, yields phenyl *p*-methoxybenzyl ketone, bright spangles, m. p. 98—99°, on treatment with silver nitrate solution. This ketone reacts with benzyl chloride in the presence of sodium ethoxide, giving phenyl  $\beta$ -phenyl- $\alpha$ -*p*-anisylethyl ketone, m. p. 135—136°, and with amyl nitrite in the cold in the presence of sodium ethoxide yielding a mixture of isomeric oximes, one in large, colourless, prismatic needles, m. p. 163—164°, soluble in ether, and the other soluble in water, m. p. 115—116°, resolidifying with m. p. 163—164°, being quantitatively transformed into the other isomeride. L. F. H.

**Attempts to Prepare Meta Condensed Ring Systems in the Aromatic Series.** P. PFEIFFER, E. PRAHL, W. FITZ, and W. STOLL (*J. pr. Chem.*, 1925, [ii], 109, 41—58).—In view of the fact that *p*-methoxyphenyl *o*-nitrostyryl ketone and *o*-nitrostyryl *p*-methoxystyryl ketone on reduction readily condense between the carbonyl group and the primarily formed amino group, yielding 2-*p*-methoxyphenylquinoline and 2-*p*-methoxystyrylquinoline, attempts have been made to obtain a nine-membered ring system by reduction of *m*-nitrocinnamylidene-*p*-methoxyacetophenone:

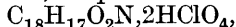


Conditions which lead to quinoline condensation with the *o*-nitro compounds uniformly yield the *m*-aminoketone when the *m*-nitro compound is reduced.

*p*-Methoxyphenyl *o*-nitrostyryl ketone, greenish-yellow, m. p. 113—115°, is obtained from *o*-nitrobenzaldehyde and *p*-methoxyacetophenone in presence of alcoholic sodium hydroxide. *p*-Methoxyphenyl *m*-nitrostyryl ketone, yellow, m. p. 153°; *o*-nitrostyryl *p*-methoxystyryl ketone, greenish-yellow, m. p. 124°; *m*-nitrostyryl *p*-methoxystyryl ketone, yellow, m. p. 159—160°; *m*-nitrocinnamyl-

*ideneacetophenone*, yellow, m. p. 157—158°; *m*-nitrocinnamylidene-*p*-methoxyacetophenone, golden-yellow, m. p. 175—176°; and *p*-anisylidene-*m*-nitrocinnamylideneacetone, golden-yellow, m. p. 167°, were similarly prepared. The colour reactions of these nitro-ketones with sulphuric and with trichloroacetic acid are described.

Reduction of *p*-methoxyphenyl *m*-nitrostyryl ketone with stannous chloride and hydrogen chloride in acetic acid gives the *p*-methoxyphenyl *m*-aminostyryl ketone, orange-yellow, m. p. 139—141° (benzoyl derivative, m. p. 161—162°). *m*-Aminostyryl *p*-methoxystyryl ketone, orange-yellow, m. p. 146—148° (perchlorate,



Bordeaux-red); *m*-aminocinnamylideneacetophenone, yellow, m. p. 152—153° (hydrochloride,  $\text{C}_{17}\text{H}_{15}\text{ON}, \text{HCl}$ , colourless, perchlorate,  $\text{C}_{17}\text{H}_{15}\text{ON}, 2\text{HClO}_4, 2\text{H}_2\text{O}$ , dark red; *p*-anisylidene-*m*-aminocinnamylideneacetone, ochreous yellow, m. p. 162° (black perchlorate; hydrochloride,  $\text{C}_{20}\text{H}_{19}\text{O}_2\text{N}, \text{HCl}$ , brownish-yellow), were similarly prepared. Reduction of *p*-methoxyphenyl *o*-nitrostyryl ketone under similar conditions gives 2-*p*-anisylquinoline, colourless, m. p. 125—126° (canary-yellow perchlorate,  $\text{C}_{16}\text{H}_{13}\text{ON}, \text{HClO}_4$ ; hydrochloride,  $\text{C}_{16}\text{H}_{13}\text{ON}, \text{HCl}$ , greenish-yellow), whilst *o*-nitrostyryl *p*-methoxystyryl ketone similarly yields anisylidenequininaldine (Bialon, A., 1902, i, 828), the orange-yellow perchlorate,



and orange-yellow hydrochloride of which are described. R. B.

**photoDypnopinacolins.** M. DELACRE (*Bull. Soc. chim.*, 1925, [iv], 37, 440—452).—On exposing *albodypnopinacolin* in alcoholic solution to the action of sunlight, a mixture of  $\alpha$ - and  $\beta$ -*photo*-dypnopinacolins with a trace of  $\beta$ -benzopinacolin is produced (cf. A., 1896, i, 591). When treated with potassium hydroxide (A., 1896, i, 662),  $\alpha$ -*photodypnopinacolin* yields a mixture of  $\gamma$ - and  $\delta$ -*photodypnopinacolins*.  $\gamma$ -*photo*Dypnopinacolin gives a carmine-red coloration with concentrated sulphuric acid.  $\delta$ -*photo*Dypnopinacolin is unchanged on treatment with acetic acid or anhydride, absorbs bromine giving a resin, and on treatment with potassium hydroxide yields a substance,  $\text{C}_{32}\text{H}_{24}\text{O}$  or  $\text{C}_{32}\text{H}_{26}\text{O}$ , m. p. 212—213°, unacted on by acetyl chloride. On exposure to sunlight,  $\beta$ -*photodypnopinacolin* is transformed into  $\alpha$ -*photodypnopinacolin* and a reddish-brown resin similar to that obtained by the irradiation of  $\alpha$ -*photodypnopinacolin* itself.  $\beta$ -*luteo*Dypnopinacolin, on exposure to sunlight gives some *albodypnopinacolin*, and  $\gamma$ -*luteo*-dypnopinacolin yields a substance,  $\text{C}_{32}\text{H}_{26}\text{O}$ , m. p. 204—205°. Treatment of this substance with potassium hydroxide yields silky needles, m. p. 184°. A theoretical discussion of the papers of this series (cf. A., 1920, i, 236) is appended. L. F. H.

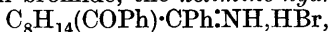
**Unsaturated 1:4-Diketones. I. Halogen Derivatives of Dibenzoylethylene and Related Substances.** J. B. CONANT and R. E. LUTZ (*J. Amer. Chem. Soc.*, 1925, 47, 881—892).— $\alpha\beta$ -*Dichloro- $\alpha\beta$ -dibenzoylthane*, m. p. 167°, is obtained by the action of chlorine on *trans*-dibenzoylethylene (cf. Conant and

Lutz, A., 1923, i, 685; Oddy, *ibid.*, 1098) and also by the action of dry hydrogen chloride on dibenzoylacetylene in chloroform. An *isomeride* is obtained, together with the above product, by the action of chlorine on a suspension of *cis*-dibenzoylethylene in chloroform at  $-20^{\circ}$ .  $\alpha\beta$ -Dichloro- $\alpha\beta$ -ditoluoylethane, m. p.  $210^{\circ}$ ,  $\alpha\beta$ -di-(4-chlorobenzoyl)-, m. p.  $201^{\circ}$ ,  $\alpha\beta$ -di-(6-chloro-m-toluoyl)-, m. p.  $207^{\circ}$ , and  $\alpha\beta$ -dibromo- $\alpha\beta$ -di-(2 : 4 : 6-trimethylbenzoyl)-ethane, m. p.  $207^{\circ}$ , were prepared similarly from the *trans* isomerides of the corresponding unsaturated diketones. When either of the isomerides of the above dichlorodibenzoylethane is dissolved in acetic anhydride containing concentrated sulphuric acid, it is converted into 3 : 4-dichloro-2 : 5-diphenylfuran, m. p.  $91^{\circ}$ .  $\alpha$ -Chloro- $\alpha\beta$ -dibenzoylethylene was obtained in a labile ( $\alpha$ ) form, m. p.  $53^{\circ}$ , by the action of absolute alcoholic hydrogen chloride on dibenzoylacetylene, and in a stable ( $\beta$ ) form, m. p.  $75^{\circ}$ , by refluxing an alcoholic solution of either of the above dichlorodibenzoylethanes. The labile form is converted into the stable isomeride when it is exposed to sunlight in chloroform solution in presence of a trace of iodine. Both isomerides are reduced by titanous chloride to  $\alpha$ -chloro- $\alpha\beta$ -dibenzoylethane.  $\alpha$ -Bromo- $\alpha\beta$ -dibenzoylethylene, m. p.  $88^{\circ}$ , is obtained, analogously to the above chloro derivative, together with a *compound*, m. p.  $126^{\circ}$ . A labile isomeride was not obtainable. It is reduced by titanous chloride to dibenzoylethane. Labile and stable modifications of  $\alpha\beta$ -dichloro- $\alpha\beta$ -dibenzoylethylene, m. p.  $66^{\circ}$  and  $162^{\circ}$ , respectively, were prepared by the action of chlorine on dibenzoylacetylene in chloroform. Corresponding isomerides of  $\alpha\beta$ -dibromo- $\alpha\beta$ -dibenzoylethylene, m. p.  $108^{\circ}$  and  $213^{\circ}$ , respectively, were also prepared. Tetrabromo- $\alpha\beta$ -dibenzoylethane, m. p.  $188-188.5^{\circ}$ , is obtained by brominating dibenzoylacetylene in acetic acid at  $100^{\circ}$ .  $\alpha$ -Methoxy- $\alpha\beta$ -dibenzoylethylene, m. p.  $108.5^{\circ}$ , and  $\alpha$ -phenoxy- $\alpha\beta$ -dibenzoylethylene, m. p.  $92^{\circ}$ , are obtained respectively by the action of sodium methoxide in methyl alcohol, and sodium phenoxide in ether, on dibromodibenzoylethane. The following similarly constituted ethylenes are described :  $\alpha$ -methoxy- $\alpha\beta$ -ditoluoyl-, m. p.  $100^{\circ}$ ;  $\alpha$ -ethoxy- $\alpha\beta$ -dibenzoyl-, m. p.  $103^{\circ}$ ;  $\alpha$ -m-tolyloxy- $\alpha\beta$ -dibenzoyl-, m. p.  $104.5^{\circ}$ ;  $\alpha$ -p-tolyloxy- $\alpha\beta$ -dibenzoyl-, m. p.  $165^{\circ}$ ;  $\alpha$ -methoxy- $\alpha\beta$ -di-(4-chlorobenzoyl)-, m. p.  $131^{\circ}$ ;  $\alpha$ -methoxy- $\alpha\beta$ -di-(6-chloro-m-toluoyl)-, m. p.  $123.5^{\circ}$ ;  $\alpha$ -methoxy- $\alpha\beta$ -di-(2 : 4-dimethylbenzoyl)-, m. p.  $117.5^{\circ}$ , and  $\alpha$ -methoxy- $\alpha\beta$ -di-(2 : 4 : 6-trimethylbenzoyl)-ethylene, m. p.  $120^{\circ}$ . 4-Methoxy-2 : 5-diphenylfuran, m. p.  $115^{\circ}$ , was obtained by reducing  $\alpha$ -methoxy- $\alpha\beta$ -dibenzoylethylene with zinc and acetic acid.  $\alpha$ -m-Tolyloxy- $\alpha\beta$ -dibenzoylethane, m. p.  $111^{\circ}$ , is obtained by reducing the corresponding ethylene with chromous chloride.  $\alpha$ -Amino- $\alpha\beta$ -dibenzoylethylene, yellow, m. p.  $137.5^{\circ}$ , was prepared by the action of alcoholic ammonia on dibromodibenzoylethane.  $\alpha$ -Amino- $\alpha\beta$ -ditoluoylethylene, similar, has m. p.  $136^{\circ}$ . Alcoholic potassium hydroxide afforded similarly  $\alpha$ -hydroxy- $\alpha\beta$ -dibenzoylethylene, yellow, m. p. indefinite, giving a green copper salt. The following ethylene derivatives were prepared by the Friedel-Crafts reaction from fumaroyl chloride :  $\alpha\beta$ -di-(6-chloro-m-toluoyl)-, pale yellow, m. p.  $167^{\circ}$ ;  $\alpha\beta$ -di-(4-chloro-m-toluoyl)-, pale yellow, m. p.

158°;  $\alpha\beta$ -di- $\alpha$ -naphthoyl-, pale yellow, m. p. 140°, and  $\alpha\beta$ -di-(4-bromobenzoyl)-ethylene, yellow, m. p. 188·5°. F. G. W.

**Diketones and Mixed Ketones derived from the  $\alpha$ -Mononitrile of Camphoric Acid and from Methyl Cyanocampholate.**

A. HALLER and F. S. LEGAGNEUR (*Compt. rend.*, 1925, **180**, 881—886).—The methyl ester of camphoric acid  $\alpha$ -mononitrile is prepared by adding methyl alcohol to the product of interaction of isonitrosocamphor and thionyl chloride. It reacts with magnesium phenyl bromide, and by treating the product with ice-water and hydrogen bromide, the *ketimine hydrobromide*,



m. p. 211—213°,  $[\alpha]_{\text{D}}^{25} -53^\circ 16'$  in alcohol, is deposited. This is converted by boiling alcohol containing a little hydrogen chloride into 1 : 3-dibenzoyl-1 : 2 : 2-trimethylcyclopentane, m. p. 118°,  $[\alpha]_{\text{D}}^{20} -60^\circ 10'$  in benzene; the *monoxime*, m. p. 199—200°, is regarded as the  $\alpha$ -compound, since it may be obtained directly from the ketimine hydrobromide. The ethereal solution from the Grignard reaction yields diphenyl, together with 1-benzoyl-1 : 2 : 2-trimethylcyclopentane-3-carboxylamide, m. p. 172—175° (softening from 120°),  $[\alpha]_{\text{D}}^{18} +44^\circ 51'$  in alcohol (*oxime*, m. p. 194—196°), converted by alcoholic potassium hydroxide or by hydrogen chloride into (inactive) 1-benzoyl-1 : 2 : 2-trimethylcyclopentane 3-carboxylic acid, m. p. 169°.

Methyl cyanocampholate and magnesium phenyl bromide give 1-benzoyl-1 : 2 : 2-trimethyl-3-phenacylcyclopentane, m. p. 115°,  $[\alpha]_{\text{D}} +43^\circ 35'$  in benzene, together with a *substance*, m. p. about 180°, and methyl benzoylcampholate (cf. Haller and Weimann, A., 1907, i, 278). By increasing the proportion of Grignard reagent, the substance, m. p. 180°, is not obtained, but 1-benzoyl-1 : 2 : 2-trimethyl-3-cyanomethylcyclopentane (?), m. p. 140—141°, may be isolated, together with a small amount of a *substance*,  $\text{C}_{17}\text{H}_{23}\text{ON}$ , m. p. 195—197°. F. M. H.

**Compounds of the Diphen succindene Series. VII. Oxidation of Diphen succinda-9 : 12-dione to Phthalic Acid and Benzil-*oo'*-dicarboxylic Acid.** K. BRAND and O. LOEHR (*J. pr. Chem.*, 1925, [ii], **109**, 353—358; cf. A., 1920, i, 486).—

Diphen succinda-9 : 12-dione,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CO}\cdot\text{CH} \\ \text{CH}\cdot\text{CO} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$ , is slowly oxidised on boiling with nitric acid, more rapidly in the presence of vanadium pentoxide, yielding benzil-*oo'*-dicarboxylic acid and phthalic acid, together with a small quantity of a *substance*,  $\text{C}_{16}\text{H}_8\text{O}_6$  or  $\text{C}_{32}\text{H}_{14}\text{O}_{12}$ , m. p. 236°. A mixture of chromic and acetic acids does not attack diphen succinda-9 : 12-dione although dilute potassium permanganate gives an 81% yield of benzil-*oo'*-dicarboxylic acid. The different behaviour in these two cases is attributed to the conversion of the diphen succindadione, under the influence of alkali in the latter case, into the more readily oxidised alkali salt of 9 : 12-dihydroxydiphen succindadiene (cf. Reimer, A., 1882, 200). These results confirm the structure previously assigned to diphen succinda-9 : 12-dione by Roser (A., 1888, 1301). R. B.

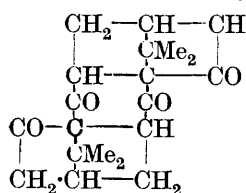
**Compounds of the Diphenysuccindene Series. VIII. Dinitedrodiphenysuccinda-9:12-dione.** K. BRAND and O. LOEHR (*J. pr. Chem.*, 1925, [ii], **109**, 359—375; cf. preceding abstract).—With the object of preparing compounds of the diphenysuccindene series substituted in the phenylene ring, the authors have attempted to condense nitro- $\alpha$ -phenylcinnamonitriles with hydrogen cyanide. Although  $\alpha$ -phenylcinnamonitrile condenses readily in the presence of piperidine, the presence of a nitro group in the *o*- or *p*-position completely inhibits addition of hydrogen cyanide, and in the case of the *m*-nitro- $\alpha$ -phenylcinnamonitrile addition takes place only with difficulty (cf. Frost, A., 1889, 597). The resulting *m*-nitrodiphenylsuccinonitrile,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{CN})\cdot\text{CHPh}(\text{CN})$ , m. p. 175—182°, appears to be a mixture of isomerides in varying proportions, and when heated with hydrochloric acid at 150—170° is converted (yield 80%) into *m*-nitrodiphenylsuccinic acid, which sinters at 229°, m. p. 235°. Attempts to condense this acid to nitedrodiphenysuccindadione failed. On boiling with potassium cyanide and ammonium chloride in alcoholic solution with or without piperidine, *o*-nitro- $\alpha$ -phenylcinnamonitrile is converted into a substance,  $\text{C}_{17}\text{H}_{13}\text{ON}_3$ , m. p. 233°. Attempts to obtain the *o*-nitrodiphenylsuccinonitrile by condensing mandelonitrile with phenylacetoneitrile also failed.

*p*-Methoxy- $\alpha$ -phenylcinnamonitrile readily condenses with potassium cyanide in alcoholic solution in the presence of ammonium chloride, yielding *p*-methoxydiphenylsuccinonitrile, m. p. 193°, hydrolysed by dilute sulphuric acid to *p*-methoxydiphenylsuccinic acid, m. p. 221°. All attempts to condense this to the diphenysuccindadione failed. On nitration with potassium nitrate and sulphuric acid in ice or with nitric acid and sulphuric acid at -5°, diphenysuccindadione is converted into a dinitro derivative, sintering at 234°, m. p. 241°. This is regarded as the 2:6-dinitrodiphenysuccinda-9:12-dione, (1) from its oxidation by potassium permanganate in the presence of magnesium sulphate to 4-nitrophthalic acid (yield 57%), and (2) from the formation of 6-nitro derivatives on nitration of hydrindone (Braun and Heider, A., 1916, i, 729), and of *pp'*-dinitrodiphenylsuccinic acid on nitration of diphenylsuccinic acid (Reimer, A., 1882, 200). On reduction with tin and hydrochloric acid, the dinitro derivative is converted into a diamino compound,  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2$ , which, together with its hydrochloride, does not melt at 280°. By replacing sodium ethoxide with piperidine in the condensation of nitrobenzaldehydes with phenylacetoneitrile, the authors obtain better yields and purer products. *o*-Nitro- and 2:4-dinitro-benzaldehydes yield dark, viscous oils. From salicylaldehyde and phenylacetoneitrile,  $\alpha$ -phenylcoumarin is obtained.

R. B.

**Relations Between Chemical Constitution and Camphor-like Physiological Action in Compounds not of the Camphor Series.** E. WEDEKIND (*Z. angew. Chem.*, 1925, **38**, 315—317).—A number of substances have been examined in the endeavour to obtain one more soluble than camphor and resembling it in its

physiological action. The conditions necessary for this action were found to be the presence of a six-membered ring containing an *isopropyl* group in the meta position to the keto group, but the presence or absence of methyl groups or of double bonds was without serious influence. An isomeride of camphor, 3-methyl-5-*isopropyl*- $\Delta^2$ -*cyclohexenone*, was found to have the physiological properties of camphor in a very high degree, and it is also easily soluble in sodium salicylate solution. It has been introduced into therapeutics under the name "Hexeton." The corresponding *m-isopropylcyclohexenone* and *m-isopropylcyclohexanone* also have a camphor-like action, but the *o*- and *p-isopropylcyclohexanones* have not. Tetrahydrocarvone shows the camphor-like action,



but this is absent from the *n*-propyl compounds tried. The five-membered ring compound, camphorone, is inactive, as also is the corresponding saturated dihydrocamphorone. Both these ketones are only slightly soluble in sodium salicylate solution. Complex derivatives of ketopinic acid (A., 1924, i, 639) show quite different physiological action, dinorcamphocyclohexanedione (annexed formula) being toxic and producing death after very strong lowering of blood-pressure.

P. M.

### Simplified Preparation of certain Organic Compounds.

**II. Chloro-*p*-benzoquinone.** H. VAN ERP (*Ber.*, 1925, 58, [B], 663—665; cf. van Erp, A., 1912, i, 28).—Chloro-*p*-benzoquinone, m. p. 56—56.5° (corr.), is prepared in good yield by the addition of 2-chloro-*p*-nitrophenol dissolved in a mixture of glacial acetic acid and saturated aqueous sulphur dioxide solution to granulated zinc and aqueous acetic acid and subsequent addition of the filtered solution to a mixture of ice, powdered potassium dichromate, and sulphuric acid. 2 : 6-Dichloro-*p*-benzoquinone is prepared similarly from 2 : 6-dichloro-*p*-nitrophenol. H. W.

**Anthraquinone Derivatives.** E. G. BECKETT, J. THOMAS, and SCOTTISH DYES, LTD. (Brit. Pat. 230116).—Nitration of 1-phthalimidoanthraquinone at 15—20° in sulphuric acid gives a dinitro derivative which is hydrolysed by 85% sulphuric acid at 85° to a *dinitro-1-aminoanthraquinone*, m. p. above 300°. This is reduced by alkaline sodium sulphide solution at 80° to a *triaminoanthraquinone*, bronze crystals, m. p. 258—260°, giving a *benzoyl* derivative, reddish-purple crystals with copper reflex, m. p. above 300°. [Cf. B., 1925, 394.] E. H. R.

**Monoazides of Anthraquinone.** K. BRASS and O. ZIEGLER (*Ber.*, 1925, 58, [B], 755—764; cf. Schaarschmidt, A., 1916, i, 856).—Anthraquinone-2-azide, m. p. 160—161°, is prepared in 86.1% yield by the action of ammonia on anthraquinone-2-diazonium perbromide. It is decomposed by moderately concentrated sulphuric acid at 70—90° into 2-aminoanthraquinone and complex

dehydration products which are insoluble in alkali hydroxide and 2-amino-1-hydroxyanthraquinone, with a smaller proportion of 2-amino-1:4-dihydroxyanthraquinone which dissolves in alkali hydroxide. The separation of the aminohydroxy compounds from one another cannot be effected by crystallisation. 2-Amino-1-hydroxyanthraquinone, m. p. 226—227°, is therefore isolated through its *diacetyl* derivative, m. p. 247—248°; the presence of the hydroxy group in position 1 is established by the formation of the *boroacetate*,  $C_{20}H_{18}O_8NB$ , from 2-acetamidohydroxyanthraquinone (cf. Dimroth and Faust, A., 1922, i, 156). The presence of 2-amino-1:4-dihydroxyanthraquinone is established by the production of purpurin when the mixture of bases is heated with concentrated hydrochloric acid, whilst the relative proportions of the mono- and di-hydroxy compounds are deduced from the amounts of purpurin and alizarin thus obtained. The formation of the hydroxyamines is attributed to the addition of 1 or 2 mols. of water to the immediately-formed anthraquinonylnitrogen.

The decomposition of anthraquinone-1-azide in strongly acid solution proceeds relatively simply, yielding 1-aminoanthraquinone and products of high molecular weight which are insoluble in potassium hydroxide solution and 1-amino-4-hydroxyanthraquinone, m. p. 208° (*diacetyl* derivative, m. p. 183°). The 1 and 4 positions of the amino and hydroxy groups in the latter compound are established by its ability to yield a *diboroacetate*,  $C_{22}H_{19}O_{11}NB_2$ .  
H. W.

**Rotatory Dispersive Power of Organic Compounds. XV. Borneol, Camphor, and Camphorquinone. Origin of Complex and Anomalous Rotatory Dispersion.** T. M. LOWRY and J. O. CUTTER.—(See ii, 356.)

**Relations between Diketocineole and Buchu-camphor. VI.** G. CUSMANO and G. MASSA (*Gazzetta*, 1925, 55, 140—148; cf. A., 1923, i, 689).—The stability of the cineole bridge is found to diminish when ketocineole is converted into diketocineole, the former compound resisting the action of nascent hydrogen furnished by zinc and sulphuric acid or by aluminium-amalgam and water, whereas, under the same conditions, diketocineole unites with two hydrogen atoms at the bridge and is converted into 8-hydroxybuchu-camphor,  $OH \cdot CMe_2 \cdot CH < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CO - CO \end{smallmatrix} > CHMe$ , m. p. 78—79°, isomeric with the compound obtained by oxidising buchu-camphor in presence of platinum-black (A., 1923, i, 586). When treated with aqueous alkali hydroxide, 8-hydroxybuchu-camphor decomposes with formation of acetone and methyl-2:3-diketohexamethylene, and, by benzil transposition of the latter, 2-hydroxy-1-methylcyclopentane-2-carboxylic acid. The relationship between diketocineole and buchu-camphor is manifested also in the action on the former of dry hydrogen bromide, which converts it into a dibromobuchu-camphor, this being readily transformed into buchu-camphor by treatment with zinc and alcohol. T. H. P.



**Catalytic Action. XI. Catalytic Activity of Reduced Copper. I.** S. KOMATSU and M. KURATA (*Mem. Coll. Sci. Kyoto*, 1925, 8, [A], 35—41).—When *l*-menthol is passed over reduced copper at 300°, menthene, menthone, thymol, and cymene are formed; similarly, *l*-menthone yields menthene, thymol, and cymene. The process by which the catalyst is prepared affects the nature and extent of its activity. The oxidising activity of the copper is checked by sulphur dioxide, and reaction products, which accumulate on the surface of the catalyst, have the same effect; the dehydrating activity, however, remains constant. [Cf. *B.*, 1925, 424.] B. W. A.

**Camphor Series. V. Catalytic Action of Reduced Copper and Reduced Nickel on *l*-Menthol.** S. KOMATSU and T. YUKITOMO (*Mem. Coll. Sci. Kyoto*, 1925, 8, [A], 65—73).—When *l*-menthol is passed over reduced copper at 200° menthene and menthone are the chief products, but at 300° a large yield of thymol is obtained. To a lesser extent, reduced nickel shows a greater oxidising activity at 300° than at 200°. [Cf. *B.*, 1925, 424.] B. W. A.

**Esthonian Oil of Peppermint.** N. WEIDERPASS (*Acta Comment. Dorpat*, 1924; from *Chem. Zentr.*, 1924, ii, 2090—2091).—Esthonian peppermint, *Mentha piperita*, var. *alba et nigra*, yields an essential oil having  $d_{20}^{20}$  0.9086;  $[\alpha]_D^{20}$  -17.63°;  $n_D^{20}$  1.4584; saponification number, 0.808; ester number, 10.384; acetyl number, 180.41. It contains total menthol 50.21%, menthone 17.21%, *l*- and *d*-limonene, cineole, and the methyl esters of valeric and acetic acids. The dry plant contains up to 0.5% of oil. G. W. R.

**Constituents of some Indian Essential Oils. XVII. Abietic Acid from the Rosin of *Pinus longifolia*, Roxb.** M. G. RAO and J. L. SIMONSEN (*Indian For. Rec.*, 1925, 11, 207—214).—The chief acid present in the rosin of *Pinus longifolia*, Roxb., is abietic acid. After purification by Steele's method (*A.*, 1922, i, 739), it has m. p. 168—169°,  $[\alpha]_D^{20}$  -95.3° in alcohol (cf. Virtanen, *A.*, 1921, i, 669; Ruzicka and Schinz, *A.*, 1923, i, 818), and is identical with the acid similarly obtained from *P. palustris*. No isomerides are present. It gives a dibromide, dihydrobromide, monohydriodide, and nitrosochloride identical with those obtained by Aschan and Virtanen (*loc. cit.*) from their higher-melting acid. The action of hydrochloric acid yields a *dihydrochloride*,  $C_{20}H_{32}O_2Cl_2$ , m. p. 205°, a *monohydrochloride*,  $C_{20}H_{31}O_2Cl$ , m. p. 197°, and a *bimolecular monohydrochloride*,  $C_{40}H_{59}O_3Cl$ , decomp. about 310°. An unsaturated *hydroxyabietic acid*,  $C_{20}H_{32}O_3$ , m. p. 230°, optically inactive (*methyl ester*, m. p. 110°; *silver salt*, white, amorphous powder), is obtained by boiling the dihydrochloride with a solution of sodium hydrogen carbonate. M. J.

**Constituents of some Indian Essential Oils. XVI. Rate of Oxidation of *d*- $\Delta^3$ -Carene and other Terpenes in the Presence of Catalysts.** M. G. RAO (*Indian For. Rec.*, 1924, 11, 197—206).—Experiments on the absorption of oxygen by *d*- $\alpha$ -pinene, *d*- $\Delta^3$ -carene, *d*- $\Delta^4$ -carene, *d*- $\alpha$ -thujene, and ordinary

Indian turpentine from the rosin of *Pinus longifolia* show that, for the preservation of terpenes, pyrogallol is by far the most effective anticatalyst. Quinol inhibits oxidation for only a short time, whilst mannitol, ethyl tartrate, and diphenylamine are quite ineffective (cf. Moureu and Dufraisse, A., 1923, i, 91). When oxidation once begins it proceeds rapidly, even when an anti-catalyst is present, and the absorption curve has the same form as that of the unimpeded oxidation curve. Pyrogallol cannot be detected after the reaction and apparently undergoes slow oxidation, which must be completed before the terpene is attacked. With *d*- $\Delta^3$ -carene (cf. Simonsen, T., 1920, 117, 570), complete absorption of the available oxygen under the conditions employed took place in 43 days in presence of 0.001% of pyrogallol as opposed to 10 days without an anticatalyst. Similar results were obtained with the other terpenes investigated. With turpentine itself, 97.5% of the oxygen was removed in 4 days in the absence of a catalyst. With 0.001% of pyrogallol, oxidation did not take place until the sixty-second day and was complete after 76 days. Corresponding figures for oxidation in air are given.

M. J.

**Sicilian Eucalyptus Oil.** R. INVIDIATO (*Boll. Chim. Farm.*, 1925, 64, 193—196).—Eucalyptus oil obtained by distilling leaves gathered from Sicilian *Eucalyptus globulus* during the blossoming of the plant compares favourably with the Australian oil. [Cf. B., 1925, 424.]

T. H. P.

***Eucalyptus piperita* and its Essential Oils, with Special Reference to their Piperitone Content.** I. A. R. PENFOLD and F. R. MORRISON (*J. Proc. Roy. Soc. N.S. Wales*, 1924, 58, 124—127).—Steam-distillation of the leaves and terminal branchlets of *Eucalyptus piperita* gives 2.15% of an oil ( $d_{15}^{25}$  0.8972,  $\alpha$   $-59.78^\circ$ ,  $n_D^{20}$  1.481) containing piperitone (44%) and phellandrene. Tentative reference is made to another form of *E. piperita* (variety "A") giving 0.7% of oil containing little piperitone, much phellandrene and eudesmol, and 20% of cineole.

B. F.

**Essential Oils of *Melaleuca erubescens* (Otto), and *M. hypericifolia* (Smith).** A. R. PENFOLD (*J. Proc. Roy. Soc. N.S. Wales*, 1924, 58, 182—188).—The leaves and terminal branchlets were steam-distilled in each case. *Melaleuca erubescens* yielded 0.44% of a pale lemon-coloured oil ( $d_{15}^{25}$  0.907,  $\alpha$   $+5.25^\circ$  to  $-0.65^\circ$ ,  $n_D^{20}$  1.4667, ester number 1.72—13.46, ester number after acetylation 30.36—52.94) containing cineole (48%),  $\alpha$ -pinene, limonene, dipentene,  $\alpha$ -terpineol, sesquiterpene, and a phenol (trace). *M. hypericifolia* yields 0.98% of a yellow oil ( $d_{15}^{25}$  0.9210,  $\alpha$   $+1.82^\circ$ ,  $n_D^{20}$  1.461, ester number 7.4, ester number after acetylation 20.89, all these being average values), which contains cineole (78%), dipentene, limonene,  $\alpha$ -pinene, sesquiterpene, and a trace of a phenol and a paraffin.

B. F.

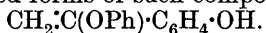
**Essential Oil of *Boronia saffrolifera* (Cheel).** A. R. PENFOLD (*J. Proc. Roy. Soc. N.S. Wales*, 1925, 58, 230—233).—The leaves and terminal branches of the plant yield on distillation

1.45% of a yellow oil ( $d_{15}^{25}$  1.034,  $\alpha$  +3.79°,  $n_{20}$  1.518, ester number 13.67, ester number after acetylation 29.33) which contains safrole (70—75%), *d*- $\alpha$ -pinene, methyleugenol, and traces of a phenol and a paraffin. [Cf. *B.*, 1925, 337.] B. F.

**Phenol Resins and Resinoids.** L. H. BAEKELAND and H. L. BENDER (*Ind. Eng. Chem.*, 1925, **17**, 225—237; cf. *J. Ind. Eng. Chem.*, 1909, **1**, 149; 1913, **5**, 506; A., 1914, i, 423; Redman, Weith, and Brock, A., 1914, i, 308).—Published information relating to the formation of these substances is reviewed and a general theory advanced. The compounds, although hitherto all classed together as “phenol resins,” form two distinct groups. There are those that are fusible and resemble the natural resins in properties; these are called “novolaks” (Baekeland, *loc. cit.*, 1913). There are also the infusible and inert substances having a variety of names in commerce; these are to be called “phenol resinoids.”

Phenol does not interact with *n*-butaldehyde alone, but when a little hydrogen chloride is added, reaction, accompanied by some evolution of heat, sets in and in 7 days the mixture becomes jelly-like, but contains crystals in suspension. The crystalline compound, representing 35—38% of the whole, is  $\alpha\alpha$ -*pp'*-dihydroxydiphenylbutane, m. p. 136°, b. p. 270—273°/22 mm. The resin, eventually obtained by evaporation of its toluene solution as a hard, brittle mass, has the same empirical formula and molecular weight (cryoscopic determinations) as the crystals, but, on this basis, only one phenolic hydroxyl group is present; it is therefore considered to be *phenyl*  $\alpha$ -*p*-hydroxyphenylbutyl ether. When this resin is distilled at 22 mm. the distillate (passing over between 260° and 310°) crystallises, and 79% of the calculated amount of *pp'*-dihydroxydiphenylbutane is thus obtained. Both the latter and the resin (which is a typical “novolak”) yield, when heated at 180° with 10% of their weight of hexamethylenetetramine, a “phenol resinoid.” When *pp'*-dihydroxytetraphenylmethane is similarly treated at 290°, it also affords an infusible, insoluble, “resinoid.” If the mixture of phenol and benzophenone chloride from which the *pp'*-dihydroxytetraphenylmethane is prepared is quickly heated, a product is obtained which closely resembles the “novolak” resins and yields, moreover, some *p*-hydroxytriphenylcarbinol when hydrolysed with hydrochloric acid. This appears to be *phenyl* *p*-hydroxytriphenylmethyl ether; when heated, it is converted into the diphenol, and with hexamethylenetetramine it affords a “phenol resinoid.”  $\alpha$ -Phenoxybutyl alcohol, b. p. 172—177°, is obtained by interaction of the hydrogen sulphite compound of *n*-butaldehyde and sodium phenoxide in aqueous solution at 70°. When this compound is heated with hexamethylenetetramine at 180° no true “resinoid” is produced, and only a small proportion is converted into a fusible resin. When sodium phenoxide and formaldehyde hydrogen sulphite interact, the solution being subsequently acidified, a resin is produced; this dissolves in sodium hydroxide, has the empirical formula,  $C_{13}H_{12}O_2$ , and a molecular weight (in acetic acid) of 264. It is considered to be chiefly *phenyl* *p*-hydroxyphenyl-

*methyl ether*. It resembles in every way the fusible "novolak" obtained commonly from phenol and formaldehyde. When the latter is distilled (at 20 mm.), some *pp'*-dihydroxydiphenylmethane is obtained, but the bulk forms an infusible mass possessing "saliretin" characteristics. Other experimental evidence, however, indicates that the common "novolak" is a phenyl ether, and, in fact, suggests that it also is simply phenyl *p*-hydroxyphenylmethyl ether. Phenyl methylmethylene ether, prepared from formaldehyde hydrogen sulphite, methyl alcohol, and sodium phenoxide, is an unstable oil, readily converted into a resin by the action of hydrochloric acid. *Diphenyl methylene ether*, b. p. 290—296°, obtained by interaction of methylene chloride and sodium phenoxide in alcohol at 150°, is comparatively stable; it affords a resin only after standing in contact with hydrochloric acid for several weeks. When benzylidene chloride and phenol interact, eventually at 180°, a red, resinous mass of molecular weight (in acetic acid) about 274, together with a little *pp'*-dihydroxytriphenylmethane, is produced. This is considered to be phenyl *p*-hydroxydiphenylmethyl ether. When heated at 180° with hexamethylenetetramine, it affords an insoluble "resinoid." *pp'*-Dihydroxytriphenylmethane also yields a "resinoid" when similarly treated. Other experiments are described the results of which support the general thesis that the "novolaks" are ethers and are the primary products; that intramolecular rearrangement, with substitution in the para position, then takes place, followed by, or simultaneously with, condensation with more formaldehyde; and that the commercial "resinoids" are chiefly polymerised forms of such compounds as



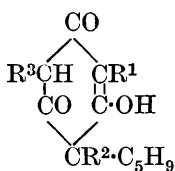
W. A. S.

**Rhamnicoside, a New Glucoside, the Source of China Green, found in the Bark of the Stem of the Purgative Buckthorn.** M. BRIDEL and C. CHARAUX (*Compt. rend.*, 1925, **180**, 1047—1049; cf. this vol., i, 621).—By extraction of the glucosidic complex with 90% alcohol, *rhamnicoside*,  $\text{C}_{26}\text{H}_{30}\text{O}_{15}\cdot 4\text{H}_2\text{O}$ , is obtained as colourless needles, having no definite m. p.,  $\alpha_D - 78\cdot 12^\circ$  in alcohol at 70°. It is hydrolysed by dilute sulphuric acid with production of equimolecular quantities of dextrose, xylose, and *rhamnicogenol*,  $\text{C}_{15}\text{H}_{12}\text{O}_6$ , whilst boiling water leaves the two sugars combined together as primeverose. The glucoside, treated with dilute aqueous sodium hydroxide, yields a clear solution and colourless crystals, both of which are extremely sensitive to light, which produces an intense violet colour in the solution. Evaporation leaves a green residue, a still brighter colour being obtainable by substituting calcium or barium for sodium hydroxide in the process. The solution and the residue have strong tinctorial properties, and it is clear that China green is derived from this glucoside. A list is given of the species of *Rhamnus* from which the glucoside is obtainable.

G. M. B.

**Bitter Principles of Hops.** W. WÖLLMER (*Ber.*, 1925, **58**, [B], 672—678; cf. Wöllmer, A., 1916, i, 494; Wieland, this vol., i, 276).—Lupulon,  $\text{C}_{26}\text{H}_{38}\text{O}_4$ , m. p. 90·5—92°, is isolated from

lupulin after removal of humulon as the lead salt according to the method of Lintner and Barth (A., 1898, i, 678). It behaves as a weak, monobasic acid containing no carboxyl group. It gradually develops a reddish-brown colour with ferric chloride. The nature of the oxygen atoms cannot be established in the customary manner since semicarbazide, benzoyl chloride and pyridine, and sodium acetate and acetic anhydride, yield only resinous products. By means of magnesium alkyl iodide, the presence of two hydroxyl groups is established. Towards sodium hydroxide lupulon is much more stable than humulon. Catalytic hydrogenation of lupulon gives  $\beta$ -methylbutane and a substance,  $C_{21}H_{34}O_4$ , which could be obtained only as a viscous resin and is characterised as the *tribenzoate*,  $C_{42}H_{46}O_7$ , m. p. 164—165°. The compound,  $C_{21}H_{34}O_4$ , is transformed by oxygen in alcoholic solution in the presence of lead acetate into the *lead* salt of tetrahydrohumulon, from which *tetrahydrohumulon*,  $C_{21}H_{34}O_5$ , m. p. 82—84°, is prepared (the *copper* salt is described). Three of the five oxygen atoms are present in hydroxyl groups, but the mode of attachment of the remaining two could not be established by the usual reagents. Tetrahydrohumulon differs from humulon in its behaviour when hydrogenated,



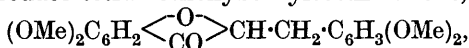
(I.)

since it does not suffer fission or yield the expected tetrahydroxy product,  $C_{16}H_{24}O_5$ . Its relationship to humulon is, however, established by its transformation by sodium hydroxide solution into *isol*(?)-hexoic acid and dihydrohumulic acid (cf. Wöllmer, *loc. cit.*). The properties of lupulon are in accordance with the constitution, (I), in which  $R^2$  is  $C_5H_{11}$ ,  $C_5H_7$ , or, most probably,  $C_5H_9$ , whereas  $R^1 + R^3 = C_{10}H_{20}O$ ,  $C_{10}H_{16}O$ , or, most probably,  $C_{10}H_{18}O$  (cf. Wieland's formula for humulon). H. W.

**Constitution of Picrotoxin.** M. BAKUNIN and F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], **30**, 166—174).—Thermal analysis of the system picrotin–picrotoxinin (cf. Barth von Barthenau and Kretschy, A., 1881, 286; 1882, 412; Paternò and Ogliastro-Todaro, A., 1881, 440; Schmidt, A., 1884, 845; Paternò and Nasini, A., 1886, 970; Meyer and Bruger, A., 1899, i, 226; Sielisch, A., 1912, i, 790, 886; Horrmann, A., 1912, i, 709) indicates clearly the existence of a compound containing about 40% of picrotin. The optical activities of mixtures of the two compounds in absolute alcohol lie almost exactly on a straight line, mixtures containing about 40% of picrotin appearing to show very slight divergences. If picrotoxinin has the formula  $C_{15}H_{16}O_6$ , the hydrate would contain either 5.8% or 3.94% of water, according as its composition is  $C_{15}H_{16}O_6\cdot H_2O$  or  $3C_{15}H_{16}O_6\cdot 2H_2O$ ; the author finds 5.01—5.64%, whilst Schmidt (*loc. cit.*) gave 4.67—5.59%. As intermediate figures are obtained for the percentage of methyl alcohol in the crystals containing it, it remains uncertain whether the hydrate and the methyl alcoholate are mixtures or whether the molecule of picrotoxinin is somewhat greater than is represented by the above formula. T. H. P.

**Tannins and Similar Substances. XIX. Constitution of Catechin.** K. FREUDENBERG, H. FIKENTSCHER, and W. WENNER (*Annalen*, 1925, **442**, 309—322; cf. this vol., i, 419).—Phloroglucinaldehyde dimethyl ether and  $\omega$ -bromoacetoveratone yield 4 : 6-dimethoxy-2-(3' : 4'-dimethoxybenzoyl)coumarone, m. p. 166°, which is reduced by sodium and amyl alcohol to 4 : 6-dimethoxy-2-(3' : 4'-dimethoxybenzyl)coumarone, m. p. 91—92° (monobromo derivative, m. p. 142°), and 2-hydroxy-4 : 6 : 3' : 4'-tetramethoxy- $\alpha$ -diphenylpropane (isolated as the *p*-nitrobenzoate, m. p. 137°). Since the benzyl compound is not identical with tetramethylanhydroepicatechin, the latter substance must have the alternative structure (*loc. cit.*),  $(\text{OMe})_2\text{C}_6\text{H}_2 < \begin{smallmatrix} \text{O} \\ \text{C} \\ \text{CH}_2 \cdot \text{CH} \end{smallmatrix} \text{C}_6\text{H}_3(\text{OMe})_2$ . This con-

ception is strengthened by the observation that tetramethylanhydroepicatechin is converted in moist acetic acid solution into 3' : 4'-dimethoxyphenyl  $\beta$ -2-hydroxy-4 : 6-dimethoxyphenylethyl ketone, m. p. 137·5° [the corresponding pentamethoxy derivative is identical with the synthetic product, m. p. 113—114°, described previously (*loc. cit.*)], which is identical with the product obtained by hydrogenation of 3' : 4'-dimethoxyphenyl  $\beta$ -2-hydroxy-4 : 6-dimethoxystyryl ketone (cf. Pratt, Robinson, and Williams, A., 1924, i, 306). Synthetic 3' : 4'-dimethoxyphenyl  $\beta$ -2-hydroxy-4 : 6-dimethoxyphenylethyl ketone and tetramethylanhydroepicatechin are converted by hydrogen chloride in indifferent media into the same *hydrochloride*,  $\text{C}_{19}\text{H}_{21}\text{O}_5\text{Cl}$ , m. p. 161—162° (decomp.), which is hydrogenated to 5 : 7 : 3' : 4'-tetramethoxyflavan, m. p. 111—112°. Reductive fission of tetramethylanhydroepicatechin yields 2-hydroxy-4 : 6 : 3' : 4'-tetramethoxy- $\alpha$ -diphenylpropane (*p*-nitrobenzoate, m. p. 141—142°), whereas tetramethylanhydrocatechin yields an isomeric phenol (*p*-nitrobenzoate, m. p. 108—109°; *p*-nitrobenzoate of the corresponding pentamethoxy derivative, m. p. 104—105°). Attempts to reduce tetramethoxybenzylcoumaranone,



by Wolff's method have led to the isolation of two isomeric *semi-carbazones*, m. p. 171° and 155° (decomp.), respectively.

Improved methods are described for the preparation of phloroglucinol dimethyl ether, phloroglucinaldehyde dimethyl ether, trimethylcatechone, and trinitrophloroglucinol. H. W.

**Gallotannin. XIII. Identity of Digallic Acid from Gallotannin with Synthetic *m*-Digallic Acid.** M. NIERENSTEIN, C. W. SPIERS, and P. R. HATCHER (*J. Amer. Chem. Soc.*, 1925, **47**, 846—850).—The identity of synthetic *m*-digallic acid (cf. Fischer and Freudenberg, A., 1913, i, 479) with the *m*-digallic acid obtained from gallotannin (cf. Nierenstein, A., 1910, i, 265) is established by melting-point determinations of mixtures of the synthetic and naturally-derived acids, of mixtures of synthetic methyl pentamethyl-*m*-digallate (m. p. 128—129°) (cf. Fischer and Freudenberg, *loc. cit.*; Fischer, Bergmann, and Lipschitz, A., 1918, i, 172) with that obtained by the action of diazomethane on the naturally-

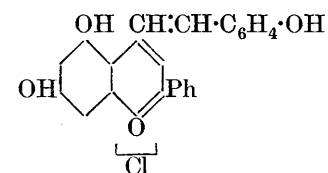
derived product (m. p. 127—128°), and of mixtures of the corresponding penta-acetyl derivatives (m. p. 208—209°). When penta-acetyl-*m*-digallic acid is hydrolysed with ammonium hydroxide, the filtrate obtained after separation of the *m*-digallic acid deposits, when evaporated, *p*-digallic acid, m. p. 290—291° (decomp.), the rearrangement being due to the formation of an intermediate ring compound as suggested by Fischer, Bergmann, and Lipschitz (*loc. cit.*), which on further hydrolysis can undergo scission in two ways, one of which leads to the expected *m*-digallic acid, the other to *p*-digallic acid. This observation offers an explanation of previous differences in the reported m. p. of *m*-digallic acid, the pure acid having m. p. 271°.

F. G. W.

**3-Chlorobenzopyrylium Derivatives.** L. R. RIDGWAY and R. ROBINSON (*J. Chem. Soc.*, 1925, **127**, 767—768).— $\omega$ -Chloroacetophenone condenses with 2-hydroxy-3-ethoxybenzaldehyde in acetic acid saturated with hydrogen chloride, and addition of hydroferrichloric acid precipitates 3-chloro-8-ethoxy-2-phenylbenzopyrylium ferrichloride (annexed formula), maroon prisms, m. p. 155°. In like manner,  $\omega$ -chloroacetylanisole gives 3-chloro-4'-methoxy-8-ethoxy-2-phenylbenzopyrylium ferrichloride, brick-red plates, m. p. 150°. The ferrichlorides yield colourless  $\psi$ -bases from which the yellow oxonium salt can be regenerated.

C. H.

**Styrylbenzopyrylium Salts. IV.  $\gamma$ -Styryl Derivatives of 5 : 7-Dihydroxy- and 5 : 7-Dimethoxy-2-phenyl-4-methylbenzopyrylium Chlorides.** G. H. WALKER and I. M. HEILBRON (*J. Chem. Soc.*, 1925, **127**, 685—689; cf. Buck and Heilbron, *ibid.*, 1923, **123**, 2521).—5 : 7-Dihydroxy-2-phenyl-4-methylbenzopyrylium chloride (Bülow and Wagner, A., 1901, i, 400) condenses with *p*-hydroxybenzaldehyde in boiling absolute alcohol in a current of hydrogen chloride to form 4' : 5 : 7-trihydroxy-2-phenyl-4-styrylbenzopyrylium chloride (annexed formula), m. p. 260°. 5 : 7-Dihydroxy-4'-methoxy-2-phenyl-4-styrylbenzopyrylium chloride is similarly prepared from anisaldehyde. *p*-Dimethylaminobenzaldehyde condenses without hydrogen chloride to form 4'-dimethylamino-5 : 7-dihydroxy-2-phenyl-4-styrylbenzopyrylium chloride (ferrichloride, m. p. 270°, hydrochloride, perchlorate, and diperchlorate are described).



phenyl-4-styrylbenzopyrylium chloride (ferrichloride, m. p. 270°, hydrochloride, perchlorate, and diperchlorate are described).

5 : 7-Dimethoxy-2-phenyl-4-methylbenzopyrylium chloride, m. p. 180° (+ $\frac{1}{2}$ H<sub>2</sub>O +  $\frac{1}{2}$ HCl) (ferrichloride, m. p. 215°), prepared from phloroglucinol dimethyl ether and benzoylacetone, condenses with *p*-hydroxybenzaldehyde, salicylaldehyde, vanillin, or *p*-dimethylaminobenzaldehyde in a similar manner to give the following derivatives of 2-phenyl-4-styrylbenzopyrylium chloride : 4'-hydroxy-5 : 7-dimethoxy derivative, m. p. 230°; 2'-hydroxy-5 : 7-dimethoxy derivative, m. p. 110° (+H<sub>2</sub>O); 4'-hydroxy-3' : 5 : 7-trimethoxy

derivative, m. p.  $210^{\circ}$ ; 4'-dimethylamino-5 : 7-dimethoxy derivative, m. p.  $190^{\circ}$  (*ferrichloride* described). As with salts of the 7-hydroxy- $\gamma$ -styryl series (*loc. cit.*), a deep blue or violet colour is developed on adding alkali to the red aqueous-alcoholic solutions of all chlorides containing a *p*-hydroxyl group in the styryl residue. With the *p*-methoxy analogues, quinonoid formation is impossible and the red colour is unchanged. As in the  $\alpha$ -styryl series, the 7-hydroxyl group retards the quinonoid rearrangement, which occurs on dilution alone when this is absent. C. H.

**Styrylbenzopyrylium Salts. V. Distyryl Derivatives of 7-Hydroxy-2 : 4-dimethylbenzopyrylium Chloride.** I. M. HEILBRON, G. H. WALKER, and J. S. BUCK (*J. Chem. Soc.*, 1925, 127, 690—696).—The successive condensation of two aldehyde molecules (identical or different) with 7-hydroxy-2 : 4-dimethylbenzopyrylium chloride is studied. Mixtures are not obtained and it is assumed that the  $\alpha$ -methyl reacts in preference to the  $\gamma$ -methyl radical. Anisaldehyde and vanillin behave exceptionally in giving  $\gamma$ -mono-condensation products. All the substances containing a *p*-hydroxyl group in either styryl residue change from red to blue on adding alkali to their solutions, but not on dilution alone (*cf.* preceding abstract).

7-Hydroxy-2 : 4-dimethylbenzopyrylium chloride, from resorcinol and acetylacetone (Bülow and Wagner, A., 1901, i, 400), condenses at  $40^{\circ}$  with 1 mol. of *p*-hydroxybenzaldehyde in formic acid saturated with hydrogen chloride to form 4 : 7-dihydroxy-2-styryl-4-methylbenzopyrylium chloride, m. p.  $260^{\circ}$  ( $+1\text{H}\cdot\text{CO}_2\text{H}$ ). 7-Hydroxy-4'-methoxy-2-styryl-4-methylbenzopyrylium chloride, purple prisms, m. p.  $160^{\circ}$ , is formed from anisaldehyde in the same way, but if the aldehyde is added to the boiling solution there is formed the isomeric 4-styryl-2-methyl compound, blue-black needles, m. p.  $150^{\circ}$  ( $+1\text{H}_2\text{O}$ ). Vanillin gives 4' : 7-dihydroxy-3'-methoxy-4-styryl-2-methylbenzopyrylium chloride, the only brown monostyryl chloride in the series. 3' : 4' : 7-Trihydroxy- and 7-hydroxy-4'-dimethylamino-2-styryl-4-methylbenzopyrylium chlorides are formed normally from protocatechualdehyde and *p*-dimethylaminobenzaldehyde, respectively.

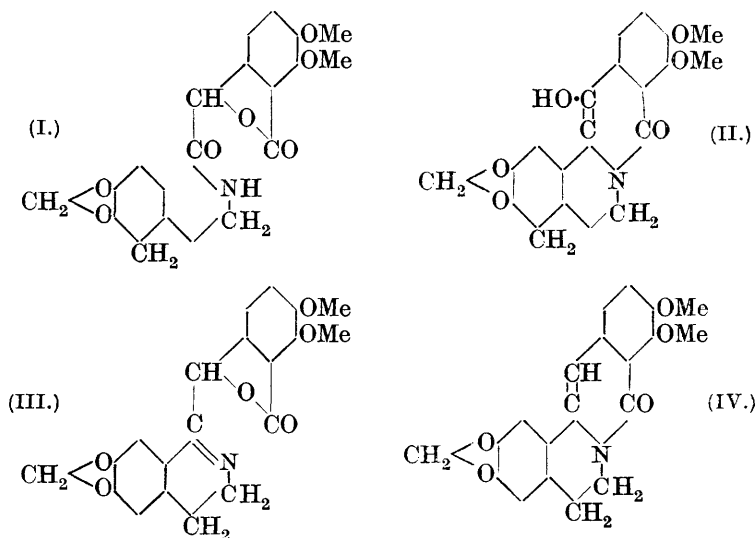
The following substituted 2 : 4-distyrylbenzopyrylium chlorides are prepared in hot absolute alcohol in a stream of hydrogen chloride : 4' : 4'' : 7-trihydroxy derivative, m. p.  $240^{\circ}$  ( $+1\text{H}_2\text{O}$ ), from the dimethylpyrylium chloride and 2 mols. of *p*-hydroxybenzaldehyde; 7-hydroxy-4 : 4''-dimethoxy derivative, m. p.  $170^{\circ}$  ( $+1\text{H}_2\text{O}$ ), from the purple monoanisyl chloride and anisaldehyde; 4''-dimethylamino-7-hydroxy-4'-methoxy derivative, m. p.  $200^{\circ}$  ( $+2\text{H}_2\text{O}$ ), from the purple monoanisyl chloride and *p*-dimethylaminobenzaldehyde; 4' : 7-dihydroxy-4''-methoxy derivative, m. p.  $220^{\circ}$  ( $+1\text{H}_2\text{O}$ ), from the mono-*p*-hydroxyphenyl chloride and anisaldehyde, or from the blue monoanisyl chloride and *p*-hydroxybenzaldehyde; 4'' : 7-dihydroxy-4'-methoxy derivative, m. p.  $160^{\circ}$  ( $+2\text{H}_2\text{O}$ ), from the purple monoanisyl chloride and *p*-hydroxybenzaldehyde; 3' : 4' : 7-trihydroxy-4''-methoxy derivative, m. p.  $240^{\circ}$  ( $+2\text{H}_2\text{O}$ ), and 3'' : 4'' : 7-



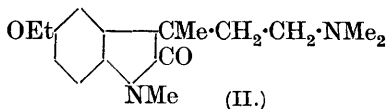
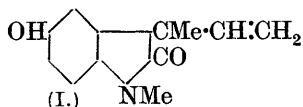
*trihydroxy-4'-methoxy* derivative, m. p.  $210^{\circ}$  ( $+2\text{H}_2\text{O}$ ), from the blue and the purple monoanisyl chlorides, respectively, with protocatechualdehyde; *3' : 4' : 7-trihydroxy-3'' : 4''-methylenedioxy* derivative, m. p.  $255^{\circ}$  ( $+2\text{H}_2\text{O}$ ), from the dihydroxyphenyl chloride and piperonal; *3'' : 4'' : 7-trihydroxy-3' : 4'-methylenedioxy* derivative, m. p.  $200^{\circ}$ , from 7-hydroxy-3' : 4'-methylenedioxy-2-styryl-4-methylbenzopyrylium chloride and protocatechualdehyde; and *4'' : 7-dihydroxy-3'-methoxy-3' : 4'-methylenedioxy* derivative, m. p.  $180^{\circ}$  ( $+2\text{H}_2\text{O}$ ), from the same chloride and vanillin. C. H.

**Rây's Supposed Triethylene Trisulphide.** G. M. BENNETT and W. A. BERRY (*J. Chem. Soc.*, 1925, 127, 910; cf. T., 1923, 123, 2178, footnote).—The supposed triethylene trisulphide is shown by molecular weight determination and by direct comparison with a specimen of diethylene disulphide to be identical with the latter substance. M. J.

**Synthesis of Oxyberberine.** I. W. H. PERKIN, jun., J. N. RÂY, and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 740—744).—The  $\beta$ -piperonylethylamide (I) of meconinecarboxylic acid (Freundler, A., 1914, i, 860), heated with phosphoryl chloride for 5 hrs. on the steam-bath, gave in one experiment dioxyberberine (II), but on repetition the main product was a substance, probably (III), which was converted by zinc dust and acetic acid into oxyberberine (IV). As by-product there was obtained a yellow, crystalline substance, m. p.  $230^{\circ}$ , which seems to be a chloromethylnoroxyberberine. A synthesis of oxyberberine is also a synthesis of berberine and of derived alkaloids such as canadine and palmatine. C. H.

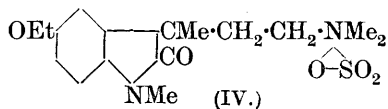
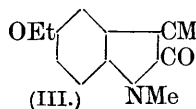


**Derivatives of Oxeserine.** M. POLONOVSKI and M. POLONOVSKI (*Compt. rend.*, 1925, **180**, 1273—1275; cf. this vol., i, 151, 293).—Oxeserolene (I), when hydrogenated in presence of colloidal palladium, yields (by reduction of the vinyl group to ethyl) *dihydro-oxeserolene*, m. p. 200°. The methiodide of oxeseretholemethine



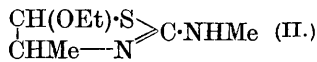
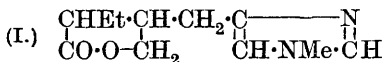
( $\psi$ -geneseretholemethine) (II) on prolonged heating at 200° in a vacuum yields (cf. A., 1918, i, 505) trimethylamine methiodide and oxeserolene ethyl ether. Stedman and Barger (this vol., i, 292) have described a compound, dehydroeseretholemethine, identical with the  $\psi$ -geneseretholemethine previously obtained by Polonovski and Polonovski (*loc. cit.*).

When treated with hydrogen peroxide eseretholemethine yields not only oxeseretholemethine but also the corresponding *amine-oxide* (III), m. p. 60°,  $[\alpha]_D^{20}$   $-38^\circ$ , *hydrochloride*, m. p. 198°. When reduced with zinc and hydrochloric acid the amine-oxide gives oxeseretholemethine, but with sulphur dioxide it gives some *ester* (IV), m. p. 193—194° (decomp.), hydrolysed readily by hot water



to oxeseretholemethine and sulphuric acid. The amine-oxide is obtained by treating oxeseretholemethine itself with hydrogen peroxide. The latter similarly converts oxeserimethine and oxeserolemethine into the corresponding *amine-oxides*. L. F. H.

**Relation of Pilocarpidine to Pilocarpine. Synthesis of 1:4- and 1:5-Dimethylglyoxalines.** R. BURTLES, F. L. PYMAN, and J. ROYLANCE (*J. Chem. Soc.*, 1925, **127**, 581—591).—That pilocarpidine is the imino compound corresponding with pilocarpine is now confirmed by its conversion by methylation into a mixture of pilocarpine and an isomeride, *neopilocarpine* (I), m. p. 39—40° (*hydrochloride*, m. p. 177°; *nitrate*, m. p. 94—95°; *picrate*, m. p. 117—119°). Boiled with alkali, the new base is



partly racemised, like pilocarpine, with formation of the stereoisomeric *isoneopilocarpine* (*picrate*, m. p. 125—126°; *nitrate*, m. p. 105—106°). 1:5-Dimethylglyoxaline, the degradation product of *isopilocarpine*, is synthesised by an extension of the Wohl-Mareckwald method.  $\alpha$ -Bromopropionacetal, b. p. 69°/14 mm., is converted by treatment with alcoholic ammonia into  $\alpha$ -aminopropionacetal, b. p. 79—80°/40 mm., or with alcoholic methylamine into

$\alpha$ -methylaminopropionacetal,  $(\text{OEt})_2\text{CH}\cdot\text{CHMe}\cdot\text{NHMe}$ , b. p. 66—69°/16—18 mm. From the latter by the action of thiocyanic acid there is obtained 2-thiol-1:5-dimethylglyoxaline, m. p. 261—262°, which is oxidised by hot dilute nitric acid to 1:5-dimethylglyoxaline, identical with the product from isopilocarpine. The condensation product of  $\alpha$ -aminopropionacetal with methylthiocarbimide gives, on boiling with 5*N*-hydrochloric acid, three products: (a) 2-thiol-1:4-dimethylglyoxaline, m. p. 211—212°, unchanged by concentrated hydrochloric acid at 150°, oxidised by hot dilute nitric acid to 1:4-dimethylglyoxaline, m. p. 167—168°; (b) 2-methylamino-5-ethoxy-4-methyl-4:5-dihydrothiazole (II), m. p. 52° (picrate, m. p. 158°; chloroplatinate, m. p. 201°), which is slowly converted by boiling dilute mineral acids into compound (a), and by concentrated hydrochloric acid at 150° into compounds (a) and (c) together with 2-methylamino-4-methylthiazole, m. p. 71·5—72·5° (hydrochloride, m. p. 228°; hydriodide, m. p. 194°; chloroplatinate, m. p. 180°); (c) 2-ethylthiol-1:4-dimethylglyoxaline (picrate, m. p. 105°; hydrochloride, m. p. 125—127°). The last-named thiazole is also prepared by Traumann's method (A., 1889, 414) from chloroacetone and methylthiocarbamide (m. p. of the base and its salts are much higher than previously recorded). It is not converted by hydrochloric acid at 150° into 2-thiol-1:4-dimethylglyoxaline.

$\alpha$ -Propionacetalylphenylthiocarbamide, m. p. 110°, from  $\alpha$ -aminopropionacetal and phenylthiocarbimide, is hydrolysed by 5*N*-hydrochloric acid to 2-thiol-1-phenyl-4-methylglyoxaline, m. p. 190—191°, but the main product is 2-anilino-5-ethoxy-4-methyl-4:5-dihydrothiazole (as II; picrate, m. p. 163—165°). Parallel results are obtained by hydrolysis of acetalylphenylthiocarbamide and probably also with acetalyl-*m*-xylylthiocarbamide. The former, m. p. 96°, yields 2-thiol-1-phenylglyoxaline, m. p. 181—182°, and 2-anilino-5-ethoxy-5:4-dihydrothiazole,  $\text{C}_{11}\text{H}_{14}\text{ON}_2\text{S}$ , m. p. 92—93° [picrate, m. p. 198°; Wohl and Marckwald (A., 1889, 624, 866; 1892, 1326) give  $\text{C}_{11}\text{H}_{16}\text{O}_2\text{N}_2\text{S}$ , m. p. 94°, picrate decomp. 190°]. The ethoxy base is hydrolysable to 2-thiol-1-phenylglyoxaline, 2-anilinothiazole (picrate, m. p. 198—199°), and 2-ethylthiol-1-phenylglyoxaline, b. p. 310°/772 mm. (picrate, m. p. 119—120°). C. H.

**Does Nicotine Combine with Calcium Ions?** R. M. CHAPIN (*J. Amer. Chem. Soc.*, 1925, 47, 892—894; cf. A., 1924, ii, 635).—The apparent union of calcium and nicotine (cf. Graham and Carr, A., 1924, i, 816) is due to adsorption. The observation that a solution of calcium chloride becomes acid on the addition of nicotine is not confirmed. F. G. W.

**Preparation of 4-Tetrahydroquinolone and of Intermediate Products.** BRITISH DYESTUFFS CORPORATION, LTD., W. H. PERKIN, and G. R. CLEMO (Brit. Pat. 230607).—A patent incorporating results previously abstracted (A., 1924, i, 1103). 4-Tetrahydroquinolone has m. p. 45°, not 144° as previously stated.

E. H. R.

**3-Nitropyridine and its Derivatives.** A. KIRPAL and E. REITER (*Ber.*, 1925, 58, [B], 699—701).—The nitration of pyridine  $b\ b^*$

to 3-nitropyridine (cf. Friedl, A., 1912, i, 299; 1913, i, 754) depends for its success on the presence of a trace of iron, used, *e.g.* as wire. The nitro compound is reduced by aluminium amalgam in ethereal solution to 3-hydroxylaminopyridine [ $\beta$ -3-pyridylhydroxylamine], m. p. 109°; any 3-aminopyridine produced is retained by the aluminium hydroxide. 3-Nitrosopyridine, m. p. 94°, obtained by oxidising 3-hydroxylaminopyridine with potassium dichromate in sulphuric acid solution, shows the colour changes typical of nitroso derivatives. H. W.

**Mechanism of Fischer's Synthesis of Indoles.** S. BODFORSS (*Ber.*, 1925, 58, [B], 775—785).—In explanation of the production of indoles from ketonearylhydrazones (Fischer, A., 1884, 1180), the following scheme has been suggested by Reddelien (A., 1912, i, 363):  $\text{CH}_2\text{R}''\cdot\text{CR}''\cdot\text{N}\cdot\text{NPhR}''' + \text{H}_2 \rightarrow \text{CH}_2\text{R}''\cdot\text{CR}''\cdot\text{NH} + \text{NHPHR}''' \rightarrow \text{NH}_3 + \text{CHR}''\cdot\text{CR}''\cdot\text{NPhR}''' \rightarrow \text{C}_6\text{H}_4 \begin{smallmatrix} \text{CR}'' \\ \text{NR}''' \end{smallmatrix} \gg \text{CR}'' + \text{H}_2$ . Since, however, the reaction is quantitative in certain cases, it appears improbable that the initial decomposition occurs, and, further, the coloration which develops during the change (attributed by Reddelien to decomposition) is only transitory. Also it appears improbable that the intermediate ketimine should escape hydrolysis completely in the presence of concentrated acid and frequently at a high temperature. More direct evidence against Reddelien's hypothesis is deduced from the observation that the course of the change is not influenced by the addition of an amine differing from that assumed to be produced during the primary change. Thus the phenylmethylhydrazone of pyruvic acid and benzylaniline give 1-methylindole-2-carboxylic acid, whereas the phenylbenzylhydrazone of pyruvic acid and methylaniline afford 1-benzylindole-2-carboxylic acid. Similarly, 2:3-diphenylindole and 1-methyl-2:3-diphenylindole are derived respectively from deoxybenzoinphenylhydrazone and methylaniline and from deoxybenzoinphenylmethylhydrazone and aniline. 1-Methylindole-2-carboxylic acid is derived from aniline and the phenylmethylhydrazone of pyruvic acid, and 2:3-diphenylindole is obtained from deoxybenzoinphenylhydrazone and *p*-bromoaniline. The production of 2-phenylindole when acetophenoneanil is melted with phenylhydrazine zincchloride has been attributed by Reddelien (*loc. cit.*) to the oxidising action of the latter substance; the observation that acetophenone-*p*-tolil also yields 2-phenylindole (together with *p*-toluidine) under similar conditions shows, however, that the primary change is replacement of the anilo group by the phenylhydrazine residue (cf. Reddelien, A., 1922, i, 145) followed by normal ring closure of the hydrazone.

According to Reddelien's hypothesis the reaction is accompanied by a continuous, inter-molecular hydrogen exchange which might be expected to impart a pronounced, negative potential to a platinum foil immersed in the reaction mixture. This, however, is not observed in the case of the phenylmethylhydrazone of pyruvic acid. The validity of the method is established by the

observation that the potential of a platinum-air electrode sinks rapidly when placed in a methyl-alcoholic solution of benzaldehyde, pyruvic acid, and  $\beta$ -naphthylamine, from which 2-phenylnaphtho-cinchonic acid is being formed with simultaneous production of hydrogen (cf. Jones and Evans, T., 1911, **99**, 334), or in a solution in which 2-methylpyridine-4 : 6-dicarboxylic acid is being generated by the auto-condensation of ammonium pyruvate,  $3\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{NH}_3 = \text{C}_8\text{H}_7\text{O}_4\text{N} + \text{H}_2 + \text{CO}_2 + 3\text{H}_2\text{O}$ .

1-Benzylindole-2-carboxylic acid, m. p.  $196^\circ$  (decomp.), and deoxybenzoin-*p*-bromophenylhydrazone, m. p.  $138^\circ$ , are described incidentally. H. W.

**Relationship of Thyroxin to Tryptophan.** C. S. HICKS.—(See ii, 473.)

**Preparation of Substituted Hydantoins.** T. J. THOMPSON, H. L. BEDELL, and G. M. BUFFETT (*J. Amer. Chem. Soc.*, 1925, **47**, 874—876).—Syntheses of 4-phenyl-4-ethylhydantoin (nirvanol) and its homologues were carried out (a) by converting the appropriate ketones into the cyanohydrins by Albert's method (cf. A., 1916, i, 821) and then converting these into the acetonitriles by heating their solutions in absolute alcohol at  $85^\circ$  in sealed tubes after saturating with ammonia, the remaining steps being those of Read's synthesis (A., 1922, i, 954); and (b) by the action of alkali hypobromites on the appropriate disubstituted cyanoacetamides (cf. U.S.P. 1285703; Swiss Pats. 72561, 74094). The following compounds are described: phenylethyl-, m. p.  $117^\circ$ ; phenylpropyl-, m. p.  $120^\circ$ ; phenylisopropyl-, m. p.  $130^\circ$ ; phenylbutyl-, m. p.  $126^\circ$ ; and phenylisobutyl-cyanoacetamide, m. p.  $100^\circ$ ; phenylpropyl-, m. p.  $165$ — $166^\circ$ ; phenylisopropyl-, m. p.  $211^\circ$ ; phenylbutyl-, m. p.  $204$ — $205^\circ$ ; and phenylisobutyl-hydantoin, m. p.  $177$ — $178^\circ$ . Phenylpropyl- and phenylisobutyl-hydantoins have about the same physiological effect as "nirvanol," the remaining homologues having no hypnotic action. F. G. W.

**Preparation of 1-*p*-Sulphophenyl-3-methyl-5-pyrazolone.** G. REEVES (*J. Chem. Soc.*, 1925, **127**, 911—912).—1-*p*-Sulphophenyl-3-methyl-5-pyrazolone, ordinarily prepared under conditions which do not favour primary enolisation of the ethyl acetoacetate in its condensation with phenylhydrazine-*p*-sulphonic acid, is obtained satisfactorily pure and in excellent yield when conditions are favourable to this enolisation (cf. Ingold, T., 1921, **119**, 329).

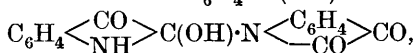
M. J.

**Tautomerism of Amidines.** V. Methylation of Glyoxalines by Diazomethane. Bromination of 4(or 5)-Phenylglyoxaline. W. G. FORSYTH and F. L. PYMAN (*J. Chem. Soc.*, 1925, **127**, 573—581; cf. T., 1910, **97**, 1814; A., 1924, i, 1112).—The yields of 5 : 1- and 4 : 1-isomerides obtained by methylation of 2 : 5(2 : 4)-dibromo-4(5)-methylglyoxaline are 55% and 1.2%, respectively, with methyl sulphate alone, 63% and 6.3% with diazomethane. Similarly, with methyl sulphate alone 5(4)-bromo-4(5)-methylglyoxaline gives 63% of 5-bromo-1 : 4-di-

methylglyoxaline (*hydrogen oxalate*, m. p. 96°) and only 0.1% of the isomeride. 5(4)-Bromo-4(5)-phenylglyoxaline gives pure 5-bromo-4-phenyl-1-methylglyoxaline, m. p. 88—90° (*picrate*, m. p. 226°) in 73% yield. The same product is obtained by the action of bromine (1 mol.) on 4-phenyl-1-methylglyoxaline. From 4(5)-nitroglyoxaline and diazomethane are obtained a 58% yield of 5-nitro-1-methylglyoxaline, m. p. 153°, and only 1.3% of the isomeride, m. p. 134°; whilst with methyl sulphate and alkali it gives 19% of the 5-nitro and 59% of the 4-nitro compound. Methylation of 4(5)-phenylglyoxaline by diazomethane yields 20% of 5-phenyl-1-methylglyoxaline, m. p. 138—139°, and 41% of the 1 : 4-isomeride, m. p. 241°. It thus appears that in each case the more basic isomeride greatly predominates except when methylation is performed in the presence of alkali.

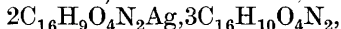
5(4)-Bromo-4(5)-phenylglyoxaline, m. p. 242—245° (*hydrochloride*, *nitrate*, m. p. 127°, and *picrate*, m. p. 188—189°, are described), is formed in 64% yield, together with 11% of 2 : 5(2 : 4)-dibromo-4(5)-phenylglyoxaline, m. p. 197—198°, by bromination of 4(5)-phenylglyoxaline. The bromine in these compounds is not removed by aqueous sodium sulphite at 100°, but is reduced at higher temperatures. In 2-bromo-4(5)-phenylglyoxaline, m. p. 153°, synthesised by the method used for 2-bromo-4(5)-methylglyoxaline (T., 1923, 123, 494), the stabilising effect of the phenyl group is less evident. Ethyl 2-thiol-4(5)-phenylglyoxaline-5(4)-carboxylate, m. p. 219°, prepared from ethyl  $\alpha$ -aminobenzoylacetate hydrochloride and potassium thiocyanate, is oxidised by hot dilute nitric acid to ethyl 4(5)-phenylglyoxaline-5(4)-carboxylate, m. p. 225°, from which the above 2-bromo-4(5)-phenylglyoxaline is obtained by bromination, followed by hydrolysis and decarboxylation. The ethyl amino-benzoylacetate required was obtained from ethyl isonitrosobenzoylacetate, prepared by an improved method. C. H.

**Isatoid and the So-called "Isatole."** A. HANTZSCH (*Ber.*, 1925, 58, [B], 685—692; cf. Heller, A., 1920, i, 766; 1921, i, 891; Heller and Benade, A., 1922, i, 582; Hantzsch, A., 1921, i, 597; 1922, i, 1177).—Silver isatin is converted by benzoyl chloride at the atmospheric temperature primarily into *O*-benzoylisatin, which is hydrolysed by traces of water to the corresponding non-isolable enol; this condenses with unchanged *O*-benzoylisatin giving *O*-benzoylisatoid, from which the benzoyl group is readily removed by water, thus yielding *isatoid*,  $\text{CO}-\text{C}(\text{OH})\cdot\text{N}\cdot\text{C}_6\text{H}_4$  or  $\text{C}_6\text{H}_4\cdot\text{N}(\text{OH})\text{C}\cdot\text{CO}$



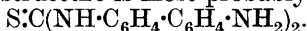
m. p. 178—182°. (The possibility of the second structure is established by the almost quantitative conversion of methylisatoid into a phenylhydrazone.) The compound is closely allied to Heller's "isatole," prepared by the action of warm benzoyl chloride on impure silver isatin. The non-existence of Heller's "structural association" and the similarity of "isatole" to "3-hydroxy-indazole" which has been shown to be di-3-hydroxyindazole (cf.

Hantzsch, this vol., i, 702) render it impossible to consider "isatole" an isomeride of isatin; until the termolecular nature of Heller's product in solution is firmly established, it appears equally justifiable to regard the compound, if existent, as an isomeride of isatoid, one substance having the dienolic and the other the open keto-enolic form (see above). *Silver isatoid*,



m. p.  $204^\circ$ , is prepared from isatoid and silver acetate or by the action of benzoyl chloride on pure silver isatin; it dissolves in solutions of alkali hydroxides without separation of silver oxide, but this property is not attributable to its complex nature, as it is also shared by the normally-constituted *silver methylisatoid*,  $\text{C}_{17}\text{H}_{11}\text{O}_4\text{N}_2\text{Ag}$ ; the compounds are therefore regarded as *N*-salts. Isatin and mercuric acetate in aqueous-alcoholic solution yield *N-mercuri-isatin*,  $(\text{C}_8\text{H}_4\text{O}_2\text{N})_2\text{Hg}\cdot\text{H}_2\text{O}$ . *Silver 5-bromoisatin* and silver 3 : 5-dichloroisatin are converted by cold benzoyl chloride into *N-benzoyl-5-bromoisatin*, m. p.  $195\text{--}196^\circ$ , and *N-benzoyl-3 : 5-dichloroisatin*, m. p.  $145\text{--}146^\circ$ . H. W.

**Action of Carbon Disulphide on Benzidine.** G. ROSSI and B. CECCHETTI (*Gazzetta*, 1925, **55**, 97—99).—The crystalline compound formed together with thiocarbobenzidine (cf. Borodin, *Jahresber.*, 1860, 356) by the action of carbon disulphide on benzidine and regarded by Strakosch (A., 1872, **25**, 503) as an isomeride of thiocarbobenzidine, forms a diazo derivative which may be coupled to give a compound still containing sulphur. It decomposes at above  $200^\circ$  and its structure is most probably



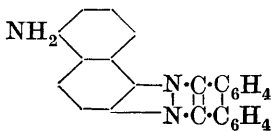
T. H. P.

**Dinitro- and Triamino-naphthalenes.** C. FINZI (*Annali Chim. Appl.*, 1925, **15**, 55—62).—Conditions are given for the separation of 1 : 5-dinitronaphthalene which yield better results than the procedure described by Friedländer (A., 1900, i, 150).

1 : 2 : 5-Triaminonaphthalene, prepared by coupling 1 : 5-diaminonaphthalene with *p*-diazotoluene and reducing the violet-blue dye thus formed by means of tin and hydrochloric acid, forms a white, crystalline trihydrochloride, which gives a violet-blue coloration with hydrochloric acid and ferric chloride, and a tribenzoyl derivative,  $\text{C}_{10}\text{H}_5(\text{NHBz})_3$ , m. p.  $268^\circ$ . It condenses (1) with phenanthraquinone to form 7-amino-2 : 3-diphenyl- $\alpha\beta$ -naphthoquinoxaline (annexed formula), which does not melt at  $300^\circ$ , and (2) with benzil, giving 7-amino-2 : 3-diphenyl- $\alpha\beta$ -naphthoquinoxaline, yellow needles, m. p.  $208^\circ$ .

1 : 4 : 8-Triaminonaphthalene, similarly obtained from 1 : 8-diaminonaphthalene, forms a trihydrochloride, gives a red coloration with a deficit of nitrous acid and a wine-red coloration with hydrochloric acid and ferric chloride, and reacts with neither phenanthraquinone nor benzil.

T. H. P.



**Supposed "3-Hydroxyindazole" and the so-called "Structural Association" of G. Heller.** A. HANTZSCH (*Ber.*, 1925, **58**, [B], 680—685).—The compound, m. p. 206°, obtained by heating *o*-aminobenzhydrazide in the presence of quinoline at 200—210° (described by Heller and Köhler [*A.*, 1923, i, 850] as 3-hydroxyindazole and by Thode [*A.*, 1904, i, 347] as benzisopyrazolone) is bimolecular in phenol, camphor, and probably in acetone, in which it dissolves somewhat sparingly; it is therefore to be regarded as *di*-3-hydroxyindazole,

as *di*-3-hydroxyindazole, 
$$\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{NH} \\ \text{NH}\cdot\text{N}(\text{OH})\cdot\text{C}\cdot\text{C}_6\text{H}_4 \end{array}$$
 Heller's 2-acetyl-

3-hydroxyindole [*di*-1-acetyl-3-hydroxyindazole] is bimolecular in phenol and camphor. Heller's bis-*N*-acetylindazolyl 3-ether has the

structure, 
$$\begin{array}{c} \text{C}_6\text{H}_4\cdot\text{C}\text{---}\text{N}\cdot\text{N}\cdot\text{Ac} \\ \text{N}\cdot\text{N}\text{---}\text{C}\cdot\text{C}_6\text{H}_4 \\ \text{O} \end{array}$$

Repetition of Heller's experiments has shown that 4-hydroxyquinaldine is unimolecular in phenol, bimolecular in camphor, but not termolecular in acetone. 4-Hydroxyquinoline is bimolecular in camphor, but could not be examined in other solvents. These substances behave in solution therefore in much the same manner as acetic acid, alcohols, and phenols, which are associated in the majority of non-ionising solvents, but unimolecular in all hydroxylated media. A difference exists, however, in that these compounds with the group  $\text{C}(\text{OH})\cdot\text{N}$  are bimolecular in camphor, in which the simple, nitrogen-free phenols (*p*-bromophenol, *p*-cresol, thymol,  $\alpha$ -naphthol) are unimolecular. This difference is not principally in nature, since the tendency of solvents towards the unimolecular fission of simple hydroxy compounds varies greatly. Thus the majority of phenols and carboxylic acids are bimolecular in benzene, in which trinitrobenzoic acid, triphenylcarbinol, and triphenylacetic acid are strictly unimolecular. Trichloroacetic acid, in contrast to acetic acid, is not only strictly unimolecular as vapour, but forms equilibrium mixtures of little bi- and much uni-molecular forms in solvents in which acetic acid is bimolecular. Heller's conception of "structural association" is founded on incorrect experiments and should be abandoned.

H. W.

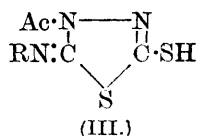
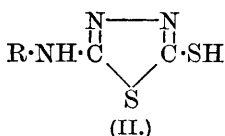
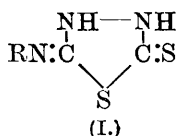
**Physiological Action of certain Benzthiazoles and Mercaptan Derivatives.** R. F. HUNTER (*J. Chem. Soc.*, 1925, **127**, 911).—Hot solutions of 4'-amino-1-phenyl-5-methylbenzthiazole (*J. Soc. Chem. Ind.*, 1923, **42**, 302) in contact with the skin develop an unpleasant form of eczema. The vapour of the thiocresol resulting from alkali fusion of this compound, like that of its lower homologue *o*-aminothiophenol (cf. Hofmann, *Ber.*, 1887, **20**, 2251), produces intense irritation and swelling.

M. J.

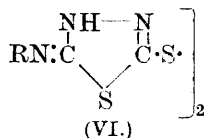
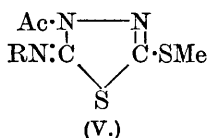
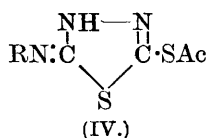
**Constitution of the so-called Dithiourazole of Martin Freund. III. Synthesis of some Monosubstituted Thiodiazoles.** P. C. GUHA and H. P. RÂY (*J. Amer. Chem. Soc.*, 1925, **47**, 385—390; cf. *A.*, 1922, i, 875, 876).—The following substituted thiosemicarbazides, obtained by the action of hydrazine



hydrate on the respective appropriate thiocarbimides (cf. Pulvermacher, A., 1894, i, 76; Busch and Ulmer, A., 1902, i, 575), are described: 4-*m*-xylyl-, m. p. 184°; 4-*p*-bromophenyl-, m. p. 189°; and 4-*m*-chlorophenylthiosemicarbazide, m. p. 130°. An isomeric *p*-bromophenylthiosemicarbazide, m. p. 110°, was obtained by adding hydrazine hydrate to a dilute alcoholic solution of *p*-bromophenylthiocarbimide. By heating the above thiosemicarbazides with an equivalent of carbon disulphide and alcoholic potassium hydroxide in sealed tubes at 100°, substituted 5-imino-2-thion-2:3:4:5-tetrahydro-1:3:4-thiodiazoles (5-amino-2-thiol-1:3:4-thiodiazoles) (I) or (II), were obtained. 5-Tolylimino-2-thion-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 219°, yields a nitroso derivative, yellow, m. p. 228°; a methyl derivative, m. p. 134°; a diacetyl derivative, m. p. 234—236° after contracting at



200°, readily hydrolysed to the monoacetyl derivative (III), pale yellow, m. p. 152°; and an isomeric monoacetyl derivative (IV), light yellow, m. p. 198—200°. 5-Tolylimino-4-acetyl-2-methylthiol-4:5-dihydrothiodiazole (V), m. p. 89—90°, was obtained from



either of the above monoacetyl derivatives by the action of methyl iodide, and from the methyl derivative and acetic anhydride. By the action of iodine in alcohol on the 5-tolylimino derivative (I), the disulphide (VI), m. p. 232°, was obtained. The monoacetyl derivative (III) afforded similarly a disulphide, m. p. 245°, identical with that obtained by acetylating (VI). 5-Xylylimino-2-thion-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 230° (decomp.), yielded similarly a disulphide, m. p. 114° (decomp.) [acetyl derivative, m. p. 130° (decomp.)]. 5-*p*-Bromophenylimino-2-thion-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 220° [diacetyl derivative, m. p. 161°; monoacetyl derivative, m. p. 205°; methyl derivative, m. p. 212°; methyl-acetyl derivative, m. p. 91°], yields a disulphide, amorphous, m. p. 216°. 5- $\alpha$ -Naphthyl-, m. p. 225°, and 5-*m*-chlorophenyl-2-thion-2:3:4:5-tetrahydro-1:3:4-thiodiazole, m. p. 240°, and the disulphide of the latter, m. p. 156°, were prepared.

F. G. W.

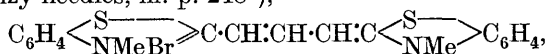
**Action of Benzoyl Chloride on 4- and 1-Phenylthiosemicarbazide.** E. FROMM and A. TRUKA (*Annalen*, 1925, 442, 150—159; cf. Fromm, Soffner, and Frey, A., 1924, i, 93).—4-Phenylthiosemicarbazide is converted by benzoyl chloride in

the presence of sodium hydroxide into the *tetrabenzoyl* derivative,  $\text{NPhBz} \cdot \text{CS} \cdot \text{NBz} \cdot \text{NBz}_2$ , m. p.  $148^\circ$ . When, however, the substances are allowed to react in the presence of chloroform as diluent, a mixture of *5-anilino-4-benzoyl-2-phenyl-1:3:4-thiodiazole*, m. p.  $184^\circ$ , and *1:2-dibenzoyl-4-phenylthiosemicarbazide*, m. p.  $195^\circ$ , is formed. The constitution of the former substance is established by its production by the benzoylation of *3-anilino-2-phenyl-1:3:4-thiodiazole* (cf. Pulvermacher, A., 1894, 304; Marekwald and Bott, A., 1897, i, 205), the structure of which is confirmed by its failure to yield lead sulphide when boiled with an alkaline solution of lead oxide and its inability to give a benzyl derivative. The position of the benzoyl groups in *1:2-dibenzoyl-4-phenylthiosemicarbazide* follows from its failure to condense with benzaldehyde, whereby the absence of a free amino group is established, and its conversion by boiling, dilute alkali hydroxide into *3-thiol-4:5-diphenyl-1:2:4-triazole*, m. p.  $287^\circ$ . The latter substance is converted by benzyl chloride in the presence of alcoholic sodium ethoxide into *3-benzylthiol-4:5-diphenyl-1:2:4-triazole*, m. p.  $165^\circ$ , and by an excess of benzoyl chloride into *3-thion-2-benzoyl-4:5-diphenyl-2:3-dihydro-1:2:4-triazole*, m. p.  $164^\circ$ . The action of benzoyl chloride on *4-phenylthiosemicarbazide* in the absence of diluent yields *5-anilino-2-phenyl-1:3:4-thiodiazole* and *3-thiol-4:5-diphenyl-1:2:4-triazole*. The behaviour of *4-phenylthiosemicarbazide* is thus analogous to that of *4-o-anisylthiosemicarbazide*, and differs from that of the corresponding *4-o-tolyl* derivative (cf. Fromm, Soffner, and Frey, *loc. cit.*).

*1-Phenylthiosemicarbazide* is converted by benzoyl chloride (Schotten-Baumann) into *1-benzoyl-1-phenylthiosemicarbazide*, m. p.  $223^\circ$ . The constitution of the compound is established by the observations that it evolves nitrogen when treated with nitrous acid and is converted by dilute alkali hydroxide into *3-thiol-1:5-diphenyl-1:2:4-triazole*, m. p.  $188^\circ$ . The latter substance is stable towards acids and alkalis. It is converted by benzyl chloride in alkaline solution into *3-benzylthiol-1:5-diphenyl-1:2:4-triazole*, m. p.  $100^\circ$ , and by benzoyl chloride and alkali hydroxide into *3-thion-2-benzoyl-1:5-diphenyl-2:3-dihydro-1:2:4-triazole*, m. p.  $139^\circ$ . The latter compound can also be obtained by treatment of *1-phenylthiosemicarbazide* with an excess of benzoyl chloride in alkaline solution if the temperature is not moderated; it is converted by benzoyl chloride in boiling alkaline solution into *3-benzylthiol-1:5-diphenyl-1:2:4-triazole*. *1-Phenylthiosemicarbazide* and benzoyl chloride in the presence of boiling chloroform yield a mixture of a *dibenzoyl-1-phenylthiosemicarbazide*, m. p.  $188^\circ$ , which does not contain a free amino group and is converted by protracted boiling in alkaline solution into *3-thion-2-benzoyl-1:5-diphenyl-2:3-dihydro-1:2:4-triazole*, and a substance, m. p.  $212^\circ$ , to which the constitution  $\text{N} \begin{smallmatrix} \text{CS} \\ \text{CPh} \end{smallmatrix} \text{N} \cdot \text{NPhBz}$  is ascribed, since it is transformed by alkali hydroxide into *1:4-dibenzoyl-1-phenylthiosemicarbazide*, m. p.  $188^\circ$ . The action of benzoyl chloride on *1-phenylthiosemicarbazide* in the absence of diluent gives a mixture of

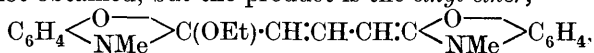
highly benzoylated compounds which has not been examined completely.  
H. W.

**Thio- and Oxa-cyanines.** W. KÖNIG and W. MEIER (*J. pr. Chem.*, 1925, [ii], 109, 324—344; cf. A., 1924, i, 669; 1922, i, 1188).—1-Methylbenzthiazole (König and Treichel, A., 1921, i, 738) affords a *methiodide*, m. p. 219°, and a *methobromide*, m. p. 206°. When the methoperchlorate (*loc. cit.*) is treated in acetone suspension with sodium hydroxide, it yields 2-methyl-1-methylenebenzthiazoline, m. p. 166°. This substance, when heated alone or in solution, is converted into a compound which dissolves in acids to yield a purple dye, apparently identical with the “thiazole-purple” or 1:1'-dimethylstreptomono-vinylene-2:2'-thiocyanine, the bromide (blue-bronzy needles, m. p. 248°),



of which is obtained (yield, 85%) by treating the above 1-methylbenzthiazole methobromide, in nitrobenzene, pyridine, or acetic anhydride solution, with an excess of ethyl orthoformate or anhydrous sodium formate at 150—160°. The *iodide* has m. p. 254°, and the *perchlorate* has m. p. 250° (decomp.). This compound shows absorption bands at  $\lambda$  558 and  $\lambda$  526 in alcoholic solution and dyes mordanted cotton or viscose-silk in bluish-red shades. It is resistant to acids and is affected by alkalis less than its quino-cyanine analogues.

1-Methylbenzoxazole combines with methyl iodide at 100° to give the *methiodide*, m. p. 200°, which is hydrolysed by hot water to *N*-methyl-*o*-acetamidophenol (Lees and Shedden, T., 1903, 83, 756). The *methosulphate* has m. p. about 75°. When the methiodide is treated with ethyl orthoformate in boiling acetic anhydride “oxazole-yellow,” 1:1'-dimethylstreptomono-vinylene-2:2'-oxacyanine iodide (formula analogous to that above, cf. also below) is obtained. This substance forms scarlet needles, m. p. 259°, and the corresponding *sulphate* (from the above methosulphate) has m. p. 267°; it shows absorption bands (in alcohol) at  $\lambda$  485 and  $\lambda$  456, and dyes mordanted cotton in reddish-yellow shades. It is more resistant to acids than its sulphur analogue, but is decomposed by alkalis. When it is treated with absolute alcoholic sodium hydroxide the carbinol base is not obtained, but the product is the *ethyl ether*,



yellow needles, m. p. 212°.

The relationships between colour and constitution among the above dyes and their known analogues are discussed at length, emphasis being laid on the influence on one another of the various possible alternative conjugated chains.  
W. A. S.

**6-Chlorophenoxarsine.** E. E. TURNER and A. B. SHEPPARD (*J. Chem. Soc.*, 1925, 127, 544—547).—*o*-Aminodiphenyl ether, m. p. 41.5°, b. p. 160—162°/12—15 mm. (*benzoyl* derivative, m. p. 75°), was obtained from the tin double salt (cf. Ullmann, A., 1896, i, 605) by treatment below 0° with excess of potassium hydroxide.

*o*-Phenoxybenzeneazo- $\beta$ -naphthol melts at 135°. *o*-Phenoxyphenylarsinic acid, prepared from diazotised *o*-aminodiphenyl ether and sodium arsenite, is converted into *o*-phenoxyphenyldichloroarsine by the sulphurous-hydriodic-hydrochloric acid method. The orange-red oil so obtained loses hydrogen chloride when distilled at 10 mm. and gives 6-chlorophenoxarsine, m. p. 122°, identical with the product prepared from diphenyl ether and arsenious chloride in presence of aluminium chloride. The sulphur ring-analogue is not obtained from diphenyl sulphide, arsenious chloride, and aluminium chloride at 175–185°, the only product isolated being diphenylene disulphide.

C. H.

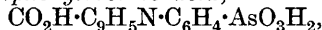
**Asymmetric Compounds of Quinquevalent Arsenic.** J. A. AESCHLIMANN (*J. Chem. Soc.*, 1925, **127**, 811–815; cf. Michaelis, A., 1902, i, 516; Winmill, *J. Chem. Soc.*, 1912, **101**, 720; Burrows and Turner, *J. Chem. Soc.*, 1921, **119**, 426).—Unsuccessful attempts were made to resolve compounds of the type  $abcAs\cdot O$ , in which one of the groups a, b, and c contained an acidic radical for combination with an active base. These included *oo'*-dicarboxydiphenylarsinic anhydride (cf. A., 1924, i, 1358); *o*-carboxydiphenylmethylarsine oxide, m. p. 242°, obtained by the action of hydrogen peroxide on the arsine, which was prepared by an improved method from magnesium phenyl bromide and *o*-carboxyphenylmethylarsinous anhydride; and a *sulphonic acid*, m. p. 249°, of phenyl- $\alpha$ -naphthylmethylarsine oxide (Burrows and Turner, *loc. cit.*).

Certain quaternary salts were also prepared for investigation: Phenyl- $\alpha$ -naphthylmethylarsine gives with bromoacetic acid an *additive* compound, m. p. 145–150° (decomp.). 6-Ethylphenoxarsine, colourless oil, obtained from magnesium ethyl bromide and 6-chlorophenoxarsine (*sulphonic acid*, m. p. above 300°), is oxidised to 6-ethylphenoxarsine oxide, m. p. 99°, and forms stable additive compounds with bromoacetic acid and alkyl iodides: 6-carboxymethyl-6-ethylphenoxarsonium bromide; 6:6-diethylphenoxarsonium iodide, m. p. 193°; and 6-methyl-6-ethylphenoxarsonium iodide, m. p. 186–193°, according to rate of heating. No resolution of the latter was obtained by conversion into 6-methyl-6-ethylphenoxarsonium d-bromocamphorsulphonate, m. p. 153°.

Phenyl  $\alpha$ -naphthyl ether condenses with arsenious chloride in presence of aluminium chloride giving 7-chloro- $\alpha\beta$ -naphthaphenoxarsine, m. p. 168°.

M. J.

**Carboxyquinolylphenylarsinic Acid and Derivatives.** K. OGDEN and R. ADAMS (*J. Amer. Chem. Soc.*, 1925, **47**, 826–830).—*p*-4-Carboxy-2-quinolylphenylarsinic acid,



m. p. not below 270°, was obtained by condensing acetophenone-*p*-arsinic acid with isatin in aqueous alcohol in presence of sodium hydroxide. It forms a *disodium* salt, and yields, on esterification with ethyl and methyl alcohols, the corresponding *carbethoxy*, m. p. 117–119° (decomp.), and *carbomethoxy* derivatives, m. p. 153°, respectively, whilst reduction with sodium hyposulphite affords *p*:*p'*-di-4-carboxy-2-quinolylarsenobenzene, m. p. not below 250°.

*p*-4-Carboxy-6-methyl-2-quinolylphenylarsinic acid, m. p. not below 250° (*methyl* and *ethyl* esters, m. p. not below 275°), and *p*:*p'*-di-4-carboxy-6-methyl-2-quinolylarsenobenzene, reddish-brown, m. p. not below 250°, were prepared similarly. *Acetophenone-p*-arsinic acid, m. p. not below 250°, is described. The above derivatives are more toxic and less trypanocidal than salvarsan and arsanic acid.  
F. G. W.

**Derivative of Cupreine containing Arsenic.** F. X. ERBEN and N. SCHNIDERSCHITSCH [with W. VIS] (*Ber.*, 1925, **58**, [B], 693—695).—*Sodium dihydrocupreine-5-azobenzene-p*-arsinic acid, decomp. 218° after darkening, is prepared by the addition of a diazotised solution of *p*-aminophenylarsinic acid in hydrochloric acid to a solution of dihydrocupreine in *N*-sodium hydroxide in the presence of sodium acetate, the conditions being so adjusted that the mixture is finally just neutral with respect to the monosodium salt. The corresponding free acid has m. p. (indef.) 215° after darkening at 170°; like the sodium salt, it absorbs oxygen during desiccation. This property is not shared by the hydrochloride (+2H<sub>2</sub>O).  
H. W.

**Influence of Neutral Salts on Gelatin. III. Influence on the Action of Trypsin on Gelatin.** E. STIASNY and S. R. D. GUPTA (*Collegium*, 1925, 57—64).—Trypsin was allowed to act on a 1% gelatin solution, with or without the addition of sodium thiocyanate, nitrate, chlorate, chloride, or sulphate. The proteolytic effect of the trypsin is little affected by salts other than the thiocyanate, which hinders it slightly. The formaldehyde and Van Slyke figures showed that 0.1*N*-solutions of neutral salts increase the peptolytic action of the trypsin slightly, but that stronger solutions cause it to diminish again. Proteolysis is complete in 4 hrs.; peptolysis occurs mainly in the first 24 hrs., but still proceeds after 6 days, when 20% of the nitrogen originally present becomes titratable by formaldehyde. This is one-third of the complete hydrolysis, showing that the latter cannot be attained with trypsin. This agrees with the view (Ssadiikov and Zelinsky) that the last elements of proteins are not amino-acids only but diketopiperazines which are not included in the formaldehyde titration. The effect of neutral salts on the hydrolysis of gelatin by trypsin is very different from their effect on the hydrolysis of collagen. Sodium thiocyanate retards the peptolytic action of trypsin on both collagen and gelatin; other neutral salts do not. [Cf. *B.*, 1925, 412.]  
D. W.

**Halogenated Proteins. IV. Bromofibrin.** A. J. J. VANDELVELDE (*Rec. trav. chim.*, 1925, **44**, 224—228; cf. this vol., i, 91).—A solution of bromine in carbon tetrachloride converts fibrin into a bromofibrin (N=8.06%, Br=41.1%) without liberation of hydrogen bromide. This material, treated with water or alkalis, gives substances of variable composition containing less bromine, the greater part of the bromine which passes into solution being present as hydrobromic acid. The bromofibrin is converted by heating at 100° into a substance (N=11.0%, Br=35.4%) which

shows a similar behaviour with water and alkalis except that the insoluble substances produced contain a higher proportion of bromine than those from the original bromofibrin. G. M. B.

**Coagulation of Albumins and  $\beta$ -Albumins.** M. A. RAKUSIN and A. ROSENFELD (*Z. Unters. Nahr. Genussm.*, 1925, **49**, 38—39).—A  $\beta$ -modification of albumin was obtained by heating coagulated albumin with water under pressure for 12 hrs. The modified material was soluble in water, non-coagulable, and had a higher optical rotation than the original, although it still showed all the typical protein reactions. A. G. P.

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## Biochemistry.

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**Cell Respiration. II. Mechanism of Oxidation of Lactic Acid. III. Reactivation Experiments using Artificial Co-enzymes.** A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1925, **157**, 50—84).—The system in muscle which brings about the oxidation of lactic acid has two components, one soluble, the other relatively insoluble. The latter is a very active dehydrogenase. An oxygen activator may also be present. The soluble component is co-enzymic in character; it is heat-stable, and is neither enzyme nor protein. It is precipitated by lead acetate in neutral solution, and may be recovered in active form by decomposing the lead precipitate with hydrogen sulphide. Neither the soluble nor the insoluble component is active in absence of the other, but when both are added together in the correct proportions, lactic acid oxidation proceeds at normal speed.

Catalase is not the co-enzyme, nor can the oxidising power of washed muscle be induced by adding methylene-blue instead of the co-enzyme. Neither the reduced nor the oxidised form of glutathione is able to bring about the oxidation of lactic acid by washed muscle. There are insufficient amounts of active metallic salts in the tissues to catalyse the autoxidation of reduced glutathione, and it does not appear to be oxidised by the oxygen activated by washed muscle, although *p*-phenylenediamine, adrenaline, *p*-aminophenol, quinol, and other phenols are readily oxidised by such preparations. Washed muscle is not capable of oxidising the -SH group of thioglycollic acid. It would appear that in muscle there is a specific phenol oxydase, and not a more general system by which oxygen is activated to a definite oxidation potential. The velocity of oxidation of such phenols and phenol derivatives depends on their adsorbability by the tissue. They are able to reactivate washed muscle, and act like the co-enzyme in enabling it to oxidise lactic acid.

H. D. K.

**Influence of Oxygen Tension on Biological Oxidation.** R. J. HAMBURGER and A. VON SZENT-GYÖRGYI (*Biochem. Z.*, 1925, **157**, 298—302).—The velocity of oxidation of *p*-phenylenediamine by means of washed pig's diaphragm muscle is independent of the oxygen tension over a range of 1—0.05 atm. of oxygen.

P. W. C.

**Causes of Differences of Intensity of the Elementary Respiration of Tissues.** E. F. TERROINE and J. ROCHE (*Compt. rend.*, 1925, **180**, 1061—1063).—From a consideration of data derived from various sources concerning the respiratory intensity and composition of brain, liver, kidney, and muscle (bird and mammal) tissues, the conclusion is reached that the respiratory intensity, *in vitro*, of a tissue is directly proportional to the product of the percentage of protein and the percentage of lipid phosphorus.

G. M. B.

**Influence of Tension of Molecular Oxygen on Oxidations of Hæmoglobin.** J. M. NEILL and A. B. HASTINGS (*J. Biol. Chem.*, 1925, **63**, 479—492).—The optimum tension of oxygen for the formation of methæmoglobin by sterile extracts of pneumococci, by anærobic bacilli, and by various autoxidisable substances, and also for its spontaneous formation in sterile blood, was found to be 20 mm., at which tension 50% of the hæmoglobin is in the reduced state. The presence of 10 mm. tension of carbon monoxide inhibits the formation of methæmoglobin altogether. The course of the reaction appears to consist of the formation of an oxidising agent by combination of molecular oxygen with an autoxidisable substance and the subsequent oxidation of the ferrous iron of hæmoglobin to the ferric state. The results are in accord with the view of Conant (this vol., i, 455) that the substance oxidised to methæmoglobin is reduced hæmoglobin.

C. R. H.

**Formation of Methæmoglobin.** W. KLEIN (*Biochem. Z.*, 1925, **156**, 323—333).—From observations of the actions of iron salts and organic acids on hæmoglobin it is concluded that the formation from the latter of methæmoglobin depends on the conversion of the iron of the pigment from the ferrous into the ferric condition together with the liberation of oxygen. The use of succinic acid is recommended for the direct gasometric determination of carbon dioxide in blood.

J. P.

**Acid-Base Equilibrium. II. Determination of the Hydrogen-ion Concentration of the Blood. III. Determination of Alveolar Carbon Dioxide Tension. IV. Titrimetric Determination of Hydrogen Carbonate in the Blood.** J. HOLLO and S. WEISS (*Magyar orvosi Archivum*, 1924, **25**, 288—300, 301—306, 307—313).—II.—The diluted plasma containing indicator is divided into two portions, one of which is titrated with hydrochloric acid after addition of alkali phosphate. When equality of colour is attained, the result may be read from an empirically determined curve.

III.—The air is passed into sodium hydrogen carbonate solution,



the change in reaction of which is determined colorimetrically, and the tension calculated from an empirical curve.

IV.—Gollwitzer's criticism of Van Slyke, Stillman, and Cullen's method is rejected; modifications are available for clinical and exact work respectively.

CHEMICAL ABSTRACTS.

**Determination of Carbon Monoxide in Blood.** D. G. C. TERVAERT (*Biochem. J.*, 1925, **19**, 300—303; see also *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 832—833).—The carbon monoxide is extracted from the blood by the use of ferricyanide with evacuation. After passing the gas through strong potassium hydroxide and concentrated sulphuric acid, it is led over iodine pentoxide heated at 150°. The liberated iodine is collected in potassium iodide solution and titrated with 0.01*N*-sodium thiosulphate. Accurate results can be obtained with 10 c.c. of blood.

S. S. Z.

**Determination of Ammonia and Urea in Blood and Urine.** M. M. MURRAY (*Biochem. J.*, 1925, **19**, 294—299).—Ammonia and urea in urine and in blood can be determined by aëration in the apparatus of Cannan and Sulzer (*Heart*, **11**, 148) and subsequent titration. Urea in urine and in blood can also be determined by aspirating the ammonia from the decomposed urea and determining it colorimetrically by Orr's method (this vol., i, 184). The determination can be made with 0.2 c.c. of blood.

S. S. Z.

**Exchange of Chlorine between the Red Blood Corpuscle and the Surrounding Solution. III. Influence of the Hydrogen-ion Concentration on the Exchange.** W. BURGER (*Arch. Exp. Path. Pharm.*, 1925, **106**, 102—107).—The exchange has been examined in solutions of  $p_H$  6.7 and 7.3. After  $\frac{1}{2}$  hr. less chlorine is found in the solution of  $p_H$  6.7 than in the other. This is ascribed to a reduction in the amount of diffusion rather than to a displacement of the equilibrium, since after about 2 hrs. the difference of chlorine is much less. A definite equilibrium is probably reached in both cases in about 2 hrs. When the structure of the corpuscles has been destroyed by freezing, the amount of chlorine in the solution is considerably increased, although the amount is unaffected by the difference in the reaction of the two solutions. The addition of peptone is without effect on the amount of chlorine in the surrounding solution. The effect of anions and cations on the exchange has been determined by the addition of the nitrates of sodium, calcium, and potassium and the sulphates of sodium and potassium. In the presence of nitrate, more chlorine is found in the solution than when sulphate is present, during  $\frac{1}{2}$  hr. At the end of 2 hrs., however, there is practically no difference. Equilibrium is attained much more rapidly in the presence of nitrate than in the presence of either sulphate or phosphate. The nitrates and sulphates, respectively, of different cations all have the same effect.

O. O.

**Rate of Sinking of Erythrocytes with Reference to the Hofmeister Ionic Series.** D. VON KLOBUSITZKY (*Biochem. Z.*, 1925, **157**, 277—282).—An investigation of the influence of hypertonic salt and sugar solutions on the rate of sinking of erythrocytes

shows that the influence follows the Hofmeister series, and is inversely proportional to the concentration of the solution. P. W. C.

**Stereoisomerism and Cell-permeability.** M. OKAGAWA (*Z. physiol. Chem.*, 1925, **143**, 211—217).—Of the optically active forms of histidine, the *l*-isomeride enters the washed red blood-corpuscle of the rabbit (suspended in saline) more readily than the *d*-isomeride. H. D. K.

**Determination of Hæmoglobin.** H. B. NEWHAM, H. G. WILTSHIRE, and J. W. SCHARFF (*J. Roy. Army Med. Corps*, 1924, **43**, 359—365).—The Gower, Haldane, Fleischl, and Tallquist hæmoglobinometers are untrustworthy, and the normal value should be 108—110%, representing 15 g. of hæmoglobin per 100 c.c. The specific gravity is not accurately proportional to the hæmoglobin content. CHEMICAL ABSTRACTS.

**Formation of Bile Pigment from Hæmoglobin in Tissue Cultures.** A. R. RICH (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 415—416).—Ingestion of red blood cells by phagocytes of mesodermal origin is followed by the conversion of the hæmoglobin into bile pigment and a residue containing iron within the body of the phagocytic cell. CHEMICAL ABSTRACTS.

**Porphyrins from Blood Pigment.** A. PAPENDIECK and K. BONATH (*Z. physiol. Chem.*, 1925, **144**, 60—67).—The reduction of hæmatin with hydrazine in glacial acetic acid solution gave a product identical spectroscopically with  $\alpha$ -hæmatoporphyrin (cf. Schumm, this vol., i, 88). Electrolytic reduction of hæmatin gave, according to the conditions of the reaction,  $\alpha$ -hæmatoporphyrin, hæmatoporphyrin (Nencki and Sieber, A., 1888, 971), and mesoporphyrin; mesoporphyrin was further obtained by electrolytic reduction or catalytic hydrogenation of  $\alpha$ -hæmatoporphyrin, and by electrolytic reduction of  $\alpha$ -hæmatoporphyrin. All products were identified spectroscopically. C. R. H.

**Isolation of Adenine Nucleotide from Blood.** W. S. HOFFMAN (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 417).—Pure crystalline adenine nucleotide prepared from pig's blood agrees in chemical composition and physical properties with that prepared from yeast-nucleic acid by Jones and Kennedy. CHEMICAL ABSTRACTS.

**Uric Acid in Blood.** W. G. LENNOX and M. F. O'CONNOR (*J. Lab. Clin. Med.*, 1924, **10**, 99—103).—It seems probable that the upper limit of the uric acid concentration of normal blood by the new direct method of Folin (A., 1923, ii, 196) may be 4.5—5.0 mg. per 100 c.c. of blood. The concentration of uric acid in the blood is considerably but inconstantly higher when measured by the direct method of Benedict (A., 1922, ii, 405) or of Folin (*loc. cit.*) than when measured by that of Folin and Wu (A., 1919, ii, 308) or by the check method of Folin ("Laboratory Manual of Biological Chemistry," N. York, 1923). CHEMICAL ABSTRACTS.

**New Type of Phosphoric Acid Compound from Blood. Effect of Substitution on the Rotation of *l*-Glyceric Acid.** I. GREENWALD (*J. Biol. Chem.*, 1925, **63**, 339—349).—The proteins and lipoids of pig's blood were removed with trichloroacetic acid and the filtrate was treated with lead acetate; the solution obtained on decomposition of the lead precipitate was treated with magnesia mixture and the filtrate from the magnesium ammonium phosphate again treated with lead acetate; on addition of barium hydroxide to the solution obtained after decomposition of this second lead precipitate there was obtained a *barium* salt with the composition  $C_6H_6O_{20}P_4Ba_5 \cdot 3H_2O$ ; on dissolving this salt in the minimum amount of dilute hydrochloric acid and adding alcohol a second *barium* salt,  $C_6H_{10}O_{20}P_4Ba_3 \cdot H_2O$ , was obtained. On removal of the barium from either of these salts and heating the free acid in 5% sulphuric acid for several days at 100° there was isolated from the resulting solution a barium salt identified as barium *l*-glycerate. The original compounds isolated were therefore the penta- and tri-barium salts of *diphospho-l-glyceric acid*. The tribarium salt has  $[\alpha]_D^{20} -4.45^\circ$ ; the free acid  $[\alpha]_D^{21} -3.36^\circ$ ; after neutralisation to Congo-red with sodium hydroxide,  $[\alpha]_D^{17} -4.01^\circ$ ; after neutralisation to thymolphthalein,  $[\alpha]_D^{23} -2.73^\circ$ . The *l*-glyceric acid obtained on hydrolysis was partly racemised, the greatest rotation observed being  $[\alpha]_D -1.99^\circ$ ; attention is called to the effect of introducing two phosphoric acid groups into the molecule in increasing the molecular rotation as shown by the above figures. The amount of the compound isolated from pig's blood represented 12.2—19.3 mg. of phosphorus per 100 c.c.; the same compound was obtained in smaller yield from human and dog's blood. C. R. H.

**Concentration of Acetone Substances in Normal Blood and Urine.** R. S. HUBBARD and C. V. NOBACK (*J. Biol. Chem.*, 1925, **63**, 391—394).—The average of the results of experiments on twenty-four normal individuals shows the preformed acetone+acetoacetic acid of the blood to be 0.13 and of the urine 0.19 mg. per 100 c.c., whilst the  $\beta$ -hydroxybutyric acid of the blood is 0.30 and of the urine 0.46 mg. per 100 c.c. C. R. H.

**Influence of Intravenous Administration of Urea on the Non-protein Nitrogen of the Blood.** E. SCHILL and J. KUNZE (*Magyar orvosi Archivum*, 1924, **25**, 318—325).—After injection of urea, the non-protein nitrogen did not reach the calculated value, and became normal after 3 hrs., although the urea remained in the body for several days. Storage in the tissues must therefore take place. The increase was greater for the red cells than the serum.

CHEMICAL ABSTRACTS.

**Chemistry of the Blood during Parenteral Excitation of the Activity of Digestive Glands, especially of the Stomach.** K. ONOHARA (*Biochem. Z.*, 1925, **157**, 271—276).—Changes in total solids and chloride content of the blood have been followed in dogs for 3 hrs. after the subcutaneous injection of secretin, pilocarpine,

and atropine and the intravenous or subcutaneous injection of acetylcholine (cf. this vol., i, 322). After pilocarpine, the total solids rise and remain high for 3 hrs. and then gradually fall, whilst the chloride content sinks a little at first and either remains at this value or returns to the original value. After acetylcholine, there is an increase of total solids, but the increase is smaller than with pilocarpine. In this latter case, the greater salivation is supposed to account for the greater loss of water. The chloride values are inconsistent. After secretin, there was a rise of total solids intermediate between the values for pilocarpine and acetylcholine, but no change in chloride content occurred. With atropine, slight decrease of total solids and slight increase of chloride occurred.

P. W. C.

**Chemical Composition of Blood during Labour.** E. C. P. WILLIAMS (*Lancet*, 1924, II, 1336—1337).—There is an appreciable rise in the blood non-protein nitrogen and urea during labour, the average urea content changing from 19.0 mg. % during pregnancy to 28.2 mg. % during labour.

CHEMICAL ABSTRACTS.

**Measurement of Calcium-ion Concentration [in Blood].** O. BUDDE and E. FREUDENBERG (*Z. ges. exp. Med.*, 1924, 42, 284—295; from *Chem. Zentr.*, 1924, ii, 1812).—The values obtained for calcium-ion concentration by the method of Brinkman and Van Dam are greater than the calculated values when both the alkalinity and the phosphorus value are high; otherwise good agreement is obtained. In blood dialysates, the calcium-ion concentration is depressed by substances of the residual nitrogen group. Glycine removes calcium ions from solution, particularly at low alkalinities.

G. W. R.

**Determination of Calcium in Blood Serum by the Tisdall Method.** E. P. CLARK and J. B. COLLIP (*J. Biol. Chem.*, 1925, 63, 461—464).—Some calcium oxalate may be lost in the process of washing with dilute ammonia in the method of Tisdall (*A.*, 1923, ii, 656), and it is therefore suggested that one washing only should be given, the centrifuge tube being inverted on filter paper for 5 min. to ensure complete drainage.

C. R. H.

**Blood Calcium under Normal and Pathological Conditions.** H. A. SALVESEN (*Norsk Mag. Laegev.*, 1923, 21, 1047—1052).—The calcium content of normal serum is 9.5—10.5 mg. per 100 c.c.; in pregnancy the values are lower, also in tetany, e.g., 6.34 and 4.38 mg. Other pathological conditions were investigated.

CHEMICAL ABSTRACTS.

**Determination of Formic Acid in Blood and Urine.** F. DE EDS (*J. Lab. Clin. Med.*, 1924, 10, 59—66).—The blood is placed, by means of a pipette moistened with saturated oxalate solution, in a 100 c.c. cylinder, diluted, and diluted again, after addition of picric acid, to 100 c.c., then shaken, and the liquid filtered. An aliquot portion is heated with Fincke's mercuric chloride reagent,

and the mercurous chloride determined by addition of iodine to the acidified solution and titration of the excess. Formaldehyde, if present, is first converted into hexamethylenetetramine. Urine is distilled with steam after addition of picric acid, the distillate being kept alkaline. Mercuric chloride is added after partial evaporation and acidification and the determination continued as before. Formic acid was not found in normal blood and urine.

CHEMICAL ABSTRACTS.

**Micro Determination of Potassium in Blood-serum and other Fluids.** F. LEBERMANN (*Klin. Woch.*, 1924, 3, 1632; from *Chem. Zentr.*, 1924, ii, 1966).—The liquid is treated with cobaltinitrite reagent. The precipitate of potassium cobaltinitrite is separated and washed by centrifuging, dried at 100°, and dissolved in 27% hydrochloric acid. The potassium is determined colorimetrically, using standard solutions of potassium chloride for comparison.

G. W. R.

**Micro-determination of Blood-sugar.** K. DRESEL and H. ROTHMANN (*Biochem. Z.*, 1925, 157, 172—173).—Using the modification of the Hagedorn and Jensen technique devised previously (A., 1924, ii, 632) in which filter paper and a torsion balance are used instead of a pipette for measuring the blood, it has been found that even if the blood is allowed to dry on the paper and is left up to 4 days before the determination is made, there is no change in the sugar value.

H. D. K.

**Combined Sugar in Blood. Methods for Micro Determination. Conditions in Normal Individuals. Glycolysis and Combined Sugar.** L. CONDORELLI (*Policlinico, sez. med.*, 1924, 31, 125—144; from *Chem. Zentr.*, 1924, ii, 1812).—Combined sugar was determined in blood by comparing the results obtained with native plasma and with plasma after heating with 0.125*N*-hydrochloric acid (half saturated with potassium chloride) for 10 mins. in an autoclave at one atmosphere pressure and subsequently neutralising with sodium hydroxide solution (half saturated with potassium chloride). With normal fasting men, the average content of combined sugar was 0.042% (0.030—0.054%), forming 53% (42—72%) of the free sugar. After oral administration of 20 g. of dextrose in 50 c.c. of water both the actual and relative content of combined sugar decreased at first. Subsequently when the free sugar had reached its normal value, the combined sugar was slightly increased. Similar results were obtained after subcutaneous injection of adrenaline or pituitary extract. Inconsiderable changes in the amount of combined sugar in dogs' blood were produced by glycolysis during 24 hrs. Hydrolysis of 2% Witte peptone solution by the above method caused a slight increase in reducing power, a result which only explains to a small extent the results obtained for combined sugar. Combined sugar is considered to originate from a reserve of loose compounds of protein with dextrose.

G. W. R.

**Blood-sugar of the Goat.** K. SCHUECKER (*Biochem. Z.*, 1925, **156**, 353—364).—Two normally fed goats showed the low average blood-sugar values of 49—60, and 52—64 mg.%. After 2 days' partial starvation the blood-sugar value sank to 41 mg.% in the case of the first animal. After strenuous exercise the value rose in another case to 117 mg.%, the return to normal being slow. Small injections of adrenaline (0.5 mg.) produced a hyperglycæmia of the order 95 mg. % after 4 hrs., the return to normal values being again slow. Insulin injections produced very low blood-sugar values—17 mg.%—without accompanying collapse, unless the low value was maintained for a period of 2 hrs. J. P.

**Hypoglycæmia. Identity of Intoxication Due to Dextrose Starvation with the Hypoglycæmic Reaction.** F. FISCHLER and F. OTTENSOOSER (*Z. physiol. Chem.*, 1925, **144**, 1—59).—The toxic symptoms exhibited by rabbits which have been starved or treated with phloridzin until in a condition of hypoglycæmia are similar to those which follow overdosage with insulin, and are relieved by the administration of dextrose. In both cases, the symptoms are therefore due to the actual deficit of dextrose in the blood, any concentration below 0.07% being dangerous. The hypoglycæmia caused by starvation or by phloridzin, being due to the complete exhaustion of all carbohydrate reserves in the body, is slow in onset, is accompanied by a fall in body-weight and in temperature, and the stage of convulsions is preceded by one of intense physical weakness; the intoxication is accompanied by a disturbance of hepatic function as is shown by an abnormal urinary excretion of urobilin, the latter being shown to be hepatogenous and not enterogenous in origin. C. R. H.

**Structure of Blood-serum.** H. HANDOVSKY (*Koll.-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 292—297).—The possible rôles of secondary particles or aggregates in blood sera are discussed. The quantitative relationships between the coagulation, refraction, and viscosity of sera and the contents of albumin, pseudoglobulin, and euglobulin hold only for normal and not for pathological sera. After concentration in a vacuum, sera are relatively richer in albumin. In sera saturated with carbon dioxide the change of viscosity with time depends on the albumin-globulin ratio. The amount of cholesterol extracted by ether varies inversely with the euglobulin content. It is apparently protected in the serum by the euglobulin. Dilution of serum with water or very dilute solutions of sodium, potassium, or calcium chlorides affects the amount of cholesterol extracted by ether, but dilution with physiological salt solutions, e.g., Ringer or Tyrode, has no such effect. E. M. C.

**Inorganic Bone-forming Elements of the Blood-serum.** H. A. PETERSON (*Bull. Johns Hopkins Hosp.*, 1924, **35**, 378—381).—A definite relationship exists between the concentration of the bone-forming elements of the serum and the rate of repair of fractured bones. With  $[Ca][P]$  (mg. per 100 c.c.) < 30, fractures will not unite. Dog's serum contains much more phosphorus than human serum. CHEMICAL ABSTRACTS.

**Mechanism of the Reaction between Formaldehyde and Serum Proteins.** R. R. HENLEY (*J. Agric. Res.*, 1924, 29, 471—482).—When formaldehyde is added to serum, the proteins become less soluble in ammonium sulphate (A., 1923, i, 1253). Experiments are now described from which it is concluded that the change is chemical. Immediately on the addition of formaldehyde the titratable acidity of the serum increases considerably and the  $p_H$  decreases; thereafter the titratable acidity gradually decreases, although the  $p_H$  may continue to fall. The increase in acidity is related to the amount of formaldehyde added, but is not proportional to it. The author puts forward tentatively an explanation of the formaldehyde-gelatinification of serum. C. P. S.

**Action of Chloral Hydrate on the Proteins of Blood-serum.** M. NEŠKOVIĆ (*Glas Acad. Sci. Belgrade*, 1924, 113, 27—40).—A 2.5% solution of chloral hydrate precipitates the proteins of blood-serum even in a dilution of 1:10000. The precipitation, which usually is not complete, is due to the dehydrating action of the chloral hydrate on the proteins and is more strongly marked with the globulins than with the albumins. S. S. M.

**Determination of Fibrinogen. III.** W. STARLINGER and K. HARTL (*Biochem. Z.*, 1925, 157, 283—297).—A further survey of the methods available for the determination of fibrinogen (cf. A., 1923, ii, 890; 1924, ii, 212). In a series of parallel determinations in normal plasma, 95% of the individual variations of the results by the gravimetric method and 92% by the Kjeldahl method were less than 0.04 g.%, whilst comparing results by the two methods 80% showed differences less than 0.05 g.%. Comparing results by the gravimetric and differential refractometric methods in normal plasma, since 60% of the deviations are less than 0.05 g.%, the latter method is in general sufficiently accurate for normal plasma. Comparing the individual variations in a series of determinations in salt (citrate) plasma, it is shown that the gravimetric and Kjeldahl methods are as trustworthy for salt plasma as for normal plasma. Comparing the results by gravimetric and refractometric methods in salt plasma, since 71% of the deviations are greater than 0.04 g.%, the latter method cannot be used for salt plasma. The specific refraction for fibrinogen in normal plasma varies between 0.00209 and 0.00131 and in salt plasma between 0.00207 and 0.00097. Finally, the relative values of the interferometric, polarimetric, diaphanometric, nephelometric, and colorimetric methods are discussed. Of these, the three last-named are rapid and useful, but the constant preparation of standards is so tedious that the methods are no improvement on the gravimetric and Kjeldahl methods and they were not therefore further elaborated. P. W. C.

**Blood Coagulation in Cold-blooded Animals.** K. ŠAHOVIĆ (*Glas Acad. Sci. Belgrade*, 1923, 108, 87—92).—Experiments on frogs and fishes (*Ameiurus nebulosus*, Le Sueur), both normal and after removal of the liver, have shown that certain anticoagulants, such as nucleic acid and hirudin, act directly on the blood and not

through the liver as observed by Doyon in dogs in the case of nucleic acid. S. S. M.

**Blood Clotting and the Hofmeister Series.** J. CSAPÓ and D. VAN KLOBUSITZKY (*Biochem. Z.*, 1925, 157, 354—358).—The action of various potassium salts in inhibiting blood clotting conforms with the Hofmeister series, the anions giving the series,  $\text{SO}_4 < \text{Cl} < \text{NO}_3 < \text{Br} < \text{I} < \text{CNS}$  in the order of increasing inhibition. The anions of sodium salts give the series  $\text{Cl} < \text{NO}_3 < \text{SO}_4 < \text{I} < \text{CNS}$ , and of ammonium salts  $\text{Cl} < \text{SO}_4 < \text{NO}_3$ . For the cations, the order of increasing inhibitory action is  $\text{Na} < \text{K} < \text{NH}_4$ . J. P.

**Anti-coagulating Action of Zinc Salts.** A. LUMIÈRE and H. COUTURIER (*Compt. rend.*, 1925, 180, 1364—1366).—The polybasic acids which are so effective in preventing the coagulation of the blood *in vitro* (this vol., i, 606) have the opposite effect *in vivo*. Zinc sulphate, injected intravenously, on the other hand, prevents the clotting of the blood *in vivo* as well as outside the body, and appears to have very little harmful effect on the animal. This phenomenon may be of value in the study of body function in the absence of the higher nervous centres. The mechanism of the anti-coagulating action of zinc salts must, it is suggested, be different from that of the sodium salts of the polybasic acids. L. F. H.

**Human Blood Groups. II. Physical Chemistry of iso-Hæmagglutination.** E. WÖHLISCH and E. SCHÜTZ (*Z. Biol.*, 1924, 82, 265—277).—*iso*Hæmagglutinin is colloidal and relatively thermostable. It is unaffected when the serum is dried in a vacuum at the ordinary temperature but higher temperatures are injurious. It is susceptible to strong acids and alkalis and to strong ethyl alcohol when the exposure is prolonged. The agglutinin is precipitated by ammonium sulphate with the globulin. It appears to be denatured by lengthy dialysis against distilled water. The temperature coefficient of *isohæmagglutination* is very small. During agglutination, the cell suffers a considerable loss in its electrical charge. O. O.

**Influence of Blood-serum and of Sugars on Hæmolysis.** W. P. KENNEDY (*Biochem. J.*, 1925, 19, 318—321).—Ponder's results (A., 1921, i, 905; 1922, i, 292; 1923, i, 975) on the inhibition of saponin hæmolysis by serum are confirmed. It is also found that dextrose and lævulose inhibit, galactose accelerates, and starch has no effect on saponin hæmolysis. S. S. Z.

**Calcium Fixation by Animal Tissues. XI.** T. BREHME and P. GYÖRGY (*Biochem. Z.*, 1925, 157, 243—252).—The extent of calcium fixation is dependent, not only on external conditions, *e.g.*,  $p_{\text{H}}$ , anion effect, etc., and on the total calcium content, but also on the character of the proteins which fix the calcium. The further the isoelectric point is on the acid side, the greater is the affinity of the proteins for calcium. The following are arranged in order of decreasing affinity: nucleic acid, albumin, globulin, fibrin, and hæmoglobin. The unequal intracellular distribution of calcium,



*e.g.*, the richness of the nucleus in calcium, is explained by the different calcium affinities of the individual proteins forming the nucleus. In this connexion, the Donnan equilibrium must also be borne in mind.

P. W. C.

**Calcium Fixation in Animal Tissues. XII.** O. BUDDE (*Biochem. Z.*, 1925, 157, 253—260).—Gelatin gel under calcium phosphate solution takes up at first much calcium and little phosphorus, but later less calcium and more phosphorus. Thus the Ca/P ratio in the gelatin decreases. In practically protein-free agar gel under analogous conditions, an equal absorption of calcium and phosphorus takes place, the Ca/P ratio varying only slightly. Since the difference between the two cases lies in the protein content, it was concluded in agreement with the calcification theory of Freudenberg and György (*A.*, 1924, i, 242) that protein unites first with calcium and then with phosphate.

P. W. C.

**Nature and Production of Inorganic Structures in the Organism.** R. O. HERZOG and H. W. GONELL (*Koll.-Z.*, 1925, 36, (*Zsigmondy-Festschr.*), 44—48).—The application of the X-ray spectrograph to the study of crystal aggregates in living organisms confirms and supplements the conclusions obtained by means of their double refraction. The spines of the sea-urchin, *Heterocentrotus*, and of the star-fish give typical Laue diagrams, characteristic of single crystals. The calcium carbonate needles from sponges are too small for individual examination, but a collection gives a series of superimposed Laue diagrams. In dental enamel, the individual crystals exhibit a cylindrical or multiple fibre structure. A random arrangement of the individual crystallites, as in bone, gives X-ray diagrams of the Debye-Scherrer type. Silicic acid is deposited in an amorphous form in the organism. Egg shell gives a complicated mixture of Laue and Debye-Scherrer diagrams with a deformation structure.

E. M. C.

**Cell Permeability. I. Swelling of Gelatin under the Influence of Carbamide.** F. CHODAT.—(See ii, 521.)

**"Bound" Water in Colloids and Animal Tissues.** F. THOENES (*Biochem. Z.*, 1925, 157, 174—186).—The application to animal tissues of Rubner's method (freezing of colloid to  $-20^{\circ}$  and calorimetric determination of the amount of water present as ice at this temperature) for the free and bound water in colloids results in consistent values for such partition of water, but these do not necessarily represent the actual state of affairs in the living organism. This method gives, nevertheless, a comparative indication of the firmness with which the bound water is held in different circumstances. New-born animals show a considerably greater amount of bound water than do older animals. With increasing age there is also a decrease in the total amount of water in the tissues.

H. D. K.

**Distribution of the Residual Nitrogen in the Organism.** S. T. MADSEN (*Medicinsk Revue*, 1923, 40, 370—380).—Human

organs normally contain more residual nitrogen than the blood; the same is the case with urea. Muscular tissues give the highest residual nitrogen values, and fat the lowest; apart from pathological disturbances, a slight rise takes place before death. Determination of the residual nitrogen in the blood is not a perfect measure of the total nitrogen retention of the body. CHEMICAL ABSTRACTS.

**Significance of Copper in the Animal Organism.** G. B. ZANDA (*Biochim. terap. speriment.*, 1924, **11**, 7—21; from *Chem. Zentr.*, 1924, ii, 1810).—Using the hæmatoxylin test and the phenolphthalein (Utz) blood reaction for copper, this element was found to occur in all the organs of dogs, and of most other animals examined. Considerable amounts were found in the feathers of birds, and appreciable quantities in the shells of snails. No copper was found in butterflies, fibrin, dog's urine, or in egg-white. It is concluded that copper is a definite constituent of animal tissues.

G. W. R.

**Presence of Nickel and Cobalt in Animals.** G. BERTRAND and M. MACHEBŒUF (*Compt. rend.*, 1925, **180**, 1380—1382; cf. Bertrand and Mokragnatz, A., 1922, i, 975, 1099; 1924, i, 492).—Nickel occurs in all the organs (except muscular or fatty tissue) of mammals (including man), birds, fishes, crustaceans, molluscs, and ascidians. Especially notable is the high nickel content of the human liver, the pancreas of the bull, birds' feathers, egg yolk, and molluscs.

L. F. H.

**Determination of Lactic Acid in Animal Organs.** II. G. EMBDEN (*Z. physiol. Chem.*, 1925, **143**, 297—303).—A discussion of various modifications, notably that of Hirsch and Kauffmann, of the original method of von Fürth and Charnass, with particular regard to the removal of carbohydrates. Details are given of the technique now employed in the author's laboratory, by which, working with between 1.2 and 3.6 mg. of lactic acid, an average yield of 98% of the theoretical amount of acetaldehyde may be obtained.

H. D. K.

**Determination of Lactic Acid in Animal Organs.** O. MEYERHOF (*Z. physiol. Chem.*, 1924, **141**, 316).—Polemical. E. S.

**Extraction of Alkaloids or Various Organic Compounds contained in Organs.** R. FABRE (*Compt. rend.*, 1925, **180**, 966—967).—A pulp of the organ is subjected to aseptic proteolysis by trypsin, and from the centrifuged or filtered liquid the alkaloid may be extracted by means of a suitable solvent. The alkaloids tested were unaltered by the action of the enzyme and it is claimed that the method gives an almost quantitative extraction. [Cf. B., 1925, 334.]

F. M. H.

**Products of Putrefaction in Toxicological Analysis.** L. VAN ITALLIE and A. J. STEENHAUER (*Pharm. Weekblad*, 1925, **62**, 446—449).—A substance isolated from the bowel and stomach and their contents and the liver of a corpse gave many of the reactions of veratrine, and could only be differentiated by careful

purification, when it gave different colours on warming with sulphuric acid and in Vitali's test; nor did it give the typical physiological effect of veratrine poisoning. From the liver of a 2-months' dead corpse *p*-hydroxyphenylethylamine (tyramine) was isolated.

S. I. L.

**Toxicological Detection of Hydrocyanic Acid by Chelle's Reaction.** G. MAGNIN.—(See ii, 607.)

**Importance of Maintaining certain Differences between Cell Sap and External Medium.** W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1925, 7, 561—564).—The sap of *Valonia macrophysa* differs markedly both in composition and  $p_H$  from the surrounding sea-water. If this difference be abolished by placing the cells in the sap, most of them rapidly die. This is not due to bacterial growth in the sap, nor is the difference in  $p_H$  the primary cause.

C. P. S.

**Amphoteric Substance in the Radula of the Whelk (*Buccinum undatum*).** C. F. A. PANTIN and T. H. ROGERS (*Nature*, 1925, 115, 639—640).—Chitin-*A* of the radula of *Buccinum* combines with both anions and cations irrespective of the  $p_H$ , whilst chitin-*B* appears to be amphoteric (isoelectric point about  $p_H$  2.6).

A. A. E.

**Extractives of *Arbutia pustulosia*.** F. HOLTZ and F. THIELMANN (*Z. Biol.*, 1924, 81, 296—298).—Adenine, arginine, and *d*-lysine were isolated from this sea-urchin.

O. O.

**Chemical Investigation of the Sturgeon (*Acipenser sturio*).** O. FLÖSSNER and F. KUTSCHER (*Z. Biol.*, 1924, 81, 305—308).—Sarcosine, xanthine, methylguanidine, choline, and neosine were isolated from the sturgeon.

O. O.

**Occurrence of Methyladenine, Dimethylhistamine, Guanidine, Betaine, and Eledonine in *Geodia gigas*.** D. ACKERMANN, F. HOLTZ, and H. REINWEIN (*Z. Biol.*, 1924, 82, 278—284; cf. A., 1924, i, 906).—Guanidine has been isolated from an invertebrate for the first time. In addition to the substances given in the title, a base,  $C_7H_{14}O_2N_6$  (prepared as chloroaurate), has been isolated from *Geodia gigas*.

O. O.

**Occurrence of Sugars in Muscle Juice.** A. CONSTANTINO (*Arch. ital. biol.*, 1924, 72, 183—188; from *Chem. Zentr.*, 1924, ii, 1810).—The sugar content of the press-juice of dog's muscle was determined, after removal of proteins (Schenck) and precipitation with lead acetate, by reduction and also by fermentation. The latter method gave lower results.

G. W. R.

**Lipoids. XX. Hypocerebric Acid<sup>1</sup> (Hypohirnsäure), a New Triaminomonophosphatomonosulphatide from Human Brain.** S. FRÄNKEL and O. KARPFFEN (*Biochem. Z.*, 1925, 157, 414—424).—From the barium salts of acids obtainable from "protagon" and insoluble in benzene (cf. Fränkel and Gilbert A., 1922, i, 294), a triaminomonophosphatomonosulphatide,

$C_{101}H_{152}O_{26}N_3PS$ , m. p.  $196^\circ$ , has been isolated, to which the name *hypocerebric acid* is assigned, and in which all the nitrogen is present as amino nitrogen. On hydrolysis are obtained phosphoric acid, sulphuric acid, glycerol, aminoethyl alcohol, and  $\alpha$ -hydroxy-*n*-decoic acid,  $C_{10}H_{20}O_3$ , m. p.  $161^\circ$ . The methyl ester, m. p.  $102^\circ$ , the acetyl derivative of the methyl ester, m. p.  $123^\circ$ , and the silver and barium salts of the acid are described.  $\alpha$ -Hydroxy-*n*-decoic acid yields *n*-nonoic acid on oxidation with potassium permanganate. Glycerol is present in the lipid in approximately twice the amount required to form glycerophosphoric and sulphuric acids, and it is assumed that one molecule of aminoethyl alcohol is attached to each of the inorganic acid residues, whilst the third is linked in an unknown manner. J. P.

**Occurrence of Diastase in the Cerebrospinal Fluid.** I. COHEN (*Biochem. J.*, 1925, 19, 290—293).—Approximately 7 hrs. after death roughly 20% of cerebrospinal fluids were found to contain definite amounts of diastase. This appearance of the enzyme is a *post-mortem* change, since it is very rarely found in the cerebrospinal fluid of human beings during life. S. S. Z.

**Determination of Sugar in the Cerebrospinal Fluid.** J. CSAPÓ (*Biochem. Z.*, 1925, 157, 350—353).—The proteins present in the fluid are precipitated by Bang's method, and the filtrate is treated with Bang's carbonate-tartrate solution and with 5% copper sulphate. It is heated in the boiling water-bath and the cuprous oxide is separated by centrifuging and determined by Bertrand's method, using ferric sulphate and 0.01*N*/potassium permanganate. J. P.

**Mucous Secretion of the Cervix of the Cow.** H. E. WOODMAN and J. HAMMOND (*J. Agric. Sci.*, 1925, 15, 107—124).—In non-pregnant cows the mucus of the vagina has a lower dry matter content than that of the cervix. Both vaginal and cervical mucous show lowest dry matter content just after "heat." The amount of mucus in the cervix is also lowest at this period. During pregnancy, the cervical mucus increases both in amount and in dry matter content. The chemical nature of the mucin occurring in the cervical mucus is discussed. It is shown to belong to the class of mucins containing mucoitinsulphuric acids in their molecules. The effect of various reagents on the liquefaction of the mucous secretion is examined. G. W. R.

**Composition of Amniotic Fluid [Cow].** H. REINWEIN and H. HEINLEIN (*Z. Biol.*, 1924, 81, 283—290).—Benzoic and hippuric acids and creatinine were shown to be present, whilst histidine, methylguanidine, and a base,  $C_{13}H_{30}O_4N_2$ , were actually isolated. The base is isomeric with tetanine and contains a trimethylamine nucleus. O. O.

**Transformation of Pigments in Putrefying Flesh.** O. SCHUMM (*Z. physiol. Chem.*, 1925, 142, 314).—Since mesoporphyrin and coproporphyrin are not readily distinguishable spectroscopically. VOL. CXXVIII. i. c c

ally, the possibility of the occurrence of the former pigment in extracts of putrefying flesh (cf. this vol., i, 341) must be taken into account.

E. S.

**Bile Pigments. XIV. Treatment of Ox Gallstones.** W. KÜSTER and R. HAAS (*Z. physiol. Chem.*, 1924, 141, 279—281).—The method of preparation of bilirubin from ox gallstones (A., 1922, i, 885) has been improved. The extraction with methyl alcohol is carried out by a continuous process in an atmosphere of ammonia, thereby effecting an economy in the consumption of methyl alcohol.

E. S.

**Bile in Metabolism. Determination of Bile Acids.** E. HERZFELD and A. HAEMMERLI (*Schweiz. med. Woch.*, 1924, 54, 141—145; from *Chem. Zentr.*, 1924, ii, 1837—1838; cf. Herzfeld, *Deut. Arch. klin. Med.*, 1923, 139, 306; *Schweiz. med. Woch.*, 1923, 52, 585).—The method depends on the green coloration developed when 2 c.c. of the fluid under examination are heated for 5—6 mins. on a boiling water-bath with 0.5 c.c. of a 1% alcoholic solution of furfuraldehyde and 2 c.c. of 84% orthophosphoric acid. The coloration is produced when 0.05 mg. of alkali salts of bile acids is present. With urine, a duplicate comparison should be made, omitting the furfuraldehyde in order to eliminate errors due to urine pigments. In determinations in blood, the serum is treated with twice its volume of alcohol and then heated at 100°. The filtrate is evaporated to dryness and an aqueous solution of the residue used for the determination. Organs and faeces are extracted with alcohol after addition of sodium hydrogen carbonate, the extract being treated as above.

G. W. R.

**Detection of Urobilin in Urine and Determination of Chlorides in Blood.** RODILLON (*Ann. Chim. analyt.*, 1925, [ii], 7, 131).—The author criticises Benguerel's methods (this vol., i, 460) (a) for the detection of urobilin in urine on the grounds of length of time necessary, use of acetic acid for acidifying, the assumption of the insolubility of zinc acetate in alcohol, and the expense of using ether; and (b) the determination of chlorides in blood as already published by the author (*Presse medicale*, 1920, January, 31), and points out that pure trichloroacetic acid gives no reaction with silver nitrate.

D. G. H.

**Determination of Guanidines in Urine as Picrates.** J. S. SHARPE (*Biochem. J.*, 1925, 19, 168—170).—The urine is treated with tannic acid, the excess of which is removed with barium hydroxide. The filtrate is then evaporated to a syrup and extracted with absolute alcohol. This extraction is repeated and the residue eventually taken up in water and treated with a saturated aqueous solution of picric acid, from which the guanidines crystallise out as the picrates. Methods of differentiation and of removal of other picrates are given.

S. S. Z.

**Effect of Potassium and Calcium on the Acidity of Urine.** A. BENATT and M. HÄNDEL (*Klin. Woch.*, 1924, 3, 1621—1623; from *Chem. Zentr.*, 1924, ii, 1942).—Large doses of potassium

chloride administered for several days result in increased alkalinity of the urine, whilst calcium chloride produces the reverse effect. Calcium chloride also increases the acidity of the excreta of frogs.

G. W. R.

**Toxicity and Rate of Excretion from the Blood Stream of Calcium Chloride.** J. P. BOWLER and W. WALTERS (*Ann. Surgery*, 1924, 80, 545—550). CHEMICAL ABSTRACTS.

**Excretion of Ammonia and Fixed Base after Administration of Acid.** C. H. FISKE and S. S. SOKHEY (*J. Biol. Chem.*, 1925, 63, 309—329).—After oral administration to cats of doses of 12·5—30 c.c. of 0·1N-sulphuric acid per kg. body-weight, from 60% upwards is neutralised by ammonia and a variable proportion of the remainder by fixed base; after intravenous injection of the acid, if the injection is carried out sufficiently slowly to avoid the production of hyperpnœa, about 15% is neutralised by ammonia and the remainder by fixed base; if the injection is more rapid, with resulting hyperpnœa, the excretion of fixed base is much more than equivalent to the acid injected, the urine becomes alkaline, and the excretion of ammonia is decreased. Subcutaneous injections give results intermediate between those of oral administration and intravenous injection. No increased excretion of phosphates was observed in any experiment as the result of administration of acid.

C. R. H.

**Hydroxyproteic Acid Fraction of Urine.** E. FREUND and A. SITTENBERGER-KRAFT (*Biochem. Z.*, 1925, 157, 261—262).—Reply to Brings (this vol., i, 328). P. W. C.

**Clinical Calorimetry. XXXVII. Infection and the Ketogenic Balance.** H. B. RICHARDSON and S. Z. LEVINE (*J. Biol. Chem.*, 1925, 63, 465—473).—On a diet containing a given ratio of fatty acids to dextrose, individuals (diabetic or not) who are suffering from an infection excrete no more acetone substances than do non-infected persons. Contrary to the conclusions of Wilder and Winter (*A.*, 1922, i, 893), it is thought, therefore, that the evil effects of infection in diabetes are due to a reduction in the absolute amount of dextrose oxidised rather than to a disturbance of the ketogenic balance.

C. R. H.

**Mechanism of Acidosis.** L. BLUM and M. DELAVILLE (*Compt. rend.*, 1925, 180, 1294—1296).—Acidosis accompanies many pathological conditions and may be due to excess of keto-acids (as in diabetes), lactic acid (after intense muscular effort), or hydrochloric acid in the blood, or to a deficiency of bases (as in Bright's disease and possibly in rickets), or to a combination of the two effects, hyper-acidity and hypo-alkalinity (as in Bright's disease and occasionally in severe diabetes).

L. F. H.

**Production of Acidosis by Ingestion of Magnesium Chloride and Strontium Chloride.** J. B. S. HALDANE (*Biochem. J.*, 1925, 19, 249—250).—Ingestion of magnesium chloride or strontium chloride causes acidosis in man.

S. S. Z.

**Distribution of Unsaturated Fatty Acids, Cholesterol, and Cholesterol Esters in Experimental Anæmia.** M. BODANSKY (*J. Biol. Chem.*, 1925, **63**, 239—251).—In the blood plasma of normal dogs 57—96·5% and in the whole blood, 31—55% of the total cholesterol is in the form of esters. In anæmia produced by splenectomy or by the injection of diisopropylhydrazine, acetylphenylhydrazine, or tolylenediamine, the cholesterol esters of the plasma were generally reduced and those of the corpuscles raised in amount. No marked change in the concentration of unsaturated fatty acids in the plasma was observed in experimental anæmia, but the concentration in the corpuscles was increased (cf. Bloor, this vol., i, 609).  
C. R. H.

**Inorganic Alterations of the Lymph in Canine Anaphylactic Shock.** W. F. PETERSEN and T. P. HUGHES (*J. Biol. Chem.*, 1925, **63**, 179—196).—The lymph of dogs suffering from anaphylactic shock as the result of injections of egg-albumin shows a rise in the calcium, magnesium, phosphates, and amino-nitrogen, and a fall in the sodium and potassium contents; chlorides remain unchanged; the severity of the shock and the magnitude of the chemical changes are considerably increased by injection of adrenaline or of calcium chloride immediately before the final administration of albumin.  
C. R. H.

**Inorganic Constituents of the Serum in Cancer.** R. C. THEIS and S. R. BENEDICT (*J. Cancer Research*, 1924, **8**, 499—503).—The calcium content of the blood in cancer is low (average 9·3—9·1 mg. per 100 c.c. of serum against 9·3—10·5 mg. in normal blood). Sodium is normal; potassium is somewhat decreased in a large proportion of cases; and sodium chloride is normal. The more advanced cases have lower average figures than the non-malignant cases.

CHEMICAL ABSTRACTS.

**Iron and Blood Pigment Determinations in Normal Tissues and in Tumours.** M. YABUSOE (*Biochem. Z.*, 1925, **157**, 388—395).—An investigation of the total iron and the blood-pigment iron in normal and in carcinomatous organs of rats, and in connective tissues and fibromas. The following figures for the iron other than blood-pigment iron are given: testes 0·53, liver 0·46, kidney 0·40, tumours 0·32, and muscle 0·16 mg. iron per g. of the dried organ. The total iron of connective-tissues and of fibromas is 0·04 mg. per g.  
J. P.

**Chemical Constitution of Crystalline Lens of Eye under Normal and Pathological Conditions.** H. LABBÉ and F. LAVAGNA (*Compt. rend.*, 1925, **180**, 1186—1188).—The chemical constituents of the crystalline lens of the horse in the case of normal eyes and of those with senile cataract have been examined. The pathological crystalline lens contains a higher percentage of water and of amino-acids, but a smaller amount of albumin than that of the normal eye. Formation of cataracts is thus accompanied by degradation of the crystallin (cf. Jess, A., 1913, i, 789; 1920, i, 789).  
L. F. H.

**Induced Reactions, and Diabetes from the Point of View of Induced Oxidation.** N. M. MITTRA and N. R. DHAR.—(See ii, 576.)

**Metabolism in Diseases of the Liver. I. Carbohydrate Metabolism in Liver Disease.** A. VON FEJÉR and G. HETÉNYI (*Z. ges. exp. Med.*, 1924, 42, 670—677; from *Chem. Zentr.*, 1924, ii, 1946—1947).—Under normal liver conditions, oral administration of dextrose or lævulose results in increased consumption of oxygen, a rise in the respiratory quotient, and slight hyperglycæmia. In diseased conditions of the liver, there is no increased consumption of oxygen, a delayed rise in the respiratory quotient, and a longer and more marked hyperglycæmia. After administration of lævulose, the respiratory quotient rises more slowly and does not reach unity. It is probable that in diseased livers the synthesis and fixation of glycogen are deranged and that a considerable part of the sugar passes through unchanged. Lævulose is not directly oxidisable. It is more readily transformable than dextrose into glycogen.

G. W. R.

**Uroflavine, a New Pathological Constituent of Urine.** H. REINWEIN (*Z. ges. exp. Med.*, 1924, 42, 228—234; from *Chem. Zentr.*, 1924, ii, 1815).—Urine obtained in certain diseases of the liver, after concentration, was rendered alkaline, and extracted by shaking out with trichloroethylene, whereby a basic constituent, insoluble in water, was obtained which yielded an oily chloroaurate. The urine was further extracted three times with trichloroethylene, after acidifying with sulphuric acid. After distilling off the solvent, a brownish-yellow residue was obtained, of which the portion insoluble in water yielded *uroflavine*,  $C_{29}H_{22}O_5N_2$ , yellow rosettes, m. p. 244°. It gives a strong diazo reaction and is not identical with bilirubin or its derivatives.

G. W. R.

**A Salivary Calculus.** W. PETROU (*Z. physiol. Chem.*, 1925, 144, 97—100).—A salivary calculus was found to consist for the most part of calcium phosphate; no trace of fluorine was found. The organic constituents included uric acid, and the inner layers of the calculus gave a positive reaction for diastase.

C. R. H.

**Influence of Cod-liver Oil on the Calcium and Phosphorus Metabolism in Tetany.** S. H. LIU (*China Med. J.*, 1924, 38, 793—803).—Certain cases of tetany were accompanied by low calcium content of the blood and cerebrospinal fluid. Cod-liver oil increased the retention of calcium, and to a lesser extent of phosphorus also. The urinary excretion of these two elements at the same time increased, indicating increased absorption from the intestine.

CHEMICAL ABSTRACTS.

**Lipase. II. Relationship of Lipase to Predisposition to Human Tuberculosis: Action of Lipase on Koch's Bacillus.** G. CAPPELLI (*Reprint, Giorn. Med. Mil.*, 1925, 4).—The use of lipase in the treatment of human tuberculosis is suggested, as this enzyme effects hydrolysis either of the fatty envelope, or of the tissues,



of Koch's bacillus, which is thus disintegrated. Predisposition to pulmonary tuberculosis is probably related to a permanent defect of lipase in the lungs.

T. H. P.

**Diazo Reaction in Uræmic Sera.** L. F. HEWITT (*Biochem. J.*, 1925, 19, 171—174).—The formation of a substance giving a buff instead of a pink colour by applying the diazo test to uræmic sera, which was first observed by Andrewes (*Lancet*, 1924, i, 590), is confirmed. The test may be accelerated by boiling the reaction mixture for 30 secs. before the addition of the sodium hydroxide. The substance can be removed from serum by extraction with alcohol, but not with ether. Amyl alcohol removes it from deproteinised serum and plasma which are made alkaline. It is not volatile in steam and is irreversibly adsorbed by vegetable charcoal from an alcoholic solution. A cyclic amine may be responsible for the reaction.

S. S. Z.

**Synthetic Achievements of the Animal Organism.** E. ABDERHALDEN (*Z. physiol. Chem.*, 1925, 142, 189—190).—Certain chafers (*Anthrenus muscorum*) are able to live on pure silk threads as sole diet. Tailung silk, which differs in composition from other silks (A., 1912, i, 751), is, however, unsuitable; so also are pure silk-fibroin, wool, gelatin, casein, and mixtures of amino-acids.

E. S.

**Metabolism during Embryonic and Metamorphic Development of Insects.** D. E. FINK (*J. Gen. Physiol.*, 1925, 7, 527—543).—Experiments on the oxygen intake and the carbon dioxide output of insects indicate: (1) for insects which deposit their eggs on foliage (e.g. *Leptinotarsa decemlineata*, *Crioceris asparagi*, and *Anasa tristis*) embryonic development is characterised by a short formative period followed by a period of active growth; in species which deposit their eggs in the soil (e.g., *Cotinis nitida* and *Popillia japonica*) the formative period is greatly extended as also is the period of growth; (2) intensive histolysis occurs during the prepupal period and becomes less intensive during pupal development; (3) the energy liberated per g. of organism is much greater during embryonic development than during metamorphosis. During embryonic and pupal development the respiratory quotient varies from 0.42 to 0.71, values which resemble those obtained with hibernating forms. In some species the  $p_H$  decreases during the prepupal and early pupal stages (6.8—5.9), the change being reversed as metamorphosis is completed. In some species the  $p_H$  increases during embryonic development.

C. P. S.

**Relationship of Phosphate and Carbohydrate Metabolism.**  
**II. Effect of Adrenaline and Phloridzin on the Excretion of Phosphate.** F. N. ALLAN, B. R. DICKSON, and J. MARKOWITZ (*Amer. J. Physiol.*, 1924, 70, 333—343).—The administration of adrenaline to fasting dogs, like that of insulin or ingestion of sugar, causes a decrease followed by a large increase in the urinary excretion of inorganic phosphate; nitrogen elimination is increased. Phlorid-

zin causes a small decrease followed by a large increase in the elimination of phosphate. A. A. E.

**Pancreatic Response to Carbohydrate Ingestion.** E. L. SEVRINGHAUS and M. E. SMITH (*Science*, 1925, **61**, 92—93).—Curves correlate blood sugar concentration with food ingestion and the sense of hunger. Hyperglycæmia during food absorption appears to act as a physiological stimulus to insulin production, glycogen storage and dextrose utilisation resulting. The insulin thus produced outlasts the need for it. A. A. E.

**Synthesis of Carbohydrate in Muscle.** O. MEYERHOF, K. LOHMANN, and R. MEIER (*Biochem. Z.*, 1925, **157**, 459—491).—The glycogen content of the muscles of the frog's leg increases when it is perfused with oxygenated Ringer solution containing lactic acid. The oxygen consumption of the perfused tissues increases from 50 to 150% during the synthesis. The "oxidation quotient," i.e., the ratio of total lactic acid utilised to the equivalent amount of lactic acid oxidised, is 4.33, as in the recovery process in muscle. Of the substances said to be capable of forming sugar in the organism, e.g., dihydroxyacetone, glyceraldehyde, dihydroxymaleic acid, glycollaldehyde, methylglyoxal, and pyruvic acid, the last-mentioned substance alone can replace lactic acid in respect of these observations. In this case, the oxidation quotient of pyruvic acid is approximately 5. Similar results are obtained with muscle from warm-blooded animals. The diaphragm of rats in Ringer phosphate solution shows a normal oxygen consumption per g. (dry weight) per hr. of 5 to 6 c.c., but in the presence of lactic acid this increases to 7.5 c.c., and in the presence of pyruvic acid to 9.7 c.c. At the same time, the isolated diaphragm shows a formation of urea corresponding with a protein oxidation of 15% of the total oxidation. The formation of urea is diminished in the presence of dextrose, lactic acid, or pyruvic acid, whilst other "sugar formers" have no such effect. The elimination of ammonia is also lowered in an atmosphere of nitrogen. The livers of starved rats show an oxygen consumption in Ringer solution of 7.8 c.c.; in the presence of carbohydrate, this rises to 9.4 c.c., with lactic acid to 12.3 c.c., and with pyruvic acid to 14.9 c.c. Alanine and asparagine also increase the oxygen consumption of the liver, the ammonia production being three times increased in the presence of alanine and ten times increased in the presence of asparagine. The specific dynamic action of protein is ascribed to the synthesis of carbohydrate from the deaminised amino-acids in the presence of oxygen, through the intermediate formation of lactic or pyruvic acid.

J. P.

**Action of Fluorine Ions on the Activity and Lactacidogen Metabolism of Frog Muscle.** G. EMBDEN and H. HENTSCHEL (*Biochem. Z.*, 1925, **156**, 343—352).—In air, Ringer solution, and 0.65% sodium chloride solution the gastrocnemius and semimembranosus muscles of the frog show an increasing breakdown

of lactacidogen with increasing degrees of fatigue, but in the presence of 0.02*N*-sodium fluoride the position is reversed and increased synthesis is observed. The action of the fluoride ion on lactacidogen is therefore the reverse of that of the chloride ion. J. P.

**Effect of Calcium and some of its Antagonists on the Lactacidogen Changes in Minced Muscle.** C. EMMERICH and H. LANGE (*Z. physiol. Chem.*, 1924, **141**, 242—253).—The conversion of the inorganic phosphates present in fresh minced muscle into lactacidogen under the influence of *M*/50-calcium chloride is inhibited by the following salts, the magnitude of the inhibitory actions being in the order indicated:  $\text{MgCl}_2 > \text{KCl} > \text{NH}_4\text{Cl} > \text{NaCl}$ . The maximum effect of magnesium chloride is produced at a concentration of *M*/27; a detectable inhibitory action is, however, still present at *M*/243. When sulphates are employed instead of chlorides, the effects of sodium and ammonium, but not of magnesium and potassium, in antagonising the action of calcium chloride disappear. Hence the chloride ion is mainly responsible for the inhibitory actions in the case of ammonium and sodium chlorides. E. S.

**Effect of Sodium Chloride and Sodium Bromide on the Synthesis of Lactacidogen by Calcium Ions.** G. EMBDEN, M. KAHLERT, and H. LANGE (*Z. physiol. Chem.*, 1924, **141**, 254—264).—A quantitative comparison has been made of the power possessed by sodium chloride and sodium bromide of inhibiting the action of calcium chloride in causing the synthesis of lactacidogen (cf. preceding abstract). The relative effects of the two salts vary with the concentrations employed and also with different muscle preparations. E. S.

**Lactic Acid "Fatigue Maximum" of Different Muscles of the Frog.** H. HENTSCHEL (*Z. physiol. Chem.*, 1924, **141**, 265—278).—When exhausted by a series of single stimuli, the lactic acid content ("fatigue maximum") of the gastrocnemius is considerably greater than that of the adductor muscle of the frog. The difference is accentuated in preparations obtained from animals the pancreas of which had been extirpated some days previously. These results correspond with the greater content of the gastrocnemius in sarcoplasm in which, it is considered, the lactic acid accumulates. E. S.

**Significance of Ions in Muscular Function. V. Influence of Ions on the Lactacidogen Changes during Ageing.** A. ABRAHAM and P. KAHN (*Z. physiol. Chem.*, 1924, **141**, 161—180).—The effect of certain salts (sodium fluoride, calcium chloride) in causing the synthesis of lactacidogen (cf. Embden and Lehnartz, A., 1924, i, 903) in the fresh minced muscle or muscle press-juice from various species (toads, frogs, dogs) is considerably diminished if the minced muscle or press-juice is kept for a few hours at a temperature of 13—19°. This diminution is due neither to lack of carbohydrate nor to increased acidity, since it also occurs when

glycogen and a buffer (sodium hydrogen carbonate) are added to the fresh material. Rabbit muscle does not exhibit this ageing phenomenon. E. S.

**Significance of Ions in Muscular Function. VI. Effect of Various Anions on the Formation of Phosphoric Acid in Surviving Frog's Muscle.** H. LANGE and M. E. MAYER (*Z. physiol. Chem.*, 1924, **141**, 181—195).—Treatment of isolated muscle preparations with certain ions produces changes in the lactacidogen-phosphoric acid equilibrium which are, in general, similar to those observed by Embden and Lehnartz (*A.*, 1924, **i**, 903) in the case of minced muscle. E. S.

**Significance of Ions in Muscular Function. VII. Effect of Various Organic Anions on the Lactacidogen Changes.** H. J. DEUTICKE (*Z. physiol. Chem.*, 1924, **141**, 196—224).—The effect of organic anions on the lactacidogen-phosphoric acid equilibrium in fresh minced muscle (cf. preceding abstracts) has been studied. Of the anions employed (salts of fatty, dibasic, and hydroxy acids), the oxalate ion produced the greatest diminution in free phosphoric acid (synthesis of lactacidogen). The action of the remaining ions usually depended on the concentration employed; large concentrations caused a synthesis of lactacidogen, whilst small concentrations merely inhibited, or in some cases even promoted, the fission of this substance. The kinetics of the reaction have been investigated in the cases of lactate and oxalate. In *M/9*-lactate solution, the maximum synthesis occurred in 30 mins.; thereafter fission occurred. The synthetic action of oxalate continued for more than 10 hrs. E. S.

**Lactacidogen. IV.** G. EMBDEN and M. ZIMMERMANN (*Z. physiol. Chem.*, 1924, **141**, 225—232).—The identity of lactacidogen with the hexosediphosphate of alcoholic fermentation (cf. *A.*, 1921, **i**, 528) has been confirmed by comparison of the neutral *brucine* salts prepared from the two substances. A detailed account of the method employed for the preparation of this salt from minced muscle is given; advantage was taken of the fact that free phosphates present in the muscle could be converted into lactacidogen by the addition of sodium fluoride (cf. *A.*, 1924, **i**, 903). E. S.

**Phosphate Metabolism in Fatigued Mammalian Muscle.** S. ANDREWS (*Biochem. J.*, 1925, **19**, 242—248).—Glycogen when added to sodium fluoride acting on resting muscle causes practically a disappearance of free phosphate from the mixture, thus promoting synthesis of organic phosphorus compounds. In fatigued muscle, with as much preformed phosphate as in the resting, the synthetic action of fluoride is greatly diminished. During muscular fatigue there is a slight diminution of the total phosphate (preformed and "lactacidogen") and also of free phosphate in the muscle. S. S. Z.

**Relation between Sulphur and Nitrogen Metabolism.** H. E. C. WILSON (*Biochem. J.*, 1925, **19**, 322—337).—There is a delay  
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in the excretion of ingested protein extending over several days. This occurs whether the basal diet contains nitrogen or not and even when the feeding is followed by a short period of starvation. The sulphur moiety of the protein is first utilised both in storage and in the breakdown of the protein. There is always a delay in the excretion of nitrogen as compared with sulphur. Any delay in the excretion of sulphur is due to an active preferential retention of sulphur in the tissues. There is some evidence that the retained material can exercise a sparing action on protein breakdown in the first few days of starvation.

S. S. Z.

**Nitrogen, Sulphur, and "Formol" Nitrogen on Feeding Amino-acids.** R. W. SEUFFERT, T. ITO, and T. YOKOYAMA (*Biochem. Z.*, 1925, **156**, 255—261).—Previous results (Seuffert, A., 1924, i, 586) are substantiated and extended. A close correspondence between sulphur and nitrogen balances was not observed. The ratio of total urinary nitrogen to nitrogen determined by "formol" titration remains constant, and is not appreciably altered by feeding either amino-acids or native proteins. The "formol" nitrogen of the urine was increased but slightly by the amount of amino-acids fed, being only about 0.5—1.0% of the total nitrogen of the diet.

J. P.

**Influence of Amino-acids on the Decomposition of Proteins.** R. W. SEUFFERT and E. MARKS (*Z. Biol.*, 1924, **82**, 244—248).—An elaboration of previous work (A., 1924, i, 586) in which the effect of the addition of a simple mixture of amino-acids to a nitrogen-free diet in sparing body protein was studied. In one case, there was good correlation between the nitrogen and sulphur balance. In another case, the saving in body protein calculated from the sulphur balance was only 25% of that calculated from the nitrogen balance.

O. O.

**Deamination of Amino-acids and Transformation of Resulting Products in the Animal Organism.** Y. KOTAKE (*Z. physiol. Chem.*, 1925, **143**, 240—242).—A short summary and discussion of previous results; no new experimental data.

H. D. K.

**Metabolism of Arginine and Histidine. I. Arginine and Histidine as Precursors of Purines.** C. P. STEWART (*Biochem. J.*, 1925, **19**, 266—269).—The perfusion of arginine or histidine through the excised liver causes no perceptible increase in the production of allantoin. The hypothesis that the above amino-acids act as precursors of purines in the animal body is thus not supported. Allantoin can be precipitated as a condensation product with xanthohydrol in the presence of glyoxaline compounds. A method of controlling liver perfusion experiments is described.

S. S. Z.

**Cystine in the Nutrition of the Growing Rat.** H. C. SHERMAN and A. T. MERRILL (*J. Biol. Chem.*, 1925, **63**, 331—337).—Rats fed on a diet containing 80% of starch and having as its

sole source of protein 16—17% of a whole milk powder, showed a marked increase in their rate of growth on the addition of 0.15—0.20% of cystine; the addition of 1% of calcium carbonate was without effect.

C. R. H.

**Fate of Urocanic (Glyoxalineacrylic) Acid in the Animal Body.** M. KONISHI (*Z. physiol. Chem.*, 1925, **143**, 181—188).—When fed to dogs or rabbits, urocanic acid is fairly easily destroyed, the glyoxaline ring is broken down, and the nitrogen excreted as excess urea. There is no appreciable increase in urinary creatinine.

H. D. K.

**Urocanic Acid Formation from the Optical Isomerides of Histidine.** M. KONISHI (*Z. physiol. Chem.*, 1925, **143**, 189—192).—After injection of *dl*-histidine into a dog, only one-third of the amount of urocanic acid is found in the urine as is produced by the injection of the same weight of *l*-histidine. *d*-Histidine gives no trace of urocanic acid, which appears to be produced exclusively from the *l*-isomeride.

H. D. K.

**Fate of Glyoxalinepropionic Acid (and Iminazolelactic Acid) in the Dog.** M. KONISHI and Y. TANI (*Z. physiol. Chem.*, 1925, **143**, 193—198).—No trace of urocanic acid is found in the urine after the injection of 20 g. of glyoxalinepropionic acid into a dog; 10% of the injected acid is excreted unchanged, and a substance of undetermined constitution, probably an oxidation product of glyoxalinepropionic acid, is also present. Following the administration of *l*-glyoxalinelactic acid, either subcutaneously or by mouth, no trace of urocanic acid is found in the urine, which strongly suggests that the former acid is not an intermediate substance in the production of urocanic acid from *l*-histidine.

H. D. K.

**Kynurenic Acid Formation in the Animal Body.** Z. MATSUOKA, S. TAKEMURA, and N. YOSHIMATSU (*Z. physiol. Chem.*, 1925, **143**, 199—205).—The formation of kynurenic acid from *l*-tryptophan by rabbits is unaffected by previous *in vivo* staining of the animals with carmine. Much less kynurenic acid is produced by normal rabbits from *dl*- than from *l*-tryptophan; *d*-tryptophan, therefore, is probably not a source of kynurenic acid in this animal.

H. D. K.

**New Substance Formed from Tryptophan in the Animal Body.** Z. MATSUOKA and N. YOSHIMATSU (*Z. physiol. Chem.*, 1925, **143**, 206—210).—Together with kynurenic acid, a new substance,  $C_{13}H_{14}O_5N_2$ , yellow hexagonal plates, m. p. 195—196°, the *sulphate* of which is readily recrystallised from hot water and melts at 190°, has been separated.

H. D. K.

**Fate of Pyruvic Acid in the Animal Body and in the Surviving Liver.** Z. OTANI (*Z. physiol. Chem.*, 1925, **143**, 229—239).—On perfusion of freshly-excised dog's livers with pyruvic acid, *d*-lactic acid is produced. It is also formed, but in smaller quantities, when dextrose is perfused. This formation of lactic

acid from pyruvic acid is not brought about entirely through the intermediate stage of dextrose. H. D. K.

**Extra-hepatic Production of Bile Pigments in Surviving Organs. I. Surviving Spleen.** Z. ERNST and B. SZAPPANYOS. **II. Surviving Spleen, Kidney, and Lung.** Z. ERNST. **III. Surviving Spleen of Dogs Poisoned with Phenylhydrazine.** Z. ERNST and J. FORSTER (*Biochem. Z.*, 1925, 157, 16—29, 30—38, 39—45).—I.—Bilirubin is formed when the surviving spleen of a dog is perfused with defibrinated blood. The amount of bilirubin produced is greater the shorter the time during which the spleen is without circulation before perfusion begins. Addition of a little Ringer solution to the defibrinated blood does not affect the bilirubin production, but greater quantities of Ringer solution diminish it markedly.

II.—Bilirubin formation in the surviving spleen is not due to bacterial action, nor is it due to the washing out of bilirubin already stored in the organ. If the vitality of the spleen is low, bilirubin fails to be produced. It is not formed by the surviving kidney or lung.

III.—The bilirubin production of spleens of dogs poisoned with phenylhydrazine is increased to two or three times the normal amount. H. D. K.

**Extra-hepatic Production of Bile Pigments in Surviving Organs. IV. Surviving Spleen of Dogs Treated with Collargol or Colloidal Iron.** Z. ERNST and J. FÖRSTER (*Biochem. Z.*, 1925, 157, 492—500).—The spleen of a dog previously subjected to intravenous injections of colloidal silver or iron preparations produces bilirubin to the same extent as the spleen of a normal dog, and the method is therefore useless for investigating extra-hepatic formation of bile pigment. J. P.

**Determination of Smell Thresholds.** F. B. HOFMANN and A. KOHLRAUSCH (*Biochem. Z.*, 1925, 156, 287—294).—An apparatus is described for the determination of thresholds of smell, the quantitative basis of which depends on the measurement of the vapour pressure of mixtures of the odoriferous principle and air. The error due to the adsorption of the former is negligible. J. P.

**Potassium Chlorate: Its Influence on the Blood-oxygen-binding Capacity (Hæmoglobin Concentration), Its Rate of Excretion, and Quantities Found in the Blood after Feeding.** V. ROSS (*J. Pharm. Exp. Ther.*, 1925, 25, 47—52).—Potassium chlorate in 1% aqueous solution was administered to dogs by stomach tube, the dose being 0.5 g. per kg. body-weight. There was a temporary fall in the oxygen-binding capacity of the blood, approximately equal to that produced by an equal dose of sodium chloride in 1% aqueous solution. From 50—70% of the potassium chlorate administered was excreted within 6 hrs.; thereafter, the rate of excretion diminished. At the end of 24—48 hrs., more than 90% had been excreted. The potassium chlorate

content of the blood varied from 15 to 81 mg. per 100 c.c. 2 hrs. after administration, and from 0 to 15 mg. after 24 hrs. C. P. S.

### **Reduction of Picric Acid in the Liver, Kidney, and Spleen.**

G. GIORGI (*Polislinico, sez. med.*, 1924, **31**, 184—188; from *Chem. Zentr.*, 1924, ii, 1818).—Picric acid is eliminated in the form of picramic acid. In perfusion experiments with liver, kidney, and spleen, the strongest reduction is shown by the liver. Since a small formation of urobilin was observed in the liver perfusions, it is to be expected that large doses of picric acid would produce icterus. G. W. R.

**Nephropathic Action of the Dicarboxylic Acids and their Derivatives. III. Acids with Six to Nine Carbons.** W. C. ROSE, C. J. WEBER, R. C. CORLEY, and R. W. JACKSON (*J. Pharm. Exp. Ther.*, 1925, **25**, 59—64; cf. A., 1924, i, 1374).—When injected subcutaneously, pimelic, azelaic, adipic, and suberic acids proved to be mildly nephropathic, but were much less so than glutaric acid. Since they are approximately equal in effect, it is concluded that in the animals used (rabbits) these acids are not decomposed by direct  $\beta$ -oxidation. C. P. S.

**Nephropathic Action of the Dicarboxylic Acids and their Derivatives. IV. Mucic Acid.** W. C. ROSE and P. S. DIMMETT (*J. Pharm. Exp. Ther.*, 1925, **25**, 65—73; cf. A., 1924, i, 1374).—Mucic acid is intensely nephropathic when administered subcutaneously as the sodium salt, causing retention of nitrogen and, to a less extent, of chlorides. C. P. S.

**Chemistry of the Action of Salvarsan *In Vitro* and *In Vivo*.** J. SCHUMACHER (*Biochem. Z.*, 1925, **157**, 438—455).—The absence of action of salvarsan on spirochætes *in vitro* is ascribed to the insolubility of the arsenical in the "lipoproteins" of the micro-organism. *In vivo* salvarsan is first converted into the base, which possesses the necessary solubility, and, having penetrated the cell, it becomes attached through the amino groups to the acids of the lipoids, where its strong reducing action deprives the organism of oxygen and so kills it. J. P.

**Action of Ter- and Quinque-valent Arsenic Preparations.** J. SCHUMACHER (*Biochem. Z.*, 1925, **157**, 456—458).—The lower toxicity of quinquevalent arsenic derivatives to spirochætes as compared with tervalent derivatives is ascribed to the more acid nature of the former and the consequent greater difficulty of converting them into bases soluble in the cell lipoproteins. J. P.

**Chemo-therapeutic Properties of a Substance with a Chain of Four Arsenic Atoms.** H. G. BARBOUR, C. B. RIDOUT, and D. CLAYDON (*J. Pharm. Exp. Ther.*, 1925, **25**, 53—57).—Experiments on the rate of disappearance of trypanosomes from the blood after the injection of the monosodium salt of tetra-arsenoacetic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{As}\cdot\text{As}\cdot\text{As}\cdot\text{As}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$  (Palmer, A., 1924, i, 152) are held to indicate that some therapeutic value attaches to the chain of four arsenic atoms. C. P. S.



**Chemical Changes in the Blood Produced by Drugs. III. Phloridzin.** H. N. ETS (*Amer. J. Physiol.*, 1924, 70, 240—246).—With dogs, phloridzin administered subcutaneously causes hypoglycæmia, acidosis, and an increase in the total lipoids, cholesterol, and non-protein nitrogen of the blood. A. A. E.

**Chaulmoogra and Margosa Oils and Heterogeneous Catalysis.** F. F. NORD and G. G. SCHWEITZER (*Biochem. Z.*, 1925, 156, 269—277).—From investigations of the iodine numbers, the optical and physiological activities of preparations of chaulmoogra, margosa, and hydnocarpus oils before and after catalytic hydrogenation under pressure, it is concluded that the physiological action of these oils is greater the higher their optical activity, and is independent of the nature of the unsaturated carbocyclic residue present in the component acids. J. P.

**Pharmacological Action of Cryptopine.** R. ST. A. HEATHCOTE (*J. Pharm. Exp. Ther.*, 1925, 25, 35—45).—Cryptopine appears to paralyse the central nervous system of the toad and shows little stimulation; papaverine, on the other hand, has some stimulating effect. Experiments with isolated organs showed cryptopine to have a depressant action exactly similar to, but only about one-third as great as, that of papaverine. Neither alkaloid exerts any action on striated muscle. The dilatation of the pupil in mammals after administration of cryptopine occurs only in the late stages of systemic poisoning and is probably asphyxial in origin. The minimum lethal dose (g. per kg. body-weight) for the toad is 0.325 and for the rabbit 0.2. C. P. S.

**Pharmacological Investigation of Methylated Guanidines.** F. VON GRAEVENITZ (*Arch. Exp. Path. Pharm.*, 1925, 105, 278—298; cf. Bock, A., 1905, ii, 49; Fühner, A., 1907, ii, 901; Paton, Findlay, and Burns, A., 1915, i, 481; Schenck, A., 1910, i, 99; 1911, i, 842; 1912, i, 424, 685; Wilson, Stearns, and Janney, A., 1915, i, 626; 1916, i, 190; 1923, i, 761; 1924, i, 123, 1051; this vol., i, 377).—The pharmacological effects on frogs of  $\beta$ -methylguanidine,  $\beta\beta$ -dimethylguanidine,  $\beta\beta'$ -dimethylguanidine,  $\alpha\beta\beta'$ -trimethylguanidine,  $\beta\beta\beta'\beta'$ -tetramethylguanidine,  $\alpha\beta\beta\beta'$ -tetramethylguanidine,  $\alpha\beta\beta\beta'\beta'$ -pentamethylguanidine and its  $\alpha$ -methiodide, are described. The mono- and di-methylguanidines produce peripheral fibrillary twitches like guanidine, and are of interest from the point of view of the origin of tetanic convulsions.  $\beta$ -Methylguanidine has an irritant action,  $\beta\beta'$ -dimethylguanidine increases muscular tone, whilst  $\alpha\beta\beta'$ -trimethylguanidine produces neither curare-like paralysis nor an increase in tone, but partly nullifies the tone-increasing effect of other compounds. The higher alkylated guanidines possess the power of both increasing muscular tone and producing curare-like paralysis.  $\alpha\beta\beta\beta'\beta'$ -Pentamethylguanidine  $\alpha$ -methiodide is particularly potent, as is tetramethylammonium iodide. Of the isomeric di- and tetra-methylguanidines, the symmetrical derivatives have a slightly greater action on muscular tone. All the compounds in low concentration produce vagus inhibition, and, in higher concentrations, diastolic stoppage of the heart. L. F. H.

**Action of Narcotics of the Aliphatic Series on the Smooth Musculature of the Leech.** G. JOACHIMOGLU (*Biochem. Z.*, 1925, 156, 224—235).—Dichloromethane, chloroform, carbon tetrachloride, ethylene dichloride, ethylidene chloride, pentachloroethane, di-, tri-, and tetra-chloroethylenes produce alterations of tone and contraction of the smooth muscle freed from ganglia. Tetra- and hexa-chloroethanes produce alterations of tone only. These actions are more marked in the presence of barium. The activity of these derivatives increases in general with increasing degree of halogenation. Methyl, ethyl, propyl, *isopropyl*, butyl, *isobutyl*, and amyl alcohols produce but slight alterations of tone, propyl alcohol alone producing contractions. Acetone and ethyl ether have similar actions to those of the chlorinated derivatives.

J. P.

**Narcosis. III. Influence of General Narcosis on the Chemical Processes in the Striped Muscle of the Frog.** H. LANGE and M. E. MAYER (*Z. physiol. Chem.*, 1924, 141, 233—241).—An increase in the lactic acid content of frog's muscle occurs during ether narcosis.

E. S.

**Osmosis of certain Anæsthetics in Aqueous and Lipoid-containing Gels.** S. YUMIKURA (*Biochem. Z.*, 1925, 157, 359—370).—An investigation of the distribution of various anæsthetics between water and a gelatin gel both in the presence and in the absence of lecithin. The general conclusions are that the greater toxicity of alypin and eucaïne compared with cocaine and tutocaine to the lower animals (*e.g.*, water-flea), and the greater toxicity of cocaine compared with alypin and eucaïne to the higher animals, is correlated with the lecithin content of the animal cells, which is greater in the higher and lesser in the lower animals. Thus alypin and eucaïne, which diffuse more rapidly into gelatin in the absence of lecithin than in its presence, are more adapted to penetrate the cells of the lower animals, whilst the reverse is the case with cocaine.

J. P.

**Osmosis in Aqueous Gels With and Without Addition of Lipids.** S. YUMIKURA (*Biochem. Z.*, 1925, 157, 371—376).—The rate of diffusion of capillary active substances such as octoic acid and octyl alcohol from an aqueous solution into gelatin is greater the higher the lipid content of the gel. The phenomenon is also shown by capillary inactive substances such as butyric acid and amyl alcohol, but to a much less marked degree. J. P.

**Osmosis of certain Acids in a Gelatin Gel.** S. YUMIKURA (*Biochem. Z.*, 1925, 157, 377—382).—The rate of diffusion of various acids into gelatin follows the series: hydrochloric acid > sulphuric acid > formic acid > lactic acid, and in general the results obtained with capillary active and inactive substances do not exhibit the differences which might be expected according to Overton's theory.

J. P.

**Lipoids and the Theory of Surface Action. II.** J. TRAUBE and S. YUMIKURA (*Biochem. Z.*, 1925, 157, 383—387).—A theoretical

review of the subject in the light of the results of Yumikura (preceding abstracts). Substances with no, or with slight, surface action diffuse into aqueous gels more rapidly than substances with high capillary activity. But the reverse is the case if the gel contains lipoids, and capillary activity and lipid solubility run, in general, in parallel. J. P.

**Excretion of the Stereo-isomeric Cocaines in the Urine and their Relation to Toxicity.** E. GRUHN (*Arch. Exp. Path. Pharm.*, 1925, 106, 115—125).—*d*- and *l*-Cocaine and *d*- $\psi$ -cocaine were injected subcutaneously into cats and the amounts present in the urine determined. *l*-Cocaine was found in much greater amounts in the urine than were the other two, even when the latter were injected in doses two and three times as big. This may be due to the quicker decomposition and rate at which the *d*-forms lose their toxicity; whether this is due to adsorption or decomposition is uncertain. Cats which had convulsions after injection with *d*- $\psi$ -cocaine failed to react to *d*-cocaine, although less of the *pseudo* form was found in the urine. This may be connected with the spatial arrangement of the different molecules. After repeated injections, the toxicity does not seem to be reduced, although in some cases, particularly with *l*-cocaine, the amount in the urine decreased. O. O.

**Adsorption of Poisons by a New Plant Charcoal "Supra-Norit."** E. LAQUEUR and A. SLUYTERS (*Biochem. Z.*, 1925, 156, 303—322).—The new charcoal is compared with "carbo animalis" (Merck) as regards its power to adsorb *in vitro* oxalic acid, potassium hydrogen oxalate, mercuric chloride, strychnine nitrate, morphine hydrochloride, methylene-blue, and iodine, and in all cases is more active than the animal charcoal. J. P.

**Behaviour of Oxalacetic Acid to Animal Organs.** P. MAYER (*Biochem. Z.*, 1925, 156, 300—302).—A pulp of rabbit muscle converts oxalacetic acid into *l*-malic acid. J. P.

**Kinetics of Enzyme Action.** G. E. BRIGGS and J. B. S. HALDANE (*Biochem. J.*, 1925, 19, 338—339).—Theoretical. S. S. Z.

**Amylase.** K. SJÖBERG and E. ERIKSSON (*Z. physiol. Chem.*, 1925, 142, 215—216).—Although maltose inhibits the hydrolysis of amylopectin and amylose by extracts of germinating barley to the same extent (A., 1924, i, 1264), it does not follow that the same enzyme is concerned in the two processes. If the normalities of the substrates were known, the affinity constant for maltose (calculated according to Michaelis) might prove to be different in the two cases. E. S.

**Pancreatic Enzymes. X. Adsorption Behaviour of Pancreatic Amylase.** R. WILLSTÄTTER, E. WALDSCHMIDT-LEITZ, and A. R. F. HESSE (*Z. physiol. Chem.*, 1925, 142, 14—34).—Previous results (A., 1923, i, 507) have been confirmed. The adsorption of amylase by alumina appears to be conditioned by

the presence of co-adsorbents, one of which assists whilst another hinders the adsorption of the amylase, by the particular alumina preparation employed, and by the concentration of the solution. In the absence of co-adsorbent, amylase is devoid of adsorption affinities; definite directions for the purification of amylase preparations cannot, therefore, be given. E. S.

**Purification of Malt Amylase.** H. LÜERS and E. SELLNER (*Woch. Brau.*, 1925, 42, 97—99, 103—105, 110—112).—The method of adsorption utilised by Willstätter in the purification of enzymes has been applied to malt amylase. Commercial kaolin and purified china clay were found to be unsuitable; the best adsorption was obtained with aluminium hydroxide at a faintly acid reaction ( $p_H$  5.0); the enzyme was also adsorbed, to a less extent, from faintly alkaline solutions. The concentration, time, and temperature all exerted marked effects on the extent of adsorption. The enzyme could be dissolved out of the adsorbate by water saturated with carbon dioxide, or, better, by a phosphate solution of  $p_H$  7.38. Starting with a crude malt extract, two such adsorptions and re-solutions gave preparations of which the amylolytic activity was increased 25—30-fold; starting with a dried preparation obtained by fractional precipitation of the crude extract with alcohol, and working under optimum conditions (extremely cold weather), a final product was obtained which was ninety-three times as active as the original extract, calculated on the weight of dry substance. A further adsorption and re-solution led to a loss of activity owing to the increasing instability of the enzyme as its purification advanced. The most active preparations contained 74.4% of protein and 28.07% of carbohydrate as compared with 42.99% of protein and 43.56% of carbohydrate in the starting material. A fractional determination of the nitrogen gave results almost identical with those obtained by Sherman and Gettler (A., 1913, i, 1401) with their much less active product. The sugar-forming and starch-liquefying properties of the preparations were increased to an equal extent in the process of purification.

C. R. H.

**Carboligase. VIII. Biochemical Acyloin Synthesis.** C. NEUBERG and E. SIMON (*Biochem. Z.*, 1925, 156, 374—378).—Acetaldehyde added to yeast, previously freed from glycogen, in the presence of dextrose or sucrose results in the synthesis of acetoin.

J. P.

**Influence of Radium on the Catalase of the Liver.** A. MAUBERT, L. JALoustRE, and P. LEMAY (*Compt. rend.*, 1925, 180, 1205—1207).—In general, the effect of radium on liver catalase is similar to that of thorium-X (cf. A., 1923, i, 723; 1924, i, 808). Addition of a very small amount of radium bromide has no perceptible influence on liver catalase as measured by the decomposition of hydrogen peroxide, a slightly larger amount increases the activity of the catalase, whilst a still larger amount paralyses it. The stimulating effect is ascribed to the  $\alpha$ -rays, since radium emanation

has a stimulating but no paralysing action, and the latter action to  $\beta$ - and  $\gamma$ -rays, since the radium bromide, if introduced into the fermentation medium contained in a glass capsule, or if allowed to act on the catalase prior to fermentation in a glass capsule, has a paralysing action only.

L. F. H.

**Effect of Halogen Salts on Salivary Digestion.** W. M. CLIFFORD (*Biochem. J.*, 1925, 19, 218—220).—The chlorides of sodium, potassium, ammonium, and calcium hasten the diastatic action of saliva. Sodium and calcium fluoride, sodium and potassium iodide, sodium, potassium, ammonium, and calcium bromides do not influence the action of the enzyme. Ammonium and calcium iodides, potassium and ammonium fluorides retard the action. The hydrogen-ion concentration of these salts does not influence their action in this respect.

S. S. Z.

**Influence of Different Substances on the Diastatic Activity of Saliva.** H. WALKER (*Biochem. J.*, 1925, 19, 221—225).—Sucrose and "saccharin" in the mouth have the most marked effect in producing a very active saliva. In the case of sucrose, this is largely, if not entirely, due to its stimulating action on the ptyalin. Maltose increases the quantity of ptyalin produced, although its presence depresses the activity of the enzyme. Lactose, on the other hand, tends to inhibit the production of ptyalin, but enhances its activity. Dextrose and levulose both lower the activity of saliva, which is largely due to their depressing action on ptyalin.

S. S. Z.

**Nephelometric Investigations on the Breakdown of Glycogen by Salivary Diastase.** J. PAECHTNER (*Biochem. Z.*, 1925, 156, 249—254).—The nephelometric method of following the hydrolysis of glycogen by salivary diastase gives satisfactory results.

J. P.

**So-called Reversibility of Enzyme Action. Complete Hydrolysis of Salicin by Emulsin.** G. BERTRAND and A. COMPTON (*Ann. Inst. Pasteur*, 1925, 39, 355—364).—Salicin in various concentrations and with varying amounts of emulsin was always completely hydrolysed to saligenin and dextrose. Attempts to synthesise salicin from saligenin and dextrose in the presence of emulsin failed.

O. O.

**Mechanism of Action of Hydrogenase in the Cell.** J. GRÜSS (*Woch. Brau.*, 1925, 42, 109—110).—The addition of flowers of sulphur to a solution of dextrose undergoing yeast fermentation increased the evolution of carbon dioxide, but diminished the production of alcohol. The increased evolution of carbon dioxide was probably due to the mechanical agitation of the yeast-cells by the hydrogen sulphide produced. It is suggested that the process of fermentation consists of a primary phase in which the elements of water are added to the substrate, and a secondary phase in which alcohol is produced by the action of hydrogen on the intermediate product; on this view, the enzyme of primary

importance would be a hydrogenase; the view is supported by the diminished production of alcohol in presence of sulphur, which, by fixing the hydrogen as hydrogen sulphide, would prevent the secondary phase from taking place.

C. R. H.

**Hydrolysis of Sucrose by Invertase in Presence of  $\alpha$ -Methylglucoside.** I. J. M. NELSON and B. FREEMAN (*J. Biol. Chem.*, 1925, **63**, 365—375).—The course of hydrolysis of sucrose by yeast invertase in presence of  $\alpha$ -methylglucoside is not represented by the equation of Nelson and Hitchcock (*A.*, 1922, i, 388), the term  $N$  showing, under these conditions, a progressive increase. A study of the hydrolysis of sucrose in presence of  $\alpha$ -methylglucoside and of added invert-sugar, and also of the relative retarding effects of the invert-sugar formed during the hydrolysis in presence and in absence of  $\alpha$ -methylglucoside, shows that the presence of the latter reduces the normal retarding effect of the invert-sugar. On the other hand, the presence of  $\alpha$ -methylglucoside itself causes a retarding effect which increases in magnitude with increasing amounts of sucrose up to the optimum concentration of the latter.

C. R. H.

**Invertase. VII.** R. WILLSTÄTTER and Collaborators. **Enzyme Adsorption.** II. H. KRAUT and E. WENZEL (*Z. physiol. Chem.*, 1925, **142**, 71—96; cf. *A.*, 1924, i, 467).—The application of the process of adsorption to the purification of enzymes is discussed with special reference to invertase. A single adsorbent (*e.g.*, alumina in the case of invertase) may often be usefully employed in successive stages of the purification process under different conditions. Thus, the enzyme may be adsorbed from dilute or concentrated solution, using either small or large amounts of adsorbent; the latter may also be employed in small amount for the process of preliminary adsorption of impurities. The particular method to be adopted at any stage can be deduced from the shape of the adsorption isothermal determined at that stage. When the adsorption curve approximates to that of a pure substance no further purification can be effected with the adsorbent in use; a second adsorbent which gives an adsorption isothermal deviating from that of a pure substance must be employed for the continuation of the purification.

E. S.

**Invertase. VIII.** R. WILLSTÄTTER and K. SCHNEIDER (*Z. physiol. Chem.*, 1925, **142**, 257—305; cf. *A.*, 1924, i, 692).—A comparison has been made between the various methods of purifying invertase. Preparations which have been obtained from old yeast autolysates have a relatively large content of tyrosine (Millon's reaction) which can only be removed with extreme difficulty. On the other hand, fresh neutral autolysates (prepared by liquefying 6 kg. of the yeast with 360 c.c. of chloroform, adding an equal weight of water, neutralising at intervals with dilute ammonia, allowing autolysis to proceed until the whole of the invertase is liberated—about 48 hours—and finally centrifuging and filter-

ing) readily yield preparations of invertase which contain no tyrosine.

Active and stable preparations of the enzyme may be obtained from such fresh, neutral autolysates in the following manner. The autolysate is acidified to  $p_H$  4.5—4.8 with acetic acid, and the enzyme, together with protein, precipitated by addition of alcohol to 50%. The enzyme is removed from the precipitate by extraction with  $N/50$ -acetic acid, the extract diluted, its content of acetic acid brought to  $N/2$  (1 invertase unit in 500 c.c. of  $N/2$ -acetic acid), and the invertase adsorbed by kaolin. After washing the adsorbate, the enzyme is eluted with 0.05% ammonia, the elution neutralised with acetic acid and evaporated (at 14°) to a relatively small volume. Further protein is precipitated by adding successively calcium chloride and sulphuric acid; this precipitate must be rapidly removed by centrifuging and the solution neutralised with calcium carbonate. The filtrate is again concentrated and then dialysed. A preparation of this type is in a suitable condition for purification by fractional adsorption with alumina. The most active preparations which can be obtained in this way contain a large amount of tryptophan.

Tryptophan-free preparations may be obtained from the fresh, neutral autolysates by first precipitating the proteins with acid, then precipitating the enzyme with alcohol and simultaneously adsorbing it on calcium phosphate, eluting, and purifying further by repeated adsorption on kaolin. This process is, however, accompanied by an enormous loss in the activity of the enzyme.

It appears from these and other results that the stability of invertase preparations (similar arguments hold for other enzymes) is connected with the presence of peptides containing tyrosine or tryptophan with which the enzyme can associate. In old autolysates, association with the tyrosine peptide takes place preferentially. Since, however, this peptide is only formed during the later stages of proteolysis, the invertase, when obtained from fresh autolysates, is associated with a tryptophan peptide which is rapidly produced by the action of the yeast protease on the proteins. When such preparations are systematically purified by adsorption on alumina (cf. Kraut and Wenzel, preceding abstract), a product is finally obtained which gives an adsorption isothermal similar to that of a pure substance and cannot be further purified by the same adsorbent. Such preparations (from fresh autolysates) contain the tryptophan peptide and evidently consist of a complex formed between the invertase and one or more co-adsorbents. That this is the case is shown by the fact that the peptide can be readily removed by the use of other adsorbents or by precipitation with lead acetate; the enzyme is then obtained free from tryptophan. In the absence of the co-adsorbent, which acts as a protective agent, a considerable diminution in activity occurs and the product is again a complex formed by the association of the invertase with its own decomposition products. Thus, contrary to the views of Euler and Josephson (A., 1924, i, 1143), invertase is not a protein. Enzymic actions are, nevertheless, due to specific

substances; their chemical constitutions are, however, veiled by their instability, which is doubtless caused by the reactivity of their active groups. E. S.

**Polysaccharides. XXX. Enzymic Decomposition of Cellulose.** P. KARRER and H. ILLING (*Koll.-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 91—95; cf. this vol., i, 118, 418).—Cellulose once precipitated from “cuprammonium” solution, from viscose, or from calcium thiocyanate solution is converted almost completely into dextrose by an enzyme from the intestine of snails. The optimum reaction for the snail cellulase is about  $p_H$  5.3. Cellulose treated in the cold with zinc chloride or sodium hydroxide is hydrolysed to a smaller extent, whilst commercial viscose silk and “copper” silk are not attacked. It is suggested that the ease with which the cellulose preparations are broken down is connected with the degree of orientation or dispersion of the cellulose. E. M. C.

**Pancreatic Enzymes. XI.** R. WILLSTÄTTER and Collaborators. **Enterokinase.** E. WALDSCHMIDT-LEITZ (*Z. physiol. Chem.*, 1925, 142, 215—244).—Although the rôle of enterokinase is that of an activator rather than of an enzyme (A., 1924, i, 473), it resembles an enzyme in its properties and hence can be purified by similar methods. It is extracted from the intestinal mucosa with 0.05*N*-ammonia and, after removing the ammonia with a current of warm (30—35°) air, purified by precipitation with dilute acetic acid. The filtrate is treated with alcohol (up to 90%), which precipitates the kinase. This is dissolved in water and further impurities are removed by precipitation with tannic acid in the presence of glycerol. The enterokinase is then obtained from the mother-liquor and further purified by adsorption on alumina and kaolin. Enterokinase is most stable in neutral solution. The temperature at which it decomposes (50°) has not hitherto been found to be dependent on its state of purity. Trypsinogen cannot be activated by autolytic extracts of organs (liver, spleen, kidney) other than the pancreas. E. S.

**Pancreatic Enzymes. XII. Determination of Trypsin.** R. WILLSTÄTTER and H. PERSIEL (*Z. physiol. Chem.*, 1925, 142, 245—256).—In view of the fact that enterokinase is removed from trypsin by adsorption on alumina (A., 1924, i, 473), the method previously employed (A., 1923, i, 403) for the separation of lipase from the remaining pancreatic enzymes would undoubtedly cause a partial inactivation of the trypsin in the residual solution. A further inactivation would also result from the autolytic formation of inhibitory substances. A method for the determination of the total trypsin present in such extracts has therefore been devised for use as a control in purification experiments. It is based on the increase in acidity (as determined by titration in alcoholic solution) which occurs when a small amount of the trypsin preparation, after activation with excess of enterokinase, is allowed to act on excess of gelatin under specified conditions. Although the method is more accurate than that previously employed, it does not entirely overcome the effect of inhibitory substances. E. S.



**Pancreatic Enzymes.** R. WILLSTÄTTER and Collaborators.

**XIII. Optimum  $p_H$  for Gastric Lipase in Different Animals.** F. HAUROWITZ and W. PETROU (*Z. physiol. Chem.*, 1925, **144**, 68—75).—Extracts of gastric lipase were prepared from various animals by the method of Haurowitz and Memmen (this vol., i, 201); the amounts obtained were very variable, the enzyme being most abundant in carnivora and rodents and almost absent in birds and fishes. Tables are given of the optimum  $p_H$  for the various extracts made; no correlation could be found between the natural diet of an animal and the optimum reaction for its gastric lipase.

C. R. H.

**Enzyme Studies with Colloidal Gold.** P. UHLENBRUCK (*Koll.-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 287—291).—The decomposition of proteins by pepsin may be followed by means of the colour changes of red-gold hydrosols. With egg-white diluted to 0.4% protein content and treated with pepsin for 1—3 hrs., the gold hydrosol is changed to a clear blue; with solutions containing 1.6% of protein the colour change proceeds only to a violet-blue. The colour change agrees with change in the coagulation and serves as a measure of the amount of hydrolysis. The degree of peptisation of the gold precipitates indicates the relative sizes of the particles of the decomposition products.

E. M. C.

**Propepsin in Blood and Urine.** E. GOTTLIEB (*Skand. Arch. Physiol.*, 1924, **46**, 1—50; from *Chem. Zentr.*, 1924, ii, 2057—2058).—Propepsin in urine, serum, and plasma may be determined by the pepsin method of Fuld and Ege (cf. Ege, A., 1923, ii, 511) and expressed as the equivalent in "Armour" pepsin. With serum, a long period of digestion and great dilution is necessary. Under the same conditions, the amount of enzyme found is inversely proportional to the time of digestion. Propepsin is distinguished from pepsin by being stable at  $p_H$  7.0—10.0. At  $p_H$  3.0 it changes rapidly, at  $p_H$  4.0 slowly into pepsin. The concentration of propepsin in blood is equivalent to 0.002 mg. of "Armour" pepsin per c.c. In urine the concentration corresponds with 0.02—0.06 mg. per c.c. Propepsin corresponding with 20—50 mg. of "Armour" pepsin is excreted in the urine in 24 hrs. The daily excretion, which is fairly constant in the absence of any change of diet, depends on the activity of the ventricular glands. With hypersecretion it may be 70—150 mg., whilst with hyposcretion and achylia it may sink to 10—0 mg. The rate of formation is smaller by night than by day and increases 1—2 hrs. after meals. In the case of a dog, a single meat meal resulted in a large increase in production of propepsin even 24 hrs. later. In inanition, propepsin decreases in the urine, but does not entirely disappear. The amount of propepsin is also affected by renal activity. In two cases of chronic nephritis, whilst propepsin increased in the urine, it decreased in the blood. No propepsin was found in the urine of goats, but it occurs in the urine and serum of oxen and rabbits.

G. W. R.

**Influence of Temperature and Reaction on the Destruction and Activity of Pepsin.** R. EGE (*Z. physiol. Chem.*, 1925, 143, 159—180).—Using Armour's pepsin, and a solution of edestin as substrate, it has been confirmed that there is no definite optimum temperature for the action of this enzyme, but that the optimum varies with the length of the reaction period. At  $p_H$  1.6 and in presence of excess of substrate, the optimum in a one-hour experiment is between  $40^\circ$  and  $50^\circ$ , in a five-minute experiment about  $52^\circ$ , and in a one-minute experiment between  $56^\circ$  and  $60^\circ$ . The temperature coefficient (van't Hoff) for the activity of pepsin changes from 2.5 between  $0^\circ$  and  $10^\circ$  to 1.4 between  $40^\circ$  and  $45^\circ$ . The rate at which pepsin is destroyed depends on the reaction of the medium, the optimum  $p_H$  range for the stability of Armour's pepsin being from 3.6 to 4.6. The rate of destruction in a medium of a greater acidity than this is proportional to the hydrogen-ion concentration, whilst in a less acid medium (up to  $p_H$  7.7) it is proportional to the cube of the hydrogen-ion concentration. At a constant  $p_H$ , the rate of destruction of pepsin is markedly influenced by the temperature.

H. D. K.

**Sulphatase. V. Animal Sulphatase.** C. NEUBERG and E. SIMON (*Biochem. Z.*, 1925, 156, 365—373).—A sulphatase, capable of hydrolysing potassium phenyl sulphate and *p*-tolyl sulphate, is present in the liver, kidney, brain, and musculature of the rabbit, guinea-pig, and man. The enzyme is soluble in water, but is still active in dried preparations of these organs.

J. P.

**Sulphatase. VI. Occurrence and Behaviour of Sulphatase in Human Organs.** L. ROSENFELD (*Biochem. Z.*, 1925, 157, 434—437).—Sulphatase occurs in notable amounts in human kidney and brain. It is present also but in lesser amounts in the liver, duodenum, suprarenals, spleen, lung, muscle, small intestine, and pancreas.

J. P.

**Effect of some Potassium Salts on Succinodehydrogenase.** B. SAHLIN (*Skand. Arch. Physiol.*, 1924, 46, 64—75; from *Chem. Zentr.*, 1924, ii, 2057).—Using Thunberg's methylene-blue method with extracts prepared from horse-flesh, it was found that potassium salts inhibit dehydrogenase according to the Hofmeister series ( $CNS > F > I > Br > NO_3 > Cl > SO_4$ ). Potassium bromide and nitrate produce an almost equal inhibition of the enzyme. The precipitation of thionine by potassium salts also follows the Hofmeister series, whilst the precipitation of methylene-blue follows the series  $I > CNS > Br > Cl > F, NO_3, SO_4$ .

G. W. R.

**Xanthine Oxydase. IV. Relation of Xanthine Oxydase and Similar Oxidising Systems to Bach's Oxygenase.** (*Biochem. J.*, 1925, 19, 175—187).—The following evidence is produced in support of the view that the action of the so-called enzyme "itate" described by Haas and Hill (*A.*, 1924, i, 349, 908) is due to the coupled action of the xanthine oxydase and peroxydase of milk. When aldehyde is replaced by hypoxanthine, xanthine, and adenine, nitrites are also oxidised.

Uric acid, guanine, and caffeine cannot replace aldehyde. A number of substances which inhibit the xanthine-oxydase in milk also inhibit the oxidation of nitrites. As in the case of the xanthine-oxydase, on increasing the hypoxanthine concentration, inhibition resulted, whereas an increase in the aldehyde concentration produced an increase in the velocity of oxidation of the nitrite. When the caseinogen xanthine-oxydase preparation was used instead of the whole milk the nitrites were not oxidised unless a peroxydase of animal origin (ox liver) was added. The formation of peroxide by the oxidation of hypoxanthine, xanthine, and aldehyde in the presence of molecular oxygen by the milk oxydase has been demonstrated by various direct and indirect means.

Nitrites are also oxidised by the system succinic oxydase-succinic acid and during autoxidation of the -SH compounds cysteine and glutathione in the presence of peroxydase and molecular oxygen.

Bach's definition of oxygenase, therefore, applies to the three systems xanthine oxydase plus any one of its substrates, succinic oxydase plus succinic acid, cysteine plus glutathione. S. S. Z.

**Accelerating Influence of Protein-free Colloids on the Hydrolysis of Urea by Soya Bean Urease.** G. TAUBMANN (*Biochem. Z.*, 1925, 157, 98—102).—The addition of starch or gum arabic to the reaction mixture assists the hydrolytic action of the urease of soya bean. H. D. K.

**Enzymic Degradation and Synthesis of Carbohydrate. I. Phosphate Exchanges and Glycogen Cleavage in Muscle and in Yeast.** H. VON EULER, K. MYRBÄCK, and S. KARLSSON (*Z. physiol. Chem.*, 1925, 143, 243—264).—Fresh yeast, like fresh chopped muscle, in presence of 0.5% sodium fluoride solution, is able to synthesise organic phosphorus compounds from free phosphate. After some hours, these compounds are again hydrolysed. The addition of glycogen, dextrose, or lævulose affects, in the case of yeast, neither the velocity nor the extent of this process, but in the case of muscle (confirming the results of Embden) addition of glycogen brings about much greater synthesis of organic phosphorus compounds. Lævulose and starch have no effect on the synthesis in fresh muscle. A dried muscle preparation is also able to effect synthesis, particularly in presence of glycogen, if sodium fluoride is added. The auto-fermentation of dried yeast is completely checked by sodium fluoride.

If sodium hexosediphosphate (Bayer) is added to fresh muscle, it is hydrolysed, but in presence of sodium fluoride the hydrolysis is almost negligible. In the production of lactic acid from glycogen by fresh muscle, a reducing sugar is first formed from the glycogen; this is then esterified by addition of phosphoric acid, and the degradation of the resulting ester into lactic acid is extremely rapid. Dried muscle shows an undiminished glycogenase activity, with an optimum at  $p_H$  6.3. At this optimum, the rapidity of breakdown of the glycogen is scarcely affected by large changes in the inorganic

phosphate concentration, but lactic acid formation has an optimum in about 3% phosphate solution. Muscle glycogenase is soluble in water. Dried muscle is able to hydrolyse starch, producing a reducing sugar from it. The curve showing the relationship between  $p_H$  and velocity for muscle glycogenase is identical with that found by Sherman, Thomas, and Baldwin for pancreas amylase.

H. D. K.

**Fate of Yeast Invertase in the Animal Organism.** S. NOGAKI (*Z. physiol. Chem.*, 1925, **142**, 97—102).—When injected intravenously into rabbits and mice, highly purified preparations of yeast invertase are at first removed rapidly from the blood and disappear completely in about 24 hrs. It is not excreted in the urine. The enzyme is apparently adsorbed by the tissues, where it is slowly destroyed. That it has no antigenic character is not due to its rapid destruction or excretion.

E. S.

**Acceleration of the Fermentative Activity of Fresh Yeast by the Biocatalyst  $z$ .** H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1924, **141**, 297—308).—The biocatalyst  $z$  (this vol., i, 209) which is present in extracts of dried yeast and accelerates alcoholic fermentation by living yeast has been shown to be distinct from the co-enzyme. It possesses a much greater stability to heat than the co-enzyme; further, addition of a concentrated preparation of the latter failed to accelerate the fermentation of dextrose by living yeast whereas extracts containing  $z$  produced this effect.

E. S.

**Oxidative Deamination by a Basidiomycete Enzyme.** M. E. ROBINSON and R. A. McCANCE (*Biochem. J.*, 1925, **19**, 251—256).—A crude tyrosinase preparation from *Lactarius vellereus* does not oxidise glycine, leucine, or alanine unless certain phenols be present. Oxidative deamination of glycine has been brought about in the presence of *p*-cresol, pyrocatechol, and resorcinol. *p*-Cresol cannot be replaced in this reaction by *p*-hydroxybenzoic acid or aldehyde. The system, glycine (or any amino-acid) plus any of the phenols which help in the deamination as mentioned above plus tyrosinase reduces methylene-blue. Neither *p*-cresol nor resorcinol decolorises the dye either alone or in the presence of tyrosinase.

S. S. Z.

**Activity of the Proteolytic and Related Enzymes of certain *Hymenomycetæ* known as *Mycorrhiza*.** E. MELIN and K. HELLEBERG (*Biochem. Z.*, 1925, **157**, 146—155).—The activity of these enzymes has been studied in view of the likelihood that certain *mycorrhiza* which are associated with the roots of the larch, the pine, and the birch render more readily available for the tree some of the nitrogen of the humus. The proteolytic activity of an extract of the young fructifications of these fungi and also the activity of their deaminase varies very much from one species to another. A nuclease is present in small quantities in all the species examined. In virtue of these enzymes the *mycorrhiza*

probably assist the tree by providing simpler nitrogenous food material for it from the more complicated compounds of the humus.

H. D. K.

**Enzymes of Thermal Algæ.** R. B. HARVEY (*Science*, 1924, 60, 481—482).—*Phormidium laminosum*, growing at 65—73°, possesses no catalase and little oxydase activity, but shows strong peroxydase and probably oxydoreductase reactions. A. A. E.

**Significance of Calcium for the Genus *Citromyces*.** S. J. KUSNETZOV (*Biochem. Z.*, 1925, 157, 339—349).—The growth of *Citromyces glaber* in the presence of sucrose and potassium nitrate is optimal at  $p_H$  5.5, but growth is still obtained up to a maximum  $p_H$  of 8.7. Ammonium sulphate is the most suitable source of nitrogen, but potassium nitrate is practically of equivalent value. With increasing amounts of ammonium nitrate in the culture, calcium carbonate being present, a diminution in the citric acid formed is observed whilst the fungus itself develops more vigorously. Calcium ions have an inhibiting effect on both growth and citric acid formation in neutral and alkaline cultures, this effect being partly neutralised by the presence of magnesium ions. In acid cultures, calcium has no inhibitory action. Nitrate-nitrogen penetrates the mycelium more readily in acid than in alkaline solution, whilst the reverse effect is observed in the case of ammonium nitrogen. J. P.

**Excretion of Urea by Fungi.** N. N. IVANOV (*Biochem. Z.*, 1925, 157, 229—242).—Experiments with *Aspergillus niger*, *Penicillium glaucum*, *Rhizopus nigricans*, and *Tieghemella orchidis* lead to the conclusion that pure cultures of fungi can form urea from substrates rich in nitrogen. The urea does not remain in the mycelium of the fungi, but is excreted into the medium. Urease appears in or disappears from the culture according to the ratio of the by-products of nitrogen- or carbon-nutrition. P. W. C.

**Action of *Oidium lactis* on Tyrosine and Related Compounds.** Y. KOTAKE, M. CHIKANO, and K. ICHIHARA (*Z. physiol. Chem.*, 1925, 143, 218—228).—*p*-Hydroxyphenylpyruvic acid is partly transformed into *p*-hydroxyphenyl-lactic acid by this mould. The deamination of tyrosine by *Oidium lactis* is apparently mainly hydrolytic, although oxidative deamination with production of *p*-hydroxyphenylpyruvic acid may also take place to a small extent. The mould is capable of transforming *l*-hydroxyphenyl-lactic acid—but not the *d*-isomeride—in limited amount into *p*-hydroxyphenylpyruvic acid. H. D. K.

**Changes of Buffering and the Amino-nitrogen Increase in Nutrient Media by Bacterial Action.** L. BLEYER (*Biochem. Z.*, 1925, 157, 220—228).—The proteolysis of 20% sheep's serum, coagulated sheep's serum, gelatin, caseinogen, and Witte's peptone both by living cultures of *Bacillus pyocyaneus*, *B. prodigiosus*, and *B. proteus*, and by the corresponding bacterial enzymes in media of initial  $p_H$  6—9, is followed by an increase in amino-nitrogen

(formol titration) and by changes in buffering. Proteolytic curves obtained by plotting  $p_H$  against titration values show deviations from the straight line, the extent of deviation being different for different proteins. In most cases, the curve can be regarded as made up of two portions, each a straight line, the portion on the alkaline side being much steeper than the other portion. Witte's peptone, gelatin, and caseinogen became alkaline under the action of the living culture, whereas the enzyme preparation led to slight acidification. Acid was formed in media containing glycerol.

P. W. C.

**Putrefaction of Agmatine.** H. REINWEIN and K. L. KOCHINKI (*Z. Biol.*, 1924, **81**, 291—295).—Agmatine chloride or carbonate in a weakly alkaline medium inoculated with putrefying pancreatic tissue gave rise to putrescine after 18 days. It is suggested that arginase of vegetable origin may be able to decompose agmatine as well as arginine (cf. Kiesel, A., 1922, i, 413).

O. O.

**Mechanism of Hydrogen Production from Dextrose by *Bacillus coli communis*.** E. AUBEL and J. SALABARTAN (*Compt. rend.*, 1925, **180**, 1183—1186).—Dextrose is decomposed by *Bacillus coli* according to the equation  $C_6H_{12}O_6 = CH_3 \cdot CO_2H + C_2H_5 \cdot OH + 2CO_2 + 2H_2$  (cf. Harden, T., 1901, **79**, 610). It has been suggested that the hydrogen arises from the decomposition of formic acid, which is one of the first products of the action of the bacillus on the sugar (cf. Pakes and Jollymann, T., 1901, **79**, 386; Grey, A., 1913, i, 1024; 1914, i, 1034; 1918, i, 143; 1920, i, 699). Under certain conditions, it is possible to isolate pyruvic acid from the product of action of the bacillus on dextrose, and it is suggested that the pyruvic acid together with hydrogen is the first decomposition product of the sugar and is formed in accordance with the requirements of the equation  $C_6H_{12}O_6 = 2CH_3 \cdot CO \cdot CO_2H + 2H_2 + 12,000$  cal. The pyruvic acid thus formed thereupon breaks down to acetaldehyde which, in turn, gives acetic acid and ethyl alcohol. The process by which hydrogen is liberated by an oxidation process appears to be novel.

L. F. H.

**Reactions of Resting Bacteria in Relation to Anaërobic Growth.** J. H. QUASTEL, M. STEPHENSON, and M. D. WHETHAM (*Biochem. J.*, 1925, **19**, 304—317).—Nitrate has a powerful inhibiting influence on the velocity of reduction of methylene-blue by various hydrogen donators in presence of resting *Bacillus coli* and resting *B. pyocyaneus*. It oxidises leucomethylene-blue in presence of resting *B. coli* or *B. pyocyaneus*, but not *in vitro*. This oxidation is dependent on a thermolabile enzyme. Nitrite does not reduce methylene-blue or oxidise leucomethylene-blue in presence of resting *B. coli in vitro*. Chlorates behave similarly to nitrates. Perchlorates do not oxidise leucomethylene-blue *in vivo* or *in vitro*. Bromates and iodates both oxidise leucomethylene-blue *in vitro*. *B. subtilis* does not oxidise leucomethylene-blue in the presence of fumarate, nitrate, or chlorate. *B. coli* grows

anaerobically with pyruvic acid, lactic acid, succinic acid, fumaric acid, or glycerol as the sole source of carbon only when nitrates are present. On dextrose it grows anaerobically without nitrate. This organism produces from lactic acid aerobically and anaerobically in the presence of nitrates a relatively large quantity of pyruvic acid. When grown on lactic acid aerobically in the absence of nitrates, no pyruvic acid is produced. *B. pyocyaneus* grows well in the presence of nitrates only under strictly anaerobic conditions, on citric acid, dextrose, lactic acid, or pyruvic acid as sole source of carbon. It grows anaerobically to some extent on dextrose alone without nitrates, but not nearly to the same extent as with nitrates. Both aerobically and anaerobically it produces pyruvic acid from lactic acid in the presence of nitrates. It will, however, produce pyruvic acid from lactic acid aerobically in the absence of nitrates also. In the presence of only a trace of oxygen, this organism will grow on a citrate medium when nitrates are not present. It breaks down nitrites. No anaerobic growth was obtained with *B. subtilis*. Chlorates cannot be substituted for nitrates in anaerobic growth of *B. coli*. They have a toxic effect on the organism which is probably due to the formation of chlorites. Neither perchlorates nor maleates will induce anaerobic growth, but they have no perceptible toxic action on *B. coli* grown on lactate and nitrate under aerobic or anaerobic conditions. *B. coli* grows anaerobically on a mixture of lactate and fumarate where these substances form the sole sources of carbon and ammonia the sole source of nitrogen. Pyruvic acid is produced when resting *B. coli* is grown in contact with lactate and nitrate. When the resting organism is in contact with lactate and chlorate, chlorite and pyruvic acid are produced. No oxidation of lactate by either nitrate or chlorate occurs *in vitro*. The course of the production of nitrite and pyruvic acid during the growth of *B. coli* on lactate and nitrate has been studied. Nitrite has a toxic effect on *B. coli*. It is confirmed that nitrate is broken down by *B. pyocyaneus*.

S. S. Z.

**Symbiosis between *Chlorella* sp. and *Azotobacter Chroococcum* and Nitrogen Fixation.** C. B. LIPMAN and J. J. H. TEAKLE (*J. Gen. Physiol.*, 1925, 7, 509—511).—Compared with pure cultures of *Chlorella*, mixed cultures of *Chlorella* and *Azotobacter chroococcum* show a relatively large (although absolutely small) gain of nitrogen. The mixed culture grew much more rapidly than the culture of *Chlorella* alone.

C. P. S.

**Pyocyanine, the Blue Pigment in *Bacillus pyocyaneus*.** II. F. WREDE and E. STRACK.—(See i, 174.)

**Distribution of Nitrogen in Protein Fraction of Tubercle Bacilli.** T. B. JOHNSON and R. D. COGHILL (*J. Biol. Chem.*, 1925, 63, 225—231).—The nitrogen distribution of the protein fraction, obtained by extracting tubercle bacilli with toluene and treating the fat-free residue with dilute sodium hydroxide to remove tuberculinic acid, has been determined and the results are

in close agreement with those of Johnson and Brown (A., 1923, i, 160). The figures show a general relationship to those obtained by Chibnall (A., 1924, i, 1272; this vol., i, 215) for the proteins of spinach and alfalfa (lucerne) leaves.

C. R. H.

**Flocculation of Antimeningococcal Sera in the Presence of Alcoholic Extracts of Meningococci.** D. DE LA RIVIÈRE and É. ROUX (*Ann. Inst. Pasteur*, 1925, 39, 368—381).—Antimeningococcal sera can be flocculated in physiological saline solution containing a mixture of tincture of benzoin and an alcoholic extract of meningococci. A normal serum never shows flocculation. Filtration of the serum does not affect its capacity for flocculation. Flocculation of other sera with alcoholic extracts of the corresponding antigens was successful.

O. O.

**Acid Agglutination of Mixtures of Oppositely Charged Bacterial Cells.** L. T. WEBSTER (*J. Gen. Physiol.*, 1925, 7, 513—515).—Suspensions of *Bacterium lepi-septicum*, Types D and G, were mixed in various proportions in sodium lactate buffer solutions at  $p_H$  ranging from 2.4 to 4.7. Whilst the  $p_H$  zones in which agglutination of pure D or G took place scarcely overlapped, mixtures of the two flocculated completely in the intermediate zone. Since the mixture flocculates at a  $p_H$  at which Type D bacteria are negatively and Type G positively charged, the experiments indicate that the behaviour of bacteria in suspension is similar to that of unorganised colloidal particles, and that bacteria with like charges repel one another.

C. P. S.

**Conditions Affecting Bactericidal Power.** E. A. COOPER, D. L. WOODHOUSE, and G. E. FORSTNER (*J. Soc. Chem. Ind.*, 1925, 44, 134—138r).—Determinations of germicidal power by the Chick–Martin method with *Bacillus coli communis* as test organism gave the following phenol coefficients; cyclohexanol 0.5, acrylic acid 2.0, crotonic acid 2.2, maleic acid 4.2, fumaric acid 6.0. The results obtained by the Chick–Martin test were more consistent when the concentration of organic matter in the culture was reduced by dilution or, preferably, by centrifuging, before adding it to the disinfectant. This test shows that at 20° the coefficients of maleic and fumaric acids are respectively 28.0 and 7.3, whilst at 37° fumaric acid is the more powerful. Nitrosoanilines and nitrosophenols possess about the same power, but under a 48 hrs. “inhibitory test” the nitrosoanilines were more active. Unlike the phenols, the power of the nitrosophenols is not enhanced by the introduction of a methyl group into the nucleus. The power of nitrosoaniline increases with the substitution of one or two methyl groups either in the nucleus or the amino group; the isomeric nitrosoamines are much less powerful germicides. Nitroso-resorcinol is more active than nitrosophenol, and the introduction of a second nitroso group into nitrosoresorcinol and nitrosoaniline enhances bactericidal action. Nitrosophenol is more active in saline media than in distilled water and all the compounds tested were less active in the presence of serum. The organism acquired



a tolerance, limited to the particular germicide, when cultivated for some time in a dilute solution of the compound. *p*-Nitrosodimethylaniline was active in a concentration of 1 in 170,000.

F. B.

**Bactericidal Properties and Chemical Structure.** F. ISHIWARA (*Z. Immunitäts-forsch. exp. Ther.*, 1924, I, 40, 429—452; from *Chem. Zentr.*, 1924, ii, 1809).—Amino and alkyl derivatives of benzene have no bactericidal effect. When, however, as in toluidine, alkyl and amino groups are combined with different carbon atoms of the benzene ring, the bactericidal power is very great. The nitro group exerts as strong an effect as the alkyl group. The bactericidal effect of a phenol is increased from 3 to 10 times by substitution with an alkyl group. Increase in the number of carbon atoms diminishes the bactericidal effect of fatty acids. Both benzene and methane acquire bactericidal properties by substitution with hydroxyl, carboxyl, and chlorine. The aldehyde and sulphonic acid groups and thio compounds have a strong action, whilst ketones and unsaturated iodo compounds have weak bactericidal properties.

G. W. R.

**Synthesis of Vitamin-A by a Fresh-water Alga, *Chlorella* (sp.?).** K. H. COWARD (*Biochem. J.*, 1925, 19, 240—241).—*Chlorella* grown in pure culture promotes growth in rats subsisting on a vitamin-A free diet.

S. S. Z.

**Antirachitic Value of Irradiated Phytosterol and Cholesterol.** I. A. F. HESS, M. WEINSTOCK, and F. D. HELMAN (*J. Biol. Chem.*, 1925, 63, 305—308).—Phytosterol prepared from the unsaponifiable fraction of cotton-seed oil, which itself had no antirachitic properties, acquired such properties when irradiated in aqueous suspension with ultra-violet light; similar results were obtained with cholesterol isolated from brain-tissue and with lanolin. In view of these facts, it is tentatively suggested that the known protective influence of light against rickets may be due to activation of the cholesterol of the skin.

C. R. H.

**Antirachitic Properties Imparted to Inert Substances by Ultra-violet Irradiation.** A. F. HESS and M. WEINSTOCK (*J. Biol. Chem.*, 1925, 63, 297—304).—Antirachitic properties can be conferred, by ultra-violet irradiation, on etiolated and green wheat or lettuce leaves, but not on chlorophyll, hæmoglobin, red blood-corpuscles, cream, glycerol, or the phosphatides of egg-yolk. The previously reported (this vol., i, 212) activation of vegetable oils by irradiation can be carried out equally well in an atmosphere of nitrogen; in such activated oils the active substance is found to be in the unsaponifiable fraction. Activation conferred by ultra-violet irradiation is retained for periods of weeks by the vegetables and for at least 6 months by the oils.

C. R. H.

**Measurement of Ultra-violet Light by Means of an Acetone-Methylene-blue Solution.** T. A. WEBSTER, L. HILL, and A. EDINOW (*Brit. J. Radiol., B.I.R. Section*, 1924, 29, 335—339).—Aqueous acetone is decomposed by ultra-violet light, yielding

acetic and formic acids, with other substances. Rays of  $\lambda$  3000 Å. have the most active biological effect. CHEMICAL ABSTRACTS.

**Variations in Blood-sugar and Liver Glycogen of Pigeons Fed on Normal Diet and on Diet Deficient in Vitamin-B.** L. RANDOIN and E. LELESZ (*Compt. rend.*, 1925, 180, 1366—1368).—The pigeons were kept on constant diets, deficient in vitamin-B, by forced feeding, and it was found that under these conditions there is an increase in the free sugar in the blood and very little change in the amount of glycogen in the liver. This is contrary to the conclusions of other workers (cf. Collazo, A., 1923, i, 506), who have found a disappearance of glycogen from the liver of pigeons fed voluntarily on a diet deficient in vitamin-B.

L. F. H.

**Comparison of Dried and Evaporated Milks by a Dietetic Method.** G. A. HARTWELL (*Biochem. J.*, 1925, 19, 226—332).—The vitamin-B content of evaporated milks is lower than that of dried milks and of fresh milk. Dried milks vary in their vitamin-B content, which may be slightly greater or slightly less than that of fresh milk. This variation does not depend on the method of manufacture. Dried skim and half-cream milks are not quite so good as the same makes in full-cream. The method used in the above experiments consisted in feeding the nursing mother of a litter of rats on a diet which causes death to the offspring and adding to this diet different quantities of fresh cow's milk in order to find the least amount necessary to protect the young from spasms.

S. S. Z.

**Ultra-violet Light and the Antineuritic Vitamin.** R. R. WILLIAMS (*Science*, 1924, 60, 499).—The antineuritic food factor is completely destroyed by exposing a layer, 2—3 mm. deep, of aqueous yeast extract for a few hours to radiation from a quartz mercury lamp.

A. A. E.

**Synthesis of Vitamin-C by Germination.** E. M. HONEYWELL and H. STEENBOCK (*Amer. J. Physiol.*, 1924, 70, 322—331).—Since vitamin-C is synthesised by barley during germination, even in the dark, but not during the first 24 hrs. of soaking, or during 96 hrs. in the absence of oxygen, it is concluded that vitamin-C, although easily destroyed by oxygen, requires oxygen for its synthesis.

A. A. E.

**Nature of the Antiscorbutic Principle, Vitamin-C.** N. BEZSSONOFF (*Compt. rend.*, 1925, 180, 970—972).—From the juice of fresh cabbage is isolated a crystalline substance, m. p. about 47°, to which antiscorbutic properties are attributed. The substance contains 47.6% C, 48.2% O, and 6.2% H; it spontaneously undergoes oxidation, and the product gives the reactions of *o*-diphenol. [Cf. B., 1925, 332.]

F. M. H.

**Variations of Proportion of Urea in the Blood of a Guinea-pig under the Influence of a Diet Lacking in Antiscorbutic Factor.** L. RANDOIN and A. MICHAUX (*Compt. rend.*, 1925, 180, 1063—1066).—In a normal guinea-pig receiving a normal

diet the blood-urea is in the neighbourhood of 0.036 g./100 c.c. plasma. For a guinea-pig fed on a complete artificial diet the figure is 0.038 g. When the antiscorbutic factor is removed from the diet, the effect on the blood-urea begins to appear after about 12 days simultaneously with the other symptoms. The urea value rises to 0.075 or 0.080 g./100 c.c. after the 22nd day. G. M. B.

**Dietary Requirements for Reproduction. IV. Solubility of Vitamin-E in Organic Solvents.** B. SURE (*J. Biol. Chem.* 1925, 63, 211—223; cf. this vol., i, 212).—The addition to a basal diet, in itself insufficient for a normal reproductive cycle, of an ether, benzene, or acetone extract of wheat embryo, supplies the deficiency of vitamin-E. The residue of the wheat embryo, after exhaustive extraction with any of these solvents, is free from vitamin-E, which is thus shown to be a fat-soluble substance (cf. Mattill, Carman, and Clayton, A., 1924, i, 1389). C. R. H.

**Glutathione. Occurrence and Determination of Glutathione in Tissues.** H. E. TUNNICLIFFE (*Biochem. J.*, 1925, 19, 194—198).—The glutathione content of certain tissues has been determined and the values given. By far the greater part of the glutathione exists in the tissues in reduced form. The determination was carried out by extracting a known weight of tissue with 10% trichloroacetic acid and titrating the clear extract with 0.01N-iodine solution. Figures for the soluble organic sulphur were found to correspond well with the values obtained by titration for the sulphur present as -SH groups. S. S. Z.

**Glutathione. Relation between the Tissues and the Oxidised Dipeptide.** H. E. TUNNICLIFFE (*Biochem. J.*, 1925, 19, 199—206).—The reduction of methylene-blue by heated and unheated preparations of the muscle of the rabbit, rat, dog, and cat is slowed by increasing acidity. The combined reactions of reduction of oxidised glutathione by the above tissues and eventual reduction of methylene-blue under anaërobic conditions proceed at a greater rate than the direct reduction of methylene-blue by the tissue alone. In the reduction of an excess of oxidised glutathione by tissues, the reaction proceeds rapidly for the first 3 hrs., then becomes slower, and is complete after 5 hrs. Below a certain amount, the oxidised glutathione is practically completely reduced. Any increase in the amount of the oxidised compound beyond this limit does not bring about any further reduction. No significant difference in the rate or amount of reduction can be detected by altering the  $p_H$  or the salts of the medium. The amount of reduced glutathione formed by a given weight of a tissue preparation from an excess of the oxidised dipeptide is equivalent to the amount of methylene-blue which such a quantity of tissue reduces. On the other hand, there is a greater uptake of oxygen when the latter acts as the hydrogen acceptor than would theoretically be expected. This discrepancy is due to the presence of unsaturated fatty acid in the tissue, which is not, however, responsible for the reduction of oxidised glutathione. At  $p_H$  7.6

in the aërobic reduction of oxidised glutathione by tissues, the concentration of the sulphhydryl form is low owing to the higher velocity of the oxidation than of the reduction at this reaction. At  $p_H$  6 the reverse is the case and the concentration of the reduced glutathione increases. S. S. Z.

**Insulin.** A. I. VIRTANEN (*Ber.*, 1925, 58, [B], 696—698).—Insulin strongly activates a co-enzyme-free, dry preparation of *Bacillus casei*  $\epsilon$  and hence can function as co-enzyme. It appears therefore to facilitate the degradation of sugars in the organism by promoting the formation of zymophosphate. H. W.

**Insulin.** E. ABDERHALDEN (*Z. physiol. Chem.*, 1924, 141, 309—310).—Active preparations of insulin give a positive ninhydrin reaction when boiled for one minute with 0.1N-hydrochloric acid and neutralised with sodium hydroxide. Without this treatment a positive reaction is obtained only after prolonged boiling. E. S.

**Insulin and the Distribution of Sugar between Fluid and Non-fluid Systems.** H. HÄUSLER and O. LOEWI (*Biochem. Z.*, 1925, 156, 295—299).—A pulp of ox arteries and veins absorbs dextrose in the presence of insulin, but not when the latter is absent. In the presence of insulin, dextrose passes from the plasma into the erythrocytes, but its total amount in the whole blood remains unchanged. J. P.

**Insulin and Liver Glycogen.** C. F. CORI (*J. Pharm. Exp. Ther.*, 1925, 25, 1—33).—During the first hour of insulin action, starving rabbits or mice show no appreciable change in their liver glycogen. From the second to the sixth hour, the liver glycogen may remain constant or may decrease. Animals with a high initial glycogen content are apt to show a diminution of liver glycogen, whilst those with a lower initial content may maintain a constant value. To explain these results, the hypothesis is advanced that sugar oxidation and glycogen synthesis are linked processes; that glycogen is built up at the expense of the products of glycogenolysis which are burnt in the liver itself; and that insulin stimulates the liver to produce the energy required for the synthesis of glycogen, although enough sugar is not available for the synthesis actually to take place. This demands that glycogen synthesis should take place when an excess of sugar is present, and it is accordingly found that animals fed with dextrose show, under the influence of insulin, an increased glycogen deposition. Similarly, starving phloridzinised rabbits and cats and starving depancreatised cats and dogs build up glycogen when they receive insulin. In the liver of the normal animal about 5% of the total hydrolysable carbohydrate is not glycogen; after administration of insulin the proportion is increased to about 10%. C. P. S.

**Effect of Insulin and Adrenaline on Lactic Acid Content of Blood and Tissues.** C. F. CORI (*J. Biol. Chem.*, 1925, 63, 253—268).—The lactic acid content of the blood of rabbits and

cats (normal, phloridzinised, or depancreatized) is unchanged during insulin hypoglycæmia, unless convulsions occur, when it is much raised; the lactic acid content of the liver and muscles of mice is unaffected by insulin even when convulsions occur. Administration of adrenaline to rabbits or cats causes an increase in the lactic acid of the blood, the effect being more marked with rabbits (cf. Briggs and others, A., 1924, i, 445; also Best and Ridout, following abstract). C. R. H.

**Blood Lactic Acid after Insulin.** C. H. BEST and J. H. RIDOUT (*J. Biol. Chem.*, 1925, 63, 197—203).—Contrary to the conclusions of Briggs and others (A., 1924, i, 445), the rise in concentration of lactic acid in the blood of normal or diabetic dogs during insulin hypoglycæmia is very slight, and is in no way parallel to the fall in concentration of dextrose. C. R. H.

**Yield of Insulin from Fish.** N. A. McCORMICK and E. C. NOBLE (*Studies Biol. Sta. Canada*, 2, I, No. 7).—Extracts from islets of the flounder, sea raven, eel pout, hake, pollock, haddock, and halibut reduced the blood-sugar of rabbits from 0.12 to 0.04%; insulin from cod was investigated. CHEMICAL ABSTRACTS.

**Insulin from Fish. VII.** N. A. McCORMICK (*Bull. Biol. Board, Canada*, 1924, Dec.).—Insulin is present in all fish in quantities comparable with those found in mammals; the product has the same effect as that from the ox or pig. CHEMICAL ABSTRACTS.

**Extraction of a Parathyroid Hormone.** J. B. COLLIP. **Effect of Parathyroid Hormone on Normal Animals.** J. B. COLLIP, E. P. CLARK, and J. W. SCOTT (*J. Biol. Chem.*, 1925, 63, 395—438; 439—460; see also *Nature*, 1925, 115, 761).—I.—Fresh ox parathyroid glands were extracted with an equal volume of 5% hydrochloric acid for 1 hr. at 100°; after mechanical separation of the fat, the bulk of the proteins were removed by making the solution alkaline and then adding hydrochloric acid to the point of maximum precipitation. Oral, subcutaneous, or intravenous administration of the filtrate from this protein precipitate prevented the development of tetany in parathyroidectomized dogs or removed the symptoms of tetany if these had already set in, even although the animals were on a heavy meat diet. Coincidentally with the disappearance of tetany following a dose of the extract, the concentration of calcium in the blood, which had fallen after parathyroidectomy, rose again to its normal level, or, in cases of overdosage, above the normal. The condition of "hypercalcæmia" so produced was fatal if allowed to persist; in such cases it was possible to reduce the calcium of the blood by intravenous administration of sodium hydrogen carbonate.

II.—Injection of a single dose of parathyroid extract causes, in the normal dog, a rise in the concentration of calcium in the serum which reaches its height at about the 6th hour; successive injections may cause the calcium concentration to be doubled and collapse and death may ensue; it is suggested that the effect on the calcium of the blood of a normal animal may be used for the standardisation

of parathyroid extracts. The blood of animals in the terminal stage of fatal hypercalcaemia becomes very viscous and shows an abnormally great depression of the freezing point; the chlorides are reduced and the non-protein nitrogen is greatly increased; no change was observed in the blood-sugar, but the alkali reserve was markedly reduced in the terminal stages. C. R. H.

**Quantitative Law of Energy Exchanges in Formation of Carbohydrates from Proteins and Fats in Plants.** E. F. TERROINE, S. TRAUTMANN, and R. BONNET (*Compt. rend.*, 1925, **180**, 1181—1183).—The conversion of the proteins and fats of seeds into carbohydrates on germination has been examined from the point of view of the energy exchanges and losses. In the widely differing seeds studied it is found that there is a loss of 35% of the energy content of the proteins, and 23% of that of the fats converted into carbohydrates (cf. A., 1924, i, 804). L. F. H.

**Metachromatic Staining of Plant Cell-walls with Substantive Dyes. I and II.** F. SCHWARZ (*Ber. deut. bot. Ges.*, 1924, **42**, 21—28; 28—38).—Certain substantive dyes, on adsorption, show markedly different colours according to the degree of dispersion of the particles of the deposited colouring matter. The structure of the adsorbing tissue (*e.g.*, cell-walls of different types) in the main determines the degree of dispersion and hence the colour produced. With cell-walls consisting chiefly of cellulose and pectins, such as the walls of cambium and parenchyma cells, the colour is deposited in comparatively coarse particles, whereas with cutinised cell-walls, as in cuticular and corky tissues, the highest degree of dispersion is reached. Cell-walls of woody tissues form an intermediate group. By suitable selection of dyes, cell-walls of various types may conveniently be differentiated by the colour obtained and changes taking place during development or by the action of enzymes may be followed. Some 70 dyes have been selected and tested in this connexion and are divided into 10 groups, according to the colours given with different plant-tissues and their value for special purposes. Brilliant Congo-blue is representative of dyes suitable for distinguishing between cellulose (blue or violet) and lignin (purple or red) cell-walls, and diamine-blue between lignin (blue or dull violet) and cutin (red or orange) cell-walls. Aqueous solutions of the dyes are used; the procedure for staining sections is fully described.

C. T. G.

**Growth of Duckweeds in Mineral Nutrient Solutions With and Without Organic Extracts.** A. SAEGER (*J. Gen. Physiol.*, 1925, **7**, 517—525).—Although Detmer's solution and a modified Knop's solution proved unfavourable culture media for *Spirodela polyrrhiza*, dilution of the modified Knop's solution to ten times its original volume gave a medium which supported growth of *S. polyrrhiza* for 26 months and of *Lemna valdiviana* for 21 months without any permanent decrease in the size of the plants or in the rate of reproduction. In this dilute solution, however, growth

of *Spirodella* was stimulated by the addition of aqueous extract of autolysed yeast or of the components of peat extracted by a 1% solution of sodium hydrogen carbonate. The necessity of organic accessory foods (auximones) for the growth of green plants cannot be accepted as an established fact. C. P. S.

**Linear Relationship between the Amounts of Phosphoric Acid and of Nitrogen in the Leaves of the Adequately Nourished Vine.** H. LAGATU and L. MAUME (*Compt. rend.*, 1925, 180, 1179—1181).—A linear relationship exists between the amount of phosphoric acid and nitrogen in the leaves of the vine which has received correct manuring. This simple relation in the plant grown under optimum conditions renders easy the recognition of deficiencies or excesses of the constituents used in manuring (cf. *ibid.*, 1924, 179, 782, 932). L. F. H.

**Ripening of Seeds.** A. BLAGOVESCHENSKI (*Biochem. Z.*, 1925, 157, 201—219).—The absolute weight of the dry seed, of the ash, and of the ether extract of the dried seeds of the horse-bean (*Vicia faba minor*) increased with ripening. The absolute weight of the total, protein-, and non-protein-nitrogen increased as ripening proceeded, but expressed as percentage of the dry weight the total and protein-nitrogen showed an alternate increase and decrease, whereas the non-protein-nitrogen steadily decreased. The percentage of dextrose and sucrose decreased during ripening, but the absolute weight showed alternation. Similarly, the content of soluble polysaccharides, starch, and hemicellulose, although increasing absolutely, showed periods of storage alternating with periods of utilisation, probably due to an alternation in the relative quantities and character of the substances synthesised in the leaves. The after-ripening of material removed from the plant was also investigated. The percentage of total and protein-nitrogen, soluble polysaccharides, and hemicellulose increased and the percentage of non-protein-nitrogen, dextrose, and sucrose decreased, showing that synthesis was still taking place. The separation of non-protein nitrogenous bases of the ripened seed led to the isolation of histidine, arginine, adenine, guanine, guanidine, xanthine, hypoxanthine, uric acid, cytosine, and choline. Finally, determinations of peptase and amylase were carried out and an attempt was made to connect these enzymes with the synthetic processes taking place in the plant. P. W. C.

**Nature of the Process of Germination. Determination of Proteins by Means of Adsorption Applied to the Decomposition of Proteins in Germinating Pea Seeds.** A. FODOR and A. REIFENBERG (*Biochem. J.*, 1925, 19, 188—193).—The non-protein-nitrogen in germinating seeds increases almost equally during the process of germination whether the germination takes place in dark or in light. A high percentage of the protein derivatives formed during germination remains in the seed. In non-germinating seeds, there is a proportion of 30 : 70 of protein precipitable by acid to protein not precipitable in this way. In the

germinating seeds these two proteins are present approximately in equal parts. The protein which is precipitated by acid is dispersed by 70—80% alcohol. No phosphoproteins are present in either non-germinating or germinating seeds. The protein- and non-protein-nitrogen was determined by macerating the seed-flour in a 10% sodium chloride solution and adsorbing the proteins from the maceration liquor after filtration with iron hydroxide gel. The difference between the nitrogen content of the maceration liquor before and after adsorption gave the protein-nitrogen. The protein can be eluted from the adsorbent with various strengths of sodium hydroxide. Kaolin may also be used as an adsorbent under certain conditions. S. S. Z.

**Effect of Urea, Thiourea, and Allylthiourea on the Higher Plants.** E. NICOLAS and G. NICOLAS (*Compt. rend.*, 1925, **180**, 1286—1289).—Addition of a small amount of urea to the solution (up to 0.1%) with which plants of white mustard and dwarf kidney bean were treated had a beneficial effect on the plants but larger doses proved toxic. The urea would seem to function as a source of nitrogen when applied in small quantities (cf. Bokorny, A., 1917, i, 680; 1920, i, 43; 1922, i, 1096, 1222). Thiourea and allylthiourea proved toxic in the smallest doses applied (0.02% of the solution). The toxicity of urea in large doses is ascribed to the ammonia formed from its hydrolysis by the urease in the plant, whereas thiourea and allylthiourea are probably themselves toxic to the plant as soya-bean urease is without action on them.

L. F. H.

**Physiological Character of Ammonium Nitrate [towards Plants].** D. N. PRJANISCHNIKOV (*Z. Pflanz. Düng.*, 1925, **4A**, 242—250).—In sterile cultures and in experiments of short duration in unsterilised solutions of ammonium nitrate, maize seedlings took up much greater quantities of ammonia than of nitrate, with a corresponding increase in the acidity of the solution. Ammonium nitrate is to be regarded as physiologically acid rather than amphoteric. [Cf. B., 1925, June 26]. E. M. C.

**Iron, Sulphur, and Chlorine Contents of Grains and the Influence of Irrigation Water on Them.** J. E. GREAVES and D. H. NELSON (*Soil Sci.*, 1925, **19**, 325—330).—The content of iron in wheat, barley, and oat grains increased with the amount of irrigation water applied to the soil. The chlorine content of wheat varied similarly, but no regularity was observed in the case of oats and barley. The sulphur content of wheat increased with the amount of irrigation water, and examination of the sulphur-nitrogen ratio indicated that the increase was mainly in the form of oxidised sulphur. A. G. P.

**Influence of Light on the Absorption of Nutrients by Young Plants.** H. WIESSMANN (*Z. Pflanz. Düng.*, 1925, **4B**, 153—155).—Three lots of summer-rye plants were grown in sand, treated with a complete fertiliser, and exposed to light in the open, light from a northern window, and light from a southern window,



respectively. The dry weights of green matter and roots and the total potash and phosphoric acid content were all considerably higher for the plants exposed to the southern light than for those exposed to the northern light. The plants grown in the open had higher values for all determinations than either of the other two.

O. O.

**Carbon Dioxide as a Stimulant and a Nutrient.** W. SCHMIDT (*Z. Pflanz. Düng.*, 1925, **4B**, 162—171).—For complete germination of pine seeds an atmosphere enriched with carbon dioxide is of little benefit. In the intermediate stages, however, the treated seeds show an increased rate of germination. Excess of carbon dioxide depresses the total germination. The injurious effects of excess of the gas wear off in time.

O. O.

**Selective Absorption of Potassium by Plants.** G. ANDRÉ and E. DEMOUSSY (*Compt. rend.*, 1925, **180**, 1052—1054).—In order to test whether the occurrence of potassium salts in plants in much greater quantities than sodium salts is due to fractional diffusion, determinations have been made of the potassium and sodium in different parts of the beetroot. On July 31st the ratio K/Na was 13.9 in the central zone and 8.7 in the outermost zone, whilst on October 31st the ratios were practically equal, namely 8.1 and 7.6, respectively.

G. M. B.

**Alkaline Reaction of the Cotton Plant.** F. B. POWER and V. K. CHESNUT (*Science*, 1924, **60**, 405).—The alkalinity of the dew of the cotton plant is ascribed, at least partly, to the presence of ammonia and trimethylamine (cf. Mills, *ibid.*, 286; Smith, *J. Agric. Res.*, 1923, **26**, 192).

A. A. E.

**Reaction of the Cotton Plant.** J. A. HARRIS, W. F. HOFFMAN, and A. H. JOHNSON (*Science*, 1925, **61**, 65; cf. preceding abstract).—The tissue fluids of the cotton plant are acidic, the average  $p_H$  values being 5.25—5.46.

A. A. E.

**Relation of Pectose and Pectin in Apple Tissue.** M. H. CARRÉ (*Biochem. J.*, 1925, **19**, 257—265).—It is shown chemically and microscopically that proto-pectin (pectose) is present in apple tissue and that it is converted by hydrolysis into the soluble pectin. Tutin's assertion (*A.*, 1923, **i**, 1162) of the non-existence of proto-pectin is contested.

S. S. Z.

**Preparation of Asparagine by the Diffusion Method.** A. PIUTTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], **30**, 188—191).—The young growing cells of new vegetable tissues consist of an external membrane and protoplasmic contents which gradually contract, forming an inner membrane. The outer membrane is permeable to water and crystalloids, whereas the inner one is semi-permeable and allows only water to traverse it. At a certain stage, varying in different cases, this internal membrane is, however, permeable also to carbamide, glycerol, various alkaloids, nitrates, and asparagine. This observation forms the basis for a method of

isolating asparagine from *Lupinus albus* and *Vicia sativa* by diffusion into water. The stems may be dried in the air and extracted later, the yield of asparagine being virtually the same as is given by the fresh material. Even in presence of toluene, the enzymes of the cotyledons rapidly destroy the asparagine of the dialysed liquid. [Cf. B., 1925, 335.] T. H. P.

**Mercurialis. I. Development of a Blue Pigment on Drying.** P. HAAS and T. G. HILL (*Biochem. J.*, 1925, **19**, 233—235).—There exists in *Mercurialis* a chromogen which gives rise to a blue pigment on drying. The production of this colour is not due to enzyme action. The chromogen is most abundant in the youngest and vigorously growing parts. The pigment can be extracted from freshly-gathered plants with alcohol. By using colourless rhizomes, contamination with chlorophyll is obviated in this extraction. The pigment is not soluble in absolute alcohol. It can also be extracted from the dried plants with water and precipitated with ammonium sulphate from the extract. S. S. Z.

**Mercurialis. II. Occurrence of a Chromogen Showing a Remarkable Avidity for Free Oxygen.** P. HAAS and T. G. HILL (*Biochem. J.*, 1925, **19**, 236—239).—*Mercurialis* contains a chromogen which undergoes oxidation by gaseous oxygen in two stages, namely, with the production of a fugitive blue compound and further of a permanent yellow substance. This oxidation of the chromogen is independent of enzyme action. It is considered that there is only one chromogen concerned in the production of the fugitive blue and the permanent blue (see preceding abstract) according to conditions. S. S. Z.

**Ripening of the Kaki-Fruit. VII.** S. KOMATSU and M. ISHIMASA (*Mem. Coll. Sci. Kyōtō*, 1924, **7**, 397—401).—Although the two varieties of the fruit differ markedly in composition when unripe, the astringent variety containing less sugar and more pectin, "shibu," and acid than the sweet one, they are practically identical when ripe. In preserving the fruit by desiccation, it is found that the peeled fruit loses less sugar and more water. C. P. S.

**Kakishibu. II.** S. KOMATSU, N. MATSUNAMI, and M. ISHIMASA (*Mem. Coll. Sci. Kyōtō*, 1925, **8**, 43—49; cf. A., 1923, i, 1197).—During the fermentation of kakishibu, butyric acid, acetic acid, and mannitol are formed from the sugars of the fresh fruit. In the presence of air, the fermenting liquid becomes viscous and yields a white, translucent jelly, the insoluble part of which contains mucilage and pectin, whilst the soluble part contains shibuol. O. O.

**Genesis of Ethereal Oils in Plants.** L. FRANCESCONI, M. MANFREDI, and R. ASTENGO (*Annali Chim. Appl.*, 1925, **15**, 63—71).—Possible methods of formation of the commoner constituents of ethereal oils in plants are discussed. T. H. P.

**Oil of *Echinacea angustifolia*.** F. BISCHOFF (*J. Amer. Pharm. Assoc.*, 1924, **13**, 889—902).—The oil, 49% of which, b. p. 258·5—260°, consists chiefly of the hydrocarbon  $C_{15}H_{28}$ , has  $d$  0·792 (from dried roots), 0·802 (from moist roots),  $n_D^{25}$  1·4490.

## CHEMICAL ABSTRACTS.

**Characteristics of Oils of the *Euphorbiaceæ*.** P. GILLOT (*Compt. rend.*, 1925, **180**, 1285—1286).—The seeds of twenty species of *Euphorbiaceæ* and *Mercurialis* contain very similar essential oils with good drying properties. The physical constants of all the oils are about  $d^{15}$  0·936,  $n_D^{15}$  1·485, iodine value (Wijs) 205.

L. F. H.

**Primeverose, the Primeverosides, and Primeverosidase.** M. BRIDEL (*Compt. rend.*, 1925, **180**, 1421—1423).—Primeverose, a reducing xyloglucose, has been obtained as a product of the hydrolytic fermentation of (i) the two glucosides obtained from the roots of *Primula officinalis*, Jacq. (Goris, Mascré, and Vischniac, A., 1913, i, 576; 1920, i, 14), (ii) genticauloside (this vol., i, 336), (iii) monotropitoside (this vol., i, 347), and (iv) rhamnucoside (Bridel and Charaux, this vol., i, 621). The properties of this sugar differ from those recorded by Goris, Mascré, and Vischniac (*loc. cit.*) and are as follow:  $[\alpha]_D - 62\cdot92^\circ$ , reducing power (Bertrand) 64·7% of that of an equal weight of dextrose. The five primeverosides mentioned are widely distributed in nature and are hydrolysed by an enzyme to which the following names have been ascribed: betulase (Schneegans, A., 1898, i, 286), gaultherase (Bourquelot, A., 1896, ii, 540), and primeverase (Goris and Mascré, A., 1910, ii, 64). None of the names has been accurately derived and the name *primeverosidase* is proposed.

L. F. H.

**Glucosides of the Navel Orange.** J. A. HALL (*J. Amer. Chem. Soc.*, 1925, **47**, 1191—1195).—Whilst the hesperidin, which appears as crystal aggregates embedded in the endocarp of frozen oranges (cf. *Univ. California Agr. Expt. Sta., Bull.*, 1919, **304**, 257), disappears after 3 months in the case of navel oranges, it persists for 8 months in Valencia oranges. Filtered juice of navel oranges deposits pure hesperidin on keeping. The dried endocarp of navel oranges was extracted with methyl alcohol. Addition of ether gave a white precipitate, which on exposure to air turned to a brown gum. This dissolved in water and the solution deposited a white precipitate on keeping, which yielded hesperidin and a *substance*, m. p. 234—237°, probably closely related to hesperidin, whilst the aqueous filtrate contained dextrose. The original methyl-alcohol-ether filtrate deposited on evaporation a *substance*, m. p. 253—254°. It is concluded that the original precipitate is a mixture of hesperidin and a related compound, both in combination with dextrose, and it is suggested that the function of the hesperidin and its congener is to form a means of transferring dextrose from the chlorophyllous tissue.

F. G. W.

**Glucoside Content of Woodruff (*Asperula odorata*).** L. HERBOTH (*Arch. Pharm.*, 1925, **263**, 180—181).—An attempt has

been made to determine why the plant loses its spring odour of coumarin in summer. The plant (freed of roots) is extracted with 95% alcohol. Treatment of the extract with invertase and polarimetric observation reveal the presence of sucrose. Subsequent treatment with emulsin, polarimetric observation, and comparison with the results of Bourquelot and Hérissé (A., 1920, i, 586) show that the amounts of coumarin glucoside present in the plant in August and May bear to one another the relation 1 : 6. B. F.

**Active Principles of South African Plants.** C. F. JURITZ (*Chem. News*, 1925, **130**, 225—226).—The “bark” of the root of saffronwood (*Elaeodendron croceum*) was extracted with 60% alcohol acidified with acetic acid. After evaporation to a syrup and precipitation of resins, the residue was dissolved in dilute acid. Ether extraction of this solution yielded an alkaloidal substance to the extent of less than 0.04% of the weight of the bark. From the dilute acid solution was obtained a dull red powder, precipitable by lead acetate, which after purification darkened at 220° and decomposed at 284°. The filtrate from this red powder contained dextrose.

From the leafing tops of *Cotyledon Wallachii*, Harv., no trace of an alkaloid could be obtained, and only a minute amount of a glucoside corresponding with 0.03% of the weight of the dried plant. C. P. S.

**Rotenone, an Active Principle of the Derris Root.** S. TAKEI (*Biochem. Z.*, 1925, **157**, 1—15).—By extraction of the roots of *Derris elliptica*, Benth., with alcohol or ether, a crystalline substance,  $C_{19}H_{18}O_5$ , m. p. 163°, has been isolated, which is extremely toxic to animals when injected subcutaneously. It is insoluble in water, but soluble in organic solvents. On hydrolysis with alcoholic potassium hydroxide, an acid is obtained,  $C_{10}H_{10}O_3$ , which on fusion with alkali gives an acid (m. p. 182°) of the formula  $C_6H_2Me_2(OH)(CO_2H)$ . This is not identical with any of the three known dimethylsalicylic acids; it has been called *rotenic acid*. It may also be prepared direct from rotenone by fusion with potassium hydroxide.

Oxidation products of rotenone have been prepared, among which is *rotenonone*, obtained by the action of chromic acid in boiling acetic acid solution. Rotenonone also gives rotenic acid on fusion with potassium hydroxide. H. D. K.

**Presence of Two Alkaloids in *Aconitum Anthora*, L.** A. GORIS and M. MÉTIN (*Compt. rend.*, 1925, **180**, 968—969).—The two alkaloids of *Aconitum Anthora*, L., are separated by treatment with chloroform and ether. The one soluble in ether is named *anthorine* and the insoluble one, *ψ-anthorine*. Compared with aconitine, their toxicity is slight, that of *pseudoanthorine* being the greater. Their *sulphates* are amorphous, and *anthorine sulphate* is dextrorotatory in aqueous solution. [Cf. B., 1925, 334.]

F. M. H.

**Chemical Composition of the Hybrid of *Aconitum Anthora*, L., and *A. Napellus*.** A. GORIS and M. MÉTIN (*Compt. rend.*, 1925, **180**, 1282—1284).—The two *Aconita* differ in chemical composition, the latter containing aconitine and similar compounds and the former anethorine and  $\psi$ -anethorine (cf. preceding abstract). The hybrid of these two species (Randou) contains 0.15% of alkaloids but the quantity examined was too small for chemical investigation. Physiological tests (injection into guinea-pigs) revealed the presence of both anethorine and aconitine. The latter produces a tingling sensation on the tongue, and comparisons by this method suggest the presence of 2—5% of aconitine in the mixture of alkaloids.  
L. F. H.

**Alkaloids and Oil of Larkspur Seed (*Delphinium consolida*).** L. N. MARKWOOD (*J. Amer. Pharm. Assoc.*, 1924, **13**, 696—702).—The oil has  $d_{20}^{20}$  0.889,  $n_D^{20}$  1.4581, saponification number, 181.2, acid number, 189.2, iodine number, 87.8, acetyl number, 34.9, unsaponifiable matter, 1.28%. An alkaloid, *delnoline*,  $C_{25}H_{41}O_8N$ , has m. p. 207—209°.  
CHEMICAL ABSTRACTS.

**Extraction of *Adonis vernalis*.** O. STEPPUHN and G. PEWSNER (*Arch. exp. Path. Pharm.*, 1925, **105**, 334—342).—Extraction of the herb with ethyl or methyl alcohol by percolation or by absolute ethyl alcohol in a Soxhlet apparatus gives the same amount of product as measured by the effect on the frog's heart. Prolonged extraction with cold water, however, gives only 75% of the amount obtained by the alcoholic extractions. Although heating of the alcoholic extract for 8 hrs. has no appreciable effect, heating of the aqueous solution at 100° for 10 mins. produces a 10% diminution in potency and modifies the properties of the extract, which are then closely similar to those of *Digitalis* extract.  
L. F. H.

**Non-volatile Acids of the Strawberry, Pineapple, Raspberry, and Concord Grape.** E. K. NELSON (*J. Amer. Chem. Soc.*, 1925, **47**, 1177—1179).—Identified by the ester-hydrazide method, the non-volatile acids of the strawberry are *l*-malic (10%) and citric (90%); those of the pineapple are *l*-malic (13%) and citric (87%); of the red raspberry, *l*-malic (3%) and citric (97%), the black raspberry containing citric acid alone; and of the Concord grape *l*-malic (60%) and *d*-tartaric acids (40%).  
F. G. W.

**Chemistry of Japanese Plants. V. Chemical Composition of *Hydrangea paniculata*, Sieb.** I. S. KOMATSU and H. UEDA (*Mem. Coll. Sci. Kyōtō*, 1925, **8**, 59—63).—The inner bark of *Hydrangea paniculata*, Sieb., contains 5.3% of mucilage and 0.1% of umbelliferone. In addition, the aqueous extract contains a resin, magnesium and calcium lactates, fat, and umbelliferone glucoside. The portion insoluble in water contains umbelliferone and a resin.  
O. O.

**Constitution of Polysaccharides. III. Plant Mucilage. I.** S. KOMATSU and H. UEDA (*Mem. Coll. Sci. Kyōtō*, 1925, **8**, 51—57).—Crude mucilage prepared from the bark of *Hydrangea*

*paniculata*, Sieb., contains 14% of ash. Hydrolysis with dilute sulphuric acid for 4—5 hrs. gave a mixture of the following composition: 52% of a calcium salt of an organic acid I, 14% of *l*-arabinose and other sugars, 22% of calcium oxalate, and a little fat. The calcium salt I,  $[\alpha]_D^{20}$  in water  $+71.9^\circ$ , contains 6.12% of calcium and yields galactan and pentosan. It appears to be similar to mucilage and may bear the same relation to mucilage as pectic acid does to pectin. On hydrolysis with sulphuric acid it yields reducing sugars and a second calcium salt IIa,  $[\alpha]_D^{20}$  in water  $+67^\circ$ . Hydrolysis of I with stronger acid yields reducing sugars and another calcium salt IIb,  $[\alpha]_D^{20}$  in water  $+58^\circ$ . Both IIa and IIb yield pentosan, methylpentosan, galactan, and reducing sugars.

O. O.

**Occurrence of Acetaldehyde in Fruits and Other Parts of Plants.** C. GRIEBEL (*Z. Unters. Nahr. Genussm.*, 1925, 49, 105—110).—The presence of acetaldehyde in fruits was demonstrated by means of *p*-nitrophenylhydrazine (A., 1924, ii, 791). Acetaldehyde was detected in fruits in many stages of development and its presence is not characteristic of the ripening stages alone. In general, alcohol and aldehyde appeared simultaneously in fruits. It is suggested that acetaldehyde is a normal product of the metabolism of plants, and that its rapid production in certain fruits (notably those of the *Rosaceæ*) in the fully ripened condition is abnormal.

A. G. P.

**Chemical Components of Native Medicinal Plants. II.** J. ZELLNER (*Arch. Pharm.*, 1925, 263, 161—179).—*Pulmonaria officinalis*, L., contains in its dried leaves and stalks: light petroleum extract, 7.69%; ether extract, 2.27%; alcohol extract, 8.47%; total water-soluble matter, 34.64%; water-soluble mineral matter, 3.33%; free acids (as KOH), 0.87%; reducing sugars, 9.28%; tannins, 6.53%; total nitrogen, 1.54%; protein, 9.63%; fibre, 29.55%; ash, 15.53%. Ceryl alcohol, various higher fatty acids, and a phytosterol, m. p.  $133^\circ$ , were isolated on hydrolysis of the fat; whilst resin acids, phlobaphens, invert-sugar, and polysaccharides (yielding galactose, galactonic acid, and pentoses on hydrolysis) were also found.

*Menyanthes trifoliata*, L. (air-dried), contains: light petroleum extract, 4.89%; ether extract, 3.13%; alcohol extract, 30.13%; tannins, 7.12%; reducing sugars, 4.09%; total water-soluble matter, 38.89%; water-soluble polysaccharides (yielding galactose and mannose on hydrolysis), 5.04%; free acids (as KOH), 2.55%; water-soluble mineral matter, 7.78%; crude fibre, 20.78%; total nitrogen, 1.84%; total ash, 11.85%. The light petroleum extract yielded on hydrolysis a substance, m. p.  $144^\circ$  (acetyl derivative, m. p.  $61^\circ$ ), ceryl alcohol, a phytosterol, m. p.  $162^\circ$ , carotin, palmitic acid, resin acids, choline, and phosphoric acid. The alcohol extract contains menyanthin, now thought to have C 58.67%, H 7.74% (cf. Lendrich, A., 1892, 1262). On acid hydrolysis, it yields dextrose, a levorotatory monosaccharide, and menyanthol, now regarded as  $(C_6H_{10}O)_n$ , which yields on oxidation an acid, m. p.  $46^\circ$ , and is

either an unsaturated aliphatic aldehyde, or an alicyclic compound with a side-chain. Phlobaphens and invert-sugar are found.

*Hypericum perforatum*, L., contains in its air-dried stalks and leaves: light petroleum extract, 1.59%; ether extract, 3.3%; soluble in 95% alcohol, 16.75%; tannins, 10.85%; total water-soluble matter, 33.45%; reducing sugars, 4.02%; soluble polysaccharides (yielding on hydrolysis galactose and pentoses), 5.19%; soluble mineral matter, 4.52%; free acids (as KOH), 3.57%; pentosans, 10.91%; total nitrogen, 2.44%; protein, 15.25%; ash, 11.97%; fibre, 16.96%. On hydrolysis of the fat, the following substances were found: ceryl alcohol; the paraffins,  $C_{33}H_{68}$ , m. p. 63°, and  $C_{36}H_{74}$ , m. p. 68°; a phytosterol, m. p. 131°; various higher fatty acids, glycerol, and choline. Resin acids, phlobaphens, and invert-sugar are present. The flowers contain 12.4% of tannin, and known colouring matters, whilst the fruit fat, on hydrolysis, yields a mixture of oleic and linoleic acids. From the light petroleum fraction of the fruit, and by steam distillation of the whole plant, is prepared oil of hypericum (cf. Haensel, *Geschäftsber.*, 1904, I), which has  $d^{20}_D$  0.8778,  $[\alpha]_D +25.95^\circ$ ,  $n^{20}_D$  1.4856, and distils from below 100° to 178°, when decomposition sets in, leaving a residue which solidifies. The physical properties of the fractions distilling at 25 mm. are tabulated, and the oil contains: an indifferent substance, C 66.56%, H 9.19%, decomposing at 170° (bromo derivative, m. p. 110—113°); *d*-pinene and cadinene; and possibly ocimene, myrcene (this fraction yielding with sodium a reduction product,  $C_{10}H_{18}$ ), gurjunene, aromadendrene, an isovalerate, and cineole.

B. F.

### Chemical Constituents of the Leaves of certain Deciduous

**Trees.** K. FRICKE (*Z. physiol. Chem.*, 1925, **143**, 272—289).—In the young leaves there is an accumulation of specific food material, nitrogen, potassium, and phosphoric acid, which is greatest before flowering. There is a greater amount of sulphur and magnesium in the older leaves. In the ageing leaf structural constituents such as silica, calcium, and fibrous material increase. There is a return of specific food material out of the leaves into the storage organs in autumn.

From the ethereal extract of maple and beech leaves the following substances have been isolated: (1) a wax giving cerotic acid on saponification, (2) phytosterol, (3) phosphorus- and nitrogen-containing substances precipitable by alcohol, which give phosphoric acid and also a reducing carbohydrate on acid hydrolysis. The ether-soluble phosphorus compounds decrease in quantity as the leaf ages.

H. D. K.

**Wild Plum** (*Ximenia americana*, Linn.). ANON (*J. Dep. Agr. Union S. Africa*, 1925, **10**, 44—46).—The kernels of *Ximenia americana*, Linn., yield an oil,  $d^{15}_D$  0.9234, acid value 1.0, saponification value 170.7, iodine value 94.8, unsaponifiable matter, 3.1%; the residual meal contains water, 7.5%; proteins, 41.3%; fat, 1.6%; carbohydrates, 38.0%; fibre, 6.1%; ash, 5.5%. Alkaloids and cyanogenetic glucosides were absent.

CHEMICAL ABSTRACTS.

**Forms of Nitrogen in Lake Waters.** B. P. DOMOGALLA, C. JUDAY, and W. H. PETERSON (*J. Biol. Chem.*, 1925, **63**, 269—285).—In the water of various inland lakes soluble nitrogen is present in the form of ammonia, nitrites, nitrates, amino-acids, and proteins, the bottom water being richer than the surface water. This nitrogen reaches its maximum in the winter, a specially sharp rise, due to an increase in ammonia and nitrates, being observed in February; the plankton nitrogen increases as the soluble nitrogen decreases in the summer months, with irregularities corresponding to the successive growths of different sets of organisms.

C. R. H.

**Occurrence of Amino-acids and Other Organic Nitrogen Compounds in Lake Water.** W. H. PETERSON, E. B. FRED, and B. P. DOMOGALLA (*J. Biol. Chem.*, 1925, **63**, 287—295).—Concentrated filtered lake water gives all the usual protein reactions; figures are given of the nitrogen partition of the hydrolysis products of the residue from the evaporated water and also separate determinations of tryptophan, tyrosine, histidine, and cystine.

C. R. H.

**Acidity Produced in Salt Solutions by Sphagnum.** M. SKENE and G. L. STUART (*Nature*, 1925, **115**, 605—606).—The acid present in a salt solution after shaking with sphagnum is that of the salt employed, not humic acids.

A. A. E.

**Soil Microbiology.** S. WINOGRADSKY (*Ann. Inst. Pasteur*, 1925, **39**, 299—354; cf. *A.*, 1924, i, 1395).—A review of methods and their significance, with particular reference to those evolved by the author.

O. O.

**Influence of Micro-organisms on the Absorption of Nutritive Elements from Soil.** J. STOKLASA (*Bull. Assoc. Chim. Sucr.*, 1925, **42**, 350—357).—A comparison of the soils of plots on which various crops were grown continuously showed, after 4 years, great differences in the numbers of bacteria present and in the amount of carbon dioxide respired per unit weight of soil. A lucerne plot yielded the highest figures, sugar-beet came next, followed by wheat; all cultivated plots gave very much higher figures than an adjoining area left uncultivated. The differences in bacterial activity were reflected in the corresponding amounts of phosphoric acid and potassium taken up by the different crops from the soil. Selective absorption of anions and cations by plants, and the significance for nutrition of the differing numbers of bacteria to be found in the neighbourhood of the roots of different species are also discussed (cf. *A.*, 1924, i, 1018).

C. T. G.

**Properties of Urea in the Soil.** F. COUTURIER and S. PERAUD (*Compt. rend.*, 1925, **180**, 1433—1436; cf. Brioux, this vol., i, 491).—Urea is not adsorbed from solution by soil under sterile conditions; it is, however, quantitatively converted into ammonium salts by the micro-organisms of the soil after 48 hrs. at 17°, and after 120 hrs. at 2°. Urea can thus act as a nitrogenous fertiliser even at low temperatures.

L. F. H.



**Formation of Thiosulphates at the Expense of Sulphur by Micro-organisms of the Soil.** G. GUITTONNEAU (*Compt. rend.*, 1925, **180**, 1142—1144; cf. Demolon, A., 1912, ii, 382).—Four kinds of micro-organisms were isolated from soil and placed in an appropriate culture medium with precipitated sulphur at 25° for 16 days. The filtered liquid was practically free from sulphate. It was treated successively with cadmium carbonate and strontium nitrate to remove sulphides and sulphites. The solution then gave tests indicating the presence of thiosulphate. Determination of the thiosulphate gave the following results: Soluble sulphur (mg. per l.) determined by iodine 46.5, 19.8, 17.1, 15 for the four different micro-organisms. Probably, therefore, thiosulphate is an intermediate product in the slow oxidation of sulphur to sulphate in soil.

R. A. M.

**Copper Sulphate as Fertiliser.** DENSCH (*Landw. Jahrb.*, 1924, **60**, 139—140; from *Chem. Zentr.*, 1924, ii, 1846).—Copper sulphate applied at the rate of 30 kg. per hectare increases the yield of barley grain, but frequently depresses the yield of straw. A similar effect was produced by steeping the seed corn in 0.1—0.25% copper sulphate solution. The effect of copper sulphate in increasing the production of organic substance is mainly confined to carbohydrate formation. Protein formation is apparently unaffected. The copper is principally found in the straw, but detectable amounts were also found in the grain.

G. W. R.

**Lime-requirement of Soils. III. Influence of Soil Reaction on Biological and Physico-chemical Soil Factors.** O. ARRHENIUS (*Z. Pflanz. Düng.*, 1925, **4A**, 348—358; cf. this vol., i, 490).—Attention is drawn to the variety of soil factors concerned with the growth of crops which may be affected by changes in the reaction of the soil. In addition to a direct effect upon the higher plants, the growth of both nitrifying and nitrogen-fixing bacteria, and of many pathogenic organisms is dependent to a large extent on the degree of acidity. An increase or decrease in acidity acts very differently on different organisms; for example, the optimum  $p_H$  for nodule formation on various *Leguminosae* is by no means always the same as the optimum  $p_H$  for the growth of the host plant. Further, the state of combination of phosphoric acid in the soil and hence its solubility depends on the  $p_H$ , as also does the solubility of iron and aluminium salts. The infertility of acid soils can very rarely be due to aluminium, since only in very acid unoxidised soils are toxic amounts of aluminium detectable in solution. Knowledge of soil conditions and of the interaction of various factors on plant growth is not yet sufficient to allow of generalisations as to the effect of alterations of the reaction of the soil, e.g., by liming; each case must be considered individually.

C. T. G.

**Action of Silica in Increasing the Yield [of Plants].** O. LEMMERMAN, H. WIESSMANN, and K. SAMMET (*Z. Pflanz. Düng.*, 1925, **4A**, 265—315).—A detailed series of sand-culture experiments on the influence of silica on the yield and composition of the ash of

a number of different plants. The following are the chief conclusions reached. Silica definitely increases the yield of dry matter when there is a deficiency of phosphoric acid. This favourable action is not accounted for by a direct effect on plant growth nor does the silica merely satisfy the total mineral requirements in absence of sufficient phosphoric acid. It does not replace phosphoric acid in the nutrition of the plant, but indirectly increases the amount of phosphoric acid which can be taken up from the soil and the efficiency with which it is utilised. If readily available silica is deficient in a soil, the addition of an adequate supply will produce satisfactory yields with a smaller application of phosphatic fertiliser than would otherwise be the case. Silica apparently exerts a solvent action on the phosphate present and renders it more easily available to the plant.

C. T. G.

**Action of Silica in Increasing the Yield [of Plants] in Sand Cultures with Insufficient Phosphoric Acid.**

(I) F. DUCHON (*Z. Pflanz. Düng.*, 1925, **4A**, 316—325). (II) O. LEMMERMANN (*ibid.*, 326—330).—(I) The conclusions of Lemmermann and his colleagues (cf. preceding abstract) are criticised. The increase of yield obtained by the use of colloidal silica in sand cultures when phosphoric acid is apparently deficient is considered to be due to a favourable effect upon the physical properties of the sand, making a more efficient utilisation of the phosphoric acid present possible. The use of dung or green manure to improve the physical properties of sand reduces the amount of phosphatic fertiliser required to an extent at least equal to that brought about by silica. Natural soils contain sufficient colloidal material; the use of silica is held to have no practical importance. (II) The above criticisms are answered. The favourable action of silica, when phosphoric acid is deficient, was observed in sand cultures to which humic material had been added.

C. T. G.

**Effect of Soluble Silicates on Crop Yields and on the Utilisation of Phosphates.**

DENSCH (*Landw. Jahrb.*, 1924, **60**, 142—145; from *Chem. Zentr.*, 1924, ii, 1846).—From pot experiments with barley and analysis of the resulting ash, it is shown that when easily soluble silicates such as permutite are supplied to plants, there is no substitution of phosphoric oxide by silica in the crop, but that the soluble silicate induces a stronger growth and greater intake of plant food constituents from the soil. Light soils, poor in colloidal material, may not fix the added colloidal silicates, and an actual silicification of the plant may occur which inhibits the circulation of sap and the absorption of plant food.

G. W. R.

**Soil Conditions which Promote Nitrogen Fixation.**

N. E. WINTERS (*J. Amer. Soc. Agron.*, 1924, **16**, 701—716).—In the cases examined, the promotion of nitrogen fixation did not increase continuously with the amount of limestone, sodium nitrate, ammonium sulphate, or calcium nitrate applied.

CHEMICAL ABSTRACTS.

**Dispersion of Soil in Water under various Conditions.**

A. N. PURI and B. A. KEEN (*J. Agric. Sci.*, 1925, **15**, 147—161).—A study of the dispersion of soil when shaken with water under standard conditions. As a measure of the degree of dispersion obtained by different treatments, the authors use a dispersion factor obtained by allowing a column of suspension to settle for 24 hrs. and determining the ratio of the concentration of material in the top 8.5 cm. to the total concentration. Disintegration of soil aggregates by shaking proceeds continuously, rapidly at first and then more slowly. The change with time can be expressed  $d = a + K \log t$ , where  $d$  is the dispersion factor,  $t$  the time, and  $a$  and  $K$  are constants. In a series of experiments using the same shaking period, the dispersion factor is found to vary with the original concentration of the suspension and also with the initial moisture content. With clays, the dispersion factor decreases continuously with decrease in initial moisture content, whilst with soils a stationary value is reached when the initial moisture content is reduced to a certain value. Heating at 100° greatly reduces the dispersion factor of clays, whilst in the case of soils such decrease only occurs after heating above 110°. The effect of electrolytes is examined. Amongst mechanical methods of dispersion, trituration with a rubber pestle is most efficient.

G. W. R.

**Buffer Action of some Burma Soils.**

J. CHARLTON (*Mem. Dept. Agric. India*, 1924, **7**, 111—121).—The buffer action of a number of soils was measured by shaking the soil with varying quantities of acid and alkali, and determining the  $p_H$  value of the resulting suspension. From titration curves showing the relationship between these two quantities, the lime requirements of the soils were determined. The titration curves have the additional value of recording reserve buffering capacity against increasing acidity.

A. G. P.

**Influence of Grain Growing on the Nitrogen and Organic Matter Content of the Western Prairie Soils of Canada.**

F. T. SHUTT (*J. Agric. Sci.*, 1925, **15**, 162—177).—The author has investigated the effect of long-continued arable cultivation with grain on the amounts of nitrogen and organic matter in prairie soil. The results indicate a depletion in these soil constituents. There is evidence that the rate of loss tends to diminish so that eventually an equilibrium may be reached. Losses in nitrogen and organic matter may be neutralised by introducing grass, clover, and forage crops into the rotation.

G. W. R.

**Application and Importance of Electrometric Titration to the Determination of Soil Reactivity.**

H. NIKLAS and A. HOCK (*Z. angew. Chem.*, 1925, **38**, 195—199).—The measurement of  $p_H$  for soil suspensions is described. The graphs of  $p_H$  against the amount of alkali added during electrometric titration fall into two classes; their interpretation in terms of soil reactivity is discussed in detail. [Cf. *B.*, 1925, June 26th.]

S. K. T.

## Organic Chemistry.

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**Crystallising Point of Paraffin Wax.** A. P. BJERREGAARD (*Ind. Eng. Chem.*, 1925, **17**, 507).—Using the American m. p. method for paraffin waxes of different origin (temperature of separation of first crystals) and the English method (mean temperature of solidification of the main quantity) considerable and inconsistent differences are noted, depending on the composition of the wax with regard to the relative amounts of homologues of higher and intermediate m. p. and the difference between their m. p. [Cf. *B.*, 1925, 489.] D. G. H.

**Ethylenic Peroxides. Oxygenase of the Bach-Chodat System.** O. FERNÁNDEZ (*Anal. Fis. Quím.*, 1925, **23**, 181—185; cf. *A.*, 1921, i, 485).—Ethylenic compounds which can combine with an atom of oxygen by means of their double linkings, yield unstable peroxides which give the guaiacol reaction with peroxydases, in the same manner as the oxides of alkaloids. Certain vegetable oils, including some volatile oils, and ovolecithin yield such peroxides on treatment with hydrogen peroxide below 80°. Peroxides of this type are also obtained from ethyl cinnamate, styryl methyl ketone, and phenyl styryl ketone, respectively. G. W. R.

**Liquid Hydrocarbons Obtained in the Compression of Oil Gas.** P. LEWIS-DALE (*J. Soc. Chem. Ind.*, 1925, **44**, 189—194r).—Oil obtained by compressing oil-gas at 10 atm. had the following characteristics:  $d$  0.84,  $n_D$  1.47, iodine value 70, calorific value 23,000 B.Th.U. It contained approximately 20% of olefines (b. p. below 70°), 30% of benzene and toluene (mainly benzene), 30% of naphthenes, b. p. 70—120°, and 20% of higher benzene derivatives and polymerised olefines. Traces of a monoalkyl-acetylene, probably  $\Delta^2$ -butinene, were detected in the lowest boiling fractions, and the vapour densities etc. of the lower fractions indicated the presence of amylenes and olefines of the  $C_5H_8$  series, the iodine values indicating the presence of amylenes,  $C_5H_{10}$ , rather than the  $C_5H_8$  compounds. Traces of hexinenes appeared to be present in the benzene fraction. These results are in agreement with those of Armstrong and Miller (*T.*, 1886, **49**, 74) but separation was readily effected by fractional distillation only. R. B.

**Electron Displacement in Carbon Compounds. III. Polarity Differences in Carbon-Hydrogen Unions.** H. J. LUCAS, T. P. SIMPSON, and J. M. CARTER (*J. Amer. Chem. Soc.*, 1925, **47**, 1462—1469).—The action of alcoholic potassium hydroxide on  $\beta$ -bromobutane affords *cis*- (86%) and *trans*- (14%)  $\Delta^2$ -butenes, whilst  $\beta$ -bromopentane yields similarly  $\Delta^2$ -pentene

(71%) and  $\Delta^{\alpha}$ -pentene (29%). An explanation of these results from the point of view of electron displacement is given. It is suggested that, in a substitution process, the position of an entering substituent will be that at which electrons are least firmly held by carbon, and a suitable notation is suggested to indicate the direction of electron displacements, due, for example, to the difference in attraction for electrons between hydrogen and a methyl group.  $\beta$ -Bromobutane does not undergo rearrangement at  $140^{\circ}$ .

F. G. W.

**Electron Displacement in Carbon Compounds. II. Hydrogen Bromide and  $\Delta^{\beta}$ -Pentene.** H. J. LUCAS and H. W. MOYSE (*J. Amer. Chem. Soc.*, 1925, **47**, 1459—1461; cf. this vol., i, 2).— $\gamma$ -Bromopentane, prepared by the action of hydrobromic acid on the corresponding alcohol, has b. p.  $118-118.2^{\circ}/745$  mm.,  $n_D^{20}$  1.4443,  $n_D^{25}$  1.4427,  $n_D^{30}$  1.4400,  $n_D^{35}$  1.4351,  $n_D^{40}$  1.4322 (cf. Rozanov, A., 1917, i, 84). The action of hydrogen bromide on  $\Delta^{\beta}$ -pentene in glacial acetic acid yields  $\gamma$ - and  $\beta$ -bromopentanes in the proportion 78:22, with a possible variation of 8%. This result is in harmony with the hypothesis of electron displacement, but not with that of alternately polarised carbon atoms.

F. G. W.

**Preparation of True Acetylenic Hydrocarbons.** BOURGUEL (*Ann. Chim.*, 1925, [x], **3**, 191—235, 325—389).—Ground sodamide suspended in a suitable solvent is used to withdraw the elements of hydrogen halide from halogenated ethylenic hydrocarbons. A temperature of  $110-160^{\circ}$  is necessary. The acetylenes are produced as combinations of the type  $CR:C\cdot NH_3Na$ , which on decomposition with water yield the pure, non-polymerised hydrocarbons in good yields (50—85%). With the symmetrical dibromides the ethylenes  $CHR:CHR'$  are also formed. Sodamide also brings about molecular transformations; thus  $\Delta^{\delta}$ - and  $\Delta^{\gamma}$ -octinines are converted into the true octinine, and in this way higher acetylenes may be prepared from lower homologues after methylation:  $CR:CH \rightarrow CR:CMe \rightarrow CH_2R:C:CH$ .

Details are given for the preparation of many acetylenes and their derivatives, including the following:  $\Delta^{\gamma}$ -octinene,  $CBu:CET$ , b. p.  $131-132^{\circ}$ ,  $d^{21}$  0.755,  $n_D^{21}$  1.430;  $\Delta^{\beta}$ -noninene, b. p.  $161^{\circ}$  (corr.),  $d^{21}$  0.768,  $n_D^{21}$  1.434;  $\Delta^{\beta}$ -cyclohexylbutinene,  $C_6H_{11}\cdot CH_2\cdot C:CMe$ , b. p.  $77^{\circ}$  (14 mm.),  $d^{20}$  0.855,  $n_D^{20}$  1.471;  $\Delta^{\alpha}$ -cyclohexylbutinene, b. p.  $70^{\circ}$  (17 mm.),  $d^{20}$  0.845,  $n_D^{20}$  1.4615;  $\Delta^{\beta}$ -cyclohexylpentinene, b. p.  $93^{\circ}$  (17 mm.),  $d^{20}$  0.857,  $n_D^{20}$  1.4710;  $\Delta^{\alpha}$ -cyclohexylpentinene, b. p.  $84^{\circ}$  (16 mm.),  $d^{20}$  0.846,  $n_D^{20}$  1.4625;  $\Delta^{\beta}$ -cyclohexylhexinene, b. p.  $109-110^{\circ}$  (17 mm.),  $d^{20}$  0.853,  $n_D^{20}$  1.4710;  $\Delta^{\alpha}$ -cyclohexylinene, b. p.  $101^{\circ}$  (17 mm.),  $d^{20}$  0.846,  $n_D^{20}$  1.463;  $\gamma$ -methoxyallene, b. p.  $100-101^{\circ}$ ,  $d^{20}$  0.856,  $n_D^{20}$  1.424;  $\beta\gamma$ -dichloropentane;  $\gamma\delta$ -dichloroheptane;  $\Delta^{\gamma}$ -heptene, b. p.  $97-98^{\circ}$ ; cyclohexylbutinoic acid, m. p.  $69-71^{\circ}$ ; cyclohexylpentinoic acid, m. p.  $37.5-39^{\circ}$ ; cyclohexylhexinoic acid, m. p. about  $30^{\circ}$ ; cyclohexylheptinoic acid, m. p.  $40-41^{\circ}$ ; phenylbutinoic acid. The following revised boiling points are given: nonane,  $151^{\circ}$  (corr.); methyl *n*-propyl ketone,  $91-92^{\circ}$ ; true octinene,  $127-127.5^{\circ}$  (corr.).

S. K. T.

**Dependence of Rotatory Power on Chemical Constitution. XXVI. Four Alcohols containing the Vinyl Group and some Esters derived therefrom.** J. KENYON and D. R. SNELGROVE (*J. Chem. Soc.*, 1925, 127, 1169—1181).—The first four members of the homologous series of unsaturated alcohols of the general formula  $\text{CH}_2\cdot\text{CH}\cdot\text{CHR}\cdot\text{OH}$  have been prepared in optically active forms, and their rotatory powers compared with those of the corresponding saturated alcohols, in order to ascertain the effect of the ethylenic linking. This linking causes marked exaltation of optical activity, but in the case of the corresponding hydrogen phthalates of these alcohols this effect is considerably reduced or suppressed. The rotatory power of the alcohols and certain of their esters has been determined for a considerable number of wave-lengths by visual and photographic methods. A one-term equation gives calculated values for  $k_0$  and  $\lambda_0$  in close agreement with the experimental figures. Unsaturation increases the value of  $\lambda_0$ , and this is also increased in the "vinyl" series with rise in molecular weight, but diminishes in the "ethyl" series. The specific and molecular rotations have been determined in the homogeneous state, in various solvents, and at different temperatures. The presence of the double bond causes an increase in the refractive index, and the density is also greater in the unsaturated series.

*dl*-Methylvinylcarbinol was converted into the *hydrogen phthalate*, m. p. 5°, from which, by fractional crystallisation of the *brucine* salt, m. p. 120—122°, there was obtained *d*-methylvinylcarbinyl *hydrogen phthalate*, m. p. 52—53°,  $[\alpha]_D +40\cdot5^\circ$  (ethyl alcohol); the *l*-hydrogen *phthalate* has m. p. 52—53° and  $[\alpha]_D -40\cdot6^\circ$ . *dl*-Ethylvinylcarbinyl *hydrogen phthalate* was resolved by means of the *strychnine* salt, m. p. 159—160°, giving the *d*-hydrogen *phthalate*,  $[\alpha]_D +26\cdot2^\circ$ . Resolution of *dl*-*n*-propylvinylcarbinyl *hydrogen phthalate*, m. p. 62—63°, by repeated crystallisation of the *strychnine* salt, m. p. 164—166°, until this was optically pure (m. p. 170—172°), gave the *l*-hydrogen *phthalate* having m. p. 58—60° and  $[\alpha]_D -16\cdot05^\circ$  (ethyl alcohol); the *brucine* salt has m. p. 118—120°. The *l*-*n*-butylvinylcarbinyl *hydrogen phthalate*, m. p. 50—52°,  $[\alpha]_D -12\cdot6^\circ$  (ethyl alcohol), was obtained by resolution of the *strychnine* salt, m. p. 174—176°, and the *d*-*n*-butylvinylcarbinyl *hydrogen phthalate*, m. p. 50—52°,  $[\alpha]_D +12\cdot6^\circ$ , from the *morphine* salt, m. p. 114—116°.

Esters prepared from the optically active unsaturated alcohols have specific rotations of opposite sign to the alcohol from which derived; thus, *l*-*n*-butylvinylcarbinol has  $[\alpha]_D^{20} -25\cdot0^\circ$ , and the *acetate*, b. p. 165—167°/760 mm., has  $[\alpha]_D +4\cdot36^\circ$ . The following esters have also been obtained, and boiling points recorded at 760 mm.: *formate*, b. p. 115·5—116·5°, and *acetate*, b. p. 126·5—127·5°, of *d*-ethylvinylcarbinol, *formate*, b. p. 155—157°, *n*-butyrate, b. p. 198—200°, and *benzoate*, b. p. 152—153°/18 mm. of *d*-*n*-butylvinylcarbinol. Reduction of *l*-*n*-butylvinylcarbinol to the corresponding saturated alcohol showed no change in the sign of optical rotation.

C. J. S.

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**Synthetic Rhodinol.** V. GRIGNARD and R. ESCOURROU (*Bull. Soc. chim.*, 1925, [iv], **37**, 542—545).—Hydrogenation of  $\beta$ -geraniol, b. p. 114—115°/12 mm.,  $n_D^{11}$  1.47628, is effected by shaking its solution in anhydrous ether with hydrogen in presence of platinum-black until 1 mol. is absorbed per mol. of alcohol. The racemic rhodinol which results has b. p. 107—108°/12 mm.,  $n_D^{12}$  1.45147,  $d_{14}$  0.8513, and is converted by cyanic acid (cf. Behal, A., 1919, ii, 301) into the allophanate, m. p. 111—111.5°. Since ozonisation yields acetone and no lævulaldehyde it must be  $\beta$ -rhodinol,  $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , and it is identical with that of Bouveault and Gourmand (A., 1904, i, 756). Ozonisation of natural citronellol gives a mixture of formaldehyde and acetone, whence it is concluded to be a mixture of the  $\alpha$  and  $\beta$  forms.

F. M. H.

**Selective Hydrogenation of Geraniol.** V. GRIGNARD and R. ESCOURROU (*Bull. Soc. chim.*, 1925, [iv], **37**, 546—548).—When geraniol, b. p. 114—117°/12 mm., is shaken at 80—95° with hydrogen in presence of nickel (reduced at 280—290°), until 1 mol. per mol. of alcohol is absorbed, the chief product is (a) racemic "citronellol (Ni)," b. p. 114.5—116°/20 mm.,  $n_D^{18}$  1.4463,  $d_{20}^{18}$  0.8420 (which with cyanic acid gives an allophanate, m. p. 112—113°), (b) a second fraction (containing dimethyloctanol?), and (c) a fraction, b. p. 118—123°,  $n_D^{20.5}$  1.4550. From the results of ozonisation it is calculated that Java geraniol contains 22.5% of the  $\alpha$  and 82.5% of the  $\beta$  form, and that citronellol (Ni) contains 17.5% of the  $\alpha$  form, whilst "citronellol (Pt)" [the rhodinol of the preceding abstract] contains 18% of the  $\alpha$  and 85.5% of the  $\beta$  form. By a modified preparation of citronellol (Pt), it contains only 15% of the  $\alpha$  form and its allophanate has m. p. 113.5° instead of 111—111.5°.

F. M. H.

**Unsaponifiable Matter of Arctic Sperm Oil.** M. TSUJIMOTO (*Chem. Umschau*, 1925, **32**, 127—128).—Arctic sperm oil yields 43.2% of unsaponifiable matter, which consists of cholesterol, 0.4%; oleyl alcohol, above 70%; and cetyl alcohol. [Cf. B., July 26th.]

B. F.

**Production and Occurrence of Acetylmethylcarbinol in Vinegar.** V. 'T HOOFT (*Chem. Weekblad*, 1925, **22**, 272—276).—Examination of a large number of samples of vinegar showed that all those prepared by the slow oxidation methods from fruit juices which had been subjected to alcoholic fermentation contained the carbinol, which results from oxidation of the butane- $\beta\gamma$ -diol formed in the fermentation, and possibly to a smaller extent from biochemical condensation of acetaldehyde formed in the oxidation. Artificial vinegars or those prepared by rapid oxidation of alcoholic liquors do not contain the alcohol. The method of Lemoigne (A., 1920, ii, 198) gives a simple means of distinguishing the various kinds of vinegar, and may be employed for the determination of the acetylmethylcarbinol present, which may be used as a test of the quality of commercial vinegar.

S. I. L.

**Preparation of Methylalkylglycerols.** R. DELABY and G. MOREL (*Compt. rend.*, 1925, **180**, 1408—1410).—Three methods of preparation of the simpler methylalkylglycerols from the corresponding alkylpropenylcarbinols have been studied quantitatively; these methods are (i) oxidation with potassium permanganate (Reif, A., 1908, i, 847), (ii) preparation and subsequent hydrolysis of the chlorohydrin (Pastureau and Bernard, A., 1923, i, 646), and (iii) preparation of the dibromohydrin, treatment of this with potassium acetate, and hydrolysis of the diacetate by treatment with methyl alcohol (cf. Delaby, A., 1923, i, 84, 85). The yields obtained were about 18%, 12%, and 37%, respectively. *Methyl-n-propylglycerol* (*heptane- $\beta\gamma\delta$ -triol*), b. p. 162—164°/25 mm., has been obtained by the last-named method. L. F. H.

**Spontaneous Decomposition of Lecithin.** S. KATO and O. SHINODA (*Mem. Coll. Sci. Kyoto*, 1924, **7**, 339—343).—Ovo-lecithin (Merck) undergoes spontaneous decomposition on long keeping. The fatty acids are gradually separated, leaving a substance rich in phosphorus and nitrogen but poor in carbon and hydrogen. C. P. S.

**Mutarotation. VI. Solution Volumes and Refraction Constants of some Polyhydric Alcohols.** C. N. RUIBER, T. SØRENSEN, and K. THORKELSEN (*Ber.*, 1925, **58**, [B], 964—970; cf. this vol., i, 8).—The molecular solution volumes at infinite dilution at 20° of sorbitol, dulcitol, mannitol, inactive erythritol, glycerol, and ethylene glycol are 117·86, 118·36, 118·76, 86·49, 70·59, and 54·28 ml., respectively. It is thus established that differences in configuration cause a difference in the molecular volume. Comparison of the constants of sorbitol,  $\alpha$ - and  $\beta$ -dextrose, and  $\beta$ -lævulose shows that the dextroses and lævulose when crystalline cannot possibly be truly aldehydic or ketonic, respectively. The refraction constants are also recorded. In spite of differences in configuration, mannitol, dulcitol, and sorbitol have almost identical refraction constants, so that the latter, in contrast to the solution volumes, are not suited to the detection of configurative differences of polyhydric alcohols. Solutions of the hexahydroxy alcohols of identical concentration have different indexes of refraction, but this appears merely as a consequence of the difference in solution volume. Among the hexahydroxy alcohols, the index of refraction is a linear function of the concentration. The densities and optical properties of solutions of the alcohols do not appear to be affected by the age of the solutions. H. W.

**Oxidation of the Sugar Alcohols from the Stereochemical Point of View.** E. VOTOČEK and R. LUKES (*Rec. trav. chim.*, 1925, **44**, 345—351).—When *d*-sorbitol is oxidised by means of bromine in sodium carbonate solution the four products required by stereochemical theory, viz., *d*-glucose, *d*-fructose, *l*-gulose, and *l*-sorbose, are all obtained and may be separated by the difference in the solubilities of their osazones in acetone. The gulosazone (=sorbosazone) is exceedingly soluble and can be extracted from



the evaporated mother-liquor with 25% alcohol. By analogy, *l*-arabinol will yield, on oxidation, two pentoses, *l*-arabinose and *l*-lyxose, and this affords an explanation of the large divergence in the results obtained when the arabinose in the product is determined by precipitation as the phenylhydrazone, and by distillation with 12% hydrochloric acid and precipitation of the furfuraldehyde produced by phloroglucinol, respectively. J. W. B.

**Solutions of Mannito-aluminates.** P. HERASYMENKO (*Rec. trav. chim.*, 1925, **44**, 435—446).—The complex ions formed in aqueous alkaline solutions containing an aluminate and mannitol were investigated by means of cryoscopic and conductivity measurements, and the results show that several complexes are formed depending largely on the concentrations of hydroxyl ions present in the solution; the inability of Hanus and Quadrat (A., 1909, i, 762) to prove the formation of complexes between polyhydric alcohols and aluminates is explained by the small concentration of hydroxyl ions in their ammoniacal solutions. When the changes in the freezing points are plotted against the total concentration of added mannitol, the majority of the curves exhibit a maximum corresponding with complex formation. In solutions where the concentration of the aluminate ions is less than that of the hydroxyl ions, this maximum is reached when the total concentration of the mannitol corresponds to half the sum of the concentrations of aluminate and hydroxyl ions and is independent of the concentration of the aluminate. The first addition of mannitol to dilute solutions gives rise, therefore, to the formation of complexes which may be represented thus:  $\text{Al}(\text{OH})_4' + \text{M} \rightarrow [\text{Al}(\text{OH})_3 \cdot \text{MOH}']$ ;  $\text{Al}(\text{OH})_4' + \text{M} + \text{OH}' \rightarrow [\text{Al}(\text{OH})_2 \cdot \text{M}(\text{OH}')_2]$ , the prevailing one being the latter dibasic anion. When the initial concentration of the aluminate ions is greater than that of the hydroxyl ions, separation of aluminium hydroxide always occurs before the mannitol concentration corresponding to the maximum on the curve is reached, this being due to the withdrawal of hydroxyl ions from the aluminate ion which is effected when the quantity of the former ion available to combine with the mannitol molecule becomes insufficient to keep the alumina in solution. In the most concentrated solutions the formation of complex ions occurs thus:  $\text{Al}(\text{OH})_4' + 2\text{OH}' + \text{M} \rightarrow \text{complex anion}$ . Conductivity measurements show that although the complex acid has a much greater stability than aluminic acid, the difference in "strength" is not great, the dissociation of the complex being of the order of  $3 \times 10^{-10}$ . J. W. B.

**Preparation of Halogen-substituted Ethers.** H. P. FORAN (*J. Soc. Chem. Ind.*, 1925, **44**, 173—174T).—Chloromethyl ethyl ether, b. p. 79.6°, is obtained in 42—44% yield by passing dry hydrogen chloride to saturation into absolute alcohol half-saturated with formaldehyde, the temperature being kept below 65°, as compared with 4—8% yields by Henry's method (A., 1885, 882; Favre, A., 1895, i, 14).  $\beta$ -Bromodiethyl ether, b. p. 128°, is obtained in 43% yield by refluxing sodium ethoxide with 0.8 mol. of ethylene

dibromide, and fractionally distilling, after filtration from sodium bromide. About 10% of the ethylene dibromide is converted into diethyl glycol. R. B.

**Alkyl Hypochlorites.** O. G. BACKEBERG (*J. S. Afr. Chem. Inst.*, 1925, **8**, 32—35; cf. T., 1923, **123**, 2999; A., 1924, i, 703).—A résumé of work already published. B. F.

**Chlorosulphonic Acid Esters.** W. TRAUBE [with P. BAUMGARTEN, L. BAERMANN, W. LANGE, and R. JUSTH] (*Z. angew. Chem.*, 1925, **38**, 441—444).—Esters of chlorosulphonic acid act as alkylating agents on aqueous suspensions of aniline in presence of alkali or alkaline-earth hydroxides or carbonates. The reaction is complex, the ethyl ester producing at 0° mono- and di-ethylaniline together with salts of phenyl- and phenylethyl-sulphamic acids. The last-named may possibly be formed from ethyl phenylsulphamate by autoalkylation. Methyl chlorosulphonate acts similarly, although at a temperature of not less than 15—20° the whole of the aniline is converted into the sulphamic acid. Chlorosulphonic esters, alkyl halides, and particularly alkyl sulphates, alkylate phenylsulphamic acid. Aniline may thus be converted simply and completely into methylaniline by the successive actions of methyl chlorosulphonate and methyl sulphate, followed by fission of the sulphamic acid. From the mixture obtained by the action of the ethyl ester on aniline, the ethylanilines may be converted into diethylaniline, whilst the mixture of phenyl- and phenylethyl-sulphamic acids left in the alkaline solution may then be converted into methylaniline. Ethyl chlorosulphonate alkylates and also partly sulphonates an aqueous solution of monoalkylaniline in presence of alkali, but aliphatic amines are only alkylated. Alkylation of phenol is carried out only in presence of alkali, a yield of 75% of phenetole being so obtained. The esters of chlorosulphonic acid may be used for alkylating potassium salts of hydroxylamine-disulphonic acid and imidodisulphonic acid as well as disodium cyanamide. Ethyl chlorosulphonate is decomposed by hydrochloric acid to give a large proportion of ethyl chloride, the proportion of this substance obtained being almost quantitative when fuming acid is employed. Hydrobromic acid forms much ethyl bromide and but little ethyl chloride, indicating that the bulk of the halide is formed by union of the alkyl group with the halogen atom of the acid. A. COUSEN.

**Organo-magnesium Compounds. Reaction between Magnesium and Acyl Halides.** D. V. TISTCHENKO (*Bull. Soc. chim.*, 1925, [iv], **37**, 623—637).—Acyl bromides react with magnesium in dry ether, although the chlorides do not react (cf. Staudinger, A., 1908, i, 654), yielding organo-magnesium compounds of the type R·CO·MgBr. The velocity of reaction increases with mol. wt. of the acyl group in the series acetyl → isovaleryl. On treatment with water the magnesium acyl bromides are decomposed, yielding aldehydes or their condensation products. Ethyl formate

and oxalate, carbon dioxide, toluonitrile, and halides such as benzyl chloride, ethyl iodide, amyl bromide, or bromobenzene are without action. With ketones, benzaldehyde, acetic anhydride, or methyl sulphate, reaction apparently occurs, but the product on treatment with water yields only the normal decomposition products of the magnesium acyl bromide and the reagent applied. Carbonyl chloride reacts immediately, with precipitation of magnesium chlorobromide and formation of a reddish, unstable ethereal solution, containing much hydrogen chloride, which resinifies on treatment with alkali. Bromine reacts violently, yielding a diketone, an ester, and ethyl bromide, probably thus:  $R \cdot CO \cdot MgBr + Br_2 = R \cdot COBr + MgBr_2$ ;  $R \cdot COBr + R \cdot CO \cdot MgBr = R \cdot CO \cdot CO \cdot R + MgBr_2$ ;  $R \cdot COBr + Et_2O = R \cdot CO \cdot OEt + EtBr$ . Oxalyl bromide yields the same products. Magnesium acetyl bromide under these conditions yields 25% of acetic acid in addition to 30% of ethyl acetate, ethyl bromide, and a tar (40%) yielding diacetyl on treatment with sulphuric acid.

Acetyl bromide and magnesium (1 atom) in 6 vols. of ether yield an oil which on decomposition with water gives ethyl acetate (35%), diacetyl (25—30%), and a quantity of resin. If 1 vol. of ether is used and the violent reaction is modified by the addition of a few drops of mercury, the reaction product on treatment with water yields acetaldehyde, ethyl acetate (80%), traces of diacetyl, and crotonaldehyde (10%). The three last compounds are formed by condensation of the acetaldehyde first produced. Addition of acetyl chloride to the magnesium acetyl bromide modifies slightly its decomposition by water, increasing the yield of crotonaldehyde to 20%, whilst similarly methyl sulphate increases the proportion of acetaldehyde to 10%. *iso*Butyryl bromide and magnesium similarly give a yellowish-brown oil, which on decomposition with water yields *isobutaldehyde*, a fraction (30%) consisting mainly of *isobutyroin*, probably contaminated with a little *diisobutyryl*, an intermediate fraction, *isobutyroin isobutyrate* (30%), and the *diisobutyrate* of  $\beta\epsilon$ -dimethylhexene- $\gamma\delta$ -diol (5%). Magnesium and *isovaleryl* bromide react very readily and the solution on decomposition with water or dilute acid yields *isovaleraldehyde*,  $\delta$ -methyl- $\beta$ -*isopropyl*- $\Delta\beta$ -pentaldehyde, *isovaleroïn isovalerate*, and the *diisovalerate* of  $\beta\gamma$ -dimethyl- $\Delta^8$ -octene- $\delta\epsilon$ -diol, the first two fractions representing 70% of the yield. If a second molecule of *isovaleryl* bromide is added to the magnesium *isovaleryl* bromide and the product decomposed with water ethyl *isovalerate* (22%) and the corresponding quantity of ethyl bromide, *diisovaleryl*, b. p. 77.5—78°/14 mm.,  $d_4^{20}$  0.931 (*phenylhydrazone*, m. p. 78°), *isovaleroïn isovalerate* and the *diisovalerate* of *diisobutylacetylene glycol* are produced. The yield of diketone amounts to 42% of theory if the second molecule of *isovaleryl* chloride is added promptly and prolonged heating of the magnesium compound avoided. Benzoyl bromide reacts rapidly with magnesium in the presence of ether but the action is checked through the formation of a viscous precipitate which on treatment with water yields only benzoic acid and resinous products.

R. B.

**Action of Acid Chlorides on Trimethylamine.** L. W. JONES and H. F. WHALEN.—(See i, 801.)

**Sudden Pyrogenic Decomposition of Methyl Formate at a High Temperature.** (MLLE.) E. PEYTRAL (*Bull. Soc. chim.*, 1925, [iv], **37**, 562—568).—When the vapour of methyl formate is passed through a platinum tube at  $1150^{\circ}$ , the chief products are formaldehyde, carbon monoxide, hydrogen, and methyl alcohol, together with carbon dioxide and methane. From determinations of the quantities of the various products, it is concluded that the primary decomposition is:  $\text{H}\cdot\text{CO}_2\text{Me} = 2\text{H}\cdot\text{CHO}$ , and this is followed by decomposition of part of the formaldehyde:  $\text{H}\cdot\text{CHO} = \text{CO} + \text{H}_2$ . The relatively less production of hydrogen as compared with carbon monoxide is due to its absorption in partial hydrogenation of the formaldehyde:  $\text{H}\cdot\text{CHO} + \text{H}_2 \rightleftharpoons \text{MeOH}$ . The reaction,  $\text{H}\cdot\text{CO}_2\text{Me} = \text{CO}_2 + \text{CH}_4$ , is of minor importance. F. M. H.

**Rambutan Tallow as Source of *n*-Eicosoic Acid.** G. T. MORGAN and E. HOLMES (*J. Soc. Chem. Ind.*, 1925, **44**, 219r).—*n*-Eicosoic acid,  $\text{C}_{19}\text{H}_{39}\cdot\text{CO}_2\text{H}$ , was prepared from the glycerides present in Rambutan tallow extracted from seeds of *Nephelium lappaceum* obtained from Singapore and Calicut, in addition to those obtained from Ceylon (cf. *ibid.*, 1924, **43**, 346r). L. A. C.

**Acceleration of the Drying of Fatty Oils by Driers.** A. EIBNER and F. PALLAUF (*Chem. Umschau*, 1925, **32**, 81—95, 97—110).—From experiments on the drying of raw and boiled oils under scrupulously uniform conditions, it is concluded that the autocatalytic agent is the aldehyde peroxide primarily formed. Experiments with introduced catalysts lead to the following conclusions. Metals and metallic oxides act through their fatty acid salts. The effectiveness of different driers depends on the metal employed and on the solubility of its fatty acid salt in the oil to be dried, but not at all on the nature of the acid residue. Cobalt salts of fatty acids are found to be the quickest driers; manganese salts come next in efficiency, but are very sensitive to atmospheric moisture unless corrected in this respect by the addition of lead (optimum proportions appear to be those of the respective atomic weights). Resinates are more efficient than linoleates owing to their greater solubility. The speed of drying varies as the amount of metal present in soluble form, and follows the usual temperature law, doubling with every rise of  $10^{\circ}$ . Quick drying, however, is often followed by softening. The efficiency of lead driers used in oil-boiling follows the decreasing order  $\text{PbO}$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{PbO}_2$ . The loss of drying activity on the maturing of boiled oil is attributed to the precipitation of drier by incidence of low temperatures, to reaction between the soluble lead salt of the drier with free saturated acid and resultant precipitation of insoluble lead salts of the latter, and finally to the formation of relatively insoluble lead salts of hydroxy-fatty acids by oxidation. It is shown that the usual increase of weight on exposure curves of drying oils are of little value

as interpreting the progress of oxidation, since the changes measured depend on several simultaneous reactions which are influenced to different degrees by external factors, particularly the incident light. On experimental evidence, Fokin's hypothesis of semi-molecular absorption of oxygen in boiled oils is rejected, as well as a similar explanation of the small increase in weight on exposure of certain so-called non-drying linseed oils. Such behaviour is completely explained by their slow rate of drying. That driers function not merely indirectly by catalysing the formation of aldehyde peroxides, but that in the form of "mloxides" they take a direct part in the transference of oxygen, seems probable. [Cf. *B.*, 1925, 513.]

G. L. R.

**Chromic Acid Oxidation and Molecular Structure. Tariric and Stearolic Acid Derivatives.** L. J. SIMON (*Compt. rend.*, 1925, **180**, 1405—1407; cf. *A.*, 1923, i, 81, 908, ii, 432; 1924, ii, 567; this vol., i, 505).—On analysis by oxidation with chromic acid there is a carbon deficiency of nearly two atoms of carbon per molecule of the straight-chain acids: stearic, tariric, tarelaidic, taroleic, ketotariric, diketotariric, stearolic, elaidic, oleic, keto-stearic, dihydroxystearic, and behenolic acids. In derivatives of these acids containing more than one chain of carbon atoms, *e.g.*, the ethyl esters and the glycerides, there is a carbon deficiency of nearly two atoms for every carbon chain in the molecule. The carbon deficiency is attributed to formation of acetic acid which is not attacked by the oxidising agent.

L. F. H.

**Constitution of Natural Unsaturated Fatty Acids. II. Acids present in a South Georgia Whale Oil.** E. F. ARMSTRONG and T. P. HILDITCH (*J. Soc. Chem. Ind.*, 1925, **44**, 180—189T; cf. this vol., i, 504).—By the use of the methods recently developed (this vol., i, 353, 355), the authors show that the unsaturated acids from a South Georgia whale oil of good quality comprise: myristoleic acids (1—1.5%, mainly  $\Delta^4$ -tetradecenoic acid, with a smaller amount of the  $\Delta^7$ - or  $\Delta^9$ -acid); palmitoleic acid (15%), entirely  $\Delta^7$ -hexadecenoic acid; oleic acids (35%), consisting of about 95% of  $\Delta^7$ -octadecenoic acid and not more than 5% of an isomeric acid, probably  $\Delta^9$ -octadecenoic acid. Highly unsaturated acids of the series with 20 and 22 carbon atoms are also present and none of these polyethylenic acids contains a double bond nearer the carboxyl group than the  $\Delta^4$ -position; much of the unsaturation commences further along the chain and is between the 9th and 20th or 11th and 22nd carbon atom. The average total unsaturation in these acids containing 20 and 22 carbon atoms amounts to the equivalent of 4 or 5 ethylenic linkings. Tsujimoto's myristoleic acid (*A.*, 1923, i, 297) was not detected.

R. B.

**Occurrence of Highly Unsaturated Acids in Algæ.** M. TSUJIMOTO (*Chem. Umschau*, 1925, **32**, 125—126).—The ether extracts of seven species of algæ were hydrolysed, and yielded unsaturated acids. *Laminaria japonica*, Aresch, and *Sargassum sagamianum*, Yendo, contain the acid  $C_{22}H_{36}O_2$  (bromo derivative,

$C_{22}H_{36}O_2Br_8$ ), yielding on reduction behenic acid, whilst the latter plant also contains a trace of clupanodonic acid,  $C_{22}H_{34}O_2$ . The acids were purified by precipitation as the ether-insoluble polybromo derivatives (yield 0.01—0.05% of air-dried plant), being regenerated from the latter by reduction. B. F.

**Tautomerism of Dyads. III. Effect of the Triple Linking on the Reactivity of Neighbouring Atoms.** (MRS.) E. H. INGOLD (*J. Chem. Soc.*, 1925, **127**, 1199—1206).—When a hydrogen atom is attached to an ethylenic carbon atom it is firmly bound, but when attached to an acetylenic carbon atom it is easily replaced by metals, and in some cases possesses tautomeric mobility. Acetylenedicarboxylic acid is less stable than the monocarboxylic acid containing a mobile hydrogen atom, since on gently heating with water only 1 mol. of carbon dioxide is eliminated. The influence of a carbethoxy group can be transmitted through an acetylenic linking to the  $\beta$ -carbon atom. The  $\beta$ -carbon atom in ethyl propiolate is so reactive that it readily undergoes the Claisen condensation with ethyl oxalate. Since amylacetylene does not condense with ethyl oxalate the carbethoxy group increases the reactivity of the acetylenic hydrogen atom; the phenyl group has a similar, but less marked, effect. The products obtained by the Claisen condensation between methyl and ethyl propiolates and oxalic and benzoic esters are unstable, and on hydrolysis and reduction pass into fully saturated compounds. Thus, *methyl propiolate*, b. p.  $102^\circ/742$  mm., when condensed with methyl oxalate, and the product hydrolysed and reduced, gives glutaric acid as the main product; oxalic and succinic acids are also formed, as well as a small amount of pyrocatechol (due to condensation of the methyl oxalate with 2 mols. of methyl propiolate). Ethyl propiolate and ethyl benzoate, when treated in the same manner, give  $\gamma$ -phenylbutyric acid.

Propiolic esters also undergo the Michael addition reaction with ethyl fumarate. Ethyl propiolate and ethyl fumarate give a product, which when hydrolysed and reduced, yields *n*-butane- $\alpha\beta\delta$ -tricarboxylic acid and a small quantity of muconic acid.

*Ethyl  $\beta\beta$ -diethoxypropionate*, b. p.  $206^\circ/755$  mm., was obtained by the action of alcoholic sodium ethoxide on ethyl propiolate.

C. J. S.

**Gattermann's Synthesis of Aldehydes in the Case of Enols.** H. WIELAND and E. DORRER (*Ber.*, 1925, **58**, [B], 818—820).—In extension of work on the parallelism between the reactions of aliphatic and aromatic compounds (A., 1920, i, 280; 1921, i, 778; 1922, i, 1033), Gattermann's method of preparing aldehydes has been applied to aliphatic enols. Ethyl acetoacetate dissolved in benzene is converted by hydrocyanic acid and hydrogen chloride in the presence of aluminium chloride into *ethyl  $\alpha$ -formiminoacetoacetate hydrochloride*,  $COMe \cdot CH(CO_2Et) \cdot CH : NH_2 \cdot HCl$ , m. p.  $106^\circ$  (decomp.). The free ester, b. p.  $155^\circ/10$  mm., m. p.  $50$ — $52^\circ$ , has been described by Claisen (A., 1897, i, 592), who considered it to be the amino compound,  $COMe \cdot C(CO_2Et) : CH \cdot NH_2$ ; the authors

discard this conception because the substance does not react with nitrous acid. Under similar conditions acetylacetone yields formiminoacetoacetone,  $\text{COMe}\cdot\text{CH}(\text{CH}\cdot\text{NH})\cdot\text{COMe}$ , m. p.  $144^\circ$  (cf. Claisen, *loc. cit.*).  
H. W.

**Catalytic Transmutation of Maleic Acid into Fumaric Acid.** E. M. TERRY and L. EICHELBERGER (*J. Amer. Chem. Soc.*, 1925, **47**, 1402—1412).—The rates of conversion of maleic acid into fumaric acid in aqueous solution at  $99.2^\circ$  under the influence of hydrochloric acid, hydrobromic acid, and potassium thiocyanate respectively, have been measured. The reaction proceeds without formation of by-products, and its velocity is proportional to the concentration of the catalyst and to the second power of the original concentration of the maleic acid; it is unaffected by any excess of fumaric acid originally present. The velocity constant is independent of the concentration of the catalyst except in the case of hydrobromic acid, where it increases with increasing concentration of the latter. It is suggested that the conversion takes place through the primary formation of an additive complex between 1 mol. of maleic acid and 2 mols. of the catalyst, addition taking place at the carboxyl groups. This complex then becomes "activated" at the  $\cdot\text{C}\cdot\text{C}\cdot$  linking, the active form being represented as an electromeride,  $\cdot\overset{+}{\text{C}}\cdot\overset{-}{\text{C}}\cdot$ , which is free to assume the *trans* configuration. It is concluded that the stage of activation is the slowest of the series of reactions, and is the one of which the velocity is measured.

F. G. W.

**Oxidation of Fumaric and of Maleic Acid to Tartaric Acid.** N. A. MILAS and E. M. TERRY (*J. Amer. Chem. Soc.*, 1925, **47**, 1412—1418).—Fumaric or maleic acid (86 g.), or sodium hydrogen maleate to which an equivalent of hydrochloric acid has been added, in water (140—150 c.c.) is heated at  $50^\circ$  with sodium or potassium chlorate (113 g.) and 10 c.c. of a 1% solution of osmium tetroxide, for 5—9 hrs. (cf. Hofmann, Ehrhart, and Schneider, A., 1913, ii, 609). The catalyst is recovered by extraction with benzene, and attention is directed to its volatility and destructive action on mucous membranes, especially the eyes. Completion of the reaction is indicated by the stability of a test portion of the reaction mixture, after removal of the catalyst and neutralisation to litmus, to dilute bromine water in presence of excess of sodium bromide; decolorisation should not take place in less than 5 mins. The respective products, racemic and mesotartaric acids, each containing not more than 1% of the other isomeride, are obtained in a yield of 97—99.5%, and are isolated by precipitating the barium salts from neutral solution, followed by decomposition with an equivalent of sulphuric acid.

F. G. W.

**Inversion Phenomena. Stereochemistry of the Tetrahedral Carbon Atom.** R. KUHN and F. EBEL (*Ber.*, 1925, **58**, [B], 919—932).—In confirmation of Lossen's observations (A., 1906, i, 798) it is found that the addition of hypochlorous acid to maleic

acid yields exclusively the chloromalic acid, m. p.  $145^{\circ}$ , which loses hydrogen chloride in alkaline solution and passes quantitatively into fumarylglycidic acid, m. p.  $209^{\circ}$ . Since the latter acid is resolvable into its optical antipodes by means of morphine it is to be regarded as *trans*-oxidoethylene- $\alpha\beta$ -dicarboxylic acid. The *morphine* salt of the *d*-acid has m. p.  $180^{\circ}$  (decomp.),  $[\alpha]_D^{20} - 76.8^{\circ}$ . *d-trans-Oxidoethylene- $\alpha\beta$ -dicarboxylic acid*, m. p.  $180^{\circ}$  (corr., decomp.),  $[\alpha]_D^{18} + 100^{\circ}$  in aqueous solution, and the *di-ammonium* salt are described. *l-trans-Oxidoethylene- $\alpha\beta$ -dicarboxylic acid*, prepared from *d*-tartaric acid, has m. p.  $180^{\circ}$ ,  $[\alpha]_D^{18} - 100^{\circ}$  in water. Contrary to the statements of Lossen (*loc. cit.*) and Dakin (A., 1922, i, 143), the addition of hypochlorous acid to fumaric acid does not proceed homogeneously; after cautious treatment of the product with alkali hydroxide and separation of barium fumarylglycidate the mother-liquors contain *chloromalic acid* II, m. p.  $153.5^{\circ}$  (more conveniently prepared by the action of hydrochloric acid on *cis*-oxidoethylene- $\alpha\beta$ -dicarboxylic acid) which passes when treated more drastically with sodium hydroxide into *cis-oxidoethylene- $\alpha\beta$ -dicarboxylic acid*, m. p.  $149^{\circ}$ , of which the *potassium hydrogen* salt ( $+H_2O$ ), *calcium* salt ( $+2H_2O$ ), *barium* salt ( $+2H_2O$ ), and *silver* salt are described. Attempts to resolve the acid into its optical antipodes by means of alkaloids were unsuccessful; *morphine hydrogen cis-oxidoethylene- $\alpha\beta$ -dicarboxylate* has m. p.  $180^{\circ}$  (decomp.),  $[\alpha]_D^{20} - 80.8^{\circ}$ . The halogenomalic acids differ very greatly in the readiness with which the halogen atom is replaced by the hydroxy group under the influence of aqueous sodium hydroxides, the half periods under identical conditions for bromomalic acid I, chloromalic acid I, *bromomalic acid* II (m. p.  $136^{\circ}$ ), and chloromalic acid II being  $>0.5$ , 18, 600, and about 200,000 mins. respectively. A method is thus afforded for the analysis of mixtures of the chloromalic acids.

Treatment of the *trans*-glycidic acid with boiling water gives a mixture of 37% of *r*-tartaric and 63% of *mesotartaric* acids (cf. Lossen, *loc. cit.*). The *cis*-acid, on the other hand, in aqueous or alkaline solution yields exclusively *r*-tartaric acid, the change being thus comparable with the homogeneous action of hypochlorous acid on maleic acid. It appears that *cis*-compounds add homogeneously whereas mixed products arise from *trans*-substances. The exclusive production of *r*-tartaric acid from the *cis*-acid is also remarkable since, on stereochemical grounds, the formation of *mesotartaric* acid would be predicted. The fragments of the ring do not therefore appear ultimately in vicinal positions. Lossen's chloromalic acid, m. p.  $145^{\circ}$ , is transformed by water into a mixture of *r*- and *meso*-tartaric acid, whereas the chloromalic acid II, m. p.  $153.5^{\circ}$ , yields exclusively *mesotartaric* acid. It is therefore possible to convert *cis*-oxidoethylene- $\alpha\beta$ -dicarboxylic acid directly into *r*-tartaric acid or indirectly through chloromalic acid II into *mesotartaric* acid. The conception of Werner and Pfeiffer that the addition of two hydroxy groups in the *cis*-position during the oxidation of fumaric and maleic acid depends on the intermediate formation of *cis*-oxidoethylene- $\alpha\beta$ -dicarboxylic acid cannot be maintained.

The bearing of the authors' results on the stereochemistry of



$\alpha\beta$ -diols (Nametkin, A., 1923, i, 811), sugars, and the Beckmann transformation of oximes (cf. Meisenheimer, A., 1922, i, 152) is discussed in detail. The possibility of secondary changes is also considered; these are divided into changes of the first type in which unstable molecular complexes produced during the reaction undergo transformations which are not shown by the preformed molecule under identical external conditions, and those of the second type which are suffered by the final products of the reaction and can therefore be demonstrated by control experiments. H. W.

### Labile Nature of the Halogen Atom in Organic Compounds.

**XI. Halogenation of Ethyl Acetylsuccinate.** A. K. MACBETH and D. TRAILL (*J. Chem. Soc.*, 1925, **127**, 1118—1122).—Reduction of the halogen atom in the  $\alpha$ -position in 1:3-ketonic esters by means of hydrazine has been applied to halogenated acetylsuccinic esters. Bromination of ethyl acetylsuccinate, by drawing air and bromine vapour through the cooled ester, gave a product containing about 26% of the  $\alpha$ -bromo derivative. When the bromination is conducted in chloroform solution, the product is mainly the  $\gamma$ -derivative, the formation of this being attributed to the migration of the halogen atom from the  $\alpha$ -position which it first enters, induced by the presence of hydrobromic acid. When ethyl acetylsuccinate is chlorinated with sulphuryl chloride, *ethyl  $\alpha$ -chloroacetylsuccinate*, b. p. 140—142°/12 mm.,  $n_D^{20}$  1.4420, is formed; the  $\alpha$ -chloro ester is almost quantitatively reduced by hydrazine hydrate, with the formation of ethyl 3-methyl-5-pyrazolone-4-acetate, and evolution of nitrogen. Phenylhydrazine reacts with ethyl  $\alpha$ -chloroacetylsuccinate to yield *ethyl  $\beta$ -carbethoxy- $\gamma$ -benzeneazo- $\Delta^8$ -pentenoate*,  $\text{CMe}(\text{N}:\text{NPh})\text{:C}(\text{CO}_2\text{Et})\text{:CH}_2\text{:CO}_2\text{Et}$ , m. p. 188°, which on hydrolysis with alcoholic potassium hydroxide forms  *$\gamma$ -benzeneazo- $\Delta^8$ -pentenoic acid*,  $\text{CMe}(\text{N}:\text{NPh})\text{:CH}\cdot\text{CH}_2\text{:CO}_2\text{H}$ , m. p. 164—165° (decomp.). Ethyl  $\alpha$ -bromoacetylsuccinate also reacts with phenylhydrazine, but none of the compounds obtained from the chloro-ester could be isolated.

By the action of chlorine on potassium *acinitromalonic* ester in aqueous solution, there is produced *ethyl chloronitromalonate*, b. p. 127°/8 mm., which reacts with hydrazine hydrate to form the hydrazide of ethyl chloronitroacetate, scarcely any nitrogen being evolved. Alcoholic ammonia reacts similarly, yielding the corresponding ammonio derivative. Polarity effects are here manifested, since it has been shown previously (T., 1922, **121**, 911) that the strongly positive bromine atom is readily removed by reduction with hydrazine, whereas in the chloro-ester the halogen atom is less positive, and the carboethoxy group is eliminated. C. J. S.

### Stereochemistry of $\alpha\delta$ -Anhydrotetrahydroxyadipic Acids.

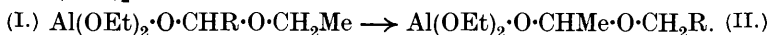
P. A. LEVENE and H. S. SIMMS (*J. Biol. Chem.*, 1925, **63**, 351—363).—Whereas the dissociation constants of the normal saccharic acids are almost identical, those of their  $\alpha\delta$ -anhydro derivatives fall into two groups corresponding to a *cis* and *trans* configuration; application of the formula of Bjerrum (A., 1923, i, 1059) to the

values determined for the two dissociation constants of each of these acids indicates a considerably greater distance between the carboxyl groups of the *trans* acids than between those of the *cis* configuration. The  $\alpha\delta$ -anhydro acids show neither mutarotation nor lactone formation. Saccharic acid has  $p_{K_1}$  3.24,  $p_{K_2}$  4.12; mucic acid,  $p_{K_1}$  3.19,  $p_{K_2}$  3.99; allomucic acid,  $p_{K_1}$  3.30,  $p_{K_2}$  4.16. Of the *cis* acids,  $\delta$ -anhydrosaccharic acid has  $p_{K_1}$  1.98,  $p_{K_2}$  4.94;  $\alpha\delta$ -anhydromucic acid,  $p_{K_1}$  2.02,  $p_{K_2}$  4.53. Of the *trans* configuration,  $\alpha\delta$ -anhydromannosaccharic acid has  $p_{K_1}$  2.81,  $p_{K_2}$  3.80;  $\alpha\delta$ -anhydro-iodosaccharic acid,  $p_{K_1}$  3.03,  $p_{K_2}$  4.00. C. R. H.

**Mucic Acid.** E. KHOTINSKA and (MME.) T. EPIFANOVA (*Bull. Soc. chim.*, 1925, [iv], **37**, 548—554).—When aqueous mucic acid is neutralised with methylamine, evaporation and distillation yield the methylamide of 1-methylpyrrole-2-carboxylic acid, together with a little 1-methylpyrrole. It is considered that the former is produced from the methylamine salt of the half methylamide of mucic acid,  $\text{NHMe}\cdot\text{CO}\cdot[\text{CH}\cdot\text{OH}]_4\cdot\text{CO}_2\text{NH}_3\text{Me}$  (I), which is formed from mucolactone which is assumed to be present in the mucic acid as impurity. In confirmation of this view, it is shown that a compound, which is regarded as I, is obtained on neutralisation of mucolactone with methylamine; with hydrochloric acid, an acid precipitate is formed, from which boiling sodium hydroxide eliminates methylamine, whilst dry distillation yields the methylamide of 1-methylpyrrole-2-carboxylic acid, accompanied by very little 1-methylpyrrole. A mucic acid solution prepared at  $0^\circ$  is heated, and by titration with alkali the amount of lactonisation is determined (cf. Hjelt, A., 1896, i, 596), but the quantity of sodium (or barium) hydroxide required to neutralise a solution of pure mucic acid, free from lactone, is appreciably less than the theoretical. With *N*-sodium hydroxide, mucic acid gives the slightly soluble anhydrous sodium salt, but the salt is more soluble if made from freshly-prepared mucic acid. A hydrated *sodium* salt is also described. F. M. H.

**Exchange of Functional Groups between Two Molecules. Passage of the Alcoholic Function into the Aldehydic Function and Inversely.** A. VERLEY (*Bull. Soc. chim.*, 1925, [iv], **37**, 537—542).—When an aldehyde is treated with excess of ethyl alcohol in presence of aluminium (or magnesium) ethoxide, the principal reaction is represented by the equation  $\text{R}\cdot\text{CHO} + \text{Me}\cdot\text{CH}_2\cdot\text{OH} = \text{R}\cdot\text{CH}_2\cdot\text{OH} + \text{Me}\cdot\text{CHO}$ , whilst Titschenko's reaction,  $2\text{R}\cdot\text{CHO} = \text{R}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}_2\text{R}$ , is secondary. Thus citronellal and ethyl alcohol yield acetaldehyde and, after acidification, citronellol, together with ethyl citronellate and citronellyl citronellate; some terpenes and sesquiterpenes are produced, but little resin. By this method, cinnamyl alcohol may be prepared from cinnamaldehyde. From the products obtained by reaction of geraniol and butaldehyde in presence of geranyl aluminate, it is concluded that the exchange of functional groups first yields citral and butyl alcohol, whilst by Titschenko's reaction are produced butyl butyrate,

geranyl geranate, geranyl butyrate, and butyl geranate. It is suggested that the catalytic cycle comprises four stages, of which the first consists in the formation of the organo-metallic derivative of a hemi-acetal (I), and the second in migration of the group  $\cdot\text{O}\cdot\text{Al}(\text{OEt})_2$ , thus :



Compound II dissociates to give  $\text{Me}\cdot\text{CHO} + \text{CH}_2\text{R}\cdot\text{O}\cdot\text{Al}(\text{OEt})_2$ ; the latter by reaction with ethyl alcohol forms  $\text{CH}_2\text{R}\cdot\text{OH} + \text{Al}(\text{OEt})_3$ . Analogous mechanisms are assigned to Titschenko's reaction and to Claisen's condensation of benzaldehyde with sodium benzyloxide.

F. M. H.

**Action of Sulphuric Acid and Sulphuric Anhydride on Acetylene Dichlorides.** H. LEPOUSE (*Bull. Soc. chim. Belg.*, 1925, **34**, 133—142).—Sulphuric acid (80—100%) does not react with acetylene dichlorides below 115° and at 120° carbonisation begins. Fuming acid containing 50% of free anhydride acts in the cold to form chlorosulphoacetaldehyde, the *barium* salt of which was isolated. Sulphuric anhydride with the acetylene dichlorides produces in the cold the compound  $\text{SO}_2\langle\begin{smallmatrix} \text{CHCl} \\ \text{—O—} \end{smallmatrix}\rangle\text{CHCl}$  which is hydrolysed by cold water to chlorosulphoacetaldehyde. The potassium salt of the aldehyde on oxidation with cold alkaline hydrogen peroxide gives in solution potassium monochlorosulphoacetate. Continued action of water vapour on the aldehyde converts it (in presence of 60% sulphuric acid) largely into chloroacetaldehyde.

A. COUSEN.

**Catalysis in Acetal Formation.** E. W. ADAMS and H. ADKINS (*J. Amer. Chem. Soc.*, 1925, **47**, 1358—1367; cf. A., 1923, i, 301).—By the use of ferric chloride (4 g.) as catalyst, a 97% yield of methylal may be obtained from methyl alcohol (2 mols.) and trioxymethylene (1 mol.). Calcium chloride is a more efficient catalyst than ferric chloride in the preparation of acetal. The same equilibrium point is reached whether calcium chloride or hydrogen chloride is used as a catalyst in the preparation of acetals, provided the reaction mixture remains homogeneous in both cases. Larger yields of acetals are obtained when sufficient calcium chloride is present to cause separation of an aqueous salt solution layer, but the greater efficiency of calcium chloride as compared with hydrogen chloride becomes less marked with the higher alcohols and aldehydes. The catalytic power of salts in promoting acetal formation appears to be connected with their ability to form alcoholates. All the known catalysts give acid solutions in water, but it is concluded that hydrogen ion is not the actual catalyst, as, for example, zinc chloride is a less efficient catalyst than calcium chloride. It is suggested that the catalytic activity is seated in the acid radical of the undissociated salt, but is modified by the basic element. The catalysis of 32 acetal condensations was investigated, and the following new acetals were prepared: *n*-butylacetal, b. p. 186°; sec.-butylacetal, b. p. 171°; methylbutylal,

b. p. 114°; *ethylbutylal*, b. p. 143°; *n-propylbutylal*, b. p. 182°; *isopropylbutylal*, b. p. 164°; *isobutylbutylal*, b. p. 203°; *isopropylpropylal*, b. p. 146.5°; *ethylisobutylal*, b. p. 138°; *isopropylisobutylal*, b. p. 158°; *isopropylfurfurylal*, b. p. 201°; *isopropylheptylal*, b. p. 240°; *benzylidenedi-n-butyl ether*, b. p. 262°; and *benzylidenediisobutyl ether*, b. p. 255°. A method for preparing *tert.*-butyl alcohol from *isobutyl* alcohol, through *isobutylene*, is described.

F. G. W.

**Relation of Structure, Affinity, and Reactivity in Acetal Formation.** H. ADKINS and E. W. ADAMS (*J. Amer. Chem. Soc.*, 1925, 47, 1368—1381).—The rates of reaction and equilibrium points of 32 acetal condensations are recorded, the reaction mixtures being in all cases 1 mol. of alcohol, 0.091 mol. of aldehyde, and 0.000465 g. of hydrogen chloride as catalyst. The velocity constants were calculated as for bimolecular reactions, and from them the decreases in free energy ( $\Delta F$ ) in the formation of acetal from aldehyde and alcohol were obtained, the affinity of acetal formation being greater the smaller the value of  $\Delta F$ . The affinity of acetal formation from acetaldehyde and the following alcohols decreases in the order: *isobutyl*, *n-butyl*, phenylethyl, methyl, *n-propyl*, ethyl, benzyl, *sec.*-butyl, *isopropyl*, *isoamyl*, *tert.*-butyl, and *tert.*-amyl alcohols. From ethyl alcohol and various aldehydes the similar order is *n*-butaldehyde, propaldehyde, acetaldehyde, *isobutaldehyde*, *m*-nitrobenzaldehyde, furfuraldehyde, benzaldehyde, cinnamaldehyde, and heptaldehyde. The same order is preserved with *isopropyl* alcohol, except that heptaldehyde, cinnamaldehyde, and benzaldehyde come after furfuraldehyde, in that order, *m*-nitrobenzaldehyde not being recorded. The difference in affinity between adjacent members of the series of aldehydes becomes less as the series is ascended. A decrease in affinity is observed when carbon atoms or a phenyl group are substituted for hydrogen atoms of the carbinol group. Similar substitution on the  $\beta$ -carbon atom of alcohols has little effect, but causes a decrease in the case of aldehydes. The highest affinities were observed when there are four carbon atoms on either the alcohol or aldehyde side of the acetal, and the lowest when the aldehyde has a double bond in the  $\beta\gamma$  position, as in benzaldehyde, cinnamaldehyde, and furfuraldehyde. The velocity of acetal formation is least with methyl alcohol, *n*-butyl alcohol being next, whilst secondary and especially tertiary alcohols react much more rapidly. Of the aldehydes examined, butaldehyde forms acetals the most slowly, whilst furfuraldehyde, benzaldehyde, cinnamaldehyde, and heptaldehyde react hundreds of times more rapidly. The results are discussed with particular reference to the conclusions of Derick (cf. A., 1911, ii, 712), and to current electronic theories.

F. G. W.

**Optimum Conditions for the Preparation of Keten from Acetone.** C. D. HURD and W. H. TALLYN (*J. Amer. Chem. Soc.*, 1925, 47, 1427—1430; cf. A., 1923, i, 312).—Keten is obtained in a yield of 35—40%, by passing acetone through a "pyrex" tube heated at 695—705°, the length of the (electric) furnace being

80 cm., at a rate of about 5 c.c. per min. From 25% to 40% of the acetone introduced is decomposed. No keten is obtained if the heated tube is of iron. F. G. W.

**Ketens. L. Additive and Polymerisation Reactions of Dimethylketen.** H. STAUDINGER (*Helv. Chim. Acta*, 1925, 8, 306—332).—**I. New Compounds of Dimethylketen and Carbon Dioxide.** [With F. FELIX and H. HARDER.]—Dimethylmalonic anhydride is prepared in good yield by the action of acetic anhydride and a trace of sulphuric acid on dimethylmalonic acid followed by removal of mineral acid by barium carbonate and of excess of anhydride in a vacuum, or, more simply, by the protracted action of acetic anhydride on dimethylmalonic acid. It decomposes at 100° in a sealed tube almost quantitatively into tetramethylcyclobutanedione, whereas in the presence of a little trimethylamine at 70—80° it affords “*tetramethylacetonedicarboxylic anhydride*” [ $\beta$ -keto- $\alpha\gamma\gamma$ -tetramethylglutaric anhydride], m. p. 78°, in 90% yield. This compound decomposes into carbon dioxide and dimethylketen when strongly heated. Its constitution is established by its decomposition by water and alkali hydroxides or aniline into dimethylmalonic and isobutyric acids or their derivatives. It is transformed by bromine into dimethylmalonyl bromide. It is converted by the successive action of hydrogen chloride and aniline in the presence of benzene into dimethylmalonanilic acid and isobutyranilide and by hydrogen chloride and alcohol into tetramethylcyclobutanedione. With phenylhydrazine it affords the phenylhydrazone of tetramethylcyclobutanedione. It is also formed by the action of carbon dioxide on a concentrated ethereal solution of dimethylketen containing a trace of trimethylamine at -80°. During the latter reaction a compound,  $C_{14}H_{18}O_7$ , m. p. 132° (decomp.) [probably a mixed anhydride of  $\beta$ -keto- $\alpha\gamma\gamma$ -tetramethylglutaric and dimethylmalonic acids since it yields dimethylketen and carbon dioxide when strongly heated and  $\beta$ -keto- $\alpha\gamma\gamma$ -tetramethylglutaric anhydride, tetramethylcyclobutanedione, and dimethylketen when cautiously heated in a vacuum at 120—130°], and a substance,  $C_{19}H_{24}O_{10}$ , are also produced.

**II. Additive Products of High Molecular Weight from Dimethylketen and Carbimides or Carbon Disulphide.** [With F. FELIX and E. GEIGER.]—Dimethylketen combines with certain carbimides (methyl- and *p*-methoxyphenyl-carbimide and methyl- and allyl-thiocarbimide are exceptions) and with carbon disulphide in the presence of trimethylamine giving products which are chemically analogous with those obtained from carbon dioxide but different physically in that they are highly polymerised (mol. wt. 2000—6000) and yield colloidal solutions. Dimethylketen and phenylcarbimide at -80° combine in the molecular ratios, 1:4 and 2:3, yielding the compounds,  $C_{32}H_{26}O_5N_4$  and  $C_{29}H_{27}O_5N_3$ ; even in the presence of an excess of phenylcarbimide, the dimethylketen becomes highly polymerised to a certain extent. Dimethylketen (2 mols.), phenylcarbimide (2 mols.), and carbon dioxide (1 mol.) yield the compound  $C_{23}H_{22}O_6N_2$ . The substances

$C_{34}H_{32}O_5N_2$  and  $C_{26}H_{26}O_9N_4$ , softening at  $215^\circ$  and  $145^\circ$ , respectively, are derived from dimethylketen (2 mols.) and  $\alpha$ -naphthylcarbimide (2 mols.), and dimethylketen (3 mols.) and *p*-nitrophenylcarbimide (2 mols.), respectively. All these substances decompose into dimethylketen and the carbimide when heated. They are transformed by alkali hydroxide in alcoholic solution into dimethylmalonanilic acid, isobutyranilide, and the corresponding urethane. Dimethylketen (5 mols.) and carbon disulphide (2 mols.) give the compound  $C_{22}H_{30}O_5S_4$ , decomp.  $160^\circ$ , whereas dimethylketen (4 mols.), carbon disulphide (2 mols.), and carbon dioxide (1 mol.) afford the substance  $C_{19}H_{24}O_6S_4$ .

[With H. HARDER.]—Dimethylketen (5 mols.) and carbonyl sulphide (2 mols.) yield the compound  $C_{22}H_{30}O_7S_2$ , decomp.  $110^\circ$  after softening at  $90^\circ$ .

**III. Polymerised Products of High Molecular Weight from Dimethylketen.** [With F. FELIX, P. MEYER, and H. HARDER.]—Amorphous *polydimethylketens* of high molecular weight are obtained by the action of a trace of trimethylamine on pure dimethylketen at  $-80^\circ$  or  $-20^\circ$ , in the presence of light petroleum or ether, or by passing dimethylketen vapour into an excess of trimethylamine at  $-80^\circ$ ; the products decompose at temperatures varying from  $100^\circ$  to above  $200^\circ$ . They are depolymerised to dimethylketen when heated, the process taking place most smoothly with the polymerides of highest temperature of decomposition. They readily absorb bromine, are converted by aniline into isobutyranilide and resinous products and by concentrated nitric acid into dimethylmalonic acid and some isobutyric acid. The latter acids are also obtained by the action of hydrogen chloride in ethereal solution. Alcoholic sodium hydroxide solution converts them into tetramethylacetone, isobutyric and dimethylmalonic acids, and an acid, m. p.  $120$ – $121^\circ$ , which has not been fully investigated. They are transformed by successive treatment with ozone and boiling water into acetone and non-volatile products from which a homogeneous material could not be separated. When heated with hydrogen under high pressure they yield non-uniform, oily products.

[With E. STIRNEMANN.]—Keten, when preserved in acetone solution for 1–2 days at  $-80^\circ$ , passes into *polyketen*,  $(C_2H_2O)_4$ , m. p. about  $53^\circ$  (decomp.), which appears to form a link between the crystalline cyclobutanedione derivatives and the colloid-disperse polydimethylketens.

**IV. Constitution of the Highly Polymerised Additive and Polymerisation Products of Dimethylketen.**—In explanation of the differences in the physical properties of the crystalline and colloidal additive and polymerisation products, it is suggested that the former contain closed rings as in the case of  $\beta$ -keto- $\alpha\alpha\gamma\gamma$ -tetramethylglutaric anhydride and analogous substances, whereas in the latter ring closure, probably on account of strain, is impossible and the compounds are thus composed of long chains of units of the type,

$$\cdots [CO \cdot CMe_2 \cdot CO \cdot NR \cdot CO \cdot CMe_2 \cdot CO \cdot NR \cdot CO \cdot CMe_2]_x \cdots$$

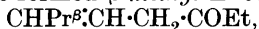
H. W.

**Action of Mixtures of Nitric Acid and Hydrochloric Acid on Acetone.**—W. J. BOYD (*J. Soc. Chem. Ind.*, 1925, **44**, 222T).—Chloroisnitrosoacetone and a mixture of dichlorodinitromethane with what appeared to be chloropicrin, were obtained by treating acetone with mixtures of concentrated hydrochloric acid and nitric acid below 50°, and at 50–80°, respectively. The action of a mixture of fuming nitric acid and sodium chloride on acetone yielded mainly chlorotrinitromethane. L. A. C.

**Action of Calcium Hydride on certain Organic Compounds.**  
**II. Methyl Ethyl Ketone.** C. PORLEZZA and U. GATTI (*Gazzetta*, 1925, **55**, 224–234; cf. A., 1924, i, 1042).—In the action of calcium hydride on methyl ethyl ketone, the resulting condensation products of high boiling point vary in both quality and proportion as the action is prolonged. Just as when other condensing agents, either acid or basic, are used, only one of the possible isomeric homomesitones is produced, namely, CMeEt:CH·COEt; as regards the higher homologues, the results obtained are analogous to those obtained by Ekeley and Hove (A., 1923, i, 997). As with acetone, so with methyl ethyl ketone, calcium constitutes a less efficient condensing agent than its hydride. On diethyl ketone, calcium hydride does not appear to exert any appreciable condensing influence. In general, the results show that condensation by means of calcium hydride, like that effected by calcium carbide (cf. Bodroux and Taboury, A., 1908, i, 854; 1909, i, 766), occurs with compounds containing the group  $\cdot\text{CO}\cdot\text{CH}_3$ . T. H. P.

**Odorants.** H. THOMS (*Arch. Pharm.*, 1925, **263**, 241–273).—

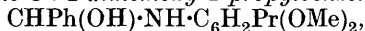
**I. Capacity for Condensation of isoButaldehyde.** [With H. KAHRE.]—From isobutaldehyde, by condensation with the appropriate alcohols in the presence of hydrogen chloride, are obtained the following derivatives: the *diisobutylacetal*, b. p. 94–95°/28 mm.; the *diisoamylacetal*, b. p. 125–127°/28 mm.; the *dibenzylacetal*, b. p. 194°/20 mm. All have an odour of fusel oil. In the presence of 10% sodium hydroxide the aldehyde condenses with various ketones, forming unsaturated ketones, the aliphatic ones being of pleasant odour. With methyl ethyl ketone there is formed  $\beta$ -methyl- $\Delta^7$ -hepten- $\epsilon$ -one,  $\text{CHPr}^8\text{:CH}\cdot\text{COEt}$ , b. p. 167°/772 mm., 53–56°/15 mm., 62–65°/23 mm.,  $d^{20}$  0.8550,  $n_D$  1.44303 (*semicarbazone*, m. p. 174–175°), which gives on addition of bromine an oil, and on catalytic reduction  $\beta$ -methylheptan- $\epsilon$ -one. With diethyl ketone there is formed  $\beta$ -methyl- $\Delta^7$ -octen- $\zeta$ -one,



b. p. 73–77°/19 mm.,  $d^{19}$  0.8628,  $n_D$  1.44533 (*semicarbazone*, m. p. 147–148°), giving on catalytic reduction  $\beta$ -methyloctan- $\zeta$ -one, b. p. 180–185°,  $d^{20}$  0.8353,  $n_D$  1.43479 (*semicarbazone*, m. p. 129°), and on reduction with sodium and alcohol  $\beta$ -methyloctan- $\zeta$ -ol, b. p. 74–79°/18 mm.,  $d^{12}$  0.8402,  $n_D$  1.43850. With methyl propyl ketone there is formed  $\beta$ -methyl- $\Delta^7$ -octen- $\epsilon$ -one, b. p. 68–78°/24 mm.,  $d^{12}$  0.9011,  $n_D$  1.47477 (*semicarbazone*, m. p. 187–188°), giving with acid potassium ferrocyanide a white precipitate, and on reduction with sodium and alcohol  $\beta$ -methyloctan- $\epsilon$ -ol, b. p. 79–84°/14 mm.

With methyl isopropyl ketone there is formed  $\beta\zeta$ -dimethyl- $\Delta\gamma$ -hepten- $\epsilon$ -one, b. p. 68—74°/16 mm.,  $d^{12}$  0.8788,  $n_D$  1.48138 (semicarbazone, m. p. 165°), giving on reduction with sodium and alcohol  $\beta\zeta$ -dimethylheptan- $\epsilon$ -ol, b. p. 173—178°. With acetophenone there is formed phenyl  $\gamma$ -methyl- $\Delta^{\alpha}$ -butenyl ketone, m. p. 137.5°. With *p*-aminoacetophenone there is formed the corresponding *p*-amino derivative, giving a yellow hydrochloride, which was diazotised and coupled with dimethylaniline, giving a solution of 4- $\gamma$ -methyl- $\Delta^{\alpha}$ -pentenoyl-4'-dimethylaminoazobenzene, the hydrochloride of which was isolated in very impure form. On treatment with urethane and hydrochloric acid, isobutaldehyde gives isobutylidenediurethane, m. p. 157°.

**II. New Derivatives of Eugenol.** [With M. KEMP.]—Nitrous acid converts dihydroeugenyl methyl ether (3 : 4-dimethoxypropylbenzene) into 6-nitro-3 : 4-dimethoxypropylbenzene. The corresponding amino compound reacts with potassium cyanate and acid to give the corresponding 6-carbamido compound, m. p. 200—201°; with ammonium thiocyanate and acid to give the 6-thiocarbamido compound, m. p. 193°; and with allyl thiocarbimide to give the *s*-6-allylthiocarbamido compound, m. p. 154°. All are of indifferent odour. The amino compound and its hydrochloride react with aldehydes giving additive compounds or azomethines and their hydrochlorides. The following are described : 6-phenylhydroxymethylamino-3 : 4-dimethoxy-1-propylbenzene,



m. p. 79—80°, and its hydrochloride, m. p. 187—189°; the corresponding 6-benzylidene compound (from the additive compound by the action of zinc chloride),  $\text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_2\text{Pr}(\text{OMe})_2$ , m. p. 85°, and its hydrochloride; the 6-*p*-dimethylaminobenzylidene compound, m. p. 80—81°, and its dihydrochloride, m. p. 206°; the 6-piperonylidene compound, m. p. 112°, and its hydrochloride, m. p. 197—198°; the 6-*o*-hydroxybenzylidene compound, m. p. 118—119°, insoluble in alkali, and its hydrochloride, m. p. 101°; the 6-*p*-methoxybenzylidene compound, m. p. 68—69°, and its hydrochloride, m. p. 135° (the former being prepared from the latter); the additive compound with cinnamaldehyde, m. p. 58—59°, and its hydrochloride, m. p. 195—198°; the 6-cinnamylidene compound, hydrochloride, m. p. 118°; the *p*-dimethylaminocinnamaldehyde additive compound, m. p. 39—40°; and the hydrochloride, m. p. 200—201°.

**III. New Asymmetric Tertiary Alcohols of High Molecular Weight, and the Direction in which they lose Water.** [With B. AMBRUS.]—From methyl nonyl ketone, by the Grignard reaction, various tertiary alcohols have been prepared. All are converted by means of acetic anhydride or sulphuric acid into ethylene hydrocarbons, the structure of the latter being determined by oxidation. In most cases the hydroxyl group removes a hydrogen atom from the largest alkyl group present. The alcohols and hydrocarbons are of faintly aromatic odour. The following substances were prepared : the known methylethylnonylcarbinol, b. p. 126—129°/10 mm.,  $d$  0.8423, which on losing the elements of water yields  $\gamma$ -methyl- $\Delta\gamma$ -dodecene, b. p. 105—107°/12 mm.,  $d$  0.7802, which gives on oxidation *n*-nonoic acid; methyl-*n*-propylnonylcarbinol, b. p.



140—142°/13 mm.,  $d$  0.8406, which on losing the elements of water yields  $\delta$ -methyl- $\Delta^{\delta}$ -tridecene, b. p. 115—117°/10 mm.,  $d$  0.788, which gives on oxidation  $n$ -nonoic acid; methylisopropylnonylcarbinol, b. p. 140—142°/14 mm.,  $d$  0.845 (which contained as by-product a hydrocarbon, b. p. 225—242°/10 mm.), which gives, on losing the elements of water,  $\beta\gamma$ -dimethyl- $\Delta\gamma$ -dodecene, b. p. 116—122°/13 mm.,  $d$  0.7858, giving on oxidation  $n$ -nonoic acid; methylisobutylnonylcarbinol, b. p. 145—150°/13 mm.,  $d$  0.8386, which on losing the elements of water yields  $\beta\delta$ -dimethyl- $\Delta^{\delta}$ -tridecene, which gives on oxidation  $n$ -nonoic acid; phenylmethyl-nonylcarbinol, decomposing on distillation, which on losing the elements of water yields  $\beta$ -phenyl- $\Delta^{\beta}$ -undecene, b. p. 166—170°/11 mm.,  $d$  0.8801, which gives on oxidation  $n$ -nonoic acid and acetophenone; benzylmethyl-nonylcarbinol, b. p. 196—200°/12 mm., 200—203°/14 mm.,  $d$  0.9217, which on losing the elements of water yields  $\beta$ -benzylideneundecane, yellow, b. p. 177—178°/12 mm., 180°/13 mm. (decomp.),  $d$  0.8790, which gives on oxidation methyl nonyl ketone and benzoic acid. B. F.

**New Reaction of the Pentoses.** G. BERTRAND (*Bull. Soc. Chim. biol.*, 1925, 7, 436—439).—A question of priority.

C. P. S.

**Thomas' Naphthol Reaction for Free and Combined Pentoses.** G. DENIGÈS (*Bull. Soc. Chim. biol.*, 1925, 7, 440—442).—A question of priority. The author re-publishes his method of identifying the individual pentoses and hexoses by their reactions with  $\alpha$ - and  $\beta$ -naphthol.

C. P. S.

**Replacement of Reactive Hydrogen Atoms in Sugars, Hydroxy- and Amino-acids by the Triphenylmethyl Residue.** B. HELFERICH, L. MOOG, and A. JÜNGER (*Ber.*, 1925, 58, [B], 872—886; cf. A., 1924, i, 500).— $d$ -Glucose is converted by triphenylmethyl chloride in the presence of anhydrous pyridine at 0° into triphenylmethyl- $\alpha$ - $d$ -glucose, m. p. (+2EtOH) 57—58° after softening at 45° or (dried), decomp. 100° after softening at 60°,  $[\alpha]_D^{25} + 59.6^\circ$  to  $+38.0^\circ$  in pyridine. The downward mutarotation is in harmony with the conception that the triphenylmethyl group is attached to the  $\zeta$  carbon atom, but the ready hydrolysis of the ether by alkali hydroxide as well as by acid is somewhat unexpected. The isolated ether is transformed by acetic anhydride in the presence of pyridine into triphenylmethyl- $\alpha$ - $d$ -glucose tetra-acetate, m. p. 129—131°,  $[\alpha]_D^{25} + 97.4^\circ$  in pyridine, whereas the action of acetic anhydride on the ether which has not been separated from the solution in which it was formed yields triphenylmethyl- $\beta$ - $d$ -glucose tetra-acetate, m. p. 163—164°,  $[\alpha]_D^{19} + 44.8^\circ$  in pyridine. The assignment of the  $\alpha$ - and  $\beta$ -configurations to the tetra-acetates is based on the comparison of their m. p. and specific rotations with those of the glucoses and their penta-acetates. Either compound is converted by phosphorus pentabromide into the known dibromoacetoglucose. Galactose yields triphenylmethyl- $d$ -galactose, m. p. (+2EtOH),

73—75° after softening at 72—73° or ( $+\frac{1}{2}$ EtOH) decomp. 108° after softening at 76°,  $[\alpha]_D^{25} +0.58^\circ$  to  $+2.24^\circ$  in pyridine. Dextrose isopropylidene ether and triphenylmethyl chloride give a syrupy product which is transformed by benzoyl chloride in the presence of pyridine into *triphenylmethyldibenzoyldextrose isopropylidene ether*, m. p. 78—79° (slight decomp.) after softening at 74°,  $[\alpha]_D^{21} -4.5^\circ$  in pyridine, or m. p. 97—99° (decomp.) after softening at 90°,  $[\alpha]_D^{21} -4.0^\circ$  in pyridine (the two substances appear to be produced irregularly under identical conditions). Gluconphenylhydrazide is readily transformed by triphenylmethyl chloride into *triphenylmethyl-d-gluconphenylhydrazide*, decomp. 101° after softening at 93° ( $+2.5\text{H}_2\text{O}$ ),  $[\alpha]_D^{25} +3.0^\circ$  in pyridine (anhydrous),  $[\alpha]_D^{25} +4.8^\circ$  in pyridine. The triphenylmethyl group is readily removed by dilute acids, whereas alcoholic potassium hydroxide converts the compound into *potassium triphenylmethyl-d-gluconate*, decomp. 198—199°,  $[\alpha]_D^{25} +7.7^\circ$  in acetone. The hydrazide is converted by benzoyl chloride in the presence of pyridine into the corresponding *tetrabenzoyl* derivative, m. p. 173° after softening at 168°,  $[\alpha]_D^{15} +36.2^\circ$  in pyridine, from which the triphenylmethyl residue is fairly readily removed by acids.

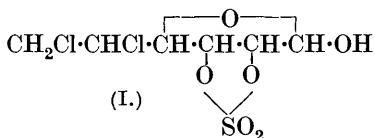
The use of triphenylmethyl chloride can also be extended to hydroxy compounds which do not belong to the sugar group. Thus, ethyl  $\beta$ -hydroxypropionate affords *ethyl  $\beta$ -triphenylmethoxypropionate*, m. p. 104—105°, which is converted by methyl-alcoholic hydrogen chloride (1%) into  $\beta$ -hydroxypropionic acid and by alcoholic potassium hydroxide (5%) into  *$\beta$ -triphenylmethoxypropionic acid*, m. p. 163—164° (the *sodium* salt is described). *p*-Hydroxybenzoic acid gives the monotriphenylmethyl ether of a dimolecular anhydride,  $\text{C}_{33}\text{H}_{24}\text{O}_5$ , m. p. 219—220°. Phenol gives phenyl triphenylmethyl ether, m. p. 103°, in poor yield; in spite of the acidic nature of the parent substance, the ether is comparatively very stable towards alkali hydroxide although readily hydrolysed by acids. During the preparation of these ethers, the formation of an additive *compound* of triphenylcarbinol and hydrogen chloride or triphenylmethyl chloride and water, m. p. 174°, is frequently observed; it is converted by warm ethyl alcohol into triphenylmethyl ethyl ether.

Carbamide and triphenylmethyl chloride in the presence of pyridine at 100° yield *ditriphenylmethylocarbamide*, m. p. 245° after softening at 243°, which is extraordinarily resistant towards alkali hydroxide. Under similar conditions thiocarbamide affords *triphenylmethylothiocarbamide*, m. p. 222° (decomp.). The possibility is thus indicated of protecting the amino groups of amino-acids and peptides by the introduction of the triphenylmethyl complex. Thus ethyl aminoacetate hydrochloride gives *ethyl triphenylmethyl-aminoacetate*, m. p. 114°, which is hydrolysed by cautious treatment with alcoholic potassium hydroxide solution to *triphenylmethyl-aminoacetic acid*, m. p. about 168°, decomp. 180° [the *sodium* and *copper* (also  $+3\text{MeOH}$ ) salts are described]. Since, however, more drastic treatment with alkali hydroxide leads to the elimination of the triphenylmethyl residue, the method appears of limited

applicability. *Ethyl dl- $\alpha$ -triphenylmethylaminopropionate*, m. p.  $100^\circ$ , is converted similarly into *dl- $\alpha$ -triphenylmethylaminopropionic acid* ( $+\frac{1}{2}\text{EtOH}$ ), the *sodium* salt of which is described. *Ethyl glycyltriphenylmethylaminoacetate*, m. p.  $161^\circ$ , *triphenylmethyl-glycylglycine*, m. p.  $180^\circ$  (decomp.) after softening at  $175^\circ$ , and the *sodium* salt of the latter are described.

Diphenylamine and triphenylmethyl chloride yield a *compound*,  $\text{C}_{31}\text{H}_{25}\text{N}$ , m. p.  $240^\circ$ , in which the triphenylmethyl residue appears to replace a nuclear hydrogen atom, since the compound is not hydrolysed by acids or alkali hydroxide, gives no indication of dissociation into radicals, and is not identical with the substance prepared by Wieland and Lecher (A., 1911, i, 569). H. W.

**d-Glucose  $\epsilon\zeta$ -Dichlorohydrin.** B. HELFERICH, G. SPROCK, and E. BESLER (*Ber.*, 1925, **58**, [B], 886—891).— $\alpha$ -Methylglucoside dichlorohydrin sulphate (cf. A., 1921, i, 497) is converted by sodium hydroxide into sodium  $\alpha$ -methylglucoside dichlorohydrin sulphate (cf. A., 1923, i, 654), which when further treated with sodium hydroxide exchanges the halogen atom (presumably) in the  $\zeta$  position for the hydroxy group thus yielding *sodium  $\alpha$ -methylglucoside  $\epsilon$ -chlorohydrin  $\gamma$ -sulphate* ( $+\text{H}_2\text{O}$ ), m. p.  $131^\circ$  (decomp.), anhydrous, m. p.  $135^\circ$  (decomp.),  $[\alpha]_D^{20} +48.9^\circ$  in aqueous solution.  $\alpha$ -Methylglucoside  $\epsilon\zeta$ -dichlorohydrin (A., 1923, i, 655) yields a *diacetate*, m. p.  $110^\circ$ , *dibenzoate*, m. p.  $117^\circ$ ,  $[\alpha]_D^{22} +180.6^\circ$  in pyridine, and *di-p-toluenesulphonate*,  $[\alpha]_D^{22} +95.8^\circ$  in pyridine. Successive treatment of  $\alpha$ -methylglucoside dichlorohydrin sulphate with ammoniacal methyl alcohol and concentrated hydrochloric acid leads to the production of *d-glucose  $\epsilon\zeta$ -dichlorohydrin*, m. p.  $180^\circ$  after darkening at  $168^\circ$ ,  $[\alpha]_D^{17} +180.05$  to  $+126.1^\circ$  in pyridine; the compound is also formed by the action of 12*N*-sulphuric acid on sodium  $\alpha$ -methylglucoside dichlorohydrin sulphate at  $70^\circ$ . Since it yields a non-crystalline *phenylosazone* and *p-nitrophenylosazone*, it must contain a hydroxy group in the  $\beta$ -position. The action of concentrated hydrochloric acid at the atmospheric temperature on  $\alpha$ -methylglucoside dichlorohydrin sulphate leads essentially to the elimination of the methyl group and



production of *d-glucose  $\epsilon\zeta$ -dichlorohydrin  $\beta\gamma$ -sulphate* (I), m. p.  $104\text{—}106^\circ$  (decomp.) after softening at  $103^\circ$ ,  $[\alpha]_D^{20}$  (initial)  $-67.96^\circ$  in water; the substance is slowly mutarotatory in aqueous solution, but the process is accompanied by hydrolysis. It is readily transformed by sodium hydroxide into *sodium d-glucose  $\epsilon\zeta$ -dichlorohydrin* (?)  $\gamma$ -sulphate.

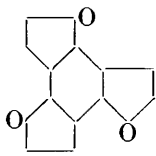
The presence of the chlorine atoms in the  $\epsilon\zeta$ -positions in the series of compounds is established by the observation that *d-glucose  $\epsilon\zeta$ -chlorohydrin* contains a free hydroxy group in the  $\beta$ -position and the probability that vicinal hydroxy groups are involved in the esterification by sulphuric acid. H. W.

**Lactose.** E. O. WHITTIER (*Chem. Reviews*, 1925, **2**, 85—125).

**Polysaccharides. XXXIII. New Sugar, Lichotriose, from Lichenin.** P. KARRER and H. LIER (*Helv. Chim. Acta*, 1925, 8, 248—249).—Lichenase, freed from cellobiase by fractional adsorption of the latter on aluminium hydroxide in weak acetic acid suspension, only attacks lichenin (reserve-cellulose) (cf. A., 1924, i, 471). When lichenin is so treated until about half is saccharified it is broken down into, chiefly, dextrose and *lichotriose*, isolated as the *osazone*, m. p. 178°,  $[\alpha]_D -46.47^\circ$  in alcohol. W. A. S.

**Electrolysis of a Colloidal Solution of Hemicellulose.** E. LENOBLE (*Chim. et Ind.*, 1925, 13, 560).—When the alkaline waste liquors from “viscose” manufacture are electrolysed the volume of the hydrogen generated is at first much more than twice that of the oxygen. Eventually the normal ratio is attained. Carbon dioxide is produced, so that the sodium hydroxide present is converted gradually into sodium carbonate. As this proceeds, hemicellulose is thrown out of solution. It is supposed that the cellulose present is oxidised completely. No hydrocarbons are produced by reduction at the cathode. W. A. S.

**Structure of Humic Acids and Coal.** J. MARCUSSE (Ber., 1925, 58, [B], 869—872).—Autoxidation of furfuryl alcohol in the presence of 1% sodium hydroxide solutions yields humic acids, which are soluble in dilute sodium hydroxide solution or ammonia. It is therefore suggested that the humic acids contain furan nuclei so united as to produce a six-membered ring (I), thus accounting for the production from them of benzenecarboxylic acids, phenols, protocatechuic acid, nitrophenols, chloroanil, etc. The presence of the furan nucleus in humic acids, lignin, lignite, and coal is indicated further by the observation that when these substances are destructively distilled and the gases evolved are passed through alcoholic hydrogen chloride solution, solid black condensation products are formed which are insoluble in alkali hydroxide, whereas the aqueous distillate gives the reactions characteristic of furan aldehydes and yields humic acids soluble in alkali hydroxides when evaporated to dryness with hydrochloric acid.



(I).

The natural transformation of humic acids into lignite can be imitated by heating them at 250° in the absence of air and presence of mineral oil, whereby pyrohumic anhydrides and humic ketones are formed. Similarly the conversion of lignite into coal can be effected by heating under pressure.

Fischer and Schrader's observation that pyrrole derivatives are produced by the distillation of natural, in contrast to artificial, humic acids is not to be regarded as evidence against the presence of the furan ring; the natural acids contain nitrogen, owing to which the furan substances are transformed into pyrroles.

H. W.

**Oxidation of Coal and of its Naphthalene Extracts.** M. OSWALD and R. PINTA (*Chim. et Ind.*, 1925, 13, 547—551).—Further experiments on Lorraine coals show that the proportion soluble in

naphthalene falls from 12—14% to 6—7% when the coal is oxidised (as on the surface of a lump). It appears that the oxidation affects chiefly the constituents that dissolve in naphthalene, and that it produces products no longer extractable. [Cf. *B.*, 1925, 485.]

W. A. S.

**Action of Nitrous Acid on Aliphatic Primary Amines, and Formation of Aliphatic Diazo Compounds.** J. BERK and P. H. HERMANS (*Chem. Weekblad*, 1925, 22, 270—272).—A theoretical paper outlining a scheme for the mechanism of the reaction. The first product is an amine nitrite, which loses water with formation of a diazo base, this product undergoing condensation to a ring compound, which loses the two nitrogen atoms, the carbon ring so formed opening by addition of the elements of water. A polymethylene ring may by this mechanism be “widened” or “contracted,” and unsaturated hydrocarbons as well as alcohols may result. An alcohol is not the direct product of the reaction.

S. I. L.

**Molecular Compounds of the Amino-acids and Diketo-piperazines.** I. P. PFEIFFER and O. ANGERN (*Z. physiol. Chem.*, 1925, 143, 265—271).—Molecular compounds of glycine anhydride and anthranilic acid (1 : 2); glycine anhydride and salicylic acid (1 : 2); sarcosine anhydride and *p*-aminobenzoic acid (1 : 1); sarcosine anhydride and anthranilic acid (1 : 2); sarcosine anhydride and skatole (1 : 2) have been prepared. The residual valencies which allow of the formation of such molecular compounds probably play an important part in the structure of the proteins. H. D. K.

**Isolation of a Product of Hydrolysis of the Proteins Hitherto Undescribed.** S. B. SCHRYVER, H. W. BUSTON, and D. H. MUKHERJEE (*Proc. Roy. Soc.*, 1925, B, 98, 58—65).—By the application to isinglass of the “carbamate” method for the separation of the products of protein hydrolysis (this vol., i, 89), the glycine fraction was found to contain a *base* which, after separation as phosphotungstate and purification by precipitation with mercuric chloride, was isolated as a deliquescent, cream-coloured powder,  $C_6H_{14}O_3N_2$ . It is very soluble in water, but insoluble in almost all organic solvents; it dissolves in a boiling mixture of pyridine and glacial acetic acid. It is strongly basic and forms salts which are extremely soluble in water. The *picrate*, *nitrate*, *copper* salt, and *chloroaurate* are described. The *base* is not precipitated by silver salts even in alkaline solution, and, in the ordinary process for the separation of the hexone bases, is therefore found in the lysine fraction. The base did not melt without decomposition, and was optically inactive owing to the method of isolation. The *tribenzoyl* compound has m. p. 68—69°. From the formation of this compound, the behaviour of the base when treated with nitrous acid, the presence of a carboxyl group, and its existence as a hydroxy compound and not as a lactone, it is suggested that the base is  $\alpha$ -diamino- $\beta$ -hydroxy-*n*-hexoic acid. The authors name it “oxylysine.” “Oxylysine” has also been isolated from the alkali-soluble protein of oats, and a method of determination based

on the method of isolation has demonstrated its presence in fish gelatin, the albumin of cabbage leaf, and edestin. It appears to be absent from (or present only in traces in) the hydrolysis products of gelatin of mammalian origin, casein, fibrin, and egg-white.

C. P. S.

**Transformation of Peptide-like Substances. IV. Hydrolytic Deamination of Amino-acids.** M. BERGMANN, A. MIEKELEY, F. WEINMANN, and E. KANN (*Z. physiol. Chem.*, 1925, **143**, 108—127).—Methyl 2-phenyloxazoline-4-carboxylate (this vol., i, 235) is transformed into the *methyl* ester of *O*-benzoylserine, m. p. 130—132°, by heating in aqueous solution for one hour at 100°. When this ester is treated with one mol. of sodium hydroxide, it is decomposed into ammonium benzoate and an oil; with excess of sodium hydroxide (2.5 mols.), on the other hand, it is transformed into *N*-benzoylserine. Strong aqueous ammonia converts it into the *amide* of *N*-benzoylserine, m. p. 164°.

Hydrolysis of anhydroglycylserine anhydride I (this vol., i, 235) with 5*N*-hydrochloric acid yields ammonia, glycine, and an *acid*, C<sub>5</sub>H<sub>7</sub>O<sub>4</sub>N, m. p. 90°; the latter yields glycine on hydrolysis with concentrated hydrochloric acid.

Ethyl 2-phenyloxazoline-5-acetate is converted by dilute hydrochloric acid into  $\gamma$ -amino- $\beta$ -benzoxybutyric acid (*picrate*, m. p. 197° decomp.; *ethyl* ester, m. p. 102° indef.) and by ammonia and alkalis into ethyl  $\gamma$ -benzamido- $\beta$ -hydroxybutyrate. On heating with excess of 5*N*-hydrochloric acid, 2-phenyloxazoline-5-acetamide (A., 1924, i, 18) is converted into  $\gamma$ -amino- $\beta$ -benzoxybutyric acid; the different behaviour with 1 mol. of acid has been described previously (*loc. cit.*).

The colour reactions described by Abderhalden and Komm (this vol., i, 175) are not specific for diketopiperazine compounds.

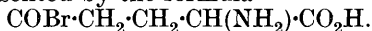
E. S.

**Racemisation. Action of Alkali on *d*-Alanyl-*d*-alanine Anhydride.** P. A. LEVENE and M. H. PFALTZ (*J. Biol. Chem.*, 1925, **63**, 661—668).—When *d*-alanyl-*d*-alanine anhydride is dissolved in 1% solution in *N*-sodium hydroxide the initial optical rotation falls rapidly and almost parallel with the increase of the amino-nitrogen, until equilibrium is reached when the latter amounts to 50% of the total nitrogen; on hydrolysing the resulting solution of the peptide with hydrochloric acid, almost optically pure *d*-alanine is obtained. If the solution contains only one equivalent of alkali, the change in rotation is much more rapid than the hydrolysis, and the alanine obtained by hydrolysing the solution after equilibrium has been attained is largely racemised. The degree of racemisation is therefore dependent on the time during which the unhydrolysed anhydride is exposed to the action of alkali. The results suggest that the racemisation of proteins by alkali may be due to the presence of ketopiperazides in the molecule.

C. R. H.

**Glutathione. Synthesis.** C. P. STEWART and H. E. TUNNICLIFFE (*Biochem. J.*, 1925, **19**, 207—217).—Glutathione has been

synthesised by two methods: (a) The acid bromide of hydantoinpropionic acid, which was prepared by the action of phosphorus tribromide on hydantoinpropionic acid, was coupled with cystine dimethyl ester, yielding di(hydantoinpropionyl)cystine. By boiling the latter with calcium hydroxide, the hydantoin ring was opened. The uramino-acid thus obtained was converted into the amino-acid by treating it with potassium nitrite and precipitating the dipeptide with mercuric sulphate. This preparation is partially racemised  $[\alpha]_{\text{H}_2\text{O}}^{15} = -30.6^\circ$ . (b) Glutamyl monobromide was prepared by treating a suspension of glutamic acid in dry toluene with phosphorus tribromide. This compound was coupled with cystine dimethyl ester, which yielded diglutamylcystine (glutathione), giving all the chemical properties of glutathione isolated by Hopkins (A., 1921, i, 635),  $[\alpha]_{\text{H}_2\text{O}}^{15} -97.4^\circ$  (natural glutathione in aqueous solution  $= -98.3^\circ$ ; in 10% hydrochloric acid  $-89.2^\circ$ ). On coupling glutamyl monobromide with aniline, glutamyl monoanilide hydrochloride,  $\text{NHPh}\cdot\text{C}_5\text{H}_8\text{O}_3\text{N}\cdot\text{HCl}$ , colourless spear-head crystals, was obtained. On oxidising the monoanilide in alkaline solution with hydrogen peroxide succinilic acid was obtained. The acid bromide from which the anilide was derived is therefore represented by the formula



The above methods are generally applicable to the synthesis of dipeptides of the type  $\text{CHRR}'\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\text{CO}_2\text{H}$ .

S. S. Z.

**Structure of the Protein Molecule.** E. ABDERHALDEN and E. KOMM.—(See i, 848.)

**Oxidation of Polypeptides and of 2 : 5-Diketopiperazines.** E. ABDERHALDEN and E. KOMM.—(See i, 848.)

**Brominated Keratin and Hydroxykeratin.** II. Z. STARY.—(See i, 847.)

**Limits of Precipitability of Gelatin by Tannin.** J. A. SMORODINCEV and A. N. ADOVA.—(See i, 847.)

**Formation of Carbamide from Ammonium Hydrogen Carbonate Solution at the Body Temperature.** F. FICHTER and W. KERN (*Helv. Chim. Acta*, 1925, 8, 301—306; cf. Fichter, Steiger, and Stanisch, A., 1919, i, 69).—Appreciable quantities of carbamide are formed in 8—14 days in moderately dilute solutions of ammonium hydrogen carbonate in pure water at  $37^\circ$  in the presence of suitable catalysts. The yields increase with increasing concentration of the solution and with increasing absorptive power of the catalyst. Animal charcoal and spongy platinum are effective. The presence of iron in the charcoal does not appear to be important.

H. W.

**Tetra-alkylsuccinimides and their Pharmacological Action.** A. W. DOX (*J. Amer. Chem. Soc.*, 1925, 47, 1471—1477).—*Azomethylethylacetoneitrile*,  $\text{CMeEt}(\text{CN})\cdot\text{N}\cdot\text{N}\cdot\text{CMeEt}\cdot\text{CN}$ , m. p.  $57^\circ$ , was obtained by the oxidation, with bromine water, of the crude

corresponding hydrazo compound obtained by the action of hydrazine sulphate and sodium cyanide on methyl ethyl ketone (cf. Thiele and Heuser, A., 1896, i, 340). On hydrolysis with 75% sulphuric acid, this yielded *s.-dimethyldiethylsuccinic acid*, m. p. 147—148° with formation of the *anhydride*, b. p. 250—255°. *dl.-α-Methylbutyric acid* was always formed during the hydrolysis of the above nitrile. *s.-Dimethyldiethylsuccinimide*, m. p. 93—94°, was prepared by heating the ammonium salt of the above dimethyldiethylsuccinic acid in a sealed tube at 170—175°. *Azodiethylacetoneitrile*, m. p. 74—75°, obtained similarly, afforded tetraethylsuccinic acid, m. p. 150—151° (cf. Walker and Walker, T., 1905, 87, 965), and *tetraethylsuccinonitrile*, m. p. 47°, together with  $\alpha$ -ethylbutyric acid. *Tetraethylsuccinimide*, m. p. 104°, was obtained by heating the acid with an equal weight of ammonium carbonate in a sealed tube at 175°. Intraperitoneal injection of solutions of the sodium salts of the above succinimides into white mice produced convulsions and general symptoms resembling those of strychnine poisoning, without any sedative action, although these compounds have, in common with nirvanol, veronal, and the dialkylhomophthalimides (cf. Lumière and Perrin, A., 1920, i, 846), the grouping  $\cdot\text{CRR}'\cdot\text{CO}\cdot\text{NH}\cdot$ .  
F. G. W.

**Creatinine.** J. KAPFFHAMMER (*Biochem. Z.*, 1925, 156, 182—189).—The creatine esters described by Dox and Yoder (A., 1923, i, 127) are derivatives of creatinine. The methyl alcohol is firmly attached to the creatinine hydrochloride, and is removed along with hydrogen chloride if the latter is eliminated.  
J. P.

**Thermochemistry of the Butenonitriles.** P. BRUYLANTS and A. CHRISTIAEN (*Bull. Soc. chim. Belg.*, 1925, 34, 144—150).—The molecular heat of combustion at constant pressure of the crotononitrile, b. p. 107.9—108.0°, is 571.9 cal., that of the isomeric crotononitrile, b. p. 120.8—120.9°, is 573.8 cal., that of vinylacetoneitrile 574.9 cal., and that of cyanocyclopropane 581.5 cal. The results point to the crotononitrile of higher boiling point as corresponding with *isocrotonic acid*.  
A. COUSEN.

**Reactions of Triethylphosphine.** J. N. COLLIE (*J. Chem. Soc.*, 1925, 127, 964—965).—Triethylphosphine reacts violently with phosphorus trichloride with liberation of phosphorus; silicon tetrachloride and sulphur monochloride behave similarly, yielding silicon and sulphur. Iodobenzene and triethylphosphine react slowly to give a *compound*,  $\text{PET}_3\cdot\text{PhI}$ , whilst trimethylene dibromide yields the *compound*,  $\text{PET}_3\cdot(\text{CH}_2)_3\text{Br}_2$ . The addition of a small quantity of triethylphosphine to chloral causes the vigorous formation of metachloral; when the reaction between triethylphosphine and chloral hydrate takes place in anhydrous ether, there is obtained an oily liquid which dissolves in water and yields a *chloroplatinate*,  $[\text{PET}_3\cdot\text{C}_2\text{H}_3\text{O}_2\text{Cl}]_2\text{PtCl}_4$ . From the products of reaction of triethylphosphine with formaldehyde and acetaldehyde the *salts*  
$$[\text{PET}_3\cdot\text{CH}_3\text{OCl}]_2\text{PtCl}_4$$
and  $[\text{PET}_3\cdot\text{C}_2\text{H}_3\text{OCl}]_2\text{PtCl}_4$  are formed.  
C. J. S.



**Organic Compounds of Tin. Stannonic Acids and some of their Derivatives.** J. G. F. DRUCE (*Rec. trav. chim.*, 1925, **44**, 340—344; cf. A., 1920, i, 426, ii, 908; 1922, i, 516, 689, 1206; 1924, i, 24, 277, 380; T., 1921, **119**, 758; 1922, **121**, 1859).—Mainly a summary of results already published. By the interaction of the alkyl halogen compounds of tin with silver cyanide the corresponding cyanides,  $R_3SnCN$ ,  $R_2Sn(CN)_2$ , and  $RSn(CN)_3$  are obtained. Hydrolysis of these compounds results in the elimination of the cyanogen group:  $R_2Sn(CN)_2 + H_2O = R_2SnO + 2HCN$ , although the tin dipropyl dicyanide yields ammonia and the hydrolysis possibly follows the normal course,  $Pr_2Sn(CN)_2 + 4H_2O = Pr_2Sn(CO_2H)_2 + 2NH_3$ .  
J. W. B.

**Organic Compounds of Lead.** G. CALINGAERT (*Chem. Reviews*, 1925, **2**, 43—83).

**Germanium. IX. Germanium Tetraethyl. Preparation and Purification of Zinc Diethyl. Analysis by Combustion of a Liquid containing Carbon and Hydrogen.** L. M. DENNIS and F. E. HANCE (*J. Amer. Chem. Soc.*, 1925, **47**, 370—377).—An apparatus is described for preparing and purifying zinc diethyl in an atmosphere of carbon dioxide with exclusion of air. From this is prepared germanium tetraethyl under the same conditions. The reaction  $2ZnEt_2 + GeCl_4 = 2ZnCl_2 + GeEt_4$  is catalysed violently by germanium tetraethyl itself, but proceeds regularly if traces of both products of the system are added with the germanium chloride. An improved method of combustion analysis for a liquid is described in which an auxiliary current of air is drawn into the combustion tube from an inlet tube ending flush with the cork. Germanium tetraethyl has the theoretical molecular weight as a vapour and in benzene solution. Its m. p. and b. p. are respectively  $-90^\circ \pm 0.2$  and  $163.5^\circ$ ,  $d^{24.5}_4$  0.9911, and  $n^{20}_D$  1.400. It is slowly attacked by chlorine, bromine, and iodine at the ordinary temperature, and is completely oxidised on prolonged boiling in nitric acid solution with ammonium persulphate.  
L. J. H.

**Hydrogenation of Benzene in Presence of Metallic Copper.** R. N. PEASE and R. B. PURDUM (*J. Amer. Chem. Soc.*, 1925, **47**, 1435—1442).—Benzene is reduced to cyclohexane when passed with excess of hydrogen at  $140^\circ$  over the active copper obtained by the slow reduction of copper oxide with hydrogen at  $150$ — $300^\circ$ . At  $140^\circ$ , the reaction is unimolecular with respect to benzene as long as the latter is present in small concentrations (0.07—0.15%). The deviation of the reaction constant noted with higher concentrations of benzene appears to indicate that reduction must be preceded by adsorption of hydrogen by the catalyst, whereas with higher concentrations of benzene, this is prevented by the preferential adsorption of the latter (cf. A., 1923, ii, 842). Measurements of the temperature coefficient of the reduction at  $160$ — $280^\circ$ , over two samples of catalyst, indicated a maximum rate of conversion, in both cases, at  $230^\circ$ , whilst the change in velocity with temperature was practically the same for the two catalysts over the same tem-

perature interval. The bearing of this anomaly on the equilibrium data of Dougherty and Taylor (A., 1923, ii, 549) is discussed.

F. G. W.

**Structure of Benzene.** J. J. VAN LAAR (*Chem. Weekblad*, 1925, 22, 286—287).—The fact that the constants  $b$  and  $\sqrt{a}$  of the gas equation are additive, and that a doubly-linked carbon atom always has the value 1.55 for  $100\sqrt{a}$  supports the symmetrical formula for benzene, the values calculated for benzene derivatives on the assumption that all the carbon atoms are doubly bound agreeing with the values found by experiment. S. I. L.

**Attempts to Synthesise Benzene by Condensation of Acetylene at a High Temperature.** A. KOVACHE and E. TRICOT (*Chim. et Ind.*, 1925, 13, 361—372, 537—547).—When acetylene is passed through a silica tube packed with fragments of quartz or porcelain and heated at about 700°, 10—40% of the gas is converted into a tar,  $d$  0.950—0.980, containing approximately 58% of benzene. The tube, however, rapidly becomes choked with carbon, part of the acetylene being decomposed. The deposit augments more rapidly and the operation becomes dangerous if the acetylene is passed into the tube too quickly. When active charcoal was used for packing the tube, the results were similar to those obtained by Zelinski (A., 1924, i, 359; 1923, i, 1169). The best temperature is about 650°. Wood charcoal, coke, "aluminous coke," porcelain, quartz, pumice, and brick all gave similar results. Active charcoal does not bring about the condensation unless it has been heated for some time, and the other materials all function better when their surfaces are covered with a thin layer of carbon (formed by decomposition of acetylene). Nevertheless, the authors conclude that Zelinski's statement that active charcoal has a specific catalytic action has no foundation in fact. In these experiments, 30—60% of the through-put, or 33—76% of the acetylene consumed, was converted into a tar containing 28% of benzene, 1.5% of toluene, and 7.5% of naphthalene. The deposition of carbon, with eventual choking of the tube, cannot be avoided by lowering the temperature, for very little condensation takes place at 500—570°. The heat of reaction will keep up the temperature in the tube, no external heat being applied, for a certain time.

When the benzene formed was quickly removed from the sphere of action, by fixing the heating tube (porcelain or silica) vertically, and fitting inside it a copper cooling tube, the tar obtained had substantially the same composition as before, although the yield on the condensation was much superior; 70—90% on the through-put, or about 90% of that actually consumed, was converted into a tar of  $d$  0.940—0.990 containing about 28% of benzene, 0.5% of toluene, and 4.3% of naphthalene. The porcelain tube became lined with a thin deposit of graphite, but this seemed to improve the yield; the copper tube, on the other hand, needed frequent cleaning. The temperature slope in the reaction space is enormous, and the energy consumed very great. When hydrogen or methane is present in the acetylene the condensation is checked, but not otherwise

affected. Neither methane nor illuminating gas (oxygen-free) condenses or deposits carbon under the above conditions. Benzene, likewise, is unaffected. The condensation of acetylene appears therefore to be the result of many simultaneous reactions, of which that producing benzene is only one.

W. A. S.

### Electrochemical Oxidation of Homologues of Benzene.

**II. Cymene.** F. FICHTER and J. MEYER (*Helv. Chim. Acta*, 1925, 8, 74—83; cf. A., 1924, i, 629; this vol., i, 381).—The electrochemical oxidation of cymene in an emulsion with aqueous sulphuric acid yields *p*-isopropylbenzaldehyde, a little *p*-isopropylbenzoic acid, *p*-acetylbenzoic acid, and terephthalic acid. The methyl group is first attacked, whereas the isopropyl residue remains intact until the conversion of methyl into carboxyl is complete. Among chemical reagents, an analogous action is effected only by manganese dioxide and permanganate in alkaline solution. When the oxidation is conducted in sulphuric acid-acetone solution, the products are *p*-isopropylbenzyl alcohol, *p*-isopropylbenzaldehyde, *p*-isopropylbenzoic acid, *p*-propenylbenzoic acid (the barium salt is described), (?) diisopropylbenzyl ether, a small quantity of a phenolic substance, and much resin. The formation of the compound  $C_{10}H_{12}(OH)_2$  (cf. Law and Perkin, A., 1905, i, 761) could not be detected.

H. W.

**F. p. of *p*-Dichlorobenzene.** N. C. COOPER (*Can. Chem. Met.*, 1925, 9, 59).—*p*-Dichlorobenzene has f. p.  $53.13 \pm 0.02^\circ$ .

CHEMICAL ABSTRACTS.

**Polarisation of Nitrosobenzene.** R. ROBINSON (*Chem. and Ind.*, 1925, 44, 456—458).—Two types of conjugated systems are distinguished: (1) that present in  $\beta$ -aminocrotonic ester, and termed "crotenoid" which is responsible for the characteristic reactions of aromatic amines and phenols and for the reactive methylene groups in the groupings,  $\cdot CO \cdot CH_2 \cdot$ ,  $\cdot CH_2 \cdot CH : CH \cdot CO \cdot$ ,  $\cdot CH_2 \cdot C : C \cdot C : C \cdot NO_2$ , etc.; (2) that present in crotonaldehyde, and comprising such groups as carbonyl associated with unsaturated centres—termed "crotonoid." Substances showing keto-enolic tautomerism are crotonoid in the ketonic and crotenoid in their enolic modifications. Nitrosobenzene and similar compounds (azo compounds and possibly sulphoxides) contain overlapping crotenoid and crotonoid systems, and the normal activations induce the addition of both positive and negative ions to the *o*-*p*-positions to the nitroso or azo groups, never to the *m*-position. The crotenoid system is involved in the *p*-substitution reactions described by Ingold, the crotonoid system in the alkaline hydrolysis of nitrosodimethylaniline. Both systems are involved in the dimerisation of nitrosobenzene. When nitrosobenzene functions as a base, positive ions or their equivalent are attracted to the nitrogen atom; when it reacts as a system analogous to carbonyl, negative ions are similarly attracted. Accordingly, although nitrosobenzene cannot be used to diagnose polarities, it can be used to determine the most reactive centres of other molecules. In correction of Gulland and Robinson's earlier statements (T.,

1923, 123, 989), the effects discussed are now regarded as better explained by general polarity of the alkyl groups. R. B.

**Reaction of certain Organic Compounds with Nitrogen Pentoxide.** L. B. HAINES and H. ADKINS (*J. Amer. Chem. Soc.*, 1925, 47, 1419—1426; cf. Schaarschmidt, this vol., i, 123, 532).—Nitrogen pentoxide and benzene react quantitatively at 0°, even in dilute carbon tetrachloride solution, with formation of nitrobenzene and nitric acid. Dinitrobenzene is not formed if rise in temperature is prevented, but equivalent quantities of nitrobenzene and nitrogen pentoxide react violently at 0° with formation of *m*-dinitrobenzene, which is not further nitrated by nitrogen pentoxide at 76°. In carbon tetrachloride solution, bromobenzene is converted by nitrogen pentoxide into the *p*-nitro derivative exclusively. Toluene affords similarly a mixture of nitrotoluenes, b. p. 228°, whilst benzoic acid is unaffected. Phenol yields picric acid, and *n*-heptane affords a mixture of liquid products, which could not be distilled. With pyridine, nitrogen pentoxide forms first an additive product from which pyridine is recovered on treatment with water. Triethylamine reacts explosively with nitrogen pentoxide, but triethylamine nitrate was the only product identified. In presence of moisture, ethylene is converted by nitrogen pentoxide into ethylene dinitrate, but is otherwise practically unattacked. Stilbene yielded a brown gum, containing 16% of nitrogen, which could not be purified. Tetrachloroethylene dissolves nitrogen pentoxide and remains unattacked in the cold, but on warming oxidation takes place with formation of trichloroacetyl chloride and oxalyl chloride. *cyclo*Hexene reacts smoothly with nitrogen pentoxide between 0° and -30°, with formation of a *nitro-alcohol*,  $C_6H_{10}(NO_2)(OH)$ , b. p. 89—92°/9 mm., a *dinitrate*, b. p. 140—144°/9 mm., and a *nitro-nitrate*,  $C_6H_{10}O_5N_2$ , crystalline, none of which could be completely purified.  $\beta\gamma$ -Dimethyl- $\Delta^8$ -butylene affords similarly a *dinitrate*, yellow, b. p. 80—90°/24 mm., and  $\beta\gamma$ -dinitro- $\beta\gamma$ -dimethyl-*n*-butane, m. p. 210—211° (cf. Bewad, A., 1906, i, 393), together with a brown *liquid*, b. p. above 120°/24 mm. F. G. W.

**Action of Acid Chlorides on Trimethylamine.** L. W. JONES and H. F. WHALEN (*J. Amer. Chem. Soc.*, 1925, 47, 1343—1352).—When trimethylamine is treated with benzenesulphonyl chloride in absolute ether, it yields benzenesulphondimethylamide and tetramethylammonium chloride. In aqueous solution, the formation of Vorländer and Nolte's salt,  $PhSO_2 \cdot NMe_3 \cdot Cl$  (cf. A., 1913, i, 1321) could not be confirmed. *p*-Toluenesulphonyl chloride reacts similarly, but benzenesulphinyl chloride in ether, and benzoyl chloride in benzene, are without action on trimethylamine. Acetyl bromide yields trimethylammonium bromide and keten (cf. Staedel, A., 1886, 940). The action of nitrosyl chloride on trimethylamine in ether yields nitric oxide, trimethylammonium chloride, and probably chlorotrimethylamine, which hydrolyses very readily with formation of formaldehyde and dimethylamine. An attempt to synthesise chlorotrimethylamine by the action of methylene

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chloride and methylene iodide on dimethylamine afforded dimethyl ammonium chloride and tetramethylmethylenediamine (cf. Henry, *Bull. Acad. roy. Belg.*, 1892, [3], **26**, 303; 1894, **28**, 368). By treating dimethylamine with methyl chloromethyl sulphate in ether in a carbon dioxide-ether freezing mixture, and evaporating the solvent, a hygroscopic residue was obtained which gave positive tests for formaldehyde and dimethylamine, and from which an orange, hygroscopic *chloroplatinate*, m. p. indefinite, was prepared, probably that of *chlorotrimethylamine*. F. G. W.

**Action of Hydroxylamine on Sulphinic Acids and their Derivatives.** H. F. WHALEN and L. W. JONES (*J. Amer. Chem. Soc.*, 1925, **47**, 1353—1357).—The product of the action of benzenesulphinyl chloride on hydroxylamine in cold ether is benzenesulphonamide, which is formed apparently by the rearrangement of benzenesulphinhydroxamic acid. A similar reaction takes place in aqueous alkaline solution. *Hydroxylamine benzenesulphinat*, m. p. 83—85°, is formed smoothly from the free acid and base in alcoholic solution. It loses water at 100—110°, but the product is again benzenesulphonamide, which is also obtained by the action of hydroxylamine hydrochloride on benzenesulphinamide in aqueous or alcoholic solution. The action of *p*-toluenesulphinyl chloride is similar.

F. G. W.

**Preparation of Hydrocarbons by the Reaction between Alkyl Sulphonates and Organo-magnesium Halides.** H. GILMAN and N. J. BEABER (*J. Amer. Chem. Soc.*, 1925, **47**, 518—525).—In the preparation of hydrocarbons by the interaction of *p*-toluenesulphonic esters and organo-magnesium halides (cf. T., 1912, **101**, 273; A., 1921, i, 664; 1923, i, 453), the best yields, in the aliphatic series, are obtained when the Grignard reagent contains the largest possible alkyl group. Magnesium aryl and aralkyl halides react equally well with all alkyl *p*-toluenesulphonates. Aryl *p*-toluenesulphonates react differently, and yield sulphones and phenols. The following *p*-toluenesulphonates were prepared by Hahn and Walter's method (cf. A., 1921, i, 651): *n*-butyl, b. p. 163—165°/3 mm.,  $d_4^{20}$  1.120,  $n_D^{20}$  1.5050; isobutyl, b. p. 163—165°/3 mm.,  $d_4^{20}$  1.125,  $n_D^{20}$  1.5050; sec.-butyl, decomposes on distillation,  $d_4^{20}$  1.140,  $n_D^{20}$  1.5100; *n*-amyl, b. p. 169—170°/3 mm.,  $d_4^{20}$  1.100,  $n_D^{20}$  1.5028; and benzyl *p*-toluenesulphonate, m. p. 55°. Syntheses, by the above method, of 18 typical hydrocarbons are described. Preparations involving the use of magnesium benzyl chloride gave an unidentified hydrocarbon, m. p. 119—120°. F. G. W.

**Alternating Polarity in Chain Compounds.** C. F. VAN DUIN (*J. Amer. Chem. Soc.*, 1925, **47**, 585—587).—A criticism of the conclusions of Conant and Kirner (A., 1924, i, 273), the irregularities in whose (bimolecular) reaction constants are explained on the termolecular mechanism of the analogous reaction between  $\alpha\beta$ -dibromo compounds and inorganic iodides, put forward by the author (A., 1924, i, 702). F. G. W.

**Alternating Polarity in Chain Compounds.** J. B. CONANT, W. R. KIRNER, and R. E. HUSSEY (*J. Amer. Chem. Soc.*, 1925, **47**, 587—589).—Reply to van Duin (cf. preceding abstract). Data derived from the rates of reaction between amyl chloride, benzyl chloride, and ethyl chloroacetate (the reactivities of which are in the ratio 1 : 200 : 2800), respectively, and potassium iodide, in acetone, show that the calculated bimolecular reaction constants are independent, within experimental error, of the original concentrations of the reactants. F. G. W.

**Synthesis of Homologues of Benzyl Chloride.** M. SOMMELET (*Compt. rend.*, 1925, **180**, 1349—1351; cf. A., 1914, i, 156).—By the condensation of methyl chloromethyl ether with toluene in the presence of stannic chloride,  $\omega$ -chloro-*p*-xylene, a *di*(chloromethyl)-toluene, m. p. 43·5°, *di-p*-tolylmethane, m. p. 28—29°, b. p. 302°/768 mm., and a chloromethyldi-*p*-tolylmethane, b. p. 198—200°/12 mm., have been obtained. Substitution of a chloromethyl group occurs in the para position whenever that position is unoccupied. The above dichloromethyltoluene is identical with that obtained by the action of chlorodimethyl ether on  $\omega$ -chloro-*p*-xylene in the presence of stannic chloride, and when treated with sodium phenoxide in alcoholic solution yields a *diphenoxymethyltoluene*,  $\text{Me}\cdot\text{C}_6\text{H}_3(\text{CH}_2\cdot\text{OPh})_2$ , m. p. 69°. *Di-p*-tolylmethane is also obtained by the reduction by means of hydriodic acid and phosphorus of *di-p*-tolyl ketone. On treatment with dimethylamine, the chloromethyldi-*p*-tolylmethane yields the corresponding *p*-tolyl $\text{dimethylaminomethyl-p-tolylmethane}$ ,  $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}_2\cdot\text{NMe}_2$ , which forms a crystalline *hydrochloride*. L. F. H.

**Decomposition of [2 : 4 : 6]-Trinitrotoluene by the Action of Sunlight.** E. WICHERT and H. DONAT (*Z. ges. Schiess- u. Sprengstoffw.*, 1925, **20**, 69—70).—Critical of Krauz and Turek's work (this vol., i, 646). The evidence of the formation of picric acid and trinitrobenzoic acid from trinitrotoluene on exposure to sunlight is inconclusive. Technical trinitrotoluene is completely stable in contact with metals and in practice is never exposed to sunlight under conditions approximating to those employed by Krauz and Turek (cf. Schultz and Ganguly, this vol., i, 647).

R. B.

**Preparation of Aromatic  $\gamma$ -Chloroallyl Derivatives and their Use in the Synthesis of Aromatic Acetylenic Hydrocarbons, Alcohols, and Aldehydes.** L. BERT (*Compt. rend.*, 1925, **180**, 1504—1506).—By the action of aromatic organo-magnesium halides on  $\alpha\gamma$ -dichloropropylene in toluene solution the substituted  $\gamma$ -chloro- $\Delta^{\beta}$ -propylenes are obtained in good yield. The aliphatic organo-magnesium halides give poor yields owing to secondary reactions. These compounds should be of use in the preparation of acetylenic hydrocarbons (cf. Bourguel, A., 1923, i, 429). On treatment with alcoholic potassium hydroxide, substituted ethyl allyl ethers are formed from the chloropropylenes as follows:  $\text{CH}_2\text{R}\cdot\text{CH}\cdot\text{CHCl} + \text{EtOH} = \text{CHR}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OEt} + \text{HCl}$ . These ethers should also prove valuable for synthetic purposes.

ff2

$\gamma$ -Chloroallylbenzene, b. p.  $97^{\circ}/18$  mm.,  $212-214^{\circ}$  (corr.),  $d_4^{14}$  1.073,  $n_D^{14}$  1.545 (dibromide, b. p.  $160^{\circ}/12$  mm.,  $d_4^{10}$  1.727,  $n_D^{10}$  1.611), on treatment with alcoholic potassium hydroxide yields *cinnamyl ethyl ether*, b. p.  $127-128^{\circ}/22$  mm.,  $d_4^{15}$  0.970,  $n_D^{15}$  1.547. The following compounds are also described: *o*- $\gamma$ -chloroallyltoluene, b. p.  $109^{\circ}/16$  mm.,  $d_4^9$  1.061,  $n_D^9$  1.545, dibromide, b. p.  $176.5^{\circ}/16$  mm.,  $d_4^{7.5}$  1.705,  $n_D^{7.5}$  1.599; *p*- $\gamma$ -chloroallyltoluene, b. p.  $112.5^{\circ}/16$  mm.,  $d_4^{11.5}$  1.053,  $n_D^{11.5}$  1.542, dibromide, b. p.  $174^{\circ}/13$  mm.,  $d_4^{10}$  1.685,  $n_D^{10}$  1.598; *p*-bromo- $\gamma$ -chloroallylbenzene, b. p.  $140^{\circ}/14$  mm.,  $d_4^{18.5}$  1.433,  $n_D^{18.5}$  1.580, dibromide, b. p.  $204^{\circ}/12$  mm.,  $d_4^{19.5}$  1.975,  $n_D^{19.5}$  1.626; *p*-methoxy- $\gamma$ -chloroallylbenzene, b. p.  $120^{\circ}/11$  mm.,  $d_4^8$  1.155,  $n_D^8$  1.553; *p*-isopropyl- $\gamma$ -chloroallylbenzene, b. p.  $146^{\circ}/30$  mm.,  $d_4^{20}$  1.019,  $n_D^{20}$  1.532, dibromide, b. p.  $186-187^{\circ}/12$  mm.,  $d_4^6$  1.580,  $n_D^6$  1.587; 2- $\gamma$ -chloroallyl-*p*-cymene, b. p.  $140^{\circ}/15$  mm.,  $d_4^{19}$  1.018,  $n_D^{19}$  1.530, dibromide, b. p.  $196^{\circ}/14$  mm.,  $d_4^{16}$  1.531,  $n_D^{16}$  1.578; *p*-isopropyl- $\omega$ -chlorobutenylbenzene (?), b. p.  $148^{\circ}/20$  mm.,  $d_4^6$  1.015,  $n_D^6$  1.537.

L. F. H.

**Nitration and Constitution of Naphthalene.** G. ODDO (*Gazzetta*, 1925, **55**, 174—184).—When naphthalene is brought into contact with either nitric acid alone or a mixture of nitric and sulphuric acids, the temperature rises and at about  $35^{\circ}$  the naphthalene begins to melt and an oil is formed which floats on the acid, the temperature rising rapidly to  $55-56^{\circ}$ . If the temperature is prevented from exceeding  $45-50^{\circ}$  by regulating the addition of the naphthalene and by cooling, and if the mixing is continued after all the naphthalene is added, pale-yellow, crystalline clots of pure  $\alpha$ -nitronaphthalene separate in theoretical yield. The floating oil is formed by addition of 1 mol. of nitric acid to 1 mol. of naphthalene, the compound thus formed then losing 1 mol. of water to yield nitronaphthalene. Similar addition of nitric acid, followed by loss of water, occurs in the nitration of 1-nitronaphthalene to 1:5- and 1:8-dinitronaphthalenes. These reactions are readily explainable on the basis of the author's structural formula for naphthalene (A., 1907, ii, 15), in which one nucleus is of aromatic and the other of alicyclic form.

T. H. P.

**Nitro Derivatives of 2-Methylnaphthalene.** V. VESELY and J. KAPP (*Rec. trav. chim.*, 1925, **44**, 360—375).—Mainly an account of work previously abstracted (cf. this vol., i, 246). The action of concentrated sulphuric acid on 2-methyl- $\alpha$ -naphthylamine nitrate yields 5-nitro-2-methyl- $\alpha$ -naphthylamine, m. p.  $136-138^{\circ}$  (acetyl derivative, m. p.  $221-223^{\circ}$ ); reduction with stannous chloride converts it into 1:5-diamino-2-methylnaphthalene. A second isomeride was isolated, but in quantity insufficient to establish its constitution. Nitration of 1-bromo-2-methylnaphthalene yields only 1-bromo-4-nitro-2-methylnaphthalene, m. p.  $100-101^{\circ}$ , identical with the product obtained by replacement of the amino group in 4-nitro-2-methyl- $\alpha$ -naphthylamine by bromine.

J. W. B.

**Replacement of Reactive Hydrogen Atoms in Sugars, Hydroxy- and Amino-acids by the Triphenylmethyl Residue.** B. HELFERICH, L. MOOG, and A. JÜNGER.—(See i, 790.)

**Phenyldiethylthiocarbamide and the Condensation of Phenylthiocarbimide with Diethylamine.** R. F. HUNTER (*Chem. News*, 1925, **130**, 338—339).—Attempts to prepare phenyldiethylthiocarbamide by the condensation of diethylamine with phenylthiocarbimide have failed (cf. Dixon, T., 1892, **61**, 539), an uncrystallisable gum only being obtained. L. F. H.

**Substituted Biurets.** E. S. GATEWOOD (*J. Amer. Chem. Soc.*, 1925, **47**, 407—412).— $\omega$ -Phenylbiuret, obtained by heating ethyl  $\omega$ -*N*-phenylallophanate with concentrated aqueous ammonia in a closed vessel at 100°, affords, on methylation, a *monomethyl* derivative, probably  $\text{NHPh}\cdot\text{CO}\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 183°, which yielded diphenylcarbamide when heated with aniline. Using aqueous methylamine in place of ammonia in the above reaction,  $\omega$ -methyl- $\omega'$ -phenylbiuret,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHMe}$ , m. p. 133°, is obtained, identical with the product obtained by heating methylcarbamide with phenylcarbimide at 80—90° for 1 hour (cf. Biltz, A., 1923, i, 1074), which yields diphenylbiuret, m. p. 210°, when heated with aniline. Ethyl *N*-phenyl-*ms*-*N*-methylallophanate could not be obtained by the action of phenylcarbamyl chloride on methyl carbamate. F. G. W.

**Preparation of Benzyaniline.** T. J. NOLAN and H. W. CLAPHAM (*J. Soc. Chem. Ind.*, 1925, **44**, 220—221t).—The best conditions for the production of benzyaniline from benzyl chloride and aniline are to add 1 mol. of benzyl chloride slowly to 2—3 mols. of aniline at 140°, the mixture being maintained at that temperature by external cooling. A method and apparatus are described for carrying out the process on a semi-manufacturing scale. L. A. C.

**Reaction of Dichloroacetic Acid with Aromatic Amines.** H. W. DOUGHTY (*J. Amer. Chem. Soc.*, 1925, **47**, 1095—1098).—Dichloroacetates of aromatic amines (cf. Wheeler and Smith, A., 1922, i, 994), when heated at 140°, are converted into the corresponding substituted dichloroacetamides. *o*-Toluidine dichloroacetate has m. p. 132.5° (Wheeler and Smith, *loc. cit.*, give m. p. 140°); *p*-toluidine dichloroacetate has m. p. 138° (Baralis, *Rev. chim. med. farm.*, **2**, 301, gives m. p. 140—141°; Wheeler and Smith, 160°);  $\alpha$ -naphthylamine dichloroacetate has m. p. 136°. Dichloroacet-*o*-toluidide, m. p. 133°, and -*p*-toluidide, m. p. 153° (cf. Rügheimer and Hoffmann, A., 1886, 159), were prepared as above.

Aniline trichloroacetate has m. p. 142—163° (decomp.), depending on the rate of heating; *aniline hydrogen trichloroacetate*, m. p. 107—108°, is obtained by the action of 2 mols. of the acid on 1 mol. of aniline in benzene. Acid dichloroacetates could not be obtained. F. G. W.

**Chemical and Electrochemical Oxidation of *as-m*-Xylidine and its Mono- and Di-methyl Derivatives.** F. FICHTER and P. MÜLLER (*Helv. Chim. Acta*, 1925, **8**, 290—300).—*as-m*-Xylidine, its mono- and di-methyl derivatives are oxidised in sulphuric acid



solution at lead dioxide or platinum anodes to 2:4-dimethyl- $\psi$ -quinol hydrate, m. p. 53—54° (cf. Bamberger and Brady, A., 1901, i, 142), which can thus be readily prepared. According to the method of working up the products, the quinol or *p*-xyloquinol or *p*-xyloquinone derived from it by transformation and subsequent oxidation are readily isolated. With *as-m*-xylidine as initial material, the same products are most conveniently obtained by the use of monopersulphuric acid as chemical oxidant, but the yields are lower than those obtained electrochemically. Dimethyl-*as-m*-xylidine is oxidised by monopersulphuric acid to the corresponding oxide, which yields a *picrate*, m. p. 138° (decomp.). [*as-m*-Xylidine *picrate* has m. p. 121—123°.] In dilute sulphuric acid solution and with low current density, the methyl group of *as-m*-xylidine is oxidised at a platinum anode yielding on the one hand a violet dye or mixture of dyes and, on the other, as a consequence of depolarisation of the anode, hydroxyxyloquinone; the latter substance is most conveniently obtained chemically by the use of ferric chloride. It resembles methyl-orange and methyl-red as an indicator for hydroxyl ions, but is preferable to these substances, since the colour changes are more decided. H. W.

### Mechanism of the Catalytic Hydrogenation of Phenols.

G. VAVON and A. L. BERTON (*Bull. Soc. chim.*, 1925, [iv], 37, 296—305).—The hydrogenation of phenols in liquid media in the presence of platinum-black or of nickel yields a mixture of the corresponding cyclohexane (19—32%) and the cyclohexanol (53—68%) (cf. Willstätter and Hatt, A., 1912, i, 545). The latter arises from further reduction of the cyclohexanone first formed. The velocity of hydrogenation of the cresols, especially *o*-cresol, is less than that of phenol and varies with the solvent used, decreasing in the following order: acetic acid, ether, ethyl acetate, alcohol. The formation of the ketone may be followed with hydroxylamine hydrochloride, titrating the hydrochloric acid liberated (cf. Bambier and Brochet, A., 1895, i, 641). The ketone formation first increases to a maximum and then decreases again to zero at the end of the reaction. This maximum is greater in acetic acid than in ether, is least in alcohol, and decreases as the initial concentration decreases. In acetic acid, the following maximum values are obtained: phenol, 35%, *o*-cresol, 16.5%, *m*-cresol, 17.5%, *p*-cresol, 15%. Hydrogenation of an equimolecular mixture of *o*-cresol and 2-methylcyclohexanone shows that the ketone is reduced more rapidly than the phenol. The actual appearance of the ketone in the reduction mixture is therefore attributed to the formation of a molecular compound of the ketone with the phenol (cf. Schmidlin and Lang, A., 1910, i, 836), which carries the ketone into the mass of the solvent so that it is only reduced on the catalyst at a later stage. The formation of these compounds of the phenol with the cyclohexanone is attended with heat development. Such molecular compounds exist in the solution but dissociate on dilution. The intermediately formed ketone can be isolated by adding semicarbazide hydrochloride, forming the semicarbazone, which undergoes reduction

to the semicarbazide (cf. Neighbors, A., 1922, i, 880). With hydroxylamine hydrochloride, the oxime first formed undergoes reduction to the *cyclohexylhydroxylamine*. *cycloHexylhydroxylamine*, obtained in 65% yield from *cyclohexanone*, and from phenol in 33% yield, has m. p. 140—141°. *2-Methylcyclohexylhydroxylamine* has m. p. 78—79°. *cycloHexylsemicarbazide*, obtained in 90% yield from *cyclohexanone*, and in 50% yield from phenol, on oxidation with acid permanganate gives a yellow azo compound,  $C_6H_{11} \cdot N:N \cdot CO \cdot NH_2$ , softening at 115°, m. p. 118—119°, which with methyl alcohol and a trace of alkali is converted into the semicarbazone. *2-Methylcyclohexylsemicarbazide*, from *2-methylcyclohexanone* in 92%, from *o*-cresol in 67% yield, has m. p. 168—169° (slight decomp.); *3-methylcyclohexylsemicarbazide*, 80% yield from the *cyclohexanone*, 60% from *m*-cresol, m. p. 142—143°; and *4-methylcyclohexylsemicarbazide*, in 90% yield from the *cyclohexanone*, 66% from *p*-cresol, m. p. 146°. The azo derivatives obtained on oxidation of these semicarbazides are unstable, but easily yield the semicarbazones. The ortho derivative yields an azo oxidation product, m. p. about 82—85°. R. B.

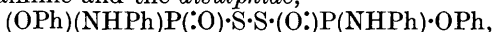
**Thiophosphoryl Chlorides of the General Formulæ  $SP(OR)Cl_2$  and  $SP(OR)_2Cl$  and Derivatives of Pentabasic Thiophosphoric Acid,  $(HO)_4P \cdot SH$ .** W. AUTENRIETH and W. MEYER (*Ber.*, 1925, 58, [B], 840—847; cf. Autenrieth and Hildebrand, A., 1898, 419).—Thiophosphoryl chloride is converted by phenol and sodium hydroxide at a temperature not exceeding 50° into a mixture of phenoxythiophosphoryl dichloride,  $SP(OPh)Cl_2$ , b. p. 133—135°/15 mm., and diphenoxythiophosphoryl monochloride,  $SP(OPh)_2Cl$ , m. p. 67°. The firmness with which the halogen atoms are retained in these compounds is remarkable. Thus, only one chlorine atom of phenoxythiophosphoryl dichloride is replaced when the compound is agitated with an excess of phenol in the presence of sodium hydroxide solution (10%), boiled with phenol dissolved in aqueous sodium hydroxide (30%), or heated with phenol under pressure at 180°; under similar conditions, diphenoxythiophosphoryl monochloride remains unchanged. Triphenyl thiophosphate is, however, produced when either chloride is heated with sodium phenoxide at 180—190°. *Tri-p-tolyl thiophosphate*, m. p. 87°, is almost exclusively obtained when thiophosphoryl chloride (1 mol.) is boiled with a solution of *p*-cresol in aqueous sodium hydroxide (25%). *p-Tolylthiophosphoryl dichloride*, b. p. 138°/12 mm., and *di-p-tolylthiophosphoryl chloride*, m. p. 53° (corresponding *amide*, m. p. 131°), are prepared by the action of thiophosphoryl chloride (1 mol.) on a solution of *p*-cresol (2.5 mols.) in a large excess of 10% sodium hydroxide solution and are separated by distillation of the moist product under diminished pressure; they are extraordinarily stable towards water. *Diphenyl p-tolyl thiophosphate*, obtained from *p*-tolylthiophosphoryl dichloride and sodium phenoxide at 180°, has m. p. 69°; *phenyl di-p-tolyl thiophosphate*, m. p. 54°, is prepared similarly from *di-p-tolylthiophosphoryl chloride*.

Thiophosphoryl chloride is converted by *p*-tolyl mercaptan (4 mols.) and sodium hydroxide solution (10%) into the *ester*,  $\text{SP}(\text{S}\cdot\text{C}_6\text{H}_4\text{Me})_3$ , m. p. 121—122°.

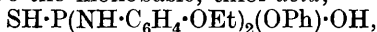
Phenoxythiophosphoryl dichloride (1 mol.) and aniline (1 mol.) in the presence of an excess of 10% sodium hydroxide solution yield the dianilide,  $\text{SP}(\text{NHPH})_2\cdot\text{OPh}$ , m. p. 126° (cf. Autenrieth and Hildebrand, *loc. cit.*), the *anilide-chloride*,  $\text{SP}(\text{NHPH})(\text{OPh})\cdot\text{Cl}$ , m. p. 153°, and the thiol acid,  $\text{SH}\cdot\text{P}(\text{NHPH})_2(\text{OPh})\cdot\text{OH}$ , m. p. 155°, which behaves as a monobasic acid towards sodium hydroxide with phenolphthalein as indicator. The acid slowly evolves hydrogen sulphide when heated, yielding the *ester-anilide*,



m. p. 126°. The sodium salt of the thiol acid is converted by iodine into aniline and the *disulphide*,



m. p. 165°. Similarly, phenoxythiophosphoryl dichloride and *p*-phenetidine give the monobasic, thiol acid,



m. p. 145°, which is transformed by iodine into *p*-phenetidine, and the *disulphide*,  $[(\text{OPh})(\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH})\text{P}(\text{O})\cdot\text{S}]_2$ , m. p. 153°.

H. W.

### 3-Nitro-4-hydroxydiphenyl and some of its Derivatives.

L. C. RAIFORD and J. C. COLBERT (*J. Amer. Chem. Soc.*, 1925, **47**, 1454—1458).—When 4-hydroxydiphenyl is treated with bromine (2.5 mols.) in carbon disulphide a *dibromo* derivative, m. p. 96°, is obtained which, on nitration, afforded a *dibromonitro* derivative, m. p. 171° (decomp.). By treating 4-hydroxydiphenyl in glacial acetic acid with nitric acid (*d* 1.2), a mixture of 3-nitro-4-hydroxydiphenyl, m. p. 66°, and a dinitro derivative (cf. Latschinoff, *J. Russ. Chem. Soc.*, 1873, **5**, 58) was obtained, from which the 3-nitro compound was separated by distillation in superheated steam. Reduction of the latter with stannous chloride in alcohol afforded 3-*amino*-4-*hydroxydiphenyl*, m. p. 208°, of which the *hydrochloride* is described. This yielded, on acetylation, 3-*acetamido*-4-*acetoxydiphenyl*, m. p. 141°, and 3-*diacetylamino*-4-*acetoxydiphenyl*, m. p. 87°. The first of these afforded, on hydrolysis, 3-*acetamido*-4-*hydroxydiphenyl*, m. p. 176°, which, on benzoylation, gave an *acetylbenzoyl* derivative, m. p. 167°, and this, on hydrolysis, afforded 3-*benzamido*-4-*hydroxydiphenyl*, m. p. 238° (*benzoate*, m. p. 234°). The latter yielded, on acetylation, the above *acetylbenzoyl* derivative, m. p. 167°. 4-Hydroxydiphenyl benzoate has m. p. 121° (cf. Kaiser, A., 1890, 897). F. G. W.

**Bismuth Salts of Pyrocatechol.** A. ROSENHEIM and I. BARUTSCHISKY (*Ber.*, 1925, **58**, [B], 891—893).—Stable bismuth salts,  $\text{R}\left[\text{C}_6\text{H}_4\left\langle\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}\right\rangle\text{Bi}\left\langle\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}\right\rangle\text{C}_6\text{H}_4\right]$ , are readily obtained by the saturation of boiling alkaline solutions of pyrocatechol with bismuth hydroxide or carbonate in the absence of air. The *ammonium*, *sodium* (+H<sub>2</sub>O), *barium* (+2H<sub>2</sub>O), and *pyridinium* compounds are described, in addition to the *potassium* and *ammonium* (+H<sub>2</sub>O)

salts of the type  $R[Bi(C_6H_4O_2)_2]_2C_6H_4(OH)_2$ . Pyrocatechol and antimonious oxide in alkaline solution yield the very stable *salt*,  $NH_4[Sb(C_6H_4O_2)_2]$ , whereas trivalent arsenic yields the strong, stable *acid*,  $H[As(C_6H_4O_2)_2]_2 \cdot 4H_2O$ .  
H. W.

**Formation of a New Dihydroxydiphenyl from Resorcinol.** B. KUBOTA, Y. FUJIMURA, and K. AKASHI (*Sci. Papers Inst. Phys. Chem. Res.*, 1925, **2**, 185—193).—When resorcinol vapour is passed over blue oxide of tungsten at 500—550°, there are formed benzene, phenol, diphenylene oxide, and 2:6-dihydroxydiphenyl, m. p. 138—138.5° (*diacetate*, m. p. 111—111.5°). When heated with zinc dust, it gives diphenylene oxide. Its absorption spectrum resembles that of *o*-hydroxydiphenyl, and not those of *m*- or *p*-hydroxydiphenyl, or of 3:4-, 2:4'-, 4:4'-, or 2:2'-dihydroxydiphenyl. The absorption curves of all these substances are given. By catalytic reduction, it gives a *hexahydro* derivative, m. p. 133.5—135° (possibly 1-phenylcyclohexane-2:6-diol), which yields, on oxidation with sodium hypobromite, phenylmalonic acid.

B. F.

**Preparation of Alkylresorcinols.** SHARP and DOHME, Inc., and A. R. L. DOHME (Brit. Pat. 224913; cf. this vol., i, 541).—The 2:4-dihydroxy-*n*-propyl- and -*n*-butylbenzene described by Johnson (A., 1921, i, 340) were impure. These compounds have been prepared in a pure state by condensing pure propionic and *n*-butyric acids, respectively, with resorcinol, purifying the ketones so produced, reducing them with zinc amalgam and hydrochloric acid, and carefully purifying the products. Thus prepared, 2:4-dihydroxy-*n*-propylbenzene has m. p. 79° and 2:4-dihydroxy-*n*-butylbenzene, m. p. 47°.  
E. H. R.

**Effect of the Acidity of Acyl on the Migration from Nitrogen to Oxygen in *o*-Aminophenols.** L. C. RAIFORD and H. P. LAN-KELMA (*J. Amer. Chem. Soc.*, 1925, **47**, 1111—1123; cf. A., 1924, i, 1304).—The action of various pairs of acylating agents on 5-chloro-3-amino-*p*-cresol and the hydrolysis of the resulting mixed diacyl derivatives have been examined. In each of eleven cases, in which both of the acyl radicals were of the type  $R \cdot CO \cdot$ , rearrangement occurred at some point in the cycle. In eight of these cases, the mixed diacyl derivatives were identical, no matter in what order the acyl groups were introduced. In these cases, the more acidic group was found to be attached to the nitrogen atom, but one exception to this was noted. No rearrangement was observed when one of the acyl groups was  $R \cdot SO_2 \cdot$ , the other being  $R \cdot CO \cdot$ . The diacetyl derivative of the above aminophenol (cf. Zincke, A., 1903, i, 756) affords 5-chloro-3-acetamido-*p*-cresol (I), m. p. 125—126°, on hydrolysis, the corresponding dibenzoyl derivative yielding similarly the benzamido derivative, m. p. 201—202°. Benzoylation of the acetamido derivative, and acetylation of the benzamido derivative, yielded the same *acetylbenzoyl* derivative, m. p. 159—160°. Hydrolysis of the di- $\alpha$ -naphthoyl derivative affords 5-chloro-3- $\alpha$ -naphthamido-*p*-cresol, m. p. 146°, which yields an *acetyl* derivative, m. p.   
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188°, identical with that obtained by  $\alpha$ -naphthoylating (I). 5-Chloro-3- $\beta$ -naphthamido-*p*-cresol (II), m. p. 169—170°, yields an acetyl derivative, m. p. 176—177°, identical with that obtained by  $\beta$ -naphthoylating (I), which gives a mixture of (I) and (II) on hydrolysis. The action of  $\alpha$ -naphthoyl chloride on (II) yielded 5-chloro-3- $\beta$ -naphthamido-*p*-tolyl  $\alpha$ -naphthoate (III), m. p. 208°. 5-Chloro-3- $\alpha$ -naphthamido-*p*-tolyl  $\beta$ -naphthoate (IV), m. p. 168—169°, was obtained similarly. Hydrolysis of (III) or (IV) yielded 5-chloro-3- $\alpha$ -naphthoamido-*p*-cresol exclusively. 5-Bromo- $\alpha$ -naphthoyl chloride, m. p. 84°, was prepared by the action of thionyl chloride on the corresponding acid. 5-Chloro-3-(5'-bromo- $\alpha$ -naphthoamido)-*p*-cresol (V), m. p. 206°, gave a  $\beta$ -naphthoate, m. p. 188—189°. The corresponding 5-chloro-3- $\beta$ -naphthamido-*p*-tolyl 5-bromo- $\alpha$ -naphthoate, m. p. 206°, was obtained similarly, and both diacyl derivatives afforded (V) on hydrolysis. 5-Chloro-3-phenylacetamido-*p*-cresol, m. p. 119°, yielded a *p*-toluate, m. p. 169—170°, identical with the product from 5-chloro-3-*p*-toluamido-*p*-cresol, m. p. 169°, and phenylacetyl chloride. 5-Chloro-3-*o*-nitrobenzamido-*p*-cresol (VI), straw-coloured, m. p. 167°, yields a *p*-nitrobenzoate, m. p. 229—230°, identical with the product from 5-chloro-3-*p*-nitrobenzamido-*p*-cresol, m. p. 206°, and *o*-nitrobenzoyl chloride. 5-Chloro-3-*m*-nitrobenzamido-*p*-cresol, m. p. 219°, yielded, on treatment with *o*-nitrobenzoyl chloride, 5-chloro-3-*o*-nitrobenzamido-*p*-tolyl *m*-nitrobenzoate, m. p. 216—217°, which is also obtained from (VI) and *m*-nitrobenzoyl chloride. 5-Chloro-3-*o*-chlorobenzamido-*p*-cresol, m. p. 138°, yielded a *p*-chlorobenzoate, m. p. 216—217°, identical with the product from 5-chloro-3-*p*-chlorobenzamido-*p*-cresol, m. p. 187°, and *o*-chlorobenzoyl chloride. 5-Chloro-3-*o*-iodobenzamido-*p*-cresol (VII), m. p. 147°, yielded a *p*-iodobenzoyl derivative (VIII), m. p. 153—155°, whilst 5-chloro-3-*p*-iodobenzamido-*p*-cresol, m. p. 202°, gave an *o*-iodobenzoyl derivative (IX), m. p. 213°. Hydrolysis of (VIII) or (IX) yielded (VII) exclusively. 5-Chloro-3-(3':5'-dinitrobenzamido)-*p*-cresol, yellow, m. p. 243—244°, afforded a benzoyl derivative, m. p. 241—242°, identical with that from the benzamido-*p*-cresol and 3:5-dinitrobenzoyl chloride. Hydrolysis of the diacyl derivative yielded the benzamido-*p*-cresol and dinitrobenzoic acid. 5-Chloro-3-benzenesulphonamido-*p*-cresol, m. p. 124—125° (acetate, m. p. 142—143°; benzoate, m. p. 169—170°); 5-chloro-3-acetamido-*p*-tolyl benzenesulphonate, m. p. 95—96°; and 5-chloro-3-benzamido-*p*-tolyl benzenesulphonate, m. p. 116—117°, are described.

F. G. W.

### Reactions of Substituted Mercapto-magnesium Halides.

H. GILMAN and W. B. KING (*J. Amer. Chem. Soc.*, 1925, 47, 1136—1143).—Magnesium *p*-tolylthiol iodide yields, when treated with allyl bromide in ether, *p*-tolyl allyl sulphide (cf. Fromm and Siebert, A., 1922, i, 542), b. p. 77—79°/2 mm.,  $d_4^{20}$  1.0044. Benzyl bromide affords similarly *p*-tolyl benzyl sulphide, and a keto sulphide is obtained from bromo- or chloro-acetophenone. Iodine yields di-*p*-tolyl disulphide, whilst dry oxygen and carbon dioxide are without action on the magnesium compound. Phenylcarbimide con-

verts the latter into *p*-tolyl phenylthiolcarbamate,  $\text{NHPh}\cdot\text{CO}\cdot\text{S}\cdot\text{C}_6\text{H}_4\text{Me}$ , m. p.  $127^\circ$ , but benzonitrile has no action. A mixture of benzaldehyde and acetophenone yields phenyl  $\beta$ -*p*-tolylthiol- $\beta$ -phenylethyl ketone (cf. Ruhemann, T., 1905, **87**, 461), probably through the intermediate formation of phenyl styryl ketone, whilst benzaldehyde or acetophenone alone yield unidentified oils. Magnesium ethylthiol iodide reacts incompletely with butaldehyde (cf. Grignard and Dubien, A., 1923, i, 896; Grignard and Fluchaire, *Bull. Soc. chim.*, 1924, **35**, 1019), only a trace of dibutanal being obtained. Magnesium benzylthiol iodide yields, when treated with phenylcarbimide, benzyl phenylthiolcarbamate, m. p.  $94\cdot5^\circ$ . Carbon dioxide has no appreciable action on magnesium  $\beta$ -naphthylthiol iodide.

F. G. W.

### Alkylation of Mercaptans by means of Sulphonic Esters.

H. GILMAN and N. J. BEABER (*J. Amer. Chem. Soc.*, 1925, **47**, 1449—1451).—Mercaptans can be converted into sulphides, in good yields, by boiling their alkaline solutions with an alkyl sulphate or an alkyl *p*-toluenesulphonate. The following sulphides are described: ethyl *n*-butyl, b. p.  $143\text{—}145^\circ$ ; benzyl ethyl, b. p.  $220\text{—}223^\circ$ ; phenyl ethyl, b. p.  $202\text{—}205^\circ$ ; *p*-tolyl methyl, b. p.  $104\text{—}105^\circ/20$  mm.; *p*-tolyl ethyl, b. p.  $101\text{—}103^\circ/2$  mm.,  $122\text{—}125^\circ/20$  mm., b. p.  $219\text{—}220^\circ$ ; *p*-tolyl *n*-propyl,  $d_4^{20}$  0.9755, b. p.  $234\text{—}235^\circ$ ,  $120^\circ/15$  mm.; and *p*-tolyl *n*-butyl sulphide, b. p.  $249\text{—}250^\circ$  (decomp. with formation of *p*-toluenesulphonic acid), b. p.  $135\text{—}138^\circ/15$  mm. The action of  $\beta$ -chloroethyl *p*-toluenesulphonate on *p*-thiocresol yielded *p*-tolyl  $\beta$ -chloroethyl sulphide, b. p.  $150\text{—}152^\circ/20$  mm., and di-*p*-tolyl ethylene disulphide. *p*-Tolyl- $\beta$ -chloroethylsulphone (cf. Fromm and Kohn, A., 1921, i, 242) has m. p.  $78\text{—}78\cdot5^\circ$ .

F. G. W.

**Preparation of Triarylmethyl Acetates.** C. S. SCHOEFFLE (*J. Amer. Chem. Soc.*, 1925, **47**, 1469—1471).—Triarylmethyl acetates are obtained, in 92—96% yields, by shaking benzene solutions of triarylmethyl halides with dry ammonium acetate, or by passing ammonia into solutions of the halides in benzene, in presence of excess of acetic acid. The halide may be produced *in situ* by the action of acetyl bromide on the benzene solution of the triarylcarbinol. Diphenyl- $\alpha$ -naphthylmethyl acetate, m. p.  $137\text{—}138^\circ$ , and phenyldi- $\alpha$ -naphthylmethyl acetate, m. p. above  $200^\circ$  (decomp.), after turning brown at about  $190^\circ$ , are described. Diphenyl- $\alpha$ -naphthylmethylamine, m. p.  $168\text{—}169^\circ$ , and phenyldi- $\alpha$ -naphthylmethylamine, m. p.  $164\text{—}165^\circ$  (cf. Schoepfle, A., 1922, i, 337), were prepared by the action of ammonia on the corresponding triarylmethyl bromides in benzene.

F. G. W.

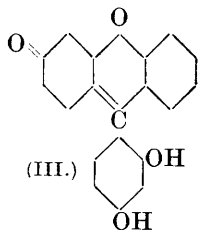
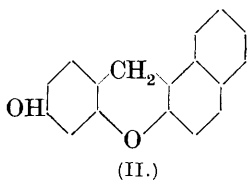
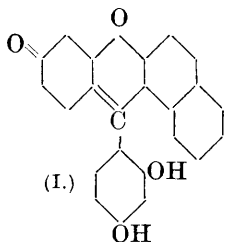
**Dissociation of Benzopinacol Derivatives.** F. F. BLICKE (*J. Amer. Chem. Soc.*, 1925, **47**, 1477).—Benzopinacol dibenzoate and dicyanotetraphenylethane (cf. Lowenbein, this vol., i, 552) develop appreciable colours, due to dissociation into tervalent carbon radicals, when heated at  $150^\circ$ . In molten naphthalene, the colour of the above cyanide is intense pink, becoming colourless on

ff\* 2

cooling. The possibility of these phenomena is foreshadowed by the author's results on the dissociation of compounds, containing the ONa and OPh groups, derived from the action of metallic sodium on aromatic aldehydes (cf. this vol., i, 37, 662). F. G. W.

**Condensation of Primary Alcohols with Resorcinol and other Hydroxy Aromatic Compounds.** R. N. SEN and N. N. SARKAR (*J. Amer. Chem. Soc.*, 1925, **47**, 1079—1091).—Compounds of the benzein type are obtained in good yield by heating together alcohols and resorcinol or similar substances with sulphuric acid (*d* 1.84) at 140—150°. The acid acts both as a condensing and oxidising agent (cf. Sen and Sinha, A., 1924, i, 288) and addition of potassium persulphate lowers the temperature necessary for the reaction. The following benzeins were prepared: resorcinol-benzein (cf. Sen and Sinha, *loc. cit.*) (benzoyl derivative, yellow, m. p. 141°; tetrabromo derivative, decomp. on heating); resorcinol-*o*-hydroxybenzein, m. p. above 250° (yields a tetrabromo derivative); resorcinol-*o*:*p*-dihydroxybenzein, orange-red, m. p. above 250° (tetrabromo derivative, decomp. above 170°); resorcinol-*m*-nitro-*p*-hydroxybenzein, m. p. above 250°; pyrogallolbenzein (from benzyl alcohol and pyrogallol); pyrogallol-*o*-hydroxybenzein (from saligenin and pyrogallol), m. p. above 250°; resorcinol-*o*:*m*:*p*-trihydroxybenzein (from 6-hydroxyfluorone and pyrogallol), red, m. p. above 230°; and a benzein,  $C_{33}H_{20}O_7$ , m. p. above 250°, from resorcinol and 3:5-dihydroxymethyl-*p*-cresol. *o*:*p*-Dihydroxybenzyl alcohol, a white powder which readily turns brick-red, was obtained from resorcinol and formaldehyde by Manasse's method (cf. A., 1894, i, 577). Resorcinol- $\beta$ -hydroxynaphthalein, orange-red, m. p. not below 250°, was obtained, together with 2':4'-dihydroxyphenylnaphthylfluorone (I), similar, from the condensation of resorcinol with  $\beta$ -hydroxynaphthylcarbinol.

Condensation of resorcinol with glycerol in presence of sulphuric acid at 130—150° (cf. Reichl, *J. Chem. Soc.*, 1880, **38**, 426) afforded a mixture of resorcinolglycerein,  $C_{15}H_{12}O_5$ , red, m. p. above 250°, and resorcinolacrolein,  $C_{15}H_{10}O_3$ , orange-yellow, m. p. similar. The former yielded a tribenzoyl derivative, brownish-yellow, and a dibromo derivative. Pyrogallol and glycerol yielded similarly pyrogallolglycerein, brown, m. p. above 250°, and pyrogallolacrolein, black, m. p. similar.



Xanthenes are obtained in good yield by the condensation of *o*-hydroxy-alcohols with an equivalent of resorcinol or  $\beta$ -naphthol

in presence of zinc chloride at 140—160°. The following are described: 3-*hydroxyxanthen*, yellow, m. p. 61° [*dibromo* derivative, m. p. 217° (decomp.)], from saligenin and resorcinol; 8-*hydroxynaphthoxanthen* (II), m. p. 122°, from  $\beta$ -hydroxynaphthylcarbinol and resorcinol; 3-*hydroxy-5-o : p-dihydroxybenzyl-7-methylxanthen*, red, m. p. above 250°; and  $\beta\beta$ -*dinaphthoxanthen* (cf. Wolff, A., 1893, i, 222).

6-Hydroxyfluorone (cf. Mohlau and Koch, A., 1895, i, 46) was obtained by condensing *o* : *p*-dihydroxybenzyl alcohol with resorcinol in presence of zinc chloride and oxidising the product in alkaline solution by means of a current of air. 9-*o* : *p*-*Dihydroxyphenyl-fluorone* (III), orange-red, m. p. above 250°, is a by-product in the preparation of resorcinol-*o*-hydroxybenzein, and is also obtained by condensing 3-hydroxyxanthene with resorcinol in presence of sulphuric acid.

F. G. W.

### Electrochemical Oxidation of Anethole and *iso*Eugenol.

F. FICHTER and A. CHRISTEN (*Helv. Chim. Acta*, 1925, 8, 332—336).

—The possibility of the smooth anodic oxidation of the propylene side-chain is established by the observation that anethole is transformed at a lead dioxide anode into anisaldehyde (yield 52%) and anisic acid (yield 25.4%). Side changes consist in the elimination of methyl from the methoxyl group and entrance of a second hydroxyl group with production of a derivative of pyrocatechol. The experimental conditions may be varied widely, since graphite, platinum, or nickel may replace lead dioxide, and the electrolyte may be a solution of sodium sulphate, carbonate, hydrogen carbonate, or mixtures of these, sodium hydroxide, or dilute sulphuric acid. The difficulty in effecting the electrolytic oxidation of *isoeugenol* to vanillin (cf. D.R.-P. 92007; Lowry and Moore, *Trans. Amer. Electrochem. Soc.*, 1922, 42, 273) is therefore attributed to the presence of the hydroxy group. In support of this view it is shown that 3 : 4-dimethoxy- $\Delta^a$ -propenylbenzene is transformable into 3 : 4-dimethoxybenzaldehyde (77.8%) and 3 : 4-dimethoxybenzoic acid (12.7%), accompanied by little resinous matter, whereas 4-hydroxy-3-methoxypropylbenzene affords much resin and *dihydroxydimethoxydipropyldiphenyl*, m. p. 152°. If, however, the hydroxyl group of *isoeugenol* is protected by using potassium *isoeugenyl* sulphate, electrolytic oxidation at a lead dioxide anode leads to the production, after hydrolysis of the product with boiling, dilute sulphuric acid, of vanillin (53.4%) and vanillic acid (25.7%).

H. W.

**Analogies between certain Reactions of Organic Peroxide and Diazo Compounds.** H. GELISSEN and P. H. HERMANS (*Ber.*, 1925, 58, [B], 984—987; cf. this vol., i, 663).—A theoretical paper in which the analogy between the actions of organic peroxides and diazo compounds towards hydrocarbons, alcohols, and water and during thermal decomposition is discussed.

H. W.

**Stable Triammine Salts.** F. L. HAHN and H. WOLF (*Z. anorg. Chem.*, 1925, 144, 128—130).—The sulphobenzoates of copper, cadmium, nickel, and cobalt yield stable, sparingly soluble salts

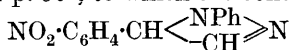


with 3 mols. of amine to 1 of sulphobenzoate, by addition of the amine to the aqueous solution of the salt; the additive compounds give conducting solutions in pure water or water containing the amine. The following *sulphobenzoates* are described: *triammine copper*, dark blue; *tripyridine copper*, bright blue, decomp.  $246^{\circ}$ ; *trianiline copper*, bright green, m. p.  $211^{\circ}$ ; *tripyridine cadmium*, decomp.  $138^{\circ}$ ; *trianiline cadmium*, white, unchanged at  $350^{\circ}$ ; *tripyridine cobalt*, strawberry coloured, darkening at  $240^{\circ}$ ; *tripyridine nickel*, bright-green, unchanged above  $300^{\circ}$ . S. I. L.

**Utilisation of *p*-Toluidine in the Synthesis of Aromatic Esters of the Novocaine Type.** M. A. SODERMAN and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1925, **47**, 1390—1395).—When *p*-toluonitrile (300 g.) is added to a mixture of sulphuric acid (1200 g.) and nitric acid (384 g.) at  $20-40^{\circ}$ , 2-nitro-4-cyanotoluene, b. p.  $171^{\circ}/12$  m., is obtained in 93% yield. This is hydrolysed quantitatively by sulphuric acid ( $d$  1.52) at  $180^{\circ}$  to 2-nitro-*p*-toluic acid, m. p.  $186-187^{\circ}$ , from which 2-nitro-*p*-toluoyl chloride, yellow, b. p.  $165^{\circ}/18$  mm.,  $185^{\circ}/36$  mm., was prepared by the action of phosphorus pentachloride. Oxidation of 2-nitro-*p*-toluic acid with potassium permanganate (cf. Johnson and Bigelow, A., 1920, i, 20) affords the corresponding nitroterephthalic acid, m. p.  $268^{\circ}$ , in 96% yield, from which nitroterephthaloyl chloride, yellow, b. p.  $174^{\circ}/8$  mm., was prepared. Interaction of the above acid chlorides with diethylaminoethyl alcohol in ether afforded respectively diethylaminoethyl 2-nitro-*p*-toluate hydrochloride, m. p.  $152-153^{\circ}$  (decomp.), and diethylaminoethyl 2-nitroterephthalate hydrochloride, m. p.  $199^{\circ}$ . From these, by reduction with tin and hydrochloric acid, diethylaminoethyl 2-amino-*p*-toluate [dihydrochloride, m. p.  $208^{\circ}$  (decomp.)] and diethylaminoethyl 2-aminoterephthalate [dihydrochloride, m. p.  $213^{\circ}$  (decomp.)] were obtained. Diethyl 2-nitroterephthalate, m. p.  $51^{\circ}$ , is described. [Cf. B., July 24th.]

F. G. W.

**Isomerism of Anilino-*m*-nitrophenylacetonitrile.** G. HELLER and G. SPIELMEYER (*Ber.*, 1925, **58**, [B], 838—840).—The condensation of *m*-nitromandelonitrile with aniline in alcoholic solution in the presence of potassium cyanide leads to the production of two interconvertible *isomerides*, yellow needles, m. p.  $102^{\circ}$ , and colourless needles, m. p.  $90^{\circ}$ , to which the constitutions



and  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{CN}) \cdot \text{NHPh}$ , are assigned. The yellow compound rapidly gives a hydrochloride, m. p.  $205-210^{\circ}$  (decomp.) after darkening at  $180^{\circ}$ , which is also obtained slowly from the colourless isomeride. Either form yields the same *acetyl* derivative, m. p.  $142.5^{\circ}$ . Anilino-*m*-chlorophenylacetonitrile could be obtained only in a colourless modification, m. p.  $83^{\circ}$ ; *p*-nitromandelonitrile does not react simply with aniline.

H. W.

**Complete Mutual Resolution of Inactive Acids and Bases.** A. W. INGERSOLL (*J. Amer. Chem. Soc.*, 1925, **47**, 1168—1173).—When *d*-camphorsulphonic acid is combined with inactive phenyl-

aminoacetic acid in aqueous solution, the *l*BdA salt separates first. After purification by recrystallisation, the pure *l*-base can be obtained from it by precipitation with ammonium hydroxide. Similar precipitation of the original mother-liquors gives the partly resolved base (*dB*+*dlB*) and when this (*a*) is combined with inactive camphorsulphonic acid, the *dB*IA salt crystallises first. Or (*b*) the pure *l*-base may be combined with 2 equivalents of inactive acid, the solution depositing first the *l*BdA salt, and leaving *l*-acid in solution. This solution is then combined with the partially resolved base, subsequent procedure being as in (*a*), the *dB*IA salt being obtained first in rather better yield. Concentration of the final liquors yields first the inactive salt, pure, and then the *dBdA* salt. The method appears to be of general application, and is exemplified further by the partial resolution of  $\alpha$ -phenylethylamine and malic acid.

F. G. W.

[Formation and Spectrochemical Behaviour of Hydrogenated Naphthalene Derivatives]. **Correction.** K. VON AUWERS (*J. pr. Chem.*, 1925, [ii], **109**, 352; cf. this vol., i, 402).— $\alpha$ -Methyl- $\beta$ -naphthoic acid has already been described by Mayer and Schnecko (A., 1923, i, 773).  $\gamma$ -Phenylbutyl alcohol (p. 403) was not used; this name is an error,  $\gamma$ -phenylpropyl alcohol being intended.

W. A. S.

**Derivatives of *p*-Hydroxymethylbenzoic Acid. I. Esters.** F. H. CASE (*J. Amer. Chem. Soc.*, 1925, **47**, 1143—1147).—The following esters of *p*-hydroxymethylbenzoic acid were prepared by boiling a solution of the acid in an excess of the appropriate alcohol in presence of a small amount of sulphuric acid: *ethyl* ester, b. p. 161—163°; *propyl* ester, b. p. 164—165°; *n-butyl* ester, b. p. 169—174°; *isobutyl* ester, b. p. 169—172°; and *benzyl* ester, m. p. 63°. The yield of the last was very low on account of ether formation from the acid itself at temperatures above 150°. The *benzoate*, b. p. 203—207°/3 mm., *p-nitrobenzoate*, yellow, m. p. 86°, *p-aminobenzoate*, m. p. 95° (*hydrochloride*, m. p. 198—203°), *urethane*, m. p. 119°, and *phenylurethane*, m. p. 107°, of the above ethyl ester, are described.

F. G. W.

**Synthesis of *p*-Thiolbenzoic Acid.** G. THOMPSON (*J. Soc. Chem. Ind.*, 1925, **44**, 196r; cf. Smiles and Harrison, T., 1922, **121**, 2022).—*p*-Aminobenzoic acid is diazotised and the diazo solution run into an alkaline solution of sodium disulphide below 5°. The crude disulphide, which could not be obtained crystalline, and charred above 290°, on reduction with sodium carbonate and iron powder is converted almost quantitatively into *p*-thiolbenzoic acid, m. p. 219° (after sublimation).

R. B.

**Di( $\alpha$ -cyanobenzoyloxy)phenylmethane, CHPh(O·CHPh·CN)<sub>2</sub>.** R. STOLLÉ (*Ber.*, 1925, **58**, [B], 975).—The compound obtained spontaneously from mandelonitrile by Wood and Lilley (this vol., i, 400) is *di*( $\alpha$ -cyanobenzoyloxy)phenylmethane; the mandelocarbyl-

amine and  $\alpha$ -hydroxybenzylmethylamine of these authors should be deleted.

H. W.

**Unsaturated Ketonic Acids. II. Experiments with  $\beta$ -Benzoylacrylic Acid and Related Compounds.** M. T. BOGERT and J. J. RITTER (*J. Amer. Chem. Soc.*, 1925, **47**, 526—535).— $\beta$ -Benzoylacrylic acid is not converted into an isomeride by the action of ultra-violet light (cf. Rice, A., 1923, i, 218; 1924, i, 287, 1314). *iso*- $\beta$ -Benzoylacrylic acid dibromide ( $\alpha\beta$ -dibromo- $\beta$ -benzoylpropionic acid), m. p.  $142^\circ$ , is obtained by treating isodibromosuccinic anhydride, prepared by the action of bromine on maleic anhydride at  $95$ — $98^\circ$  (cf. Pictet, *Ber.*, 1880, **13**, 1670), with benzene and aluminium chloride. When boiled with sodium acetate in glacial acetic acid, it is converted into the same bromobenzoylacrylic acid, m. p.  $109.4^\circ$ , as is obtained similarly from the isomeric dibromide, m. p.  $148^\circ$  (cf. Bougault, A., 1909, i, 102), prepared by the action of bromine in glacial acetic acid on  $\beta$ -benzoylacrylic acid. Both the above dibromides lose bromine, with formation of  $\beta$ -benzoylacrylic acid, when boiled with potassium iodide in alcohol, sodium thiosulphate solution being added to remove the liberated iodine which brought the reaction to an equilibrium.  $\alpha$ -Sulpho- $\beta$ -benzoylpropionic acid is obtained as the disodium salt, which darkens without melting at  $260^\circ$ , by the action of sodium sulphite on  $\beta$ -benzoylacrylic acid in aqueous solution. Attempts to regenerate a  $\beta$ -benzoylacrylic acid from this compound failed, it being hydrolysed to acetophenone by alkali, and completely decomposed by warm, concentrated sulphuric acid.  $\beta$ -m-Nitrobenzoylacrylic acid, yellow, m. p.  $188^\circ$ , is obtained from  $\beta$ -benzoylacrylic acid by the action of cold, fuming nitric acid.  $\beta$ -p-Hydroxybenzoylacrylic acid, m. p.  $134.5^\circ$ , is prepared by boiling maleic anhydride, phenol, and aluminium chloride, in benzene solution. *s*-Di(trihydroxybenzoyl)ethylene, pale yellow, m. p.  $195^\circ$  (decomp.) after darkening at  $180^\circ$ , or m. p.  $231^\circ$  after softening at  $225^\circ$  in a sealed tube, is obtained by heating maleic anhydride, pyrogallol, and zinc chloride at  $120^\circ$ . A dark red, viscous by-product of this reaction is probably the *malein*. The diketone is a very weak dye (cf. Georgievics, A., 1899, i, 803).  $\alpha$ -Methyl- $\beta$ -benzoylacrylic acid, m. p.  $153^\circ$ , is obtained by condensing citraconic anhydride with benzene in presence of aluminium chloride (cf. von Pechmann, A., 1882, 1074). Both  $\beta$ -1-naphthoylacrylic acid, pale yellow, m. p.  $150.2^\circ$ , and  $\beta$ -2-naphthoylacrylic acid, m. p.  $188^\circ$  (cf. Oddy, A., 1923, i, 1098), are obtained by condensing maleic anhydride with naphthalene in presence of aluminium chloride in benzene solution. F. G. W.

**Preparation of Derivatives of Diphenic Acid possessing the Properties of Local Anæsthetics.** C. ROBERTS and T. B. JOHNSON (*J. Amer. Chem. Soc.*, 1925, **47**, 1396—1402).—Diethylaminoethyl diphenate hydrochloride (I), was obtained as an oil by the action of diphenic chloride on diethylaminoethyl alcohol in benzene. The free base also forms an oil,  $n_D^{21}$  1.528, and it is suggested that the low melting points are due to the products being mixtures of *cis* and *trans* isomerides. Diphenanilide, m. p.  $229$ — $230^\circ$ ,

obtained analogously, was converted into the *imino-chloride*, m. p. 116—117°, by the action of phosphorus pentachloride, from which the *ethylimide*, m. p. 216—217°, and the *diethylaminoethylimide hydrochloride* (II) were obtained by treatment with the respective alcohols. Compounds (I) and (II) form satisfactory local anæsthetics. Attempts to convert diphenanilide into the aldehyde corresponding with diphenic acid, by the method of Sonn and Müller (A., 1920, i, 58) were unsuccessful.

F. G. W.

**Nitration of *p*-Carboxyphenoxyacetic Acid.** W. G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1925, 47, 1158—1162).—*p*-Carboxyphenoxyacetic acid, m. p. 280—282°, is prepared by the action of chloroacetic acid on *p*-hydroxybenzoic acid in aqueous solution in presence of excess of sodium hydroxide. When its solution in cold, concentrated sulphuric acid is treated with nitric acid (1 mol.) 2-nitro-4-carboxyphenoxyacetic acid, m. p. 247—248.5°, is obtained. When this is dissolved in sulphuric acid and treated, in the cold, with a mixture of nitric and sulphuric acids, carbon dioxide is evolved and 2:4-dinitrophenoxyacetic acid, m. p. 145—148°, obtained. The latter can be obtained also by the direct nitration of *p*-carboxyphenoxyacetic acid, which yields in addition a small proportion of 2:6-dinitro-4-carboxyphenoxyacetic acid, yellow, m. p. 182—183°.

F. G. W.

**Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. VII. Effects of Numerous Substances on the Platinum Catalysis of the Reduction of Benzaldehyde.** W. H. CAROTHERS and R. ADAMS.—(See ii, 693.)

**Brominated Additive Products of Schiff's Bases.** A. BERG (*Bull. Soc. chim.*, 1925, 37, [iv], 637—641; cf. Hantzsch, A., 1890, 50).—Schiff's bases form yellow or yellowish-red additive compounds,  $\text{CHRBr}\cdot\text{NR}'\text{Br}$ , with bromine, in which the bromine is very reactive, attacking such metals as copper and gold when the additive compound is dissolved in a dry solvent. When the Schiff's base is derived from an aromatic amine, on decomposition of the additive compound with water, one bromine atom enters the aromatic ring, and the other is eliminated as hydrogen bromide with simultaneous regeneration of the aldehyde. With additive compounds obtained from bases such as *isobutylideneisobutylamine*, water yields a brominated aldehyde and the hydrobromide of the base, e.g.,  $\alpha$ -bromo*isobutaldehyde* and *isobutylamine hydrobromide*. With the *benzylidene* derivatives of alkylamines or aralkylamines, the bromine additive product is decomposed by water in yet a third way, yielding a bromoamine and hydrogen bromide with regeneration of the aldehyde. Thus the *dibromide* of *benzylideneisobutylamine*, *decomp.* 83—84°, yields benzaldehyde and *isobutylbromoamine*,  $\text{NHBr}\cdot\text{C}_4\text{H}_9$ . Similarly, the *dibromide* of *benzylidenebenzylamine*, m. p. 141—142°, yields benzaldehyde and *benzylbromoamine*, from which benzylamine is regenerated, with liberation of bromine, by reaction with the hydrogen bromide. In some cases, as with the derivative of *isobutylideneaniline*,

several reactions occur simultaneously, in this case the principal one yielding aniline hydrobromide and  $\alpha$ -bromoisobutaldehyde.

R. B.

**Reaction between 2 : 6-Dibromocyclohexanones and Alkali.**

G. CUSMANO (*Gazzetta*, 1925, **55**, 215—218; cf. A., 1914, i, 303, 556).

—The action of 2.5% potassium hydroxide solution on 2 : 6-dibromo-2-methylcyclohexanone (cf. Wallach, A., 1918, i, 442) yields a *keto-glycol*,  $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \\ \text{CH}(\text{OH}) \cdot \text{CO} \end{smallmatrix} \text{CH}_2 > \text{CMe} \cdot \text{OH}, 2\text{H}_2\text{O}$ , m. p. about 150°

(slow heating), which gives no coloration with ferric chloride, is converted into the corresponding methylcyclohexandione at about 200°, and is isomeric with the dihydroxymethylcyclohexanone obtained by Harries (A., 1902, i, 378). It seems likely, therefore, that the intermediate terms of the reaction between 2 : 6-dibromocyclohexanones and alkali are diketones resulting from the direct substitution of the two bromine atoms by two hydroxyl groups; these diketones, by internal oxidation and reduction, would then give the dihydroxyprocatechols.

Certain of the compounds described as new by Wallach and Weissenborn (A., 1924, i, 862) were previously obtained by the author.

T. H. P.

**1 : 5-Dichloroanthrone.** E. DE B. BARNETT, J. W. COOK, and M. A. MATTHEWS (*Ber.*, 1925, **58**, [B], 976—983).—1 : 5-Di-

chloroanthranyl acetate,  $\text{C}_6\text{H}_3\text{Cl} < \begin{smallmatrix} \text{C}(\text{OAc}) \\ \text{CH} \end{smallmatrix} > \text{C}_6\text{H}_3\text{Cl}$ , m. p. 178°, is obtained by the action of acetic anhydride on 1 : 5-dichloroanthrone in the presence of pyridine. 1 : 5-Dichloroanthranyl methyl ether, m. p. 104°, and 1 : 5-dichloroanthranyl ethyl ether, m. p. 103°, are prepared from 1 : 5-dichloroanthrone and the requisite *p*-toluenesulphonate. 1 : 5-Dichloroanthrone, 1 : 5-dichloroanthranyl acetate, and 1 : 5-dichloroanthranyl methyl ether are transformed by bromine in the presence of carbon disulphide into 1 : 5-dichloro-9-bromoanthrone, m. p. 214° (decomp.), whereas anthranyl methyl ether is brominated to 9-bromoanthranyl methyl ether. 1 : 5-Dichloro-9-nitroanthrone, m. p. 168° (decomp.), is prepared by the action of nitric acid (*d* 1.42) on 1 : 5-dichloroanthrone, 1 : 5-dichloroanthranyl acetate, or 1 : 5-dichloroanthranyl methyl ether suspended in glacial acetic acid. 1 : 5-Dichloro-9-bromoanthrone is transformed by boiling aqueous acetone into 1 : 5-dichloro-9-hydroxyanthrone, by ethyl alcohol into 1 : 5-dichloroanthranlyl ethyl ether, and by sodium acetate and glacial acetic acid into 1 : 5-dichloroanthronyl acetate, m. p. 178°.

1 : 5-Dichloroanthracene is very stable towards hydrogen peroxide. It is converted by bromine in boiling glacial acetic acid solution mainly into the corresponding dibromide; if the reaction is effected in the presence of sodium acetate, it gives a difficultly separable mixture of 1 : 5-dichloroanthronyl acetate and 1 : 5-dichloro-*cis*-9 : 10-dihydroanthraquinyl diacetate, m. p. 246°. The diacetate is also obtained by the oxidation of 1 : 5-dichloroanthracene with lead tetra-acetate or by the acetylation of 1 : 5-dichloro-

*cis*-9 : 10-dihydroanthraquinol. 1 : 5-Dichloroanthraquinyl diacetate has m. p. 314° (decomp.) after darkening at 300°.

The action of organic bases on 1 : 5-dichloro-9-bromoanthrone differs from that observed with 9-bromoanthrone (T., 1922, **121**, 2059), since, in general, it leads to the replacement of the bromine atom by the basic residue. 1 : 5-Dichloro-9-dimethylaminoanthrone, m. p. 195°, 1 : 5-dichloro-9-diethylaminoanthrone, 1 : 5-dichloro-9-piperidinoanthrone, 1 : 5-dichloro-9-anilinoanthrone, m. p. 193°, and 1 : 5-dichloro-9-dimethylaminophenylanthrone, m. p. 277°, are described. 1 : 5-Dichloro-9-acetoxyanthranylpyridinium bromide,  $C_{21}H_{14}O_2NCl_2Br \cdot 0.5H_2O$ , m. p. 230° (decomp.), is prepared by the action of acetic anhydride and pyridine on 1 : 5-dichloro-9-bromoanthrone; it is converted by hydrobromic acid (30%) into 1 : 5-dichloro-9-hydroxyanthranylpyridinium bromide (or 1 : 5-dichloro-anthranylpyridinium bromide), m. p. 250° after decomposing at 150°.

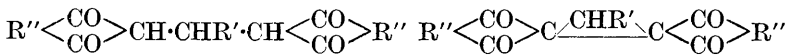
H. W.

**Perylene and its Derivatives. IX.** A. ZINKE, K. FUNKE, and A. PONGRATZ (*Ber.*, 1925, **58**, [B], 799—802).—The poor yield of *isoviolanthrone* obtained by heating 3 : 9-dibenzoylperylene with aluminium chloride (this vol., i, 383) is due, in part, to the extensive reduction of the initial material by hydrogen liberated during the action. The yield may be very materially increased by the addition of manganese dioxide to the mixture; lead peroxide, mercuric oxide, and barium peroxide are less effective. *isoViolanthrone* is readily obtained by the action of powdered potassium hydroxide on 4 : 10-dibromo-3 : 9-dibenzoylperylene in the presence of boiling aniline; the similar synthesis from 4 : 10-dichloro-3 : 9-dibenzoylperylene requires a higher temperature, which is attained by the use of quinoline. The synthesis may be extended to substituted *isoviolanthrones*. Thus, 4 : 10-dichloro-3 : 9-di-*p*-chlorobenzoylperylene, m. p. 350°, prepared from 4 : 10-dichloroperylene, *p*-chlorobenzoyl chloride, and aluminium chloride in the presence of carbon disulphide, yields 4' : 4''-dichloro*isoviolanthrone*, and 4 : 10-dichloro-3 : 9-di-*p*-bromobenzoylperylene, m. p. about 370°, appears to give a *dibromoisoviolanthrone*.

Treatment of *isoviolanthrone* suspended in nitrobenzene with glacial acetic acid, concentrated hydrochloric acid, and hydrogen peroxide gives dichloro*isoviolanthrone* identical with “indanthrene-violet 2R extra.”

H. W.

**General Method for the Synthesis of Polyspirans.** D. RADULESCU and V. GEORGESCU (*Bull. Soc. chim.*, 1925, [iv], **37**, 187—189).—Cyclic  $\beta$ -diketones are condensed with aldehydes to form derivatives of type (I), the disodium salts of which react with iodine, yielding cyclopropane derivatives (II) or with 1 : 2- or



(I.)

(II.)

1 : 3-dihalogenides to form the corresponding *cyclobutane* and *cyclopentane* derivatives. The *disodium* derivative of methylene-

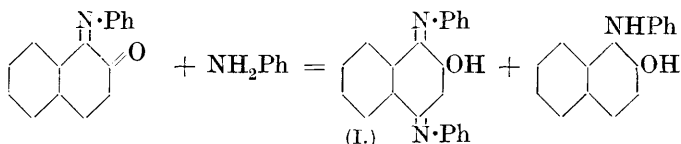
bisdimethyldihydroresorcinol (cf. A., 1897, i, 275) yields, when treated with iodine in suspension in ether, cyclopropanebis-2 : 6-diketo-4 : 4-dimethylcyclohexanedispiran, m. p. 211—212°.

The disodium derivative of methylenebisphenyldihydroresorcinol (cf. A., 1900, i, 100) yields similarly cyclopropanebis-2 : 6-diketophenylcyclohexanedispiran, m. p. 218—219°. F. G. W.

**$\beta$ -Naphthaquinone-1-arylimines.** R. LANTZ and A. WAHL (*Compt. rend.*, 1925, **180**, 1351—1354; cf. A., 1922, i, 823; 1923, i, 209, 674, 918, 1103).—When kept in air the 1-aryl-amino- $\beta$ -naphthols in alkaline solution become oxidised to deeply coloured compounds. Oxidising agents, *e.g.*, ammonium persulphate, sodium hypochlorite, iodine, and lead peroxide, have the same effect. By the action of sodium hypochlorite on 1-anilino- $\beta$ -naphthol in alkaline solution at 5°, an almost quantitative yield of  $\beta$ -naphthaquinone-1-anil,  $O:C_{10}H_6:NPh$ , is obtained. This compound has already been prepared by Euler (A., 1906, i, 369) by treating  $\beta$ -naphthol with nitrosobenzene, but in the succeeding paper (A., 1906, i, 370) the compound is erroneously described as being derived from  $\alpha$ -naphthol. 1-Anilino- $\beta$ -naphthol is regenerated on reduction of the anil with aluminium amalgam. In a similar way, 1- $\beta$ -naphthaquinone-1-anisylimine and  $\beta$ -naphthaquinone-1-p-acetamidophenylimine have been obtained from 1-anisidino- $\beta$ -naphthol and 1-p-acetamido-anilino- $\beta$ -naphthol, respectively. The anils are, in general, very unstable. L. F. H.

#### Action of Aromatic Amines on Naphthaquinonearylimines.

R. LANTZ and A. WAHL (*Compt. rend.*, 1925, **180**, 1509—1512; cf. preceding abstract, and Fr. Pat. 558117).—On treatment with aniline in acetone solution,  $\beta$ -naphthaquinone-1-phenylimine yields a mixture of 1-phenylamino- $\beta$ -naphthol and 2-hydroxy-1 : 4-naphthaquinonediphenylimine (I) the reaction being represented as follows :



In the presence of a catalyst on exposure to air, or with a mild oxidising agent, the 1-phenylamino- $\beta$ -naphthol formed is oxidised back to  $\beta$ -naphthaquinone-1-phenylimine, and thus the yield can be improved. 1-Phenylamino- $\beta$ -naphthol may be treated directly with aniline in the presence of an oxidising agent or catalyst, *e.g.*, copper oxide, which combines with the product, forming a copper derivative. On hydrolysis with dilute hydrochloric acid (I) yields 2-hydroxy- $\alpha$ -naphthaquinone-4-phenylimine (Böniger, A., 1894, i, 199). L. F. H.

**1 : 2-Benzanthraquinone (Sirius-yellow G).** E. DE B. BARNETT and M. A. MATTHEWS (*Chem. News*, 1925, **130**, 339—340).

1 : 2-Benzanthracene has m. p. 158—159°, not 141° as described

by previous workers (Graebe and Peter, A., 1905, i, 704). 9-(or 10)-Nitro-1:2-benzanthracene, m. p. 165°, is obtained by the nitration of 1:2-benzanthracene in acetic acid solution. Reduction of 1:2-benzanthraquinone yields a mixture; the first substance, probably 1:2-benz-9-anthrone, m. p. 170° (benzoate, m. p. 171—172°), gives 1:2-benzanthraquinone on oxidation with ferric chloride; the second, probably 1:2-benz-10-anthrone, an oil (benzoate, m. p. 202—203°), gives on oxidation an oil, probably a dianthrone.

L. F. H.

**Action of Magnesium *p*-Anisyl and *p*-Tolyl Bromides on Camphor.** S. LEDUC (*Compt. rend.*, 1925, 180, 1502—1503).—The substituted aryl derivatives of borneol are more easily dehydrated than the phenyl and benzyl derivatives (cf. A., 1906, i, 440). The reaction between camphor and magnesium *p*-anisyl bromide in ethereal solution gives a 20–30% yield of *p*-anisylcamphene, m. p. 85°, b. p. 178—180°/20 mm. Magnesium *p*-tolyl bromide reacts with camphor yielding a liquid, b. p. 154—157°/12 mm., which is probably a mixture of *p*-tolylborneol and *p*-tolylcamphene.

L. F. H.

#### Irreversible Catalysis of Unsaturated Cyclic Hydrocarbons.

**IV. Contact Transformation of  $\alpha$ -Pinene: Dihydropinene.** N. D. ZELINSKI (*Ber.*, 1924, 58, [B], 864—869; cf. this vol., i, 146).—Passage of *l*- or *d*- $\alpha$ -pinene over palladised asbestos at 190—200° in an atmosphere of carbon dioxide causes the production of cymene and a dihydropinene, b. p. 166.5—167.5°,  $d_4^{25}$  0.8467,  $n_D^{25}$  1.4589, identical with the product obtained by catalytic hydrogenation of pinene in the presence of nickel. The mixture of cymene and dihydropinene is transformed by hydrogen in the presence of palladium at 200° into menthane and dihydropinene. Hydrogenation of pinene at 200° in the presence of palladised asbestos gives a dihydropinene identical with that described above, whereas at 157—158° a different dihydropinene, b. p. 169—169.5° (corr.),  $d_4^{25}$  0.8351,  $n_D^{25}$  1.4531, is produced. The mechanism of the catalytic reduction of pinene depends, therefore, on the temperature and nature of the catalyst.

H. W.

**Action of Chlorine on  $\alpha$ -Pinene.** G. BRUS (*Compt. rend.*, 1925, 180, 1507—1509).—On passing dry chlorine into pure  $\alpha$ -pinene at  $-15^\circ$  to  $-20^\circ$ , a mixture of bornyl chloride (I), tricyclene dichloride (dichlorocamphane) (II), and more highly chlorinated products is obtained.



Tricyclene dichloride, monoclinic crystals, m. p. 170—171°, optically inactive, different from the orthorhombic crystalline dichloride described by Aschan (A., 1920, i, 317), is formed analogously to the dibromide (Godlewsky and Wagner, A., 1899, i, 618). L. F. H.



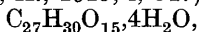
**Asymmetric Catalytic Racemisation.** A. McKENZIE and I. A. SMITH (*Ber.*, 1925, **58**, [B], 894—908; cf. T., 1923, **123**, 1962; A., 1924, i, 1066).—Complete hydrolysis of *l*-bornyl *l*- $\alpha$ -chlorophenylacetate with alcoholic potassium hydroxide solution leads to the production of a mixture of *r*- and *d*-chlorophenylacetic acids, whereas addition of a trace of alcoholic alkali to a solution of *l*-bornyl *l*-chlorophenylacetate in alcohol gives an equilibrium mixture containing 51% of *l*-bornyl *l*-chlorophenylacetate and 49% of *l*-bornyl *d*-chlorophenylacetate. It is considered that the alcoholic alkali induces inversion around the asymmetric carbon atom of the acid, thus causing racemisation, whilst the bornyl group remains unaffected, thus giving a mixture of nearly equal amounts of *l*-bornyl *l*- and *d*-chlorophenylacetates. Since, however, the *l*-bornyl ester of the *l*-acid is more rapidly formed than that of the *d*-acid, it is also more readily hydrolysed. In the initial stages of the hydrolysis the resulting potassium salt is practically inactive, whilst during this period the catalytic racemisation of the non-hydrolysed ester proceeds in such a manner as to yield a mixture of the diastereoisomerides in nearly equal amount. Towards the end of the hydrolysis, however, the concentration of the alkali is diminished to such an extent that the ratio of the *d*- to *l*-ester increases somewhat in spite of the catalyst, and the potassium salt resulting at this stage of the change is feebly dextrorotatory. The term "asymmetric catalytic racemisation" is applied to the transformation of a diastereoisomeric menthyl or bornyl ester into a mixture of esters in which one diastereoisomeride predominates after equilibrium has been established under the influence of alcoholic alkali, whereas the racemisation of a compound such as ethyl *l*-mandelate is described as symmetrical catalytic racemisation.

Esterification of *r*-chlorophenylacetic acid by *l*-borneol in the presence of hydrogen chloride at 100° followed by fractional crystallisation of the product from 96% alcohol leads to the isolation of *l*-bornyl *l*- $\alpha$ -chlorophenylacetate, m. p. 97.5—98.5°,  $[\alpha]_D^{15}$  —98.7°,  $[\alpha]_{5461}^{15}$  —116.3° in ethyl alcohol,  $[\alpha]_D^{15}$  —102.6°,  $[\alpha]_{5461}^{15}$  —120.9° in benzene, whereas *l*-bornyl *d*- $\alpha$ -chlorophenylacetate, m. p. 53—54°,  $[\alpha]_D^{15}$  +38.6°,  $[\alpha]_{5461}^{15}$  +45.8°, is obtained from the mother-liquors. *d*-Bornyl *d*- $\alpha$ -chlorophenylacetate, m. p. 97.5—98.5°,  $[\alpha]_D^{15}$  +99.1° in ethyl alcohol, is obtained by esterification of the corresponding *r*-acid with *d*-borneol and fractional crystallisation of the crude ester from 96% alcohol; *d*-bornyl *l*- $\alpha$ -chlorophenylacetate, m. p. 53—54°,  $[\alpha]_{5461}^{14}$  —44.8°, is prepared from the *l*-acid. Incomplete esterification of *r*-chlorophenylacetic acid with *l*-borneol gives a mixture of esters containing a slight preponderance of *l*-bornyl *l*-chlorophenylacetate, whilst with *d*-borneol the *d*-bornyl *d*-chlorophenylacetate is formed rather more rapidly than the diastereoisomeride. *l*-Bornyl *l*- $\alpha$ -bromophenylacetate, m. p. 91.5—92.5°,  $[\alpha]_D^{13.5}$  —95.8°,  $[\alpha]_{5461}^{13.5}$  —113.7° in ethyl alcohol,  $[\alpha]_D^{14}$  —101.1°,  $[\alpha]_{5461}^{14}$  —122.3° in benzene, is obtained from the corresponding *r*-acid followed by fractional crystallisation of the crude ester from 96% alcohol. The asymmetric action of alcoholic potassium hydroxide on *l*-menthyl *dl*-chlorophenylacetate or *dl*-bromophenylacetate on

*d*-bornyl *dl*-chlorophenylacetate and *l*-menthyl *r*-mandelate is described in detail. H. W.

**Travancore Essential Oils. III. Oil from the Resin of *Canarium strictum*, Roxb. (Black Dammar).** K. L. MOUDGILL (*J. Soc. Chem. Ind.*, 1925, **44**, 169—172T).—The resin obtained from *Canarium strictum*, Roxb., begins to melt at 110° and if heated at 150° until frothing ceases yields a brittle solid (acid value 12.5, compared with 28—30 for the raw resin). On destructive distillation, this solid yields a deep blue oil (80—85%), together with 6—7% of gaseous products, chiefly carbon dioxide, ammonia, and methane hydrocarbons, with small proportions of unsaturated hydrocarbons. The oil,  $d_4^{27}$  0.9228,  $n_D^{27}$  1.5070, ester number 11, after acetylation 28.7, acid number 0, contains heptane, "heptene," *d*- $\alpha$ -pinene, and a dicyclic sesquiterpene,  $C_{15}H_{25}$ , b. p. 262—263°, 125—127°/18 mm. (*hydrochloride*, b. p. 135—137°/18 mm.,  $\alpha_D^{20}$  —8.5°,  $d_4^{27}$  0.9660,  $n_D^{28}$  1.5136). The blue colour of the oil is due to the presence of azulene, but since the alcoholic extract of the resin does not contain azulene, it is probable that the latter is a decomposition product. The colouring-matter of the raw resin is soluble in alcohol and the alcoholic extract on distillation with steam yields *d*- $\alpha$ -pinene and a heavy oil,  $d_4^{28}$  0.9890,  $n_D^{28}$  1.5071. Extraction of the resin with acetone yielded a crystalline solid and left a brittle, light yellow residue, m. p. above 240°. R. B.

**Datiscin, a Glucoside obtained from *Datisca cannabina*, L.** C. CHARAUX (*Compt. rend.*, 1925, **180**, 1419—1421; cf. Schunck and Marchlewski, A., 1894, i, 142; Marchlewski and Korczynski, A., 1907, i, 435; Leskiewicz and Marchlewski, A., 1914, i, 856; Bargellini and Peratoner, A., 1919, i, 547).—Datiscin,



occurs to the extent of 6—10% of the dry weight of the roots and leaves of *Datisca cannabina*, L. It has m. p. 192—193°,  $[\alpha]_D^{20}$  —48.6° in alcohol; it is hydrolysed by enzymes, yielding equimolecular amounts of datiscetin (m. p. 272—273°), and a rhamnoglucose, rutinose (A., 1924, i, 659), and on hydrolysis with acids gives one molecule of datiscetin, one of dextrose, and one of rhamnose. L. F. H.

**Active Principles of the African Squill, *Urginea Burkei* (Slangkop).** E. GEORGE (*J. S. Afr. Chem. Inst.*, 1925, **8**, 14—27).—The intermediate portion of the bulb of *U. Burkei*, Baker, sun-dried, contains: ash, 3.6%; sugars; polysaccharides; much mucilage; a bitter, colourless substance—which is perhaps scillipirin (cf. Merck, *Pharm. Ztg.*, 1879, 286)—described as a glucoside, yielding on hydrolysis an amorphous, red substance, C 55.2%, H 7.1%; a bitter, amorphous, red substance, C 53.37%, H 6.15%—closely resembling scillitoxin (cf. Merck, *loc. cit.*)—described as a glucoside, which on hydrolysis reduces Fehling's solution, and yields a substance identical with the product of hydrolysis of the colourless glucoside; also a yellow substance. A review of the literature of *U. maritima* is given. B. F.

**Action of Hydrochloric Acid and Sodium on the Flavone Extracted from Red Leaves of *Prunus Pissardi*.** S. JONESCO (*Compt. rend.*, 1925, **180**, 1361—1363).—A yellow pigment with the properties of a flavone is extracted from the red leaves of *Prunus Pissardi* by long treatment with ether. Concentrated sulphuric acid dissolves the pigment producing a bluish-green fluorescent solution. On treatment with sodium amalgam and hydrochloric acid the flavone in alcoholic solution gives a red coloration which is not produced by nascent hydrogen alone, by metallic sodium, or by hydrochloric acid, but it can be obtained by treating the alcoholic solution first with sodium and then with hydrochloric acid.

L. F. H.

**Preparation of Compounds of Lecithin with Bile Acids and their Alkali Salts.** C. H. BOEHRINGER SOHN (D.R.-P. 399148; from *Chem. Zentr.*, 1924, ii, 1515—1516).—Compounds of lecithin with bile acids and their alkali salts are obtained by the usual methods. The affinity of bile acids for lecithin is so great that the *additive* compound of lecithin and sodium cholate can be obtained, for instance, by stirring lecithalbumin with an aqueous solution of sodium cholate, filtration from albuminous matter, concentration, and precipitation with alcohol. Double compounds are also described of lecithin with potassium cholate, with sodium glycocholate, with sodium apocholate, and with sodium deoxycholate.

R. B.

**Proposed International Rules for Numbering Organic Ring Systems.** A. M. PATTERSON (*J. Amer. Chem. Soc.*, 1925, **47**, 543—561; issued also as a pamphlet with *J. Chem. Soc.*, March, 1925).—Rules are given for numbering organic ring systems, as approved *provisionally* by the Committee on Organic Nomenclature of the International Union of Pure and Applied Chemistry, for details of which the original should be consulted. F. G. W.

**Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. VIII. Reduction of Furylalkylcarbinols.** J. S. PIERCE and R. ADAMS (*J. Amer. Chem. Soc.*, 1925, **47**, 1098—1104).—Reduction of furylethylcarbinol (b. p. 75—80°/1.3 mm., 86—89°/18 mm.,  $n_D^{20}$  1.476,  $d_4^{20}$  1.044; cf. Douris, A., 1913, i, 1373) in alcoholic solution by hydrogen in presence of platinum oxide is assisted by shaking the catalyst with oxygen every hour, and accelerated by addition of a trace of ferrous sulphate, but the latter is unnecessary if furfuraldehyde is rigorously excluded. The reduction products are as follows: heptan- $\gamma$ -ol (trace); ethyl-tetrahydrofurfurylcarbinol (probably as a mixture of two isomerides); heptane- $\gamma\delta$ -diol, m. p. 96—96.5° (*di-p-nitrobenzoate*, yellow, m. p. 157.5—158.5°); an *isomeride*, b. p. 205—210°/737 mm.,  $n_D^{26}$  1.4420,  $d_4^{20}$  0.9457; and heptane- $\alpha\epsilon$ -diol, b. p. 126—128°/1.8 mm.,  $n_D^{22}$  1.4571,  $d_4^{20}$  0.9705 (*di-p-nitrobenzoate*, m. p. 82—83°).

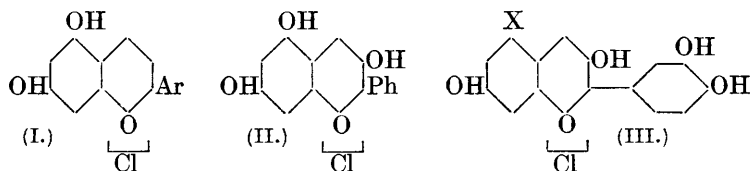
*Furyl-n-butylcarbinol*, b. p. 100—102°/2 mm.,  $n_D^{24}$  1.4720,  $d_4^{20}$  0.9914, was obtained by the action of magnesium butyl bromide on furfuraldehyde. Reduction proceeded similarly, but was retarded by the addition of ferrous sulphate. The following reduction

products were isolated: dibutylcarbinol (trace); *tetrahydrofuryl-butylcarbinol*, b. p. 99—100°/0.5 mm.,  $n_D^{21}$  1.4493,  $d_4^{20}$  0.9428 (acetate, b. p. 120—124°/18 mm.,  $n_D^{23}$  1.4396,  $d_4^{20}$  0.9682); *nonane- $\delta\epsilon$ -diol*, m. p. 124—125° (*di-p-nitrobenzoate*, yellow, m. p. 125—126°), with an *isomeride*, b. p. 120—121°/1.6 mm.,  $n_D^{23}$  1.4476; and *nonane- $\alpha\epsilon$ -diol*, b. p. 145—147°/2.7 mm.,  $n_D^{24}$  1.4560,  $d_4^{20}$  0.9370 (*di-p-nitrobenzoate*, yellow, m. p. 55.5—56°). F. G. W.

**Action of Sodium and Mineral and Organic Acids on certain Flavones.** S. JONESCO (*Compt. rend.*, 1925, **180**, 1523—1525).—On treatment with metallic sodium and subsequent addition of hydrochloric acid, the flavone obtained from *Prunus Pissardi* develops a deep red colour (this vol., i, 824). Hydrochloric acid can be replaced by sulphuric acid, the reaction proceeding as before, but if nitric acid is employed in its place the red colour quickly fades; with acetic acid, the red coloration produced is evanescent. The red pigment has been isolated, but it does not give anthocyanin reactions (cf. Willstätter and Mallison, A., 1915, i, 282).

L. F. H.

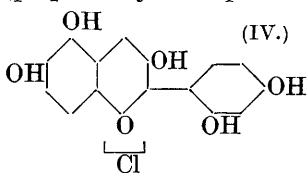
**Synthesis of Pirylium Salts of Anthocyanidin Type. VI. Polyhydroxyflavylium Salts Related to Chrysin, Apigenin, Lotoflavin, Luteolin, Galangin, Fisetin, and Morin.** D. D. PRATT and R. ROBINSON (*J. Chem. Soc.*, 1925, 1127, 1128—1138).—2-Hydroxy-4:6-dimethoxybenzaldehyde, prepared by the Gattermann method from phloroglucinol dimethyl ether, condenses in the presence of potassium hydroxide with acetophenone, 4-methoxyacetophenone, acetoveratone, and 2:4-dimethoxyacetophenone to form chalkone derivatives, which are readily converted by mineral acids into pyrylium salts, from which by demethylation are obtained, respectively, chrysinidin, apigeninidin, lotoflavinidin, and luteolinidin chlorides (I).



*Phenyl 2-hydroxy-4:6-dimethoxystyryl ketone*, m. p. 136°, warmed with concentrated hydrochloric acid, gives chrysinidin chloride dimethyl ether (*iodide*, red needles), and this by demethylation yields chrysinidin iodide and hence the chloride (I, Ar=Ph; *perchlorate*, m. p. 185° decomp.), which darkens at 130° but does not melt at 300°. Apigeninidin chloride (I, Ar=*p*-OH·C<sub>6</sub>H<sub>4</sub>; *perchlorate*, decomp. 222°), darkens at 180°. 2:4-Dimethoxyphenyl 2-hydroxy-4:6-dimethoxystyryl ketone, m. p. 154°, is quantitatively converted into 5:7:2':4'-tetramethoxyflavylium chloride, decomp. 134° (*ferrichloride*, decomp. 180°), which is demethylated to lotoflavinidin iodide (chloride, + 2H<sub>2</sub>O, darkens at 190°). Luteolinidin chloride (*iodide*, red needles) darkens at 200°.

*Galanganidin iodide*,  $C_{15}H_{11}O_4I, HI, 3H_2O$ , m. p.  $145^\circ$ , and chloride ( $+2H_2O$ ) (II) are obtained from 3:5:7-trimethoxyflavylium chloride (J., 1924, **125**, 195; cf. Willstätter and Schmidt, this vol., i, 54); fisetinidin iodide and chloride (III,  $X=H$ ) from 7-hydroxy-3:3':4'-trimethoxyflavylium chloride (T., 1924, **125**, 170). The close resemblance between fisetinidin and cyanidin indicates that cyanin chloride has probably the structure [III,  $X=(C_{12}H_{21}O_{10})\cdot O$ ].

3:5:7:2':4'-Pentamethoxyflavylium chloride, decomp.  $155^\circ$  (*ferrichloride*, decomp.  $194^\circ$ ), is obtained when hydrogen chloride is passed into an ether solution of  $\omega$ :2:4-trimethoxyacetophenone (prepared by an improved method) and 2-hydroxy-4:6-dimethoxy-



benzaldehyde. It is converted by demethylation into morinidin chloride (IV,  $+2H_2O$ ) (cf. Willstätter and Schmidt, *loc. cit.*), which darkens at  $100^\circ$  and is reduced by zinc dust and hydrochloric acid to a substance probably identical with an early transformation product

of cyanomacclurin by alkali.

5:7:3':4'-Tetramethoxyflavylium bromide has no resemblance to Drumm's product (A., 1923, i, 1221) from catechin tetramethyl ether. C. H.

**Synthesis of Pyrylium Salts of Anthocyanidin Type. VII. Preparation of the Anthocyanidins with the Aid of 2:4:6-Triacetoxybenzaldehyde.** D. D. PRATT and R. ROBINSON (*J. Chem. Soc.*, 1925, **127**, 1182—1190).—2:4:6-Triacetoxybenzaldehyde, m. p.  $151^\circ$  ( $+1\frac{1}{2}H_2O$ ), prepared by treatment of phloroglucinaldehyde with acetic anhydride and potassium carbonate, is condensed with various  $\omega$ -methoxyacetophenones (satisfactory conditions for reaction with ketones  $R\cdot COMe$  have not been discovered) to give methyl ethers of pyrylium salts containing (after hydrolysis with aqueous-alcoholic hydrochloric acid) free hydroxyl groups in positions 5 and 7.

$\omega$ -2-Dimethoxyacetophenone, b. p.  $165^\circ/15$  mm. (*semicarbazone*, m. p.  $137^\circ$ ), prepared from *o*-methoxybenzoyl chloride and ethyl sodio- $\alpha$ -dimethoxyacetoacetate, condenses with triacetoxybenzaldehyde in formic acid saturated with hydrogen chloride to give *datiscetinidin chloride* 3:2'-dimethyl ether, which darkens at  $250^\circ$ , but does not melt at  $280^\circ$ . It is demethylated to *datiscetinidin iodide* (chloride,  $+1H_2O$ , darkens at  $240^\circ$ ).  $\omega$ :3-Dimethoxyacetophenone, b. p.  $155^\circ/18$  mm. (*semicarbazone*, m. p.  $128^\circ$ ), prepared from *m*-methoxybenzoyl chloride, gives with triacetoxybenzaldehyde 5:7-dihydroxy-3:3'-dimethoxyflavylium chloride, darkening at  $195^\circ$ , decomp.  $225^\circ$ , which is demethylated to 3:5:7:3'-tetrahydroxyflavylium chloride, decomp.  $200^\circ$ . *Pelargonidin chloride* 3:4'-dimethyl ether (by a typographical error, the original paper gives it as the 3:3'-ether), from  $\omega$ :4-dimethoxyacetophenone and triacetoxybenzaldehyde, yields *pelargonidin chloride* on demethylation. *Morinidin chloride* 3:2':4'-trimethyl ether, from  $\omega$ :2:4-

trimethoxyacetophenone, darkens at 250° (*perchlorate* described), and gives morinidin chloride on demethylation. *Cyanidin chloride* 3 : 3' : 4'-trimethyl ether, from  $\omega$ -methoxyacetoveratrone, is demethylated to cyanidin chloride identical with a synthetic specimen previously authenticated (this vol., i, 423). *Delphinidin chloride* 3 : 3' : 4' : 5'-tetramethyl ether, from  $\omega$  : 3 : 4 : 5-tetramethoxyacetophenone, similarly yields delphinidin chloride (*loc. cit.*). C. H.

**Synthesis of Pyrylium Salts of Anthocyanidin Type. VIII. Synthesis of Pelargonidin Chloride and of Galanginidin Chloride.** T. MALKIN and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 1190—1195).—Bülow's method is applied to the synthesis of galanginidin and pelargonidin, but the probable formation of isomerides makes it inferior to the two other methods available.

*Phenyl  $\alpha$ -methoxy- $\beta$ -hydroxyvinyl ketone*, OMe·CBz·CH·OH, m. p. 112° (*copper salt*, m. p. 178°), prepared from  $\omega$ -methoxyacetophenone, ethyl formate, and sodium ethoxide in dry ether, condenses with phloroglucinol when hydrogen chloride is passed through the dry ethereal solution, giving *galanginidin chloride 3-methyl ether* (*perchlorate* darkens at 255—260°, but does not melt at 300°), identical with the product prepared from triacetoxybenzaldehyde and  $\omega$ -methoxyacetophenone (cf. preceding abstract). Demethylation with hydriodic acid gives galanginidin iodide.

*Anisyl  $\alpha$ -methoxy- $\beta$ -hydroxyvinyl ketone* (*copper salt* sinters at 163°, melts at 170°), from  $\omega$  : 4-dimethoxyacetophenone and ethyl formate, condenses similarly with phloroglucinol to give pelargonidin chloride 3 : 4'-dimethyl ether. The *perchlorate*, m. p. 221° (decomp.), was identical with that from Pratt and Robinson's product (preceding abstract). The pelargonidin chloride obtained by demethylation was not pure, but drastic purification gave a specimen identifiable with certainty. C. H.

**Synthesis of 5 : 5'-Dibromo-6 : 6'-dimethoxy-2 : 2'-bisoxynaphthen.** R. H. GRIFFITH and E. HOPE (*J. Chem. Soc.*, 1925, 127, 990—995).—2-Acetamido-*p*-tolyl methyl ether, m. p. 96°, b. p. 109°/15 mm., obtained by acetylation of the amine, m. p. 47°, b. p. 140°/20 mm., is brominated in acetic acid to 5-bromo-2-acetamido-*p*-tolyl methyl ether, m. p. 191°, which on hydrolysis gives 5-bromo-2-amino-*p*-tolyl methyl ether, m. p. 100° (*benzoyl derivative*, m. p. 159°; *product of coupling with  $\beta$ -naphthol*, m. p. 210°). The corresponding *hydrazine*, m. p. 192°, is converted by a boiling solution of copper sulphate into 3-bromo-*p*-tolyl methyl ether, b. p. 115°/13 mm., which by oxidation with alkaline permanganate gives 3-bromoanisic acid, m. p. 217—218° (cf. Schall and Dralle, A., 1885, 146); the constitution of this acid was confirmed by the preparation of 2-bromoanisic acid, m. p. 199° (mixed m. p. much lower), from 2-bromo-*p*-cresol methyl ether, b. p. 114°/16 mm. or 222°/760 mm. Oxidation of 5-bromo-2-acetamido-*p*-tolyl methyl ether with permanganate gives 5-bromo-2-acetamido-4-methoxybenzoic acid, m. p. 253°, which is converted by acid hydrolysis into 4-bromo-*m*-anisidine, m. p. 90—90·5° (*benzoyl derivative*, m. p. 124°), but by alkaline hydrolysis into 5-bromo-2-amino-4-methoxy-

benzoic acid, m. p. 201°, decomp. 213° (copper salt described). From this acid, by the usual methods, 5-bromo-4-methoxy-2-thiolbenzoic acid and hence 4-bromo-2-carboxy-5-methoxyphenylthiolacetic acid, m. p. 243° (decomp.) are obtained. The latter is converted by acetic anhydride and subsequent oxidation into the thioindigo, 5:5'-dibromo-6:6'-dimethoxy-2:2'-bisoxythionaphthen (annexed formula), m. p. 355—360°, which dyes cotton from the vat a shade indistinguishable from that of "helindone fast scarlet R."

The thiolacetic acid also condenses with isatin to give a blue vat dye,  $C_{17}H_{10}O_3NBrS$ , m. p. 315°, and with acenaphthenequinone to give an orange vat dye, m. p. 337°. C. H.

**Preparation of Salts of Dimethylxanthine with Organic Acids.** KNOLL U. CO., and H. VIETH (D.R.-P. 399903; from *Chem. Zentr.*, 1924, ii, 1515).—Dimethylxanthine salts with a powerful diuretic action are obtained by intimately mixing the base or its acyl or nitro derivatives with salicylic, benzoic, or other acid, alone or in the presence of water or other solvents. The salts can be resolved into their constituents by the use of solvents in which only one component is soluble. The following salts are described: of theophyllin the benzoate, salicylate (1.5 mols. salicylic acid), and cinnamate; of theobromine, the disalicylate, and a salicylate (1.5 mols. salicylic acid), the disulphosalicylate; of nitrotheobromine, the salicylate; and acetyltheobromine salicylate and salicyloyltheobromine salicylate. R. B.

**Yajeine. A New Alkaloid.** A. M. BARRIGA VILLALBA (*J. Soc. Chem. Ind.*, 1925, 44, 205—207T).—The dried stem of the plant known in the Putumayo and Caqueta river territories as "Yaje" (possibly *Hæmadictyen Amazonicum* of the *Apocynaceæ*) contains 1.5% of an alkaloid yajeine and 0.025% of a secondary alkaloid, yajenine. An acid yielding well-crystallised calcium salts is also present, together with a colouring matter readily oxidised to a scarlet substance on exposure to air. The alkaloids are obtained by extraction with dilute hydrochloric acid, precipitation with calcium hydroxide, and extraction of the dried calcareous precipitate with alcohol. The more insoluble yajeine crystallises out in oblique rhomboidal prisms, m. p. 206°, of the composition  $C_{14}H_8ON_3$ . Both the alkaloid and its salts are optically inactive. Characteristic reactions are described with auric chloride, de Frohde's, Dragendorff's, Erdmann's, and Scheibler's reagents. Both on human beings and on animals the alkaloid in small doses produced anæsthesia; larger doses on guinea-pigs produce convulsions and death, the toxic dose being about 0.2 g. per kg. body-weight. R. B.

**Amine-oxides of Alkaloids of the Tropan Group.** M. POLONOVSKI and M. POLONOVSKI (*Compt. rend.*, 1925, 180, 1755—1757; cf. Merling, A., 1893, i, 113; Wolfenstein, A., 1901, i, 613, 673; Freund, A., 1911, i, 76; Valeur and Luce, A., 1919, i, 414; Speyer and Becker, A., 1922, i, 674).—On treatment with hydrogen per-

oxide at the ordinary temperature, the alkaloids form neutral-reacting amine-oxides of the type  $R'R''R'''N:O$ , which give crystalline salts, and on treatment with sulphur dioxide give, not only sulphates, but also anhydro-sulphates, of the type  $R'R''NMe\begin{smallmatrix} O \\ \diagup \\ SO_2 \end{smallmatrix}$ ,

which are easily hydrolysed by water, giving the sulphates. These anhydro-sulphates are isomeric with the compounds obtained by Willstätter and Hug (A., 1912, i, 576). Strychnine oxide gives an anhydro-sulphate, m. p. 330°, not described by Pictet and Mattison (A., 1905, i, 816). *Hyoscyamine N-oxide*,  $[\alpha]_D -15^\circ$  in ethyl alcohol,  $[\alpha]_D -19^\circ$  in water, *hydrochloride*, m. p. 198°,  $[\alpha]_D -11.5^\circ$  in water, gives an *anhydro-sulphate*, m. p. 208°,  $[\alpha]_D^{75} -15^\circ$  in ethyl alcohol, which on hydrolysis with cold water gives hyoscyamine sulphate and, with hot water, the racemised atropine sulphate. *Atropine N-oxide*, obtained in the ordinary way or by racemisation of hyoscyamine *N-oxide*, gives a *hydrochloride*, m. p. 192—193°, and an *anhydro-sulphate*, m. p. 205°. *Tropine N-oxide* is obtained either by hydrolysis of atropine *N-oxide* or in the ordinary way, m. p. 238° (decomp.), *hydrochloride*, m. p. above 280°, *anhydro-sulphate*, m. p. 218°. *apoAtropine N-oxide*, m. p. 128°, *hydrochloride*, m. p. 205°, *salicylate*, m. p. 152°, *anhydro-sulphate*, m. p. 155°. *Homatropine N-oxide*, m. p. 138—140°, *hydrobromide*, m. p. 238°, *anhydro-sulphate*, m. p. 210°. *Scopolamine N-oxide*,  $[\alpha]_D -14^\circ$  in water, *hydrobromide*, m. p. 153°, *perchlorate*, m. p. 167°, *anhydro-sulphate*, very soluble in water. L. F. H.

**Aromatic Esters of Acylecgonines.** W. H. GRAY (*J. Chem. Soc.*, 1925, 127, 1150—1158).—The following aralkyl esters of benzoyl-*l*-ecgonine were prepared by the action of aralkyl chlorides on the sodium salt in the presence of a little pyridine: *Benzyl ester*, oily (*hydrochloride*, m. p. 171°,  $[\alpha]_D -18.62^\circ$  in 2% aqueous solution; *nitrate*, m. p. 163°, decomp.; *hydrogen sulphate*, m. p. 206—208°; *chloroaurate*, m. p. 111°; *chloroplatinate*, m. p. 210° (+2H<sub>2</sub>O) or 211° (anhyd.); *picrate*, m. p. 80°). *p-Nitrobenzyl ester*, oily [*hydrochloride*, m. p. 178.5°,  $[\alpha]_D +17.98^\circ$  in 2% aqueous solution; *nitrate*, m. p. 187°; *hydrogen sulphate*, m. p. 195°; *chloroaurate*, m. p. 154°; *chloroplatinate*, m. p. 204—205° (+2.5H<sub>2</sub>O) or 210° (anhyd.); *picrate*, m. p. 84°]. *o-Hydroxybenzyl ester*, oily (*picrate* described). The *o-acetoxybenzyl chloride*, b. p. 135°/14 mm., required for the last-named ester was prepared from acetylsaligenin by the action of thionyl chloride and diethylaniline.  $\beta$ -*Phenylethyl ester*, m. p. 100° (*hydrochloride*, m. p. 196°,  $[\alpha]_D -39.2^\circ$  in 2% aqueous solution; *chloroplatinate*, m. p. 216°; *picrate*, m. p. 66°).  $\alpha$ -*Phenylethyl ester*, oily (*hydrochloride*, *hydrobromide*, and *nitrate* very deliquescent; *chloroaurate*, m. p. 170°). The  $\alpha$ -chloroethylbenzene for this ester was made by Engler and Bethge's method (A., 1875, 65). *Phenyl-n-propyl ester*, oily (*hydrochloride* not obtained crystalline).

*Benzyltropyl-l-ecgonine* (*hydrochloride* oily; *chloroaurate*, m. p. 90°; *picrate*, m. p. 65°) was prepared in small yield by treating ecgonine hydrochloride with acetyltropyl chloride and esterifying



the product, or, better, from benzylecgonine and acetyltropyl chloride. *Benzyl-o-hydroxybenzoyl-l-ecgonine* (picrate, m. p. 67°), from benzylecgonine and salicylyl chloride, and *benzyl-2-hydroxy-3- and 4-methylbenzoyl-l-ecgonines* (picrates, m. p. 67° and 70°, respectively), from *o*- and *m*-hydroxytoluyl chlorides, were also prepared. *Benzylbenzoyl-d-ψ-ecgonine* (hydrochloride, m. p. 213°; nitrate, m. p. 168°; neutral tartrate, m. p. 155°; picrate, m. p. 80°), and *β-phenylethylbenzoyl-d-ψ-ecgonine*, m. p. 63° (hydrochloride, m. p. 197°,  $[\alpha]_D +35.0^\circ$  in 1% aqueous solution), were obtained from benzoic anhydride and the corresponding *d-ψ-ecgonine* esters.

All these substances are more active anæsthetics than cocaine, the best being benzylbenzoyl-*d-ψ-ecgonine*, *β-phenylethylbenzoyl-d-ψ-ecgonine*, and *α-phenylethylbenzoyl-l-ecgonine*. The toxicity is considerably less than that of cocaine in the first of these, and only slightly greater than that of cocaine in the second and third.

C. H.

**Alkaloids of the Columba Root. III.** K. FEIST and G. L. DSCHU (*Arch. Pharm.*, 1925, **263**, 294—305; cf. A., 1908, i, 100).—From the alcohol extract of columba root were obtained palmatine and a mixture of phenolic bases. Palmatine chloride when heated at its m. p. yields *palmatrubine*, m. p. 290—295°, which gives a reddish-yellow *hydrochloride*,  $C_{20}H_{20}O_4NCl$ , and a yellow *hydriodide*. To these substances are ascribed structures resembling that of berberrubine and its derivatives (cf. Frerichs and Stoepel, A., 1913, i, 1094; Feist and Sandstede, *Arch. Pharm.*, 1918, **256**, 1) in which the dioxymethylene group of berberine is replaced by two methoxyl groups. The phenolic bases obtained as above, on methylation with methyl sulphate, yielded palmatine methosulphate,  $C_{21}H_{22}O_4N \cdot O \cdot SO_2 \cdot OMe, H_2O$ , yellow prisms, m. p. (of dry crystals) 222°; the salts of the methylated phenolic bases are identical with those of palmatine (so-called, see below), columbamine methyl ether, and (so-called) jatteorrhizine dimethyl ether. Columbamine chloride is not homogeneous, since on treatment with potassium iodide and subsequently with sodium hydroxide it gives palmatine iodide and a *phenolic base iodide*, m. p. 210—212° (with decomp.). Jatteorrhizine iodide is also found to be a mixture, containing 85% of the iodide, m. p. 210—212°, and 15% of palmatine iodide, and it is therefore suggested that the new phenolic base from which the iodide, m. p. 210—212°, is derived be called jatteorrhizine. The methylated phenolic bases obtained in this work yielded on oxidation corydaldine, nitrogenous acids, and *o*-hemipinic acid. Palmatine iodide is the methyl ether of the new jatteorrhizine iodide, which is an isomeride of palmatrubine hydriodide.

B. F.

**Hellebore Group. V.** O. KELLER (*Arch. Pharm.*, 1925, **263**, 274—293; cf. *ibid.*, 1922, **260**, 9, and A., 1913, i, 642).—The seeds of *Delphinium Ajacis* (which contain 1.83% of alkaloids) bear in alkaloid content to the seeds of *D. hybridum*, *D. formosum*, *D. rhinante*, and *D. consolida*, respectively, the relation 10 : 4 : 3.4 : 2.5 : 1.1. *D. chinense* seeds contain alkaloids. D.

*elatum* seeds contain 1% of alkaloids, from which may be isolated a crystalline base,  $C_{33}H_{51}O_8N$ , and two amorphous bases.

[With SMECHEL.]—*D. Staphisagria* seeds, when extracted with light petroleum, afford an oil containing *n*-hexoic acid and a trace of a substance resembling delphinin. The seeds contain (according to titration and calculation as pure delphinin) 0.85% of alkaloids, from which may be isolated a trace of a new crystalline *alkaloid*, and 0.11% of pure delphinin. The latter exhibits mutarotation (in alcohol solution), having finally  $[\alpha]_D^{20} + 18.98^\circ$ ,  $n_D$  1.32945 (in alcohol). When heated with water in a sealed tube, delphinin yields benzoic acid, debenzoyldelphinin, and possibly a third *substance*. When heated with hydroxylamine, delphinin yields a substance, m. p.  $196^\circ$ , which contains 2.46% N, and is not an oxime of delphinin; hence the two oxygen atoms in delphinin which are so far unaccounted for (out of a total of nine oxygen atoms) cannot be carbonyl oxygens; they may form part of oxygen bridges or of lactone rings. When distilled with zinc dust, delphinin yields trimethylamine and pyridine. When oxidised with neutral potassium permanganate, it yields an *acid*, m. p.  $115^\circ$  (trace), a nitrogen-free *substance*, m. p.  $211^\circ$  (trace), and a *substance*, needles, m. p.  $214^\circ$ , called "X  $214^\circ$ ,"  $C_{28}H_{37}O_9N$ ,  $[\alpha]_D^{20} - 52.22^\circ$  (in 96% alcohol),  $n_D$  1.3281 (in alcohol). This substance is formed in much better yield (33.83%) if calcium permanganate be used for the oxidation, there being also formed carbon dioxide, acetic acid, possibly other fatty acids, and an undescribed *substance*. "X  $214^\circ$ " is of neutral reaction, forming no salts with acids, cannot be methylated, contains three or four methoxyl groups, and a benzoyl group. On hydrolysis, it yields benzoic acid and a little vanillin. Consideration of the amount of alkali used up in the hydrolysis leads to the view that "X  $214^\circ$ " contains a lactone or an anhydride ring, which on fission yields two acid groups. B. F.

**Strychnine and Berberine. III. Position of the Methoxyl Groups in Brucine.** F. LIONS, W. H. PERKIN, jun., and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 1158—1169).—The work of Leuchs and others has shown that brucine contains two methoxyl groups *ortho* or *para* to one another. The behaviour of certain *N*-acetyldimethoxydimethyltetrahydroquinolines towards nitric acid now indicates that the two methoxyl groups are *ortho* to one another and the positions *para* to these in the benzene nucleus are occupied.

2 : 5-Dimethoxyaniline, from nitroquinol dimethyl ether, condenses with acetylacetone to form  $\beta$ -2 : 5-dimethoxyanilinopropenyl methyl ketone, m. p.  $55^\circ$ , which is converted by concentrated sulphuric acid into 5 : 8-dimethoxy-2 : 4-dimethylquinoline, m. p.  $107^\circ$  [*hydrochloride*, m. p.  $235$ — $237^\circ$  (decomp.); *picrate*, m. p.  $190^\circ$ ]. Reduction of the quinoline with sodium and alcohol yields the tetrahydro derivative, b. p.  $170$ — $172^\circ/10$  mm. (*N*-acetyl derivative, m. p.  $85$ — $86^\circ$ ), which gives with nitric acid a dark, blood-red coloration. 6-Nitro-1-acetyl-5 : 8-dimethoxy-2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline, m. p.  $127^\circ$ , prepared by nitration of the acetyl compound,

remains yellow in sulphuric acid on addition of dichromate, indicating that the *p*-position to the quinoline nitrogen is occupied. Reduction and acetylation gives 6-acetamido-1-acetyl-5 : 8-dimethoxy-2 : 4-dimethyltetrahydroquinoline, m. p. 171°.

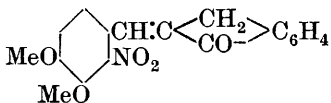
5-Bromo-4-aminoveratrole [hydrochloride, m. p. 216—218° (decomp.)] decomposes in hot water (a substance, m. p. 160—161° was isolated). By condensation with acetylacetone, it gives  $\beta$ -6-bromo-3 : 4-dimethoxyanilinopropenyl methyl ketone, m. p. 78—79°, which is converted by concentrated sulphuric acid into 8-bromo-5 : 6-dimethoxy-2 : 4-dimethylquinoline, m. p. 74—75° (hydrochloride, m. p. 136—138°), which is reduced by sodium and alcohol to 5 : 6-dimethoxy-2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. 166—167°/10 mm. (oily nitrosoamine and oily acetyl derivative were prepared). This gives with nitric acid only a yellow coloration.

$\beta$ -3 : 4-Dimethoxyanilinopropenyl methyl ketone, m. p. 79°, from 4-aminoveratrole and acetylacetone, is converted by sulphuric acid into 6 : 7-dimethoxy-2 : 4-dimethylquinoline, m. p. 81.5—82° [hydrochloride, m. p. 286° (decomp.); picrate, m. p. 239°]. The corresponding tetrahydro derivative, m. p. 73—74°, b. p. 186—189°/12 mm. [picrate, m. p. 145° (decomp.); nitrosoamine is yellow]. 1-Acetyl-6 : 7-dimethoxy-2 : 4-dimethyltetrahydroquinoline, m. p. 118°, gives a coloration with nitric acid identical with the bright orange-red given by brucine; the colour fades rather more rapidly.

$\beta$ -2 : 3-Dimethoxyanilinopropenyl methyl ketone, from 3-aminoveratrole and acetylacetone, is converted by sulphuric acid into 7 : 8-dimethoxy-2 : 4-dimethylquinoline, b. p. 189—191°/10 mm. (hydrochloride, m. p. 145°), which is reduced by sodium and alcohol to 7 : 8-dimethoxy-2 : 4-dimethyl-1 : 2 : 3 : 4-tetrahydroquinoline, b. p. 168—170°/12 mm. The N-acetyl derivative, m. p. 98—99°, gives no coloration with nitric acid.

5-Nitro-4-allylveratrole, m. p. 44°, obtained by nitration of eugenol methyl ether, is converted by reduction and acetylation into the 5-acetamido compound, m. p. 126—127°, which gives the brucine reaction with nitric acid. The same coloration is given by 5-bromo-4-acetamidoveratrole (Jones and Robinson, T., 1917, 111, 903), by 6-acetamidohomoveratrole (Luff, Perkin, and Robinson, T., 1910, 97, 1131), and by acetamidosafrrole (Foulds and Robinson, T., 1914, 105, 1963). In all these cases and with the tetrahydroquinoline mentioned above, the reaction is much less delicate than with brucine.

2'-Nitro-3' : 4'-dimethoxy-2'-benzylidene-1-hydrindone (annexed formula), m. p. 156—176°, made by condensing 2-nitroveratraldehyde with  $\alpha$ -hydrindone, was probably a mixture of isomerides. It could not be reduced to a quinoline derivative. 6'-Nitro-3' : 4'-dimethoxy-2-benzylidene-1-hydrindone, m. p. 211°, prepared similarly from 6-nitroveratraldehyde, gives on reduction the dimethoxyindenoquinoline, m. p. 188—190° (hydrochloride, m. p. 251—252°.



It could not be reduced to a quinoline derivative. 6'-Nitro-3' : 4'-dimethoxy-2-benzylidene-1-hydrindone, m. p. 211°, prepared similarly from 6-nitroveratraldehyde, gives on reduction the dimethoxyindenoquinoline, m. p. 188—190° (hydrochloride, m. p. 251—252°.

C. H.

**Acocantherine.** II. J. MOIR and J. LEWIS (*J. S. Afr. Chem. Inst.*, 1925, **8**, 11—13; cf. A., 1924, i, 758).—Acocantherine (from *Acokanthera venenata*) withstands boiling in aqueous solution, or with very dilute acid, but is sensitive to alkali hydroxide. Evidence of its great toxicity is adduced. No satisfactory method of purifying it is yet known. Evidence as to its possible identity with strophanthine is being sought. The stem and root of *A. venenata* from Port St. John's contain (toxicity basis) ten times the amount of acocantherine present in the leaves. Acocanthic acid yields a benzoyl derivative. B. F.

**Properties of Aryl Esters and Ethers of N-Piperidinoalkyl Compounds.** H. C. BRILL (*J. Amer. Chem. Soc.*, 1925, **47**, 1134—1136).— $\gamma$ -N-Piperidinopropyl benzoate (cf. Laun, A., 1884, 1054), liquid, forms a *hydrochloride*, m. p. 192°. Both base and salt possess anæsthetic properties.  $\beta$ -N-Piperidinoethyl phenyl ether, liquid, was prepared by the action of piperidine on  $\beta$ -bromoethyl phenyl ether in alcohol. The *hydrochloride*, m. p. 180°, and *hydrobromide*, m. p. 168°, possess anæsthetic properties, the latter being more irritating.  $\gamma$ -N-Piperidinopropyl phenyl ether (cf. Gabriel and Stelzner, A., 1896, i, 702) was obtained similarly. Both the *hydrochloride*, m. p. 179°, and the *hydrobromide*, m. p. 160°, possess anæsthetic properties. F. G. W.

**Pyridonemethides [Methylenedihydropyridines].** E. KOENIGS, K. KÖHLER, and K. BLINDOW (*Ber.*, 1925, **58**, [B], 933—940; cf. Mumm and Hingst, A., 1924, i, 83).—2-p-Nitrobenzylpyridine, m. p. 76°, separates from the product obtained by the nitration of a mixture of 2- and 4-benzylpyridines (details will be published elsewhere). It is converted by methyl iodide into the corresponding unstable *methiodide*, m. p. 248°, from which the stable *methochloride*, m. p. 240°, is obtained. The latter substance is readily transformed by sodium hydroxide into 2-p-nitrobenzylidene-1-methyldihydropyridine, m. p. 160°. 4-p-Nitrobenzylpyridine is isolated from the mixture just described by means of its *picrate*; it appears to yield a non-crystalline *methiodide* and *methochloride*, from which 4-p-nitrobenzylidene-1-methyldihydropyridine, decomp. 50°, is obtained by the action of sodium hydroxide. The ready production and great stability of the dihydropyridine derivatives are so unusual among pyridonemethides as to suggest that the compounds may have a betaine-like structure involving the nitro group. In this connexion, therefore, the observations have been extended to the non-nitrated compounds. The action of methyl iodide on a mixture of 2- and 4-benzylpyridines at 0° (cf. Decker, A., 1905, i, 667) affects exclusively the 4-compound and gives 4-benzylpyridine *methiodide*, m. p. 121—122°, which is moderately sensitive towards light and moisture. 2-Benzylpyridine *methiodide*, m. p. 116—117°, is prepared from 2-benzylpyridine and methyl iodide at the atmospheric temperature. When aqueous solutions of the *methiodides* are gradually treated with alkali hydroxide in the presence of benzene, the corresponding pyridonemethides are formed with less readiness than is the case with the nitrated compounds,

but their production throws little light on the constitution of the latter substances. 4-Benzylidene-1-methyldihydropyridine yields, with phenylthiocarbimide, the *additive* compound,  $C_{20}H_{18}N_2S$ , m. p.  $162^\circ$  after darkening at  $145^\circ$ , whereas 2-benzylidene-1-methyldihydropyridine gives an analogous *substance*, m. p.  $147-148^\circ$  (cf. Schneider, Gaertner, and Jordan, A., 1924, i, 551). A mixture of 2- and 4-benzylpyridines is transformed by benzaldehyde in the presence of zinc chloride into *benzylidene-2-benzylpyridine*,  $C_5H_4N \cdot CPh \cdot CHPh$ , which could not be caused to crystallise, and *benzylidene-4-benzylpyridine*, m. p.  $86^\circ$ , which are separated from one another by means of their *picrates*, m. p.  $165-166^\circ$  and  $188-189^\circ$ , respectively. *Benzylidene-2-benzylpyridine hydrochloride*, m. p.  $196-197^\circ$ , and *methiodide*, m. p.  $172-173^\circ$ , and the *hydrochloride*, m. p.  $216-217^\circ$ , and *methiodide*, m. p.  $212-213^\circ$ , of benzylidene-4-benzylpyridine are described. Treatment of the methiodides with alkali hydroxide causes the smooth elimination of benzaldehyde and production of benzylidenemethyldihydropyridines, identified as the *additive* compounds with phenylthiocarbimide. *Stilbazole methiodide*, m. p.  $215-216^\circ$ , is converted by sodium hydroxide into benzaldehyde and 1-methyl-2-methylenedihydropyridine.

H. W.

**Synthesis of 1:2-Dihydroquinaldine.** F. A. MASON (*J. Chem. Soc.*, 1925, 127, 1032-1035; cf. R  th, A., 1924, i, 555, 667).— $\beta$ -Chlorobutaldehyde diethylacetal, from crotonaldehyde and alcoholic hydrogen chloride, condenses with aniline in amyl alcohol solution in the presence of potassium carbonate, copper powder, and sodium iodide, forming  $\beta$ -*anilinobutaldehyde diethylacetal*, b. p.  $173-175^\circ/25$  mm. or  $153-154^\circ/12$  mm. (*picrate*, m. p.  $188-190^\circ$ ).  $\beta$ -*p-Ethoxyanilinobutaldehyde diethylacetal*, b. p.  $190-192^\circ/12$  mm., is similarly prepared from *p*-phenetidine (without copper powder). *p*-Chloroaniline gave a very small amount of a *substance*, m. p.  $95-97^\circ$ .

$\beta$ -Anilinobutaldehyde diethylacetal is converted by phosphoric oxide in benzene (but not by hydrochloric acid, acetic acid, or acetic anhydride) into 1:2-dihydroquinaldine, b. p.  $125-130^\circ/18$  mm. (*picrate*, m. p.  $192-193^\circ$ ). From the *p*-ethoxyanilino-acetal an unidentified oil, b. p.  $260-270^\circ/760$  mm. (*picrate*, m. p.  $190^\circ$ ; *hydrochloride*, m. p.  $234-236^\circ$  decomp.), was obtained.

No dihydroquinaldine could be detected after heating aniline with crotonaldehyde diethylacetal under reflux, or with  $\beta$ -chlorobutaldehyde diethylacetal alone at  $220^\circ$  (cf. R  th's method, *loc. cit.*).

C. H.

**Action of Formaldehyde and Substituted Alcohols on Pyrrole Derivatives and a New Synthesis of isoPhonopyrrole-carboxylic Acid.** H. FISCHER and C. NENITZESCU (*Annalen*, 1925, 443, 113-139).—Substituted pyrroles condense with formaldehyde in the presence of alkali to yield alcohols, ethyl 2:4- and 2:5-dimethylpyrrole-3-carboxylate yielding, respectively, *ethyl 2:4-dimethyl-5-hydroxymethylpyrrole-3-carboxylate*, m. p.  $119^\circ$ , and *ethyl 2:5-dimethyl-4-hydroxymethylpyrrole-3-carboxylate*, m. p.  $131-$

132°. These compounds readily lose formaldehyde on heating above their melting points, can be reduced to the corresponding aldehydes, and, by the action of methyl-alcoholic potassium hydroxide, dilute acids, or boiling water, lose formaldehyde and are converted into the dipyrrolymethanes. If the reaction mixture from the above condensation be strongly acidified while still warm, the product is termolecular *ethyl 2:4(or 2:5)-dimethyl-1-hydroxymethylpyrrole-3-carboxylate*, m. p. 169° and 175°, respectively. A similar compound, m. p. 185°, is obtained from 2:4-dimethyl-3-acetylpyrrole, but not with *ethyl 2:4-dimethylpyrrole-5-carboxylate*, which yields the corresponding *dipyrrolylmethane*, m. p. 229—230°. The other termolecular compounds yield the corresponding dipyrrolymethanes on heating above their melting points; *ethyl 2:2':5:5'-tetramethyl-4:4'-dipyrrolylmethane-3:3'-dicarboxylate* has m. p. 230°. Methylol compounds (cf. Einhorn, A., 1906, i, 245) react with substituted pyrroles introducing the group  $-\text{CH}_2\cdot\text{NR}^1\text{R}^2$  into the molecule. Thus methylol acetamide reacts with *ethyl 2:5-dimethylpyrrole-3-carboxylate* to produce *ethyl 2:5-dimethyl-4-acetamidomethylpyrrole-3-carboxylate*, m. p. 158°, whilst methylol chloroacetamide reacts with the appropriate pyrrole to produce *ethyl 2:5-dimethyl-4-chloroacetamidomethylpyrrole-3-carboxylate*, m. p. 152°, and *ethyl 2:4-dimethyl-5-chloroacetamidomethylpyrrole-3-carboxylate*, m. p. 194° (decomp.); with 2:3:5-trimethylpyrrole it yields 2:2':3:3':5:5'-hexamethyl-4:4'-dipyrrolylmethane, m. p. 196°. By the action of diethylamine (or piperidine) and formaldehyde on *ethyl 2:5-dimethylpyrrole-3-carboxylate*, is obtained *ethyl 2:5-dimethyl-4-diethylaminomethyl-(or 4-N-piperidinomethyl-)pyrrole-3-carboxylate*, both being precipitated as their perchlorates. Similarly treated, 2:3:5-trimethylpyrrole yields only the dipyrrolylmethane. Condensation of *ethyl 2:4-dimethylpyrrole-5-carboxylate* with *ethyl  $\beta$ -methoxymethylmalonate* (cf. Simonsen, T., 1908, 93, 1777) yields *diethyl 2:4-dimethyl-5-carbethoxypyrryl-3- $\beta$ -methylmalonate*,  $\begin{array}{c} \text{CMe} \\ | \\ \text{C}(\text{CO}_2\text{Et})\cdot\text{NH}\cdot\text{CMe} \end{array} \text{---} \begin{array}{c} \text{C}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2 \\ | \\ \text{C} \end{array}$ , m. p. 107°, which

on hydrolysis with aqueous potassium hydroxide yields the corresponding *malonic acid* (the 5-carbethoxy group escaping hydrolysis) and this on heating in small quantities loses 1 mol. of carbon dioxide to produce 2:4-dimethyl-5-carbethoxypyrrrole-3-propionic acid, m. p. 152°. This, on further hydrolysis with alkali, followed by strong acidification, yields 2:4-dimethylpyrrole-3-propionic acid (*isophonopyrrolecarboxylic acid*, cf. Rose and Fischer, A., 1914, i, 429). 2:4:5-Trimethylpyrrole condenses with anhydrous hydrogen cyanide and gaseous hydrogen chloride to yield 2:4:5-trimethylpyrrole-3-aldimine hydrochloride, which, on treatment with ammonia, forms 2:4:5-trimethylpyrrole-3-aldehyde, m. p. 143°. Similarly from 2:4-dimethylpyrrole the 2:4-dimethylpyrrole-5-aldehyde is obtained together with a substance,  $\text{C}_{14}\text{H}_{19}\text{N}_3$ , m. p. 174°. J. W. B.

**Formation of Pyridine Derivatives from Acyclic  $\delta$ -Diketones.** E. E. BLAISE and M. MONTAGNE (*Compt. rend.*, 1925, 30, 1760—1762).—The ketonic groups of complex  $\delta$ -diketones

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containing electro-negative groups undergo enolisation on treatment with ammonia, and dihydropyridine bases are obtained (cf. Hantzsch, A., 1886, 77; Paal and Strasser, A., 1888, 62; Wislicenus, A., 1888, 1178), but the simpler acyclic  $\delta$ -diketones give cyclohexenones on treatment with ammonia. Thus  $\gamma\gamma$ -nonadione and ammonia yield exclusively 2-methyl-3-ethyl- $\Delta^2$ -cyclohexen-1-one, b. p.  $104^\circ/17$  mm. Knoevenagel (A., 1895, i, 48) has obtained pyridine bases by the action of hydroxylamine on aryl-substituted  $\delta$ -diketones and states that acyclic  $\delta$ -diketones will not undergo this reaction, but this conclusion is shown to be inaccurate. By treatment of  $\gamma\gamma$ -nonanedione with hydroxylamine hydrochloride, or, better, by heating the dioxime with alcoholic hydrochloric acid, 2:6-diethylpyridine, b. p.  $71-73^\circ/17$  mm. (picrate, m. p.  $115^\circ$ , chloroaurate, m. p.  $92^\circ$ , chloroplatinate, m. p.  $142^\circ$ ), is obtained.

L. F. H.

**New Derivatives of the Pyridinecarboxylic Acids.** H. MEYER (*Rec. trav. chim.*, 1925, **44**, 323—328).—By the action of the acid chloride on the sodium salt of the pyridine-mono- and -dicarboxylic acids in xylene solution with the rigid exclusion of moisture, the acid anhydrides have been prepared, which, by the action of ammonia, yield the acid amides. The regenerated acids have been further characterised by the preparation of their phenyl esters. *Picolinic anhydride*, m. p. (sealed tube)  $124^\circ$ , sublimes  $140-150^\circ$ , extremely hygroscopic, *phenyl ester*, m. p.  $82^\circ$ , *amide*, m. p.  $107^\circ$ ; *nicotinic anhydride*, subliming  $200^\circ$ , m. p. (sealed tube)  $224-225^\circ$ , *phenyl ester*, m. p.  $59^\circ$ , *amide*, m. p.  $120-122^\circ$ ; *isonicotinic anhydride*, sublimes  $220-240^\circ$ , m. p. (sealed tube)  $302^\circ$  (decomp.), *phenyl ester*, m. p.  $70^\circ$ , *amide*, m. p.  $152-154^\circ$ ; *cinchoninic anhydride*, sublimes  $210-220^\circ$ , m. p. (sealed tube)  $245^\circ$  (decomp.), *phenyl ester*, m. p.  $112^\circ$ , *amide*, m. p.  $177^\circ$ ; *phenyl esters* of dipicolinic acid, m. p.  $179^\circ$ , lutidinic acid, m. p.  $136^\circ$ , *isocinchomeronic acid*, m. p.  $156^\circ$ . Pure thionyl chloride reacts with lutidinic acid to yield the normal unimolecular acid chloride, m. p.  $54-55^\circ$ , but crude thionyl chloride yields the polymeride, m. p.  $203^\circ$ , which passes into the unimolecular form on heating with pure thionyl chloride, this forming another example of the different action of the crude and pure reagent previously observed by Meyer and Turnau (cf. A., 1909, i, 419). 6-Methylpicolinic acid yields a *methyl ester*, m. p.  $29^\circ$ , which with aqueous ammonia yields the *amide*, m. p.  $116^\circ$ , whence, by the Hofmann reaction, is obtained 6-amino- $\alpha$ -picoline, m. p.  $41^\circ$ , b. p.  $205-206^\circ$ , *hydrochloride*, m. p.  $155^\circ$ , *chloroplatinate*, m. p.  $218^\circ$  (decomp.), *acetyl derivative*, m. p.  $88^\circ$ .

J. W. B.

**Occurrence of Tryptophan in Silk Fibroin.** E. HIRATSUKA (*Biochem. Z.*, 1925, **157**, 46—49).—Tryptophan has been isolated in a pure state from the products of the hydrolysis of silk fibroin with barium hydroxide. The tryptophan content is considerably greater in "wild" silk than in the cultivated variety. Colorimetric determinations by Herzfeld's method confirm the results of the isolation experiments.

H. D. K.

**Derivatives of Barbituric Acid.** V. VOORHEES and G. S. SKINNER (*J. Amer. Chem. Soc.*, 1925, **47**, 1124—1127).—*Ethyl ethyl-β-chloroethylmalonate*, b. p. 131—133°/9 mm., was prepared by the action of ethylene chloriodide on sodio ethyl ethylmalonate. When heated with the appropriate amines in ether at 100°, it yielded *ethyl ethyl-β-dimethylaminoethylmalonate*, b. p. 135—136°/10 mm., and *ethyl ethyl-β-diethylaminoethylmalonate*, b. p. 145—152°/12 mm., respectively. When treated with carbamide and sodium ethoxide in alcoholic solution at 100°, the above amines were converted into *5-ethyl-5-β-dimethylaminoethylbarbituric acid*, m. p. 171° (*hydrochloride*, m. p. 246—247°), and *5-ethyl-5-β-diethylaminoethylbarbituric acid* (*hydrochloride*, m. p. 258—260°) respectively. Neither of these showed any hypnotic properties. *Methyl acetylphenylmalonate*, b. p. 168—175°/13 mm. (*phenylhydrazone*, m. p. 126—127°), was prepared by treating sodio methyl phenylmalonate with acetyl chloride in ether. *Bromophenylbarbituric acid*, m. p. 214° with subsequent decomposition, was obtained by the action of bromine on phenylbarbituric acid in alkaline solution. A convenient method of preparing ethylene iodide from iodine chloride and ethylene in presence of water is described. F. G. W.

**Oxidation of 2 : 5-Diketopiperazines by Hydrogen Peroxide.** M. LÜDTKE (*Z. physiol. Chem.*, 1925, **143**, 158).—When oxidised by dilute hydrogen peroxide, glycine anhydride yields a crystalline substance and an oil. E. S.

**New Bases : Carbamides of Pyrazolines.** R. LOCQUIN and R. HEILMANN (*Compt. rend.*, 1925, **180**, 1757—1760).—By the action of potassium cyanate in acetic acid solution on pyrazolines, the corresponding carbamides are formed:  $\text{:NH} + \text{CHON} = \text{:N} \cdot \text{CO} \cdot \text{NH}_2$ . All the carbamides obtained are weak bases, are stable in alkaline solution, but with acids yield the parent pyrazolines, form well crystalline picrates, and give dibenzoyl derivatives. 3 : 5 : 5-*Trimethylpyrazoline-1-carbamide*, m. p. 129°, b. p. 140—141°/10 mm., *picrate*, m. p. 136—137°, on treatment with nitrous acid, yields carbamazide and mesityl oxide. 3-*Methyl-5-isopropylpyrazoline*, b. p. 75—77°/11 mm. (*benzenesulphonate*, m. p. 109—114°, *p-bromobenzenesulphonate*, m. p. 134—135°), obtained by the action of hydrazine hydrate on isobutylideneacetone, gives a *carbamide*, m. p. 116—117°, b. p. 155—157°/11 mm., *dibenzoyl derivative*, m. p. 141°. 3-*Methyl-5-isobutylpyrazoline*, b. p. 90—92°/10 mm., *benzenesulphonate*, m. p. 93—115°, yields a *carbamide*, m. p. 110—111°, b. p. 162—168°/10 mm., *dibenzoyl derivative*, m. p. 128—129°. 4-*Methyl-5-ethylpyrazoline*, b. p. 65—70°/10 mm. (*benzenesulphonate*, m. p. 118°), obtained from α-methyl-β-ethylacraldehyde by the action of hydrazine hydrate, gives a *carbamide*, b. p. 155—160°/11 mm., m. p. 100—110°. The pyrazolinecarbamides are isomeric with the semicarbazones of the αβ-unsaturated aldehydes and ketones, and the carbamide of the pyrazoline derived from mesityl oxide is identical with the side-product of interaction of semicarbazide and mesityl oxide (cf. Scholtz, A., 1896, i, 343), of which



the constitution has been in doubt (Harries and Kaiser, A., 1899, i, 637; Rupe and Kessler, A., 1910, i, 15, 93). L. F. H.

**Indazoles from *o*-Nitromandelonitrile.** G. HELLER and G. SPIELMEYER (*Ber.*, 1925, 58, [B], 834—838).—3-Cyano-2-phenylindazole-1-oxide,  $C_6H_4 \begin{smallmatrix} N(O) \\ \diagup \diagdown \\ C(CN) \end{smallmatrix} > NPh$ , m. p. 190°, is prepared by the action of aniline on *o*-nitromandelonitrile in alcoholic solution in the presence of a little sodium acetate or from *o*-nitrobenzaldehyde, aniline hydrochloride, potassium cyanide, and sodium acetate in aqueous-alcoholic solution. It is reduced by zinc dust and acetic acid to 3-cyano-2-phenylindazole, m. p. 105°, which is converted successively into 2-phenylindazole-3-carboxylic acid, m. p. 200° (decomp.) (corresponding amide, m. p. 247—248°), and 2-phenylindazole, m. p. 83—84°. 3-Cyano-2-p-tolylindazole-1-oxide, m. p. 198—199°, is prepared by the same methods as the phenyl compound or by the addition of acetic acid to an aqueous-alcoholic solution of potassium cyanide and *o*-nitrobenzylidene-*p*-toluidine, m. p. 73°; it yields successively 3-cyano-2-p-tolylindazole, m. p. 135°, 2-p-tolylindazole-3-carboxylic acid, m. p. 195° (decomp.), and 2-p-tolylindazole, m. p. 105°. 3-Cyano-2-p-chlorophenylindazole-1-oxide, m. p. 201°, 3-cyano-2-p-chlorophenylindazole, m. p. 159°, 2-p-chlorophenylindazole-3-carboxylic acid, m. p. 198° (decomp.), and 2-p-chlorophenylindazole, m. p. 138°, are described. 5-Chloro-3-cyano-2-phenylindazole-1-oxide, m. p. 226—228°, yields successively 5-chloro-3-cyano-2-phenylindazole, m. p. 147—148°, 5-chloro-2-phenylindazole-3-carboxylic acid, m. p. 200° (decomp.), and 5-chloro-2-phenylindazole, m. p. 147°.

The action of phenylhydrazine on *o*-nitromandelonitrile in alcoholic solution yields hydrocyanic acid and *o*-nitrobenzaldehydephenylhydrazone; a similar change is observed with the corresponding *meta* and *para* derivatives.

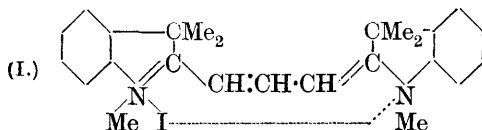
The action of hydrogen chloride on a solution of *o*-nitromandelonitrile in anhydrous ether gives 2-keto-3:6-di-*o*-nitrophenyl-1:2-di-hydro-1:4-diazine, m. p. 193°. H. W.

**Nitration of 2- and 4-Aminoquinoline.** A. E. TSCHITSCHIBABIN, D. P. WITKOVSKY, and M. I. LAPSCHIN (*Ber.*, 1925, 58, [B], 803—807).—Nitration of 2- and 4-aminoquinoline resembles the action of the corresponding pyridines (A., 1915, i, 591; 1923, i, 595) in yielding primarily stable nitroamino derivatives, although nitration in the nucleus is not entirely excluded. When isomerised, the nitro group passes into the benzenoid nucleus of the quinoline molecule.

Amination of quinoline by sodamide in the presence of xylene proceeds less smoothly than that of pyridine; the best yields (about 40%) of 2-aminoquinoline, m. p. 129.5°, are obtained by using well-stirred, dilute solutions of quinoline and very finely-divided sodamide. The base is converted by nitric acid (*d* 1.4) in the presence of sulphuric acid at 0° into 2-nitroaminoquinoline, decomp. 223—225° (the sodium and potassium salts are described),

which is converted by sulphuric acid at  $130^{\circ}$  into 6-nitro-2-aminoquinoline, m. p.  $261^{\circ}$ ; the constitution of the latter substance is established by its conversion into the known 6-nitro-2-hydroxyquinoline, m. p.  $280^{\circ}$ . Similarly, 4-aminoquinoline is converted into 4-nitroaminoquinoline, decomp.  $207^{\circ}$ , identical with the product described by Claus and Frobenius (A., 1898, i, 150) as 6-nitro-4-aminoquinoline. The compound is readily isomerised to 6-nitro-4-aminoquinoline, m. p.  $272^{\circ}$  (decomp.), which is oxidised by potassium permanganate to 5-nitroanthranilic acid. The dinitroaminoquinoline isolated by Claus and Frobenius (*loc. cit.*) is to be regarded as 6-nitro-4-nitroaminoquinoline. H. W.

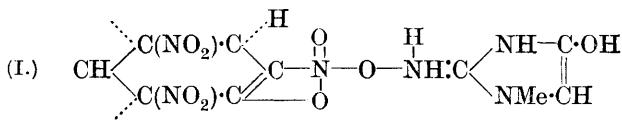
**Preparation of Polymethine Dyes.** FARBENFABRIKEN VORM. F. BAYER U. Co. (Brit. Pat. 232740).—By condensing ethyl orthoformate with 2 : 3 : 3-trimethyl- $\psi$ -indole methiodide in presence of acetic anhydride a red, basic dye is obtained having most probably the structure (I). Similar dyes can be obtained from



other cyclammonium compounds containing a reactive methyl group, e.g., 1-methylbenzthiazole or 1-methylbenzoxazole methiodide, the former giving a violet, the latter a yellow dye.

E. H. R.

**Jaffe's Reaction for Creatinine. II. Effect of Substitution in the Creatinine Molecule and a possible Formula for the Red Tautomeride.** I. GREENWALD (*J. Amer. Chem. Soc.*, 1925, 47, 1443—1448; cf. A., 1924, ii, 508).—The application of Jaffe's reaction to a number of compounds containing the creatinine nucleus indicates that red colorations are given only by those which contain the  $\cdot\text{CO}\cdot\text{CH}_2\cdot$  group, showing that the formation of a red tautomeride is due to a keto-enol rearrangement. The negative result obtained in this test with dimethylolcreatinine, in which enolisation is still possible, is due to its inability to form a picrate, as the basic nitrogen atoms are linked to  $\cdot\text{CH}_2\cdot\text{OH}$  groups. As neither 2 : 4-dinitrophenol nor 2 : 4 : 6-trinitro-*m*-cresol can replace picric acid in the test, it is concluded that two *ortho* nitro groups, as well as a hydrogen in the *meta* position, are necessary for the formation of the red tautomeride, and the following formula is suggested for the red creatinine picrate (I). *Methylcreatinine picrate*, yellow,



has m. p.  $183^{\circ}$ . Dimethylcreatinine hydriodide (cf. Kunze, A., 1911, i, 21) has m. p.  $187^{\circ}$ ; the *picrate* is soluble. By the action of

benzoyl chloride in pyridine on creatinine, a *benzoylcreatinine* was obtained as light brown plates, apparently not identical with that prepared by Urano (A., 1907, i, 192), although the two compounds, as well as a mixture of the two, have the same m. p., 190°. It is suggested that the latter is due to internal rearrangement at high temperature (cf. Schenk, A., 1911, i, 842). A dibenzoylcreatinine could not be obtained. *Tribenzoylcreatinine*, m. p. 238—240°, was prepared. *Benzylidenecetylcreatinine picrate*, yellow, m. p. 250° after softening at 230°, is hydrolysed on recrystallisation from water, alcohol, or glacial acetic acid to *benzylidenecreatinine picrate*, m. p. 260°. Reduction of benzylidenecreatinine with zinc dust and acetic acid afforded 2-benzylcreatinine (*picrate*, m. p. 206—208°). 5-Benzylcreatinine *picrate* (cf. Hennig, A., 1913, i, 1106) has m. p. 174—175°. Oxidation of the above benzylidenecetylcreatinine with alkaline permanganate afforded *acetylmethylguanidine picrate*, m. p. 160—162°, whilst Urano's benzoylcreatinine yielded similarly *benzoylmethylguanidine (hydrochloride)*, m. p. 222°; *picrate*, m. p. 180°. *Creatinine trinitro-m-tolylloxide*, m. p. 218°, is described,

F. G. W.

**General Method of Formation of 1-Phenyl-4-alkyl-1 : 2 : 3-triazoles.** A. BERTHO (*Ber.*, 1925, 58, [B], 859—864).—Diazobenzeneimide reacts with boiling alcoholic solutions of the sodium derivatives of primary aliphatic alcohols to yield aniline, 1-phenyl-4-alkyl-1 : 2 : 3-triazoles, nitrogen, and sodium hydroxide. The hydrogen necessary for the conversion of the "stable" residue,  $\text{PhN:}$ , appears to be derived from the sodium alkoxide, which is thus converted into the sodium derivative of an unsaturated alcohol, which condenses with unchanged diazobenzeneimide to the triazole. The sodium derivatives of secondary alcohols do not react in a similar manner, but cause the conversion of all the azide into aniline. Ethyl-alcoholic sodium ethoxide solution thus yields 1-phenyl-1 : 2 : 3-triazole, m. p. 56°, b. p. 172—174°/18.5 mm. 1-Phenyl-4-methyl-1 : 2 : 3-triazole, m. p. 81°, 1-phenyl-4-ethyl-1 : 2 : 3-triazole, b. p. 169—170°/12 mm., m. p. 19°, and 1-phenyl-4-isopropyl-1 : 2 : 3-triazole, b. p. 183—185°/20 mm., m. p. 29°, are similarly obtained. Small quantities of an acidic substance, m. p. 272°, are produced in all these reactions.

H. W.

#### Additive Formation of Four-membered Rings. VII. Synthesis and Division of Some Dimethylene-1 : 3-oxamines.

C. K. INGOLD (*J. Chem. Soc.*, 1925, 127, 1141—1145).—Examples of equilibria of the type  $\text{PQC} + \text{NZ} \rightleftharpoons \text{PQC}-\text{NZ} \rightleftharpoons \text{PQC:NZ} + \text{O:CXY}$  are studied. The ring-compound assumed to be formed intermediately is too unstable to be isolated, but the equilibrium may be determined in either direction by the choice of a suitable solvent.

Examples of equilibria which can be approached in ethyl acetate, chloroform, or absolute alcohol from either side are : (1) *p*-Nitrobenzaldehyde + *m*-nitrobenzylidene-*p*-nitrobenzylamine  $\rightleftharpoons$  *p*-nitrobenzylidene-*p*-nitrobenzylamine + *m*-nitrobenzaldehyde. (2)

*m*-Nitrobenzaldehyde + *p*-nitrobenzylidene-*m*-nitrobenzylamine  $\rightleftharpoons$  *m*-nitrobenzylidene-*m*-nitrobenzylamine + *p*-nitrobenzaldehyde.

The following reactions are quantitative, owing to the insolubility of one of the products in absolute alcohol: (1) *p*-Nitrobenzaldehyde + benzylidene-*p*-nitrobenzylamine  $\rightarrow$  *p*-nitrobenzylidene-*p*-nitrobenzylamine + benzaldehyde. (2) *m*-Nitrobenzaldehyde + benzylidene-*p*-nitrobenzylamine. (3) *p*-Nitrobenzaldehyde + benzylidene-*m*-nitrobenzylamine. (4) *m*-Nitrobenzaldehyde + benzylidene-*m*-nitrobenzylamine similarly. C. H.

**Constitution of Aqueous Solutions of *o*-Benzoic sulphinide (Saccharin) and *p*-Phenethylcarbamide (Dulcin).** K. TÄUFEL and C. WAGNER (*Ber.*, 1925, **58**, [B], 909—912).—As a result of an error in the calculation of the molecular conductivity, Magidson and Gorbatschov (*A.*, 1923, i, 1097) have not observed that “sodium-saccharin” is a strong electrolyte. Its degree of dissociation is therefore not appreciably depressed by the addition of an electrolyte which gives rise to sodium ions, and the sweet taste of its solutions is not affected by such addition. In the case of saccharin, undissociated molecules are practically absent from such solutions as are used in experiments on taste and the saccharin ion must therefore be regarded as solely responsible for the sweetness. The basic dissociation constant of dulcin is less than  $4 \times 10^{-15}$ ; the sweetness of its solutions is due to the dulcin molecule. The increase in sweetness caused by the mixture of saccharin and dulcin in solution is not due to salt formation, but is an additive phenomenon; the apparent exaltation is attributable to the small concentration of each component, since each, under these conditions, develops its maximum sweetening action. H. W.

**Benzthiazole Series. III. Pseudo-bases of the 1-Substituted Benzthiazole Quaternary Salts.** L. M. CLARK (*J. Chem. Soc.*, 1925, **127**, 973—975; cf. Mills, Clark, and Aeschlimann, T., 1923, **123**, 2353).—The  $\psi$ -bases are substituted thiophenols, oxidisable by air or iodine to the disulphides. 2 : 2'-*Di*-(*acetylmethylamido*)diphenyl disulphide, m. p.  $171^\circ$ , is prepared either from 1-methylbenzthiazole methiodide by air oxidation in ammonia solution or from 2 : 2'-*di*-(methylamino)diphenyl disulphide by acetylation; 2 : 2'-*di*-(*acetylethylamido*)diphenyl disulphide, m. p.  $103^\circ$ , from the ethiodide; 2 : 2'-*di*-(*acetylmethylamido*)-5 : 5'-*dimethyl*-diphenyl disulphide, m. p.  $129^\circ$ , from 1 : 5-dimethylbenzthiazole ethiodide; and 2 : 2'-*di*-(*benzoylmethylamido*)diphenyl disulphide, m. p.  $164^\circ$ , is obtained either from 1-phenylbenzthiazole methiodide, m. p.  $218^\circ$ , or from *di*-(methylamino)diphenyl disulphide by benzoylation.

The constitution of bis-2-methylbenzthiazoline-1 : 1'-spiran (*loc. cit.*, p. 2365) is confirmed by hydrolysis with 90% formic acid, the products being 2-methylbenzthiazolone, m. p.  $76^\circ$ , and 2 : 2'-*di*-(*formylmethylamido*)diphenyl disulphide, m. p.  $106$ — $107.5^\circ$ .

C. H.

**Influence of Methyl and Sulphonic Acid Groups as well as Other Substituents on the Colour of Azo Dyes.** E. WANNER (*Z. angew. Chem.*, 1925, **38**, 513—519).—The displacement of the

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maxima of the principal absorption bands in the spectra of dyes of the type Benzo-light-red-8BL. (from aminoazobenzene-*p*-sulphonic acid and benzoyl J-acid) by the introduction of various substituents has been determined.

Methyl radicals were introduced by using a series of homologues of aminoazobenzenesulphonic acid, and further parallel series of colours were obtained in which benzoyl J-acid was replaced by J-acid, acetyl J-acid, and J-acid carbamide. A series of Y-acid colours was also prepared. The wave-lengths of the absorption maxima were measured in aqueous solution, and in general a positive (bathochrome) displacement was observed. The strongest effect was obtained when the methyl groups were *ortho* to the amino group. Substitution in the *meta* position only produced one-sixth of the displacement. A small negative (hypsochrome) effect was noticed when the methyl group was in the other ring of the aminoazobenzenesulphonic acid and *ortho* to the azo group. The fastness of the colours to acid and alkali was considerably increased and the fastness to light slightly improved by the introduction of methyl groups.

The effect of sulphonic acid groups was determined by comparing dyes of the above type derived from aminoazobenzene and its homologues, with the dyes from the corresponding sulphonic acids. The spectra were examined, using water, alcohol, concentrated sulphuric acid, and in certain cases formic acid (85%) as solvents. A positive effect was usually obtained in which *para* produced a larger displacement than *meta* substitution. Two exceptional cases showing negative effects were observed in a series of Y-acid colours in changing from aminoazobenzenedisulphonic acid to aminoazotoluenedisulphonic acid, and also in a series of  $\beta$ -naphthol colours in going from the mono- to the di-sulphonic acid of aminoazobenzene. The introduction of sulphonic acid groups markedly improved the fastness to light.

The displacement produced by methoxyl groups was strongly positive, and the fastness to light was considerably increased.

The introduction of amino, nitro, and chloro groups into the acetyl group of acetyl J-acid produced only very slight colour changes. A comparison of the dyes derived from J-acid, acetyl J-acid, benzoyl J-acid, and J-acid carbamide showed that whilst the acetyl group had only a small positive effect, the action of the benzoyl radical was much greater, and the effect of the carbamide group was four times as great as that of the benzoyl group. F. R.

**Action of Hydrogen Chloride on *cyclo*Hexylideneazine and on *cyclo*Pentylideneazine.** W. H. PERKIN, jun., and S. G. P. PLANT (*J. Chem. Soc.*, 1925, 127, 1138—1141).—*cyclo*Hexylideneazine is converted into octahydrocarbazole by hydrogen chloride in tetrahydronaphthalene at 180° (Perkin and Plant, A., 1924, i, 1104), but under similar conditions *cyclopentylideneazine*, m. p. 25°, b. p. 130—132°/22 mm., yields no pyrrole derivative but *tricyclotrimethylenebenzene*,  $C_6\left(\begin{smallmatrix} <CH_2> \\ <CH_2> \end{smallmatrix}CH_2\right)_3$ , m. p. 97°, identical

with Wallach's product (A., 1897, i, 425) from *cyclopentanone* and hydrogen chloride. *cycloHexylidenecyclopentylideneazine*, b. p. 140—145°/12 mm., is obtained by heating together *cyclohexanone-hydrazone* and *cyclopentanone*. It gives no pyrrole derivative under the above conditions.

The objections of von Braun and Bayer (this vol., i, 428, and *Ber.*, 1925, 58, [B], 389) to the structure suggested for the octa-hydrocarbazole from *cyclohexylideneazine* are answered by the preparation of the strongly basic tetramethylpyrrole (Fischer and Bartholomäus, A., 1912, i, 901), and by the methylation of tetraphenylpyrrole to *tetraphenyl-1-methylpyrrole*, m. p. 210°. C. H.

**Arylazides.** V. E. BAMBERGER (*Annalen*, 1925, 443, 192—210; cf. A., 1924, i, 227, 281, 282).—Mainly experimental details of results previously reported and discussed (cf. A., 1921, i, 716). Benzylimide treated with hydrogen sulphide in hydrochloric acid solution is converted into di-*p*-aminobenzyl sulphide. J. W. B.

**Reduction of Phenylhydrazones.** R. C. GOODWIN and J. R. BAILEY (*J. Amer. Chem. Soc.*, 1925, 47, 167—174).—Reduction of acetonephenylhydrazone with hydrogen in presence of colloidal platinum in 95% alcoholic solution affords *s*-phenylisopropylhydrazine,  $\text{NHPh}\cdot\text{NPr}^3$ , b. p. 162°/25 mm.,  $d$  0.9720,  $n^{20}_D$  1.5463 (hydrochloride, m. p. 202°; oxalate, m. p. 189°; monobenzoyl derivative, m. p. 113.5°; dibenzoyl derivative, m. p. 140°), which is oxidised on exposure to air to  $\beta$ -benzeneazopropane, reddish-yellow, b. p. 110°/28 mm.,  $d$  0.9443,  $n^{20}_D$  1.5249. It yields a *diphenyldiisopropyltetrazine*, m. p. 163°, when treated with formaldehyde (cf. Knorr and Weidel, A., 1909, i, 965) and combines with phenylcarbimide and -thiocarbimide to form, respectively, 1 : 4-diphenyl-2-isopropyl-semicarbazide,  $\text{NHPh}\cdot\text{NPr}^3\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 146° (benzoyl derivative, m. p. 162°), and -thiosemicarbazide, m. p. 153°. Treatment with potassium cyanate in acetic acid affords 1-phenyl-2-isopropylsemicarbazide, m. p. 119° (nitroso derivative, m. p. 156°). 2-Phenyl-1-isopropylsemicarbazide, m. p. 209° (benzoyl derivative, m. p. 181°), obtained by reducing acetone-2-phenylsemicarbazone (cf. Goodwin and Bailey, this vol., i, 318) with hydrogen in presence of colloidal platinum, yields, on oxidation with permanganate in aqueous solution,  $\beta$ -benzeneazopropane, whilst in acetone solution a white, crystalline solid is obtained. 2-Phenyl-1-isopropylurazole,  $\text{NH}\cdot\text{CO} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{NPr}^3$ , m. p. 165°, is obtained when either of the above semicarbazides is heated with carbamide at 200—240°. 1-iso-Propylurazole, m. p. 190°, is obtained similarly from 1-isopropylsemicarbazide. *s*-Phenylcyclohexylhydrazine, b. p. 226°/100 mm., obtained by catalytic reduction of *cyclohexanonephenylhydrazone*, is described. F. G. W.

**Aromatic Chlorovinylarsines.** A. F. HUNT and E. E. TURNER (*J. Chem. Soc.*, 1925, 127, 996—999).—Acetylene is slowly absorbed by a cooled solution of aluminium chloride in phenyldichloroarsine and gives, after treatment with ice and hydrochloric acid, *phenyl-*  
g g\* 2

$\beta$ -chlorovinylchloroarsine,  $\text{AsPhCl}\cdot\text{CH}\cdot\text{CHCl}$ , b. p.  $140\text{--}145^\circ/10\text{ mm.}$ , and phenyl- $\beta\beta'$ -dichlorodivinylarsine, b. p.  $155^\circ/10\text{ mm.}$  The latter product is also obtained by the action of magnesium phenyl bromide on  $\beta\beta'$ -dichlorodivinylchloroarsine; it forms *additive* compounds with silver nitrate,  $[\text{AsPh}(\text{CH}\cdot\text{CHCl})_2, \text{AgNO}_3]$ , m. p.  $142^\circ$ , chloroplatinic acid, and mercuric chloride, and gives a gummy *methiodide*.

1-Phenylarsenopyrrole was not obtained in identifiable amount by heating the arsine with sodium in toluene. A cold solution of aluminium chloride in phenyldichloroarsine deposits a pale yellow *additive* compound,  $\text{AsPhCl}_2\cdot\text{AlCl}_3$ , on keeping a short time; after longer keeping mixtures of high-boiling condensation products are formed. If the solution is not cooled during absorption of acetylene, benzene and  $\beta$ -chlorovinylchloroarsine result.

Arsenious chloride combines with phenylacetylene to give  $\alpha$ -chlorostyryldichloroarsine, b. p.  $108\text{--}110^\circ/12\text{ mm.}$ , and  $\alpha\alpha'$ -dichlorodistyrylchloroarsine, b. p.  $170\text{--}175^\circ/12\text{ mm.}$  C. H.

**Mercuration of Aromatic Substances. I. Toluene.** S. COFFEY (*J. Chem. Soc.*, 1925, 127, 1029—1032).—Pure toluene, prepared by hydrolysis (superheated steam and sulphuric acid) of pure *p*-toluenesulphonamide and boiling within  $0.1^\circ$  at  $109.4^\circ/743\text{ mm.}$ , was refluxed with mercuric acetate and after partial separation of mono- from poly-mercuri compounds, the former were converted quantitatively into a mixture of bromotoluenes, which by oxidation to bromobenzoic acids, was shown to contain *o*-, *m*-, and *p*-compounds in the ratio 43 : 13 : 44. Boiling saturated aqueous solutions of the three bromobenzoic acids, prepared by oxidation of pure bromotoluenes from purified toluidines, contained 4%, 1%, and 0.15% of the *o*-, *m*-, and *p*-acids, respectively; the solubilities of the barium salts at  $18^\circ$  were: *o*-, 23%; *m*-, 0.65%; *p*-, 0.85%; and at  $100^\circ$ , *m*-, 3.4 g., *p*-, 2.25 g. per 100 c.c. C. H.

**Organic Compounds of Mercury.** A. ALBERT (*Brit. Pat.* 208151, 209767).—By the action of mercuric oxide on a sodium hydroxide solution of acetophenone-*p*-arsinic acid (*Brit. Pat.* 206507), and acidification of the solution, a crystalline product is obtained having marked therapeutical properties. The corresponding antimonie acid gives a similar product. Instead of the ketones themselves, their hydrazones or semicarbazones may be used, giving mercury compounds also having therapeutical properties. E. H. R.

**Pyocyanine, the Blue Pigment in *Bacillus pyocyaneus*** II. F. WREDE and E. STRACK (*Z. physiol. Chem.*, 1925, 142, 103—119).—Improved yields of pyocyanine (this vol., i, 174) are obtained when the bacillus is cultivated in Merck's "Ragibouillon" at  $p_{\text{H}}$  7.8. Pyocyanine crystallises with  $10\text{H}_2\text{O}$ . It reacts with semicarbazide and thiosemicarbazide, forms a *dinitrosoamine* (*chloroaurate*,  $\text{C}_{26}\text{H}_{22}\text{O}_4\text{N}_6\cdot\text{HAuCl}_4$ ), and is decomposed quantitatively into 2 mols. of hemipyocyanine [*chloroaurate*,  $\text{C}_{13}\text{H}_{12}\text{ON}_2\cdot\text{HAuCl}_4$ , m. p.  $179^\circ$ ; *chloroplatinate*,  $(\text{C}_{13}\text{H}_{12}\text{ON}_2)_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$ ] on treatment with 1% sodium hydroxide for 24 hours. Hemipyocyanine,

m. p. 157—158°, has now been obtained in a pure state. It forms a nitrosoamine, a *methyl ether*, m. p. 169° (*chloroaurate*, m. p. 203—205°), and an *ethyl ether*, m. p. 124° (*chloroaurate*, m. p. 193—194°), does not react with ketone reagents, and when distilled with zinc dust under diminished pressure yields phenazine. Pyocyanine, which thus contains two tertiary and two secondary nitrogen atoms and probably two carbonyl groups, is probably composed of 2 mols. of hemipyocyanine united symmetrically by peptide linkings. In hemipyocyanine the hydrogen from the imino group migrates to the oxygen and forms a phenolic hydroxyl group. Alternative structures for pyocyanine are suggested. E. S.

**Oxyhæmin and Its Salts.** A. HAMSIK (*Spisy Lékařské Fakulty Masarykovy University V Brně, ČSR*, 1924, 2, 1—12; from *Chem. Zentr.*, 1924, ii, 2661).—The *potassium* salts of oxyhæmin,  $C_{34}H_{31}O_5N_4K_2Fe$  and  $C_{34}H_{30}O_5N_4K_3Fe$ , are obtained by the action of alcoholic potassium hydroxide on  $\alpha$ -chlorohæmin or oxyhæmin anhydride; the reaction affords a means of distinguishing  $\alpha$ -oxyhæmin anhydride from the  $\beta$ -compound. Preparations obtained by incomplete extraction of blood contain only the  $\alpha$ -compound; on complete extraction, the  $\beta$ -compound is also present. The tripotassium salt, containing both  $\alpha$ - and  $\beta$ -forms, is obtained by treating with alcoholic potassium hydroxide the precipitate formed on neutralising blood extract. Glacial acetic acid yields oxyhæmin anhydride free from chlorine, whilst the corresponding *calcium*, *barium*, *silver*, and *lead* salts are obtained from the appropriate acetate in methyl-alcoholic solution. R. B.

**Porphyrins. VIII. Formation of Porphyrin from Hæmin.** W. KÜSTER and R. HUTTENLOCHER (*Z. physiol. Chem.*, 1924, 141, 282—290).—When methyl(chloro)hæmin is reduced catalytically or with zinc and acetic acid a substance is obtained which gives a porphyrin spectrum but still retains the iron. Apparently partial reduction occurs. This is provisionally interpreted on the basis of the formulæ recently proposed (*Z. f. Probleme der Gärung*, vol. 1; cf. also *Z. physiol. Chem.*, 1924, 133, 126). E. S.

**Natural Porphyrins. XIII. Conversion of Hæmoporphyrin into Mesoporphyrin and its Degradation to Aetioporphyrin.** H. FISCHER and R. MÜLLER (*Z. physiol. Chem.*, 1925, 142, 120—140).—That hæmoporphyrin contains an unsaturated side-chain is shown by its reduction to mesoporphyrin with hydriodic acid in glacial acetic acid solution. Mesoporphyrin, when converted into its phyllin and decarboxylated, yields an aetioporphyrin which is identical with that obtained from chlorophyll. Hæmoporphyrin, hæmoporphyrin ester, and aetioporphyrin are scarcely distinguishable spectroscopically; their spectra are only little different from those given by mesoporphyrin and its ester. The carboxyl group evidently has little influence on the spectrum. E. S.



**Natural Porphyrins. XV. Tetramethylhæmatoporphyrin Ester and its Conversion into Ooporphyrin Ester.** H. FISCHER and R. MÜLLER (*Z. physiol. Chem.*, 1925, **142**, 155—174).—The tetramethyl ester of hæmatoporphyrin may be obtained in four forms according to the method of preparation: A, m. p. 185°; B, m. p. 178.5°; C, m. p. 140°; D, m. p. 110°. Of these, A and D are crystallographically identical. B, C, and D are probably stereoisomerides. Since, on heating in a vacuum, they all lose two mols. of methyl alcohol with the formation of the dimethyl ester of ooporphyrin, it is probable that the isomerism is caused by a double bond in one of the side-chains. E. S.

**Porphyryns.** O. SCHUMM (*Z. physiol. Chem.*, 1925, **142**, 209—214).—Polemical against H. Fischer. E. S.

**Isolation from Caseinogen of an Amino-acid of the Indole Group with the Composition  $C_{11}H_{14}O_3N_2$ .** E. ABDERHALDEN and H. SICKEL (*Z. physiol. Chem.*, 1925, **144**, 80—84).—On hydrolysing, with 25% sulphuric acid, the substance isolated by the authors (A., 1924, i, 1101) from the products of tryptic digestion of caseinogen, after crystallisation from water and before drying in a vacuum at 105°, tyrosine and proline were obtained. The substance is therefore not a tryptophan derivative but a dipeptide of tyrosine and proline or of tyrosine with  $\delta$ -hydroxy- $\alpha$ -aminovaleric acid. The failure to recognise these products of hydrolysis previously was due to the formation, by the original compound, under the conditions of desiccation described, of an anhydride, which on hydrolysis gives very small amounts of tyrosine and proline together with unidentified products. C. R. H.

**Coagulation of Caseinogen in Acid Solution in Presence of Calcium Salts.** L. LINDET (*Compt. rend.*, 1925, **180**, 1462—1463).—Addition of lactic acid to milk precipitates the casein; if a further quantity of lactic acid is added to the washed coagulated casein it dissolves, forming a clear gel, from which the casein is again precipitated by the addition of calcium chloride, the precipitate containing only a minute amount of calcium salts. Phosphoric acid can replace lactic acid in these experiments with the same results. L. F. H.

**Complexes containing Calcium Salts of Caseinogen and Phosphoric Acid, and their Coagulation by Rennin.** C. PORCHER (*Compt. rend.*, 1925, **180**, 1534—1536; cf. A., 1922, i, 1041, and preceding abstract).—On treating caseinogen with increasing quantities of lime, complexes of decreasing hydrogen-ion concentration are obtained. Caseinogen complexes with  $p_H$  less than 7 are not coagulated by rennin. For the coagulation of caseinogen by rennin it is necessary to have present an alkaline-earth salt of a polybasic acid, such as phosphoric, lactic, arsenic, silicic, or carbonic acid, which can form a stable colloidal complex with the caseinogen. On keeping the caseinogen concentration and hydrogen-ion concentration of such a complex constant and adding increasing amounts of a salt such as calcium phosphate,

the rapidity of formation and solid consistency of the coagulum, formed by heating or by rennin, are increased. L. F. H.

**Action of Carbon Dioxide on Calcium Caseinogenate. Colloidal Calcium Carbonate.** C. PORCHER (*Compt. rend.*, 1925, **180**, 1788—1790).—The passage of carbon dioxide into an alkaline lime-caseinogen complex (cf. preceding abstract) induces the coagulation of the casein. The coagulum consists entirely of casein, but the conditions of formation and physical properties of the solid are determined by the nature and method of formation of the calcium carbonate present. L. F. H.

**Limits of Precipitability of Gelatin by Tannin.** I. A. SMORODINCEV and A. N. ADOVA (*Z. physiol. Chem.*, 1925, **144**, 255—258).—The addition of a solution obtained by diluting a 4% solution of tannin in 50% alcohol with ten times its volume of water or 50% alcohol precipitates aqueous gelatin solutions (0.005%,  $p_H=4.91$ ), whereas if the tannin solution be diluted with 0.9%, 10%, 33% (satd.) sodium chloride solution, then 0.003% gelatin solutions ( $p_H=4.96$ ) are precipitated. Aqueous gelatin solutions are precipitated more readily than in the presence of sodium carbonate and hydrogen carbonate; 0.25% gelatin solutions were not precipitated by tannin in presence of sodium carbonate ( $p_H=10.06$ ), whilst solutions containing less than 0.013% of gelatin are not precipitated in presence of hydrogen carbonate ( $p_H=8.95$ ). Aqueous gelatin solutions containing less than 0.003% are not precipitated by tannin. P. W. C.

**Action of Alkalis on Keratin.** M. BERGMANN and F. STATHER (*Collegium*, 1925, 109—110).—The product of the action of cold sodium sulphide solution on wool or of hot sodium sulphide solution on horsehair was dried, hydrolysed, and precipitated with alkali, and the sulphur content determined. The cystine content of the wool was lowered slightly by the sodium sulphide treatment. The cystine content of the horsehair was practically all destroyed by hot sodium sulphide. D. W.

**Brominated Keratin and Hydroxykeratin.** II. Z. STARY (*Z. physiol. Chem.*, 1925, **144**, 147—177).—When human hair is subjected to the action of bromine in acetic acid solution or to hydrogen peroxide in 4*N*-sulphuric acid for a long time, the chief product obtained is a protein of high molecular weight, which is easily soluble in alkali, precipitated from solution by acids, of constant composition, and easily hydrolysed by trypsin. It does not give the carbonyl, picric acid, or dinitrobenzene reaction. On the other hand, keratoses produced by the action of alkali or acid give these tests, but are resistant to trypsin. It is suggested that the ring systems present in the keratin molecule are caused to pass into polypeptide chains which are then readily attacked by trypsin (cf. A., 1924, i, 1007). P. W. C.

**The Carbohydrate Group of Glucoproteins.** S. IZUMI (*Z. physiol. Chem.*, 1925, **142**, 175—188).—The amount of reducing

sugar (glucosamine) produced during the hydrolysis of ovomucoid is too large to be accounted for as chondroitin sulphuric acid. The occurrence of the latter in this protein is hence improbable (cf. Levene, A., 1918, i, 554).

The amount of glucosamine formed during the hydrolysis of ovalbumin remains constant even after several crystallisations.

E. S.

**Oxidation of Polypeptides and of 2 : 5-Diketopiperazines.**

E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1925, **144**, 234—240).—The hydrogen peroxide oxidation method does not appear entirely satisfactory for distinguishing polypeptides and 2 : 5-piperazines.

P. W. C.

**Molecular Compounds of Amino-acids and Diketopiperazines.** P. PFEIFFER and O. ANGERN.—(See i, 794.)

**Transformation of Peptide-like Substances. IV.** M. BERGMANN and others.—(See i, 795.)

**Composition of Proteins. VI. Gliadin.** N. TROENSEGAARD and E. FISCHER (*Z. physiol. Chem.*, 1925, **142**, 35—70).—The product of the reduction of acetylglutadin with sodium and amyl alcohol (cf. A., 1924, i, 890) has been fractionated. From analyses of the various fractions as well as from their behaviour on acetylation and methylation, it is concluded that the basic fractions consist mainly of pyrrole derivatives and that the acid fractions are similarly largely heterocyclic.

E. S.

**Composition of the Proteins. VI. Correction.** N. TROENSEGAARD and E. FISCHER (*Z. physiol. Chem.*, 1925, **143**, 304).—Errata in certain formulæ.

H. D. K.

**Structure of the Protein Molecule.** E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1925, **143**, 128—132).—In confirmation and extension of previous work (this vol., i, 175), it is shown that polypeptides, with the exception of glycylglycine or of peptides containing this grouping, are completely deaminated on oxidation with zinc permanganate; diketopiperazines, peptones, and proteins, on the other hand, give varying yields of oxamide. The crystalline substance previously obtained from polypeptides was a mixture of ammonium nitrate and acetate.

E. S.

**Constitution of Proteins.** E. ABDERHALDEN (*Z. physiol. Chem.*, 1925, **142**, 306—313).—Polemical. Reply to Herzog (this vol., i, 450).

E. S.

**Constitution of Proteins.** M. BERGMANN (*Z. physiol. Chem.*, 1925, **144**, 276—277).—It is claimed that Abderhalden gives inadequate recognition of the author's work in this field. P. W. C.

**Isolation of a Product of Hydrolysis of Proteins.** S. B. SCHRYVER and others.—(See i, 794.)

**Physical Chemistry of Proteins. V. Molecular Weights of Proteins. Minimal Molecular Weights of certain Proteins.**—(See ii, 641.)

## Biochemistry.

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**Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen. IX. Muscular Activity and Carbohydrate. Metabolism in the Normal Individual.** K. FURUSAWA (*Proc. Roy. Soc.*, 1925, **B**, 98, 65—76; cf. A., 1924, i, 1128, 1363; this vol., i, 92).—By subtracting the values for the normal consumption of oxygen and production of carbon dioxide from the values obtained during exercise, the author calculates the respiratory quotient for the “excess metabolism” due to the exercise itself. Muscular exercise lasting only for a short time gives a *R.Q.* of 1.0, and is therefore performed at the expense of carbohydrate alone, whether the diet be normal or consist mainly of fat. As the duration of the exercise is prolonged, the *R.Q.* of the excess metabolism falls slowly in the case of the normal diet, more rapidly in the case of the fatty diet. It is concluded that the primary fuel of contraction in the human muscle is carbohydrate, and that fat or protein is used later, presumably to replenish the store of carbohydrate which has disappeared.

C. P. S.

**Production of Carbon Dioxide by Nerve.** G. H. PARKER (*J. Gen. Physiol.*, 1925, **7**, 641—669).—The rate of production of carbon dioxide by nerve is determined in a modified Osterhout respiratory apparatus. The lateral-line nerve of the dogfish discharges carbon dioxide rapidly for about 30 mins., and thereafter steadily, but at a lower rate for several hours. Handling the nerve has no effect on the carbon dioxide output, but cutting produces an immediate transitory increase. Carbon dioxide is a true product of nerve metabolism. In quiescent nerve, the rate of carbon dioxide production varied from 0.0071 to 0.0128 mg. per g. of nerve per minute, and averaged 0.0095 mg. For stimulated nerve, the average rate was 15.8% higher. It is concluded that chemical change is a factor in nerve transmission.

C. P. S.

**Hæmoglobin System. I. Classification of Reactions.** G. S. ADAIR (*J. Biol. Chem.*, 1925, **63**, 493—497).—The various equilibria occurring in a simplified model of blood—namely, the system hæmoglobin, oxygen, water, carbon dioxide, and sodium hydroxide—are classified. Past work on the three main reactions of hæmoglobin, with carbon dioxide, sodium hydroxide, and oxygen respectively, is reviewed and a plan of work outlined for the study of these three reactions and of the influence of the other components on each, using the same solution of human hæmoglobin throughout. Some of the results obtained (cf. following abstracts) are summarised graphically.

G. M. B.

**Hæmoglobin System. II. Theory of Reactions which do not obey the Law of Constant Proportions.** G. S. ADAIR (*J. Biol. Chem.*, 1925, **63**, 499—501).—In a case of polycythæmia

the carbon dioxide expelled on oxygenation of the blood was normal, though the amount of hæmoglobin was 50% above the normal. A thermodynamic treatment of the equilibrium where one component fails to obey the law of constant proportions leads to the relation  $d \log p_{\text{O}_2}/d \log p_{\text{CO}_2} = Z$ , where  $Z$  is the number of mols. of carbon dioxide expelled per mol. of hæmoglobin oxygenated, and has the value 0.35 for normal blood and 0.25 in the above-mentioned case. The relation has been confirmed experimentally. G. M. B.

**Hæmoglobin System. III. Equilibrium of Hæmoglobin and Carbon Dioxide.** G. S. ADAIR (*J. Biol. Chem.*, 1925, **63**, 503—513).—The wide range in the observed quantity of carbon dioxide combined with hæmoglobin is found to be due to undialysed base (cf. Parsons, A., 1920, i, 508). A method is described for preparing pure human hæmoglobin by dialysis against a saturated solution of carbon dioxide at 0°, the product then giving reproducible values for the combined carbon dioxide. At a pressure of 40 mm. this amounts to 0.32 mol. of carbon dioxide per mol. of hæmoglobin, whilst  $\text{HbO}_2 = 0.29$  mol. The  $\text{Hb-CO}_2$  dissociation curve has been investigated up to pressures of 760 mm. of carbon dioxide. It is of the parabolic type reproducible by means of the Freundlich adsorption equation. The maximum combined carbon dioxide is not less than 3 mols. A study of the osmotic pressure and membrane equilibrium of hæmoglobin and carbon dioxide indicates that the compound  $\text{Hb}(\text{CO}_2)_2$  is a hydrogen carbonate 70% ionised. The osmotic pressure has the exceptionally high value of 650 mm. The  $p_{\text{H}}$  inside the corpuscle may be from 7.25 to 7.35. At  $p_{\text{H}}$  7.3,  $[\text{H}] = 0.5 \times 10^{-7}$  and the  $\text{Hb-CO}_2$  value is 0.143. A blood with 20 vols. % of oxygen should have 2.86 c.c. of carbon dioxide combined with hæmoglobin. In very severe acidosis, the combined carbon dioxide may rise to 5 c.c., an appreciable fraction of the total.

G. M. B.

**Hæmoglobin System. IV. Reproduction of Carbon Dioxide Curves of Blood with an Artificial Mixture of Hæmoglobin and Sodium Bicarbonate.** G. S. ADAIR (*J. Biol. Chem.*, 1925, **63**, 515—516).—A mixture containing 0.00843 mol. of pure human hæmoglobin (of 18.9 vols. % oxygen capacity) and 0.0434 mol. of sodium hydrogen carbonate gave carbon dioxide dissociation curves in close agreement with those from normal blood both fully oxygenated and fully reduced.

G. M. B.

**Hæmoglobin System. V. Relation of Hæmoglobin and Bases.** G. S. ADAIR (*J. Biol. Chem.*, 1925, **63**, 517—527).—A series of determinations is recorded of the base bound and the buffer value for both pure human hæmoglobin solutions and whole blood over a wide range of  $p_{\text{H}}$  values, and their interpretation is discussed in detail. The most efficient buffer action is at  $p_{\text{H}}$  7.4, the blood reaction. Using Van Slyke's notation,  $\beta_0(\text{HbO}_2)$  is  $2.47 \pm 0.07$ ,  $\beta_{\text{R}}(\text{Hb})$  is  $2.31 \pm 0.1$ . The buffering effect of human hæmoglobin is 7% less than that of horse hæmoglobin. The base bound on oxygenation rises from 0.08 at  $p_{\text{H}}$  6.6 to 0.51 at  $p_{\text{H}}$  7.4

and 0.55 at  $p_H$  7.8, the figure at blood reaction being 25% less than Van Slyke's figure for horse hæmoglobin at the same reaction. True values of the base bound by the hæmoglobin are calculated, and the results are in accord with the mass law, assuming the presence of five independent acid groups in the hæmoglobin, all of equal strength, the constant being about 1/17.4 that of carbonic acid. The experimental data are represented approximately by the formulæ: Total base bound =  $5 (7 \times 10^5 [OH]) / (1 + 7 \times 10^5 [OH])$ , and apparent base bound = total base bound -  $3 \cdot 10^6 [H] / (1 + 10^6 [H])$ , in each case with an error of  $\pm 0.5$ .  
G. M. B.

**Hæmoglobin System. VI. Oxygen Dissociation Curve of Hæmoglobin.** G. S. ADAIR (*J. Biol. Chem.*, 1925, **63**, 529—545).—Oxygen dissociation curves have been constructed for solutions of dialysed human hæmoglobin containing only small traces of acid or base; for solutions containing in addition sodium hydrogen carbonate and having  $p_H$  values of 6.0 to 8.36; and for solutions in isotonic salt solutions of  $p_H$  8.08 (0.1M-potassium chloride + M/15-disodium hydrogen phosphate). The various theories of the oxygen hæmoglobin equilibrium are reviewed. The oxygen data can be reconciled with Adair's determination of the molecular weight of hæmoglobin (*J. Physiol.*, 1923, **58**, iv) by the hypothesis that the complex  $Hb_4(O_2)_4$  is built up and broken down into  $Hb_4$  and oxygen in stages. Methods of correction for the acid change on oxidation are worked out, proving that the curve in distilled water is of practically the same shape as in blood, rather than the hyperbola required by the law of mass action.

The linear relation between  $p_H$  and affinity for oxygen found by Barcroft and Peters for blood is found to apply to homogeneous hæmoglobin solutions only over a narrow range. The base bound on oxidation is calculated from this curve by the equation  $\Delta B = -\delta \log [O_2] / \delta p_H$ . The variation of the affinity for oxygen with varying hæmoglobin and salt concentrations, and at temperatures varying from 21.5° to 48° has been studied. The heat of reaction of pure human hæmoglobin with oxygen is about 13,600 cal. per mol. of oxygen.  
G. M. B.

**Clinical Colorimetric Determination of Hæmoglobin.** H. KÄMMERER and A. SCHAULIN (*Münch. med. Woch.*, 1924, **71**, 1271—1273; from *Chem. Zentr.*, 1924, ii, 2413).—Blood, after dilution with water containing carbon monoxide, is compared colorimetrically with standard carboxyhæmoglobin solutions.  
G. W. R.

**Standard Solution for Sahli's Hæmometer.** A. K. J. KOUMANS (*Nature*, 1925, **115**, 946—947).—An aqueous infusion of tea leaves containing "antiformin" is a stable and satisfactory comparison solution for Sahli's hæmometer.  
A. A. E.

**Microturbidimeter.** O. E. CONKLIN.—(See ii, 708.)

**Adenine Nucleotide from Blood.** W. S. HOFFMANN (*J. Biol. Chem.*, 1925, **63**, 675—679).—Pig's blood was freed from

coagulable protein and the concentrated filtrate treated with lead acetate to precipitate nucleotides; after recovery from the lead precipitate and a second such treatment there was obtained from the crude nucleotides a crystalline brucine salt; on removal of the brucine this gave crystalline adenine nucleotide. [Cf. Jackson, A., 1924, i, 783.]  
C. R. H.

**The Aldehyde contained in Blood.** R. FABRE (*Bull. Soc. Chim. biol.*, 1925, 7, 429—435).—Acetaldehyde is shown to be present in blood by isolation of its condensation product with dimethyldihydroresorcinol. A method of determination based on the reduction of mercuric salts gave the following results (mg. of acetaldehyde per litre): ox, 0.24—0.48; horse, 0.32—0.61; dog, 0.32; human (normal), 0.32—0.50; human (nephritic), 0.81. In the depancreatized dog the quantity is greatly increased, but is reduced almost to zero by administration of insulin.  
C. P. S.

**Blood Calcium. I. Calcium Content of Blood. II. Serum Calcium during Menstruation. III. Blood Calcium during Hypertonia. IV. Effect on Blood Calcium of Administration of Atropine-Calcium.** E. KYLIN and B. SILFVERSVÄRD (*Z. ges. exp. Med.*, 1924, 43, 47—57; from *Chem. Zentr.*, 1924, ii, 2408).—The calcium content of the blood under the age of 40 is 10.75—12.0 mg. %. Above 40, the corresponding values are 10.6—11.5 mg. %. During menstruation there is generally an increase in blood calcium, although under pathological conditions a decrease is sometimes observed. Oral administration of atropine-calcium causes a temporary increase in blood calcium.  
G. W. R.

**Nephelometric Determination of Calcium and Magnesium.** L. KRISS (*Biochem. Z.*, 1925, 158, 203—204).—In presence of ammonium salts magnesium gives no cloud with the sulphuricinoleate reagent of Rona and Kleinmann (A., 1923, ii, 433). Thus the nephelometric determination of calcium in presence of magnesium can easily be carried out if enough ammonium salts be added.  
H. D. K.

**Simple Micro Method for Determination of Sugar or of Reducing Substance in Blood.** L. LORBER (*Biochem. Z.*, 1925, 158, 205—210).—The method is based on that of Allihn, the precipitated cuprous oxide being centrifuged down, washed with distilled water, dissolved in nitric acid, excess of ammonia and hydrogen peroxide added, and the blue colour (which is proportional to the amount of reduced copper) examined colorimetrically against a standard of known copper content. In the blood determinations, the proteins are first precipitated by tungstic acid and removed by centrifuging, the clear liquid being used; 0.3 c.c. of normal blood is required for each determination. It is claimed that this method is particularly useful where a large number of sugar determinations have to be made in a limited time.  
H. D. K.

**Microtitration.** P. B. REHBERG (*Biochem. J.*, 1925, 19, 270—277).—A micro-burette, from which a standard solution can be

delivered in accurately measured quantities as small as 0.1 mm.<sup>3</sup>, is described. The titration is carried out in a definite volume and to a definite hydrogen-ion concentration, which is ascertained by comparison with a standard control tube. Corrections are made according to the indicator used, the volume of the liquid titrated, and the dissociation constants of the acid and alkali used.

S. S. Z.

**Determination of Carbamide in 0.1 c.c. of Blood by Micro-titration.** P. B. REHBERG (*Biochem. J.*, 1925, **19**, 278—280).—Oxalated blood is treated with urease and the ammonia produced, after addition of potassium carbonate and subsequent aëration, is received into *N*/30-acid and titrated with *N*/30-alkali by means of a micro-burette (see preceding abstract).

S. S. Z.

**Determination of Carbamide in Blood, Cerebro-spinal Fluid, and Urine, using Permuted.** G. Y ROIG and K. HELMHOLZ (*Deut. med. Woch.*, 1924, **50**, 1217—1218; from *Chem. Zentr.*, 1924, ii, 2413).—Carbamide is converted into ammonium carbonate by means of urease. The solution of the ammonium salt is allowed to react with permuted and ammonia is determined in the ammonium permuted by nesslerisation.

G. W. R.

**Physico-chemical Constants of Sera. I. Variations of the Electrical Conductivity with Dilution.** P. LASSEUR, F. GIRARDET, and H. VERMELIN (*Bull. Soc. Chim. biol.*, 1925, **7**, 401—418).—The conductivity of human serum varies from 109 to  $126 \times 10^{-4}$ , and appears to be independent of the state of nutrition and of the condition of health or disease. The conductivity of the cerebro-spinal fluid is similarly constant at  $137 \times 10^{-4}$ . Dilution of the serum with pure water not only alters the magnitude of the conductivity, but shows differences between individual sera beyond the limits of experimental error. The authors are studying the extent to which this fact may be utilised in pathology. No such differences occur in diluted cerebro-spinal fluid.

C. P. S.

**Hydrogen-ion Concentrations in the Blood of Insects.** R. W. GLASER (*J. Gen. Physiol.*, 1925, **7**, 599—602).—The  $p_H$  of the blood of grasshoppers and of house flies has a range 7.2—7.6; of the large American roach, 7.5—8.0; of *Malacosoma americanum*, 6.4—7.4; and of *Bombyx mori*, 6.4—7.2. In the forms observed, blood  $p_H$  does not appear to be directly related either to age or to metamorphosis.

C. P. S.

**Influence of Time of Coagulation of Blood on Toxicity of Serum.** A. LUMIÈRE and R. COURJON (*Compt. rend.*, 1925, **180**, 1778—1780).—Experiments on the blood of a number of mental patients show that if the time of coagulation of the blood be shortened by heating, the serum is more toxic to guinea-pigs than the serum obtained from blood allowed to coagulate slowly at a lower temperature.

L. F. H.

**Sugar Content of the Cerebro-spinal Fluid and its Relation to the Blood-sugar.** G. M. GOODWIN and H. J. SHELLEY (*Arch. intern. Med.*, 1925, **35**, 242—258).—The sugar content of "normal"



cerebro-spinal fluid varied from 40 to 77 mg. per 100 c.c. or from 45 to 65% of the concentration in the blood. After the ingestion of dextrose, the concentration in both blood and fluid increased and the relation between the two changed. Low values for the sugar content of the fluid were obtained in meningitis and in cerebro-spinal syphilis.

CHEMICAL ABSTRACTS.

**Distribution of Carbon in Cerebro-spinal Fluid.** M. POLONOVSKI and G. GALBRUN (*Compt. rend. Soc. Biol.*, 1924, **91**, 565—567; from *Chem. Zentr.*, 1924, ii, 2274; cf. A., 1924, i, 1126).—In normal cerebro-spinal fluid the mean carbon content was 0.10—0.11%; in pathological cases values up to 0.135% were found. The following data are given for the distribution of carbon, with the corresponding values in pathological cases in brackets: uric acid 0.004 (0.0036)%; protein 0.010 (0.039)%; dextrose 0.023 (0.023)%; indeterminable carbon 0.074 (0.0746)%. In each case the figures given are maximum values.

G. W. R.

**Natural Hæmatin-like Pigments and their Related Porphyrins.** O. SCHUMM (*Z. physiol. Chem.*, 1925, **144**, 272—275).—In putrefying horse flesh, in human blood seeded with bacteria from such flesh, and in fæces in cases of intestinal hæmorrhage, a hæmatin-like substance can be shown spectroscopically to be present which is very similar to, but not necessarily identical with, the "myohæmatin" of McMunn.

P. W. C.

**Bile-acids. XII. A Calculus from the Rennet-sac of a Goat. XIII. Presence of Deoxycholic (Choleic) Acid in the Hydrolysed Bile of the Goat.** M. SCHENK (*Z. physiol. Chem.*, 1925, **145**, 1—17, 95—100).—XII.—A large calculus from the rennet-sac of a goat was found to contain about 75% of cholic acid and 5% of choleic acid, both in the free state; the former was obtained in pure crystalline condition; the latter could not be obtained pure, but was identified by means of its acetic acid and xylene derivatives. There were also obtained small amounts of stearic and palmitic acids which were contaminated with traces of cholesterol; no bile pigments could be demonstrated. The residue of the calculus, which was insoluble in acetone, consisted of vegetable and inorganic material, including traces of iron.

XIII.—From the mixture of bile-acids resulting from the alkaline hydrolysis of the bile of the goat there was obtained about 4% of cholic acid and 0.4% of choleic acid, the latter being isolated in the form of its acetic acid derivative; the quantities are calculated from the whole bile.

C. R. H.

**Guanidine Compounds in the Extractives of Ox-testicles.** H. MÜLLER (*Z. Biol.*, 1925, **82**, 573—580).—Creatine, choline (as chloroaurate), hypoxanthine (as picrate), *d*-lactic acid (as the zinc salt), and methylguanidine (as chloroaurate) were identified in the extracts. Failure attended the attempts to isolate arginine, dimethylguanidine, and putrescine.

O. O.

**Proximate Composition of certain Pacific Coast Fish.** D. B. DILL (*Ind. Eng. Chem.*, 1925, **17**, 629—630; cf. A., 1921, i, 834).—Analyses showing total solids, ether extract, ash, and total nitrogen are given for a large number of food fish of the Pacific coast. [Cf. B., July 24th.] D. G. H.

**Concentration of Citric Acid in Cow's Milk and its Relation to the Chlorine : Sugar Ratio.** F. KIEFERLE, J. SCHWAIBOLD, and C. HACKMANN (*Z. physiol. Chem.*, 1925, **145**, 18—36).—Citric acid in milk was determined by preliminary removal of the proteins with phosphotungstic acid, conversion of the citric acid in the filtrate into pentabromoacetone by the method of Stahre (A., 1897, ii, 290), followed by separation of this precipitate in a special centrifuge tube graduated so that the volume of the precipitate could be accurately measured. In this way it was found that the average concentration of citric acid in normal cow's milk was 0.27%. Minor variations were observed between different normal cows and between different fractions of the milk from the same cow; in order to obtain significant results it was therefore necessary to compare samples of milk from the same teat of the same cow. Observing this precaution, a parallelism was demonstrated between the concentration of citric acid and that of lactose; hence those milks which were deficient in citric acid had a high chlorine : sugar ratio (Koester, *Schweiz. Milchztg.*, **46**). The lowest concentration of citric acid observed was 0.12%. C. R. H.

**Colorimetric Determination of Acetone in Urine.** M. H. P. SITSSEN (*Pharm. Weekblad*, 1925, **62**, 622—623).—A procedure suitable for colorimetric determination, employing sodium nitroprusside, is described. S. I. L.

**Separate Determination of Potassium and Sodium in Urine.** O. VON DEHN (*Z. physiol. Chem.*, 1925, **144**, 178—180).—Kramer and Tisdall's method (A., 1921, ii, 412, 463) for the determination of potassium and sodium in blood-serum is modified and made applicable to urine. The limits of error are 1.5—2.0%. P. W. C.

**Nitrogen Distribution in the Hydroxyproteic Acid Fraction of Urine.** S. EDLBACHER (*Z. physiol. Chem.*, 1925, **144**, 278—279).—Reply to Brings (this vol., i, 328). P. W. C.

**Red Pigment obtained by Treatment of Normal Human Urine with *p*-Dimethylaminobenzaldehyde.** G. SCHEFF (*Biochem. Z.*, 1925, **158**, 167—169, 170—175).—The crystalline pigment separated by Hári is a condensation product of *p*-dimethylaminobenzaldehyde with a normal constituent of urine. A spectrophotometric method is described for the quantitative determination of this pigment. It appears to be derived from the protein of the dietary, and particularly from the meat. H. D. K.

**Phylloerythrin. II.** H. FISCHER and H. HILMER (*Z. physiol. Chem.*, 1925, **143**, 1—8).—The new porphyrin isolated by Kémeri (this vol., i, 188) is probably phylloerythrin (cf. A., 1916, i, 574).

It has been found in the faeces of individuals on both vegetarian and meat diets. The bone marrow from a patient who died of pernicious anæmia has been found to contain coproporphyrin in addition to some Kammerer's porphyrin. It is suggested that the complete synthesis of the blood pigment had not occurred owing to the lack of the necessary iron.  
E. S.

**Iodine Value of Coprosterol.** H. DAM (*Biochem. Z.*, 1925, **158**, 76—80).—Hanuš' method and the pyridine sulphate dibromide method give fairly constant values of about 10 for the iodine number of coprosterol (theoretical value 0). Winkler's method gives much higher values, which, moreover, vary with the experimental conditions. The coprosterol content of a mixture of coprosterol and cholesterol may be determined empirically by the pyridine sulphate dibromide method.  
H. D. K.

**Glycolysis.** E. NEGELEIN (*Biochem. Z.*, 1925, **158**, 121—135).—Glycolysis of cancer tissue (Flexner-Jobling rat carcinoma) or of the retinal tissue of the rat gives rise to lactic acid only. New micro-methods are described, together with a modified form of reaction flask, for the measurement of glycolysis both in Ringer's solution or in presence of serum. Both the aërobic and the anaërobic glycolysis of cancer tissue are as great in rat serum as in Ringer solution. Carcinoma tissue glycolyses some 9% and sarcoma tissue about 10% of its weight of glucose per hour aërobically. The absolute amount of glycolysis in blood is considerably smaller, being only 1/60th to 1/100th of that of cancer tissue. The anaërobic glycolysis of nucleated erythrocytes is about the same as that of non-nucleated red cells; the aërobic glycolysis of goose's blood (nucleated corpuscles) is practically nil, whilst that of rabbit's blood (non-nucleated corpuscles) is a large fraction of the total glycolysis.  
H. D. K.

**Diastase in the Urine in Pancreatic Diseases.** T. S. HANSEN (*Medicinsk Rev.*, 1924, **41**, 321—340).—Normally the urinary diastase varies within narrow limits; its concentration is influenced by the chlorine concentration and acidity of the urine, but a large variation indicates a pathological pancreatic condition.

CHEMICAL ABSTRACTS.

**Excretion of Ketone Substances and  $\beta$ -Hydroxybutyric Acid in Depancreatized Dogs.** H. BIERRY and F. RATHERY (*Compt. rend. Soc. Biol.*, 1924, **91**, 534—537; from *Chem. Zentr.*, 1924, ii, 2275).— $\beta$ -Hydroxybutyric acid is excreted in the urine in considerable amount by depancreatized dogs, even when fat-free meat is administered. Ketonic substances may be completely absent from the urine.  
G. W. R.

**Effect on the Blood-sugar of Fish of Various Conditions, including Removal of the Principal Islets (Isletectomy).** N. A. McCORMICK and J. J. R. MACLEOD (*Proc. Roy. Soc.*, 1925, **B**, **98**, 1—29).—The blood-sugar content of salt-water fishes immediately after catching varies considerably even among individuals

of the same species. Exposure of the fish to air, as in catching, causes marked hyperglycæmia. Placing the fish in stagnant water has a similar effect, and the rate of development of the hyperglycæmia is increased by raising the temperature of the water. The hyperglycæmia slowly subsides when the fish are returned to the sea or to frequently changed water, the blood-sugar reaching a normal level after 2—4 days or even longer. The amount of glycogen in the liver also varies considerably, but does not appear to be directly related to the normal blood-sugar level or to the degree of hyperglycæmia induced by asphyxia. Evidence has been obtained of the existence in the blood of non-reducing carbohydrates which may, by their hydrolysis, account for part of the asphyxial rise in blood-sugar. In *Myoxocephalus* the fat content of the liver is much less variable than the glycogen. There is no reciprocal relation between the two, and the ratio of liver-weight to body-weight is no index of the amount of either, or both, fat and glycogen in the liver. Glycolysis does not occur in the blood of *Myoxocephalus* kept at room temperature for 10 hrs. Intramuscular injection of adrenaline rapidly produces marked hyperglycæmia; injection of insulin, however, has only a slight effect. Removal of the principal islets in *Myoxocephalus* is followed by marked hyperglycæmia. It was not possible to correlate this with the glycogen content of the liver, but the livers of the isletectomised fish showed increased fat and decreased glycogen as compared with the controls. C. P. S.

#### Variations in the Blood-sugar of Splenectomised Dogs.

H. BIERRY, F. RATHERY, and L. LEVINA (*Compt. rend. Soc. Biol.*, 1924, **91**, 537—539; from *Chem. Zentr.*, 1924, ii, 2275).—After removal of the spleen from dogs there is an increase both in the free and the combined sugar in the blood. G. W. R.

**Retention and Excretion of Nitrogen in Hypertrophy of the Prostate.** N. A. NICOLAYSEN (*Medicinsk Rev.*, 1924, **41**, 1—15).—The fluctuation of nitrogen excretion during the pre- and post-operative periods was recorded; two cases in which the azotæmia rose to more than 0.2% were fatal.

CHEMICAL ABSTRACTS.

**Tetany of Parathyroid Deficiency and the Calcium of the Blood and Cerebro-spinal Fluid.** A. T. CAMERON and V. H. K. MOORHOUSE (*J. Biol. Chem.*, 1925, **63**, 687—720).—The calcium of the cerebro-spinal fluid in normal dogs averages 53% of that of the blood-serum, and it is suggested that this figure represents the true diffusible calcium of the blood more accurately than the figures previously derived from dialysis experiments *in vitro*. If plasma, rapidly separated from oxalated normal blood by centrifuging, is treated with more oxalate, more calcium is slowly precipitated; this is taken to indicate that the remaining 47% of the calcium is in an organic compound which dissociates slowly on removal of calcium ions; after clotting, the part of the calcium in organic combination is more readily dissociable; in normal blood,

the calcium of the serum is equal to that of the plasma. It is thought that, under normal conditions, the calcium of the blood is kept uniform by the presence of a constant amount of a specific organic compound which combines with part of the calcium, rendering it non-diffusible. In the tetany of parathyroidectomy there is an absolute decrease in both fractions of the serum calcium, the total amount of which finally approximates to that in the cerebro-spinal fluid; the plasma calcium is higher than the serum calcium, owing to more complete removal of the organic compound with the clot, and the proportion of diffusible calcium in the plasma is higher than normal. The results indicate that the determining factor in the tetany of parathyroidectomy is the reduction in the inorganic calcium of the plasma which is secondary to a reduction in the organic compound.

C. R. H.

**Chemical Composition of Normal and Luetic Sera.** A. A. SOLARI (*Anal. Asoc. Quím. Argentina*, 1924, **12**, 421—432).—From an examination of a number of normal sera and of sera giving the positive Bordet-Wassermann test it is concluded that there is no quantitative relationship between specificity and the relative amounts of colloidal and non-colloidal nitrogen compounds present.

G. W. R.

**Effect of Adsorption Compounds on Infectious Diseases.** F. BERING (*Kolloid-Z.*, 1924, **35**, 374—375).—A description is given of the results obtained when "salluen," an adsorption compound of bismuth and arsenic, is tested on syphilitic patients. On intravenous injection the chemo-therapeutical index reaches the value 1 : 8, and after 15—30 mins. a strong fall in the refractometric serum-value is observed. Ultrafiltration experiments showed that the greater portion of the preparation is not dialysable out of serum; the smaller dialysable portion contains nitrogen-free bismuth. Full details of the clinical effects are given. D. C. J.

**New Oxido-reduction System and its Biochemical Significance.** H. HAEHN and A. PÜLZ (*Woch. Brau.*, 1925, **42**, 115—117, 121—123).—When acetaldehyde and methylene-blue are added to a mixture of primary and secondary alkali phosphates of  $p_H$  7.1 and glycine at 74° the dye is decolorised in a few minutes. The glycine-phosphate mixture splits up water into hydrogen and hydroxyl. The hydrogen reduces the dye to the leuco-base and the hydroxyl forms hydrogen peroxide which oxidises the aldehyde to an acid. Such a system will function only when all the components mentioned are present, and a similar series of reactions may take place in the cell. Arsenates perform the same function as phosphates, and glycine can be replaced by other amino-acids. *d*-Alanine is far more effective than the *l* form, and the inactive form is intermediate in effect. The activity of the system is susceptible to the presence of foreign substances. Ethyl alcohol and lecithin, for instance, have an activating effect, whilst chlorides restrict the activity somewhat. Attention is directed to the similarity between the system and the Schardinger reaction. O. O.

**Significance of Acetaldehyde Production in Frog's Muscle, and its Manifold Relationships to Respiration.** C. NEUBERG and A. GOTTSCHALK (*Biochem. Z.*, 1925, **158**, 253—256).—A definite and quantitative relationship exists between the carbohydrate oxidised by a chopped, respiring frog's muscle and the acetaldehyde produced in the same system. The acetaldehyde fixed by calcium sulphite represents from 37 to 45% at least of the carbohydrate oxidised, and it is concluded that acetaldehyde is a normal step in the oxidation of the greater part of the carbohydrate metabolised by muscle. H. D. K.

**Origin and Destiny of Cholesterol in the Animal Organism.**  
**XIV. Cholesterol Metabolism in Normal Breast-fed Infants.** F. W. FOX and J. A. GARDNER (*Proc. Roy. Soc.*, 1925, **B**, **98**, 76—92).—In the first few days of life, while the colostrum is changing to true milk and the meconium is being got rid of, the output of sterol is greater than the intake. During the next two weeks the output and intake are practically equal. As the age advances the balance becomes decidedly positive, and utilisation of the sterol in the diet appears to take place. Since there is a rapid increase of weight during the early months of life there must be a corresponding increase in the total sterol of the body to a much greater extent than can be accounted for by the absorption from the food. Hence the experiments confirm the conclusion (A., 1922, i, 89) that there must be some organ in the body capable of synthesising cholesterol. The sterol content of the diet, however, is a source of supply that cannot be disregarded. C. P. S.

**Behaviour of Ornithine, Lysine, and Putrescine in the Surviving Liver.** K. FELIX and H. ROTHLEDER (*Z. physiol. Chem.*, 1925, **143**, 133—140).—There is no appreciable decomposition. E. S.

**Formation of Lactic and Phosphoric Acids in the [Salivary] Gland.** E. SCHMITZ and F. CHROMETZKA (*Z. physiol. Chem.*, 1925, **144**, 196—218).—The amounts of phosphoric and lactic acids liberated on addition of hexosephosphoric acid and of nucleic acid to a pulp of the submaxillary and parotid glands of the horse are determined. Comparison of the relative amounts (g.-mols.) of these two acids leads to the conclusion that nucleic acid is more probably the intermediate source of energy for the gland and not hexosephosphoric acid. P. W. C.

**Calcium and Phosphorus Metabolism. III. Absorption and Fixation in the Skeleton.** S. V. TELFER (*Quart. J. Med.*, 1924, **17**, 245—259).—The absorption of phosphorus is difficult to restrict except by a large excess of calcium in a diet poor in phosphorus. The fixation of phosphorus in the skeleton is dependent on that of calcium. Excess of phosphorus is excreted in the urine.

CHEMICAL ABSTRACTS.

**Effect of Cooking on Metabolism of Meat.** C. RICHEL, jun., and R. MONCEAUX (*Compt. rend.*, 1925, **180**, 1688—1689).—Experiments on dogs show that raw meat is preferable to cooked

meat except in cases of kidney damage. When the meat is cooked there is an increase in the amount of chlorides, total nitrogen, urea, and phosphates in the urine. L. F. H.

**Significance of Enterotropic Uric Acid for the Physiology and Pathology of Uric Acid Metabolism.** T. BRUGSCH and J. ROTHER (*Z. physiol. Chem.*, 1925, **143**, 48—58).—When injected into guinea-pigs, uric acid is excreted partly in the urine (urotropic uric acid) and partly in the bile (enterotropic uric acid). The latter portion is destroyed in the small intestine. Folin, Berglund, and Derrick's view (*J. Biol. Chem.*, 1924, **60**, 361) that the rapid disappearance of uric acid from the blood is due to its destruction by some unknown factor present in the blood is incorrect. E. S.

**Psychological Effects on the Calcium Content of Blood-serum. [Psychophysical Reactions.]** F. GLASER (*Klin. Woch.*, 1924, **3**, 1492—1493; from *Chem. Zentr.*, 1924, ii, 2408—2409).—The calcium content of the blood may be depressed by hypnotic suggestion to 2.16 mg. %. G. W. R.

**Effect of Intravenous Injection of Inorganic Chlorides on Composition of Blood and Urine.** M. WHELAN (*J. Biol. Chem.*, 1925, **63**, 585—620).—Dogs were injected intravenously with solutions of sodium, potassium, calcium, magnesium, and ammonium chlorides in amounts up to 0.1 g. per kg. in 10% aqueous solution; no ill-effects were observed. In all cases there was found an increased concentration of chlorides in the urine, whereas that in the blood remained almost unaltered. The changes in the hæmoglobin concentration following the injections were small and variable. The concentration in the blood of the cation of the salt injected was increased considerably in the cases of calcium and magnesium and to a much less extent in those of sodium and potassium. Magnesium chloride always caused a diuresis and calcium chloride always increased the acidity of the urine; otherwise the effects of the salts on the composition of the urine were variable. C. R. H.

**Action of Inorganic Salts on the Secretion of the Isolated Kidney.** F. EICHHOLTZ and E. H. STARLING (*Proc. Roy. Soc.*, 1925, **B**, **98**, 93—113).—Calcium, working on a background of potassium, leads to an increase of chloride excretion and water output, due to decreased reabsorption in the tubules. Salts of these metals, if given separately, have no definite effect. Inorganic phosphates antagonise the action of potassium and calcium by converting the calcium ion into a colloidal form to which the glomerular membrane is impermeable. Cyanide increases the permeability of the glomerular membrane and allows the colloidal phosphates to appear in the urine. C. P. S.

**Creatine Content of Muscles Contracted by Chemicals. Criticism of the Theory of Pekelharing and Hoogenhuyze.** O. REISSER and F. HAMANN (*Z. physiol. Chem.*, 1925, **143**, 59—70).—Stimulation of muscles contracted by certain substances (caffeine, veratrine, potassium thiocyanate, calcium chloride, acetylcholine)

does not cause a production of creatine greater than that produced in normal muscle. Hence the theory of Pekelharing and Hoogenhuyze (A., 1910, ii, 324) can no longer be maintained. E. S.

**Effect of Addition of Fluorine to the Diet of the Rat on the Quality of the Teeth.** E. V. MCCOLLUM, N. SIMMONDS, J. E. BECKER, and R. W. BUNTING (*J. Biol. Chem.*, 1925, **63**, 553—562).—The addition, to an otherwise satisfactory diet, of 0.0226% of sodium fluoride causes, in the rat, overgrowth of the maxillary incisors and erosion of the mandibular incisors accompanied by inferior development of the tooth substance and also of the bones of the skull. C. R. H.

**Specificity of the so-called Arsenic Receptor in the Higher Animals.** C. VOEGTLIN, H. A. DYER, and C. S. LEONARD (*J. Pharm. Exp. Ther.*, 1925, **25**, 297—307).—The toxic effect of 3-amino-4-hydroxyphenylarsenious oxide on rats is inhibited by intravenous injection of reduced glutathione. Cysteine has a similar but much weaker effect. The toxicity is also reduced if the animal is fed on a mixture of glutamic acid and cystine, a fact which affords indirect evidence of the mode of formation of glutathione in the body. The SH group of glutathione may be regarded as the so-called arsenic receptor of mammalian protoplasm. C. P. S.

**Effects of Arsonium, Phosphonium, and Sulphonium Compounds on the Autonomic Nervous System.** R. HUNT and R. R. RENSHAW (*J. Pharm. Exp. Ther.*, 1925, **25**, 315—355).—The phosphorus, arsenic, antimony, and sulphur analogues of tetramethylammonium iodide have a muscarine-like action. The arsenic and antimony compounds are least active, the sulphur most active, but all are less active than the nitrogen compound. The sulphur and phosphorus compounds have a marked stimulating nicotine-like action, the sulphur being the more active, although less so than the nitrogen compound. The arsenic and antimony compounds have no such action. The sulphur and phosphorus compounds have also a paralysing nicotine-like action. The phosphorus compound has a curare-like action about equal to that of the sulphur compound, but only 1/10—1/20 that of the nitrogen compound; even in larger doses, the arsenic and antimony analogues do not show this action. The order of toxicity for mice (the nitrogen compound being the most toxic) is N, P, As, S, Sb. *Iodomethyltrimethylammonium iodide* has a marked muscarine action similar to, but greater than, that of the arsenic analogue. Unlike the arsenic compound, it has also an intense stimulating (nicotine) action, and a paralysing (nicotine) action. It is twice as toxic for mice as the arsenic compound. *Acetoxyethyltrimethylammonium iodide* has a marked stimulating (nicotine) action; the sulphur analogue has no such action. *Formyltrimethylarsonium bromide* has neither muscarine nor nicotine actions on the circulation. The *phosphorus analogue* of choline has a marked muscarine action, which is even greater in the acetyl derivative. *Neurine*, unlike its arsenic analogue (which is less toxic), has marked muscarine



and nicotine (stimulating and paralysing) actions. The *ethyl* ester of betaine has a pronounced muscarine action greater than that of choline or neurine. It has a stimulating nicotine action, and is about 6 times as toxic as choline. *Chloroacetylcholine* has a muscarine action greater than that of choline, but only about 1/1000 that of acetylcholine. It has a marked stimulating action on the cardioinhibitory centre, and has a stimulating nicotine action. For mice, it is about twice as toxic as choline. *Choline nitrate* has pronounced muscarine and nicotine (stimulating and paralysing) actions. The various new compounds used in this investigation are to be described in another paper. C. P. S.

**Narcotic Effect of Derivatives of Barbituric Acid.** T. A. REDONNET (*Compt. rend. Soc. Biol.*, 1924, **91**, 829—830; from *Chem. Zentr.*, 1924, ii, 2535—2536).—"Veronal," "luminal," "dial," their sodium and dimethylamine salts, and "sommifen," in contrast to "adalin," cause death in *Cyprinus auratus* a few minutes after narcosis. If the fish is placed in water before respiratory paralysis sets in, recovery takes place after a few hours. Inability to swim and narcosis with general anæsthesia are produced respectively by "veronal" in 150 and 345 mins., by "dial" in 125 and 265 mins., by "luminal" in 140 and 340 mins., by "adalin" in 20 and 145 mins., 0.0005*N*-solutions being used in each case. Similar experiments on frogs are recorded. With white mice deep narcosis by "sommifen" (1.6 c.c. per kg., given subcutaneously) is followed by death. Preliminary injection of 3 mg. of lobeline does not modify the effect of 0.2 g. of "luminal." With cats, intravenous injection of more than 0.5 c.c. of "sommifen" causes death. Doses up to 0.65 c.c. may be neutralised by previous injection of 3 mg. of lobeline. G. W. R.

**Variations in the  $p_H$  of Solutions of Cocaine Hydrochloride Subjected to Sterilisation.** A. LIOT (*J. Pharm. Chim.*, 1925, [viii], **1**, 474—478).—The author discusses the effect of sterilisation on the anæsthetic value of cocaine hydrochloride. An aqueous solution containing 2 g. of cocaine hydrochloride and 0.8 g. of sodium chloride per 100 c.c. was placed in a series of 2 c.c. glass ampoules, some of which were then tyndallised for various periods at 60°, whilst others were sterilised at temperatures varying from 100° to 120° for 15 mins. The  $p_H$  varied from 5.4 for the sample tyndallised at 60° for 1 hr. to 3.7 for that sterilised at 120°. In view of the fact that cocaine hydrochloride is more effective as an anæsthetic in solutions of high rather than of low  $p_H$ , it should not be sterilised at temperatures above 100°, and best of all should be tyndallised for 3 hrs. at 60°. B. F.

**Metabolism Study of Ethylene Anæsthesia.** H. A. OBERHELMAN and H. A. DYNIEWICZ (*J. Amer. Med. Assoc.*, 1924, **83**, 2012—2014).  
CHEMICAL ABSTRACTS.

**Effect of Ethylene Anæsthesia on the Acid-Base Balance of Blood.** C. D. LEAKE (*J. Amer. Med. Assoc.*, 1924, **83**, 2062—2065).  
CHEMICAL ABSTRACTS.

**Induced Antisepsis : Bactericidal Action of Sodium Hypochlorite without Contact with the Bacteria.** P. B. VARILLA and E. TECHOUEYRES (*Compt. rend.*, 1925, **180**, 1615—1618).—It is suggested that the antiseptic action of sodium hypochlorite solution is not a chemical effect, but is due to rays (similar to ultra-violet rays) emitted by the solution. Immersion of a quartz tube containing dilute sodium hypochlorite solution in a bacterial suspension has resulted in a diminution in the number of bacteria present. L. F. H.

**Affinities Existing between Substrate and Enzyme and their Specificity.** H. VON EULER (*Z. physiol. Chem.*, 1925, **143**, 79—88).—A theoretical paper in which it is suggested that, during the inversion of sucrose by invertase, the enzyme first unites with the substrate at two points, one of which is in the lævulose and the other in the dextrose portion of the molecule. Corresponding with this there should be two separate affinity constants controlling the combination between invertase and sucrose; the relation of these to Michaelis' affinity constant can be deduced from the law of mass action. Projected work on the basis of these considerations is outlined. E. S.

**Arginase.** S. EDLBACHER and P. BONEM (*Z. physiol. Chem.*, 1925, **145**, 69—90).—The optimum hydrogen-ion concentration for the action of arginase is at  $p_H$  9.5—9.8; at this reaction the breakdown of arginine is almost quantitatively complete after 2 days. The enzyme shows a high degree of specificity, since it does not act on guanidine-acetic acid, guanidine-propionic acid, or agmatine. The arginylarginine prepared by Fischer and Suzuki (A., 1906, i, 73), which they were unable to hydrolyse, gives a 95% yield of arginine on boiling for 14 hrs. with 25% sulphuric acid; when this dipeptide is exposed to the action of arginase the carbamide formed indicates the hydrolysis of one guanidine group only; in view of the negative result with agmatine it is suggested that the guanidine group which is attacked belongs to the arginine group of which the carboxyl is free; this assumption is further supported by the observation that the methyl ester of arginine is scarcely attacked by arginase.

Details are given of the distribution of arginase in the different organs of animals of numerous species (cf. Hunter and Dauphinee, this vol., i, 104). C. R. H.

**Behaviour of Polymethylated Sugars towards Emulsin.** R. KUHN and H. H. SCHLUBACH (*Z. physiol. Chem.*, 1925, **143**, 154—157).—Neither tetramethyl- $\beta$ -methylglucoside nor heptamethyl- $\beta$ -methyl-lactoside is hydrolysed to an appreciable extent by emulsin (cf. Irvine and Cameron, T., 1905, **87**, 900). Hence Armstrong's theory that the enzyme is united to the sugar molecule by means of the residual affinities of the oxygen atoms contained in the latter lacks experimental support. E. S.

**Influence of the Reaction of the Medium on Digestion by Papain.** R. FABRE and R. FROSSARD (*J. Pharm. Chim.*, 1925, [viii], **1**, 472—474).—The papain used (ash 0.2%) was purified by

alcoholic precipitation and dialysis. Dry fibrin (pig) was digested with papain in solutions of known  $p_H$  at  $70^\circ$  (which is found to be the optimum temperature), and the proteolytic activity of the papain determined. The maximum activity of papain occurs at  $p_H$  7. B. F.

**Autolysis. III. Autolytic Processes in Liver Pulp.** O. STEPPUHN and X. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1925, 158, 38—49).—During the autolysis of liver pulp, added proteins like caseinogen are hydrolysed in a different way in acid ( $p_H$  3.8) and in neutral ( $p_H$  7.0) solution. Whereas in an acid medium proteolysis falls off at a regular rate, in a neutral medium it decreases more rapidly, but a phase of more intense proteolysis is almost always observed. This may be due to destruction of anti-trypsin, which is known to occur in serum. There is probably more than one proteolytic enzyme concerned in autolysis. H. D. K.

**Proteolytic Enzymes of the Liver.** L. UTKIN-LJUBOVZOV (*Biochem. Z.*, 1925, 158, 50—64).—If a fine suspension of liver in distilled water is acidified to  $p_H$  4.7—5.0, 70% of the protein is precipitated, and proteolytic enzymes are found both in the precipitate and the filtrate. The enzymic action of the filtrate on caseinogen shows two maxima, one at  $p_H$  5.2—5.4, and the other at  $p_H$  3.0—3.4, with a definite minimum between corresponding with the isoelectric point of caseinogen. There is no detectable hydrolysis of this protein above  $p_H$  7.5 by the filtrate. If, however, the precipitate be treated with acetone and dried, it is found to contain an enzyme capable of hydrolysing caseinogen in alkaline solution with an optimum at  $p_H$  7.5—7.6. There are present in liver, therefore, three proteolytic enzymes with different  $p_H$  optima. H. D. K.

**Test for Diffusible Ions. II. Ionic Nature of Pepsin.** J. H. NORTHROP (*J. Gen. Physiol.*, 1925, 7, 603—614; cf. A., 1924, i, 473).—The ratio of the concentration of pepsin in particles of gelatin or coagulated egg-white to the concentration outside is the same as the ratio for chlorine or bromine ions under the same conditions. This is true over the range of  $p_H$  from 1 to 7, and in the presence of various salts and acids. Therefore, pepsin is probably a univalent ion. Also, the enzyme does not form a compound with gelatin, and the degree of dissociation is unaffected by changes in  $p_H$  in the range in which the enzyme is active. Near the isoelectric point of gelatin, the enzyme is adsorbed on the surface of the protein particles. This action is irreversible, and is profoundly influenced by the concentration of electrolytes. It does not occur in electrolyte-free solution, nor when the salt concentration exceeds  $0.2M$ . C. P. S.

**Enzymic Synthesis of Protein. IV. Effect of Concentration on Peptic Synthesis.** H. BORSOOK and H. WASTENEYS (*J. Biol. Chem.*, 1925, 63, 563—574; cf. this vol., i, 102, 472).—Between concentrations of substrate (products of peptic hydrolysis of egg-albumin) corresponding with about 8% and 25% of protein,

the amount of protein synthesised by pepsin at  $p_H$  3.9 increases directly with the concentration; at concentrations below 8% no synthesis takes place; as the concentration increases above 25% the amount of protein synthesised increases more slowly, and in great concentration it decreases again. No evidence of the disappearance of the enzyme during the synthesis could be obtained. The addition of egg-albumin or of synthesised protein inhibits the synthesis in direct proportion to the amount added. Peptic hydrolysis of egg-albumin can only proceed to completion when the concentration of protein is 6% or less. C. R. H.

**Enzymic Synthesis of Protein. V. Synthesising Action of Trypsin.** H. WASTENEYS and H. BORSOOK (*J. Biol. Chem.*, 1925, **63**, 575—578).—By the action of trypsin on a solution of the products of peptic hydrolysis of egg-albumin a product was obtained having similar properties to the protein synthesised by pepsin under like conditions; the optimum reaction for tryptic synthesis was found to be  $p_H$  5.7. The observation of Henriques and Gjaldbæk (A., 1912, ii, 1188) that, in neutral or alkaline solutions, hydrolysis takes place at the same time as synthesis was confirmed.

C. R. H.

**Investigation of Tryptic Digests by Folin's Colorimetric Method for Determination of Amino-acids.** J. ELLINGHAUS (*Z. physiol. Chem.*, 1925, **145**, 40—44).—After removal of undigested protein with sodium tungstate and sulphuric acid, the amino-acid nitrogen was determined in the filtrate by the colorimetric method of Folin (A., 1922, ii, 536); the results so obtained were compared and shown to agree well with those obtained by the methods of Van Slyke (A., 1911, ii, 779) and of Sørensen.

C. R. H.

**Dried Yeast.** H. SOBOTKA (*Z. physiol. Chem.*, 1925, **145**, 91—94; cf. A., 1924, i, 802).—Comparison of the rate of fermentation by cell-free yeast juice and by an aqueous suspension of yeast indicates that the zymase is entirely combined with the plasma of the yeast cells and is not set free in the process of drying. The results of Euler and Westling (this vol., i, 203) regarding the relative inhibitory action of phenols towards fresh and dried yeast are criticised on the ground that these authors failed to take into account the mass relation between the phenol and the dried cell-substance of the yeast.

C. R. H.

**Presence of Argon in Gases Produced by Alcoholic Fermentation of Dextrose.** A. PICTET, W. SCHERRER, and L. HELFER (*Compt. rend.*, 1925, **180**, 1629—1632).—A small, variable amount of an inert gas, giving the spectrum of argon when excited in a Geissler tube, has been isolated from the gaseous products of the alcoholic fermentation of dextrose in the presence of various mineral salts. The proportions of oxygen, nitrogen, and argon present in the gas produced by the fermentation are in some cases very similar to those in which they occur in air. It is suggested that the potassium present, which is radioactive and emits  $\beta$ -rays, may

give rise to argon, the atomic number of which is one less than that of potassium.

L. F. H.

### Enzymic Degradation and Synthesis of Carbohydrates.

II. H. VON EULER, K. MYRBÄCK, and R. NILSSON (*Z. physiol. Chem.*, 1925, **144**, 137—146).—At  $p_H$  8.5 both fresh top- and bottom-yeasts cause fermentation. Whereas dry top yeast causes strong fermentation, dry bottom yeast under the same conditions is without action. In top fermentations, addition of phosphate does not result, in either neutral or alkaline solution, in any appreciable change in velocity. The same result was obtained with yeast which had been washed to remove soluble phosphate.

Similar experiments with pyruvic acid show that at  $p_H$  4.5, at first a very rapid fermentation takes place corresponding with the decomposition of the pyruvic acid, followed by a very slow evolution of carbon dioxide due to the autofermentation of the yeast. The action on pyruvic acid is greatly inhibited at  $p_H$  8.5. It appears therefore that carboxylase is more readily inhibited by alkali than zymase.

P. W. C.

**Fermentation of Galactose by Yeast after Previous Treatment with this Sugar.** H. VON EULER and R. NILSSON (*Z. physiol. Chem.*, 1925, **143**, 89—107).—The fermentation of galactose by living yeast which has been "acclimatised" to this carbohydrate is accelerated by the biocatalyst  $z$  (this vol., i, 209, 745) but not by the co-enzyme. The process of "acclimatisation" is not peculiar to living yeast; it also takes place with dry yeast which has been thoroughly sterilised by treatment with alcohol. In the latter case the fermentation is accelerated by the addition of the co-enzyme.

E. S.

**Coproporphyrin Synthesis by Yeast and Influencing Factors.** II. Analysis of Crystalline Copper Coproporphyrin from Fresh Yeast and the Increase of Porphyrins by the Addition of Substances. H. FISCHER and H. FINK (*Z. physiol. Chem.*, 1925, **144**, 101—122).—Pure coproporphyrin is isolated from fresh yeast zymocasein (Lüers and Nowak, this vol., i, 338; cf. A., 1924, i, 459, 894, 1129; this vol., i, 307). Cerevisin also contains coproporphyrin. The influence of heavy metal salts on coproporphyrin synthesis in yeast is studied. Ferrous sulphate (concentration 1/4000), copper sulphate (1/250,000—1/100,000), lead acetate and arsenious oxide (each 1/100,000), and sodium vanadate (1/5000) added to the nutrient liquid led to increased coproporphyrin synthesis. Addition of asparagine and aspartic acid led to the formation of both coproporphyrin and Kämmerer's porphyrin. Samples of wine yeast contained coproporphyrin chiefly as copper salt (due to the treatment of the vine stems with copper sulphate). The origin of the porphyrins in yeast is discussed.

P. W. C.

**Lactic Acid Fermentation.** I. A. I. VIRTANEN (*Z. physiol. Chem.*, 1925, **143**, 71—78).—In the lactic acid fermentation of dextrose by *Bacillus casei*  $\epsilon$  and *Streptococcus lactis* (cf. A., 1924,

i, 915, 1145), the first stage of the process is the formation of a hexosediphosphate. The esterification of the sugar is conditioned by the presence of a co-enzyme, which may be removed from dry preparations of the bacteria by washing with water. Both the hexosediphosphate and the co-enzyme are considered to be identical with those concerned in alcoholic fermentation. E. S.

**Origin of  $\beta$ -Hydroxybutyric Acid Obtained by Microbial Processes.** M. LEMOIGNE (*Compt. rend.*, 1925, **180**, 1539—1541; cf. A., 1924, i, 353, 695).—On extraction with chloroform, *Bacillus M.* yields an amorphous substance giving, on hydrolysis,  $\alpha$ -crotonic acid, which is probably the precursor of the  $\beta$ -hydroxybutyric acid obtained from these bacteria after autolysis.

L. F. H.

**Voges-Proskauer Reaction [for *Bacillus coli aerogenes*].** C. S. LINTON (*J. Amer. Waterworks Assoc.*, 1925, **13**, 547—549).—Successful results with the Voges-Proskauer test depend on the period and temperature of incubation. The production of acetyl-methylcarbinol by organisms of the *aerogenes* group is transient. The practice of using portions of material remaining from the methyl-red test for the Voges-Proskauer reaction is untrustworthy owing to the prolonged incubation involved. A. G. P.

**Decomposition of Proteins and Amino-acids by Various Groups of Micro-organisms.** S. A. WAKSMAN and S. LOMANITZ (*J. Agric. Res.*, 1925, **30**, 263—281).—The fungi *Trichoderma koningi* and *Zygorhynchus molleri* utilised glycine, alanine, phenylalanine, asparagine, and glutamic acid, and also caseinogen as sources both of nitrogen and carbon. In the absence of carbohydrates, the amount of growth and of ammonia production increased with the amount of available carbon in the amino-acid. The two bacteria studied behaved differently. *Bacillus cereus* was unable to attack glycine, alanine, or phenylalanine, and attacked glutamic acid and asparagine only to a limited extent; caseinogen and other proteins, however, were decomposed very rapidly. *B. fluorescens* was unable to decompose caseinogen, but acted very rapidly on the amino-acids. Caseinogen was very readily decomposed to ammonia by a mixture of the two bacteria. The addition of a carbohydrate to a culture solution may increase the amount of protein decomposition, but reduce the ammonia production. An *Actinomyces* utilised both the amino-acids and protein as sources of energy and allowed an accumulation of ammonia, even in the presence of dextrose. The amount of ammonia liberated from amino-acids by micro-organisms depends on the carbon-nitrogen ratio of the compound. E. M. C.

**Oxidation and Reduction by *Pneumococcus*. VIII. Nature of the Oxidation-Reduction Systems in Sterile *Pneumococcus* Extracts.** J. M. NEILL and O. T. AVERY (*J. Exp. Med.*, 1925, **41**, 285—298).—One system is thermo-stable, combines slowly with molecular oxygen, and in its absence causes reduction of methylene-blue and methæmoglobin. The presence of the second

component markedly accelerates the reactions; this substance is thermolabile, non-reactive, and (unlike the former) not removed by washing the *pneumococcus* cells. CHEMICAL ABSTRACTS.

**Oxidation-Reduction of Hæmoglobin and Methæmoglobin.**

**I. Changes induced by *Pneumococci* and by Sterile Animal Tissues.** J. M. NEILL (*J. Exp. Med.*, 1925, **41**, 299—313).—Conversion of hæmoglobin into methæmoglobin and *vice versa* by living *pneumococci* or their sterile extracts depends on the presence or absence of molecular oxygen, the equilibrium between hæmoglobin and methæmoglobin being determined at will by the oxygen pressure. The disappearance of methæmoglobin from the bloodstream is discussed. CHEMICAL ABSTRACTS.

**Pyocyanine, the Blue Pigment in *Bacillus pyocyaneus*.** **II.** F. WREDE and E. STRACK.—(See i, 844.)

**Polysaccharide Produced by *Aspergillus niger*.** D. SCHMIDT (*Biochem. Z.*, 1925, **158**, 223—252).—The polysaccharide produced by this mould is identical with amylose. Glycogen is not formed in amounts which can be recognised macrochemically. Starch production runs parallel with acid formation. The nitrogen/carbohydrate relationship in the medium affects the formation of starch, the amount of the latter increasing with diminution in this ratio. Paradextran ("fungose") is a possible precursor of the starch of this mould.

The hydrolysis of amylose by acids and various enzymes follows one of two paths, leading on the one hand (acids and diastases derived from moulds or bacteria) to substances giving a red colour with iodine, and on the other (malt or pancreatic diastase, emulsin) to substances showing a diminishing blue coloration with iodine.

H. D. K.

**Influence of certain Factors in the Development of the Flagellate *Prowazekia (Bodo) edax*.** **I. Hydrogen-ion Concentration.** H. RAABE (*Bull. Soc. Chim. biol.*, 1925, **7**, 383—400).—The initial  $p_H$  of the culture influences considerably the rate of growth of *Prowazekia edax*. Growth proceeds most rapidly at  $p_H$  6.2—6.6, more slowly at higher  $p_H$ , and only feebly in definitely alkaline solution. At  $p_H$  below 6.2, growth commences slowly, and becomes more vigorous as the  $p_H$  approaches the optimum. In every case, the period of growth is succeeded by a period in which the number of individuals slowly decreases until life almost ceases. Maintenance of the  $p_H$  at the optimum level, of sufficient nourishment, and of an adequate surface to allow of oxygen absorption at a sufficient rate, are alike unable to prevent this cessation of growth. When all these conditions have been provided the decisive factor appears to be the accumulation of waste products.

C. P. S.

**Contrasts in the Cell Sap of Valonias and the Problem of Flotation.** W. J. V. OSTERHOUT and M. J. DORCAS (*J. Gen. Physiol.*, 1925, **7**, 633—640).—*Valonia macrophysa* sinks in sea-

water, and its sap contains potassium and sodium in the proportion of 5.72/1. In the closely related *V. ventricosa*, which grows in similar environment and floats in sea-water, the potassium/sodium ratio is 0.0278/1. The saps show other differences in chemical composition.

C. P. S.

**Influence of Vitamin-A and of Vitamin-B on Unbalanced Diets.** S. ÉDERER (*Biochem. Z.*, 1925, **158**, 197—202).—Vitamin-B has a beneficial effect on the assimilation of protein or of carbohydrate from a diet made up almost entirely of the one or the other. The animal maintains its weight curve at a higher level, and also lives longer if yeast be added to such a diet than if the diet is supplemented with the same weight of cod-liver oil. Both A and B vitamins must be present for the animal to survive long on a fat diet.

H. D. K.

**Growth Factors. III.** H. VON EULER, H. WIDELL, and E. ERIKSON (*Z. physiol. Chem.*, 1925, **144**, 123—131).—Arachis oil, which before exposure shows no growth-increasing activity, after irradiation with ultra-violet light, has a definite growth-increasing action. It is supposed that under the action of ultra-violet light a factor related to the growth-promoting fat-soluble vitamin, provisionally designated R, is formed. Since hardened arachis oil gives a negative result, it is concluded that the double bond is the grouping sensitive to irradiation. Oleic acid is faintly activated, stearic acid is not. The double bond of the phytols in green plants is supposed to be concerned in the formation of vitamins. It is not found possible, however, to distinguish between the irradiated and non-irradiated oil by means of Drummond's vitamin-A colour reaction (cf. A., 1924, i, 588; this vol., i, 209; *Z. physiol. Chem.*, 1924, **141**, 297).

P. W. C.

**Growth Factors. IV. Influence of Excess of *lD* [Fat-soluble Growth-promoting Factor] on the Growth of Rats.** H. VON EULER and H. WIDELL (*Z. physiol. Chem.*, 1925, **144**, 132—136).—When 10% of lemon juice (containing normally sufficient vitamin-C) is added to the drinking water and the animal fed on a standard diet containing excess of *lD*, considerable growth occurs for 60—90 days, but this is followed by a rapid fall in body-weight and death. The view is expressed that the normal amount of vitamin-C is insufficient in presence of excess of the *lD* factor (of cod-liver oil).

P. W. C.

**Ultra-violet Radiations and Antirachitic Substances.** J. C. DRUMMOND and T. A. WEBSTER.—(See ii, 630.)

**Action of Piperidine on Calcium Deposition.** S. ÉDERER (*Biochem. Z.*, 1925, **158**, 193—196).—Feeding of piperidine salts to rats on a rachitic diet delays the onset of rickets, or, in higher concentrations, will cure the disease. An amount of piperidine corresponding with 1.5% of the weight of the diet assists in the



taking up of the requisite mineral substances and the deposition of bone, but is less efficient in this respect than is cod-liver oil.

H. D. K.

**Influence of Fluorine and Iodine on Reproductive Power of Rats and on the Growth of the Young.** P. MAZÉ (*Compt. rend.*, 1925, **180**, 1683—1684).—Rats fed on a balanced diet containing skimmed milk powder are not able to reproduce unless potassium iodide and fluoride are added to the diet, when they are also enabled to feed their young sufficiently to promote growth. Phosphates appear to play no part in conferring reproductive power.

L. F. H.

**Glutathione. Synthesis.** C. P. STEWART and H. E. TUNNICLIFFE.—(See i, 795.)

**Effect of Insulin on the Lactic Acid in the Blood.** J. A. COLLAZO and J. LEWICKI (*Biochem. Z.*, 1925, **158**, 136—143).—Insulin administered in large quantities to starving normal animals causes at first, as a result of dyspnoea, a rise in blood lactic acid, which, however, has nothing directly to do with the physiological activity of insulin. Following moderate doses of insulin, there is usually in normal starving men and rabbits a fall in the level of this acid in the blood. With dogs, even larger doses produce no rise in the blood lactic acid, provided respiration is artificially controlled. The simultaneous administration of insulin and sugar—the more normal physiological process—usually produces an increase in blood lactic acid.

H. D. K.

**Action of Trypsin on Insulin.** D. A. SCOTT (*J. Biol. Chem.*, 1925, **63**, 641—651).—Insulin is inactivated immediately by the addition of trypsin to its solution at  $p_H$  2.5; as much as 80% may be recovered by increasing the acidity to  $p_H$  1.5 and heating at 80° for 30 mins.; smaller amounts can be recovered by treatment of the solution with excess of acid alcohol or of a solution of benzoic acid in alcohol, or by the addition of sodium benzoate; trypsin inactivated by heat has no effect on insulin. After incubation over-night with trypsin, insulin is no longer recoverable. It is suggested that the first action of trypsin is to adsorb the insulin and that this is followed by proteolytic destruction of the latter. Injection of trypsin immediately after insulin in amounts which, *in vitro*, would have inactivated the insulin had no effect on the action of the latter *in vivo*.

C. R. H.

**Physiology and Distribution of Flavones.** G. KLEIN and O. WERNER (*Z. physiol. Chem.*, 1925, **143**, 9—32).—The presence of flavones has been demonstrated in a large number of plants; in many cases the various organs of the plant were examined separately. Factors affecting their occurrence are discussed.

E. S.

**Photosynthesis of Carbohydrates.** M. J. GALWIALO (*Biochem. Z.*, 1925, **158**, 65—75).—In presence of sunlight, sugar is produced from a saturated solution of carbon dioxide in water if the electrolytes derived from the ash of the roots of plants, and

an enzyme derived from leaves containing chlorophyll, are also present in the solution. On keeping for 4 days in the sunlight, the sugar content of the solution diminishes, but at the same time a solid, giving a light blue colour with iodine, separates from the reaction mixture on evaporation.

H. D. K.

**Regional and Seasonal Distribution of Potassium in Plant Tissues.** E. S. DOWDING (*Ann. Bot.*, 1925, **39**, 459—474).—All meristematic cells are particularly rich in potassium. The wood of the mature root of the spruce contains no potassium in winter. In spring (also in winter if the plant is grown in a greenhouse), the potassium content of the vascular system increases in all the organs of the spruce. When the spruce bud elongates, potassium is transferred within the embryonic cone to the next year's meristem and to the embryonic leaves. In the mesophyll of the mature spruce leaf, the potassium content increases in early winter, and decreases in early spring; in summer, the potassium forms a network of granules between the chloroplasts, in winter it is concentrated near the laked chloroplasts.

C. P. S.

**Hydrogen-ion Concentration in Seeds.** A. NÉMEC (*Compt. rend.*, 1925, **180**, 1776—1778).—The hydrogen-ion concentration of the aqueous extract of the pulverised seeds of 38 plants studied varies from  $p_H$  4.2 to 6.5, and lies between wide limits in different members of the same species. In general, the hydrogen-ion concentration of the seeds is the same as that of the soil in which the plant flourishes best.

L. F. H.

**Micro- and Histo-chemical Demonstration of Free and Bound Oxalic, Succinic, Malic, Tartaric, and Citric Acids.** G. KLEIN and O. WERNER (*Z. physiol. Chem.*, 1925, **143**, 141—153).—The acids are sublimed in an evacuated flask containing an internal cooler. Sublimation occurs at the temperatures (bath) indicated: oxalic 110°, succinic 130°, malic 145°, citric 170°, tartaric 195°. With small quantities practically complete separation can be effected by fractional sublimation. The temperatures at which sublimation occurs serve to identify the acids, which can be further characterised by conversion into the strontium (oxalic), lead (succinic), or silver (malic, citric, and tartaric) salts. In some cases, the sublimate consists of the anhydride of the acid; this can be readily converted into the acid by treatment with dilute ammonia. When the method is applied to plant or animal tissue this is first treated with phosphoric acid, disintegrated, and dried. Results of the investigation of some plants are given.

E. S.

**Determination of Xanthophyll by Means of the Spectrophotometer and the Colorimeter.** F. M. SCHERTZ (*J. Agric. Res.*, 1925, **30**, 253—261; cf. A., 1924, ii, 359).—Spectrophotometric determinations of xanthophyll in ether solutions are accurate to about 3%, whilst colorimetric determinations, in comparison with Lovibond slides 5, 10, and 20 yellow, are accurate only to 17%. Spectrophotometric measurements provide a more reliable test for purity than do the melting points. The specific transmissive

index of xanthophyll in ether solution is 2.089 for the mercury line 4358 Å. A curve is given for the relative positions of the edge of the absorption bands of carotin and xanthophyll for solutions of various concentrations; this curve may be used to detect the presence of, and distinguish between, the two pigments.

E. M. C.

**Coagulation of Pectin.** M. W. KOPACZEWSKI (*Bull. Soc. Chim. biol.*, 1925, 7, 419—428).—In the coagulation of pectin by pectase calcium salts may be replaced by those of barium, strontium, magnesium, and, particularly, copper and iron. These salts have also a coagulating action of their own—in the case of copper and iron, stronger than that of pectase. Salts of the alkali metals do not antagonise the action of pectase, for which they are, indeed, necessary. Coagulation takes place best at a neutral reaction and is prevented by acids. When, however, neutral solutions of pectin and pectase, in presence of electrolytes, are mixed, the reaction becomes acid. No such change takes place in the absence of electrolytes. After the development of this acid reaction, pectin is no longer coagulable by alcohol; nor is pectase in absence of electrolytes. Alcohol coagulation is still possible after pectin, in presence of electrolytes, has been mixed with boiled pectase.

C. P. S.

**Toxicity of Juice Extracted from Succulent Onion Scales.** J. C. WALKER, C. C. LINDEGREN, and F. M. BACHMANN (*J. Agric. Res.*, 1925, 30, 175—187).—The toxins in onion scales are of two types: one which is volatile and disappears from the extracted juice fairly quickly, and the other which is relatively thermostable and non-volatile. The amount of the former in onion bulbs decreases during storage and sprouting. The toxicity of these substances towards a number of bulb parasites has been examined. Both toxins behave similarly in this respect. There appears to be no connexion between the resistance of the onion to fungous attacks and the effect of the toxins on fungi. O. O.

**Seed Hairs of the Milkweed.** A. W. SCHORGER (*Ind. Eng. Chem.*, 1925, 17, 642).—The unicellular lignified hairs of the milkweed, *Asclepias syriaca*, were found to have the following percentage composition: lignin, 22.2; pentosans, 34.6; "methylpentosans," 1.1; methoxyl, 3.6; cellulose, 60.4;  $\alpha$ -cellulose in cellulose, 58.6; material soluble in alcohol, 4.3; in ether, 1.4; and ash, 1.0.

D. G. H.

**Phytosterol from Bulb Scales of the Genus *Lilium*.** M. MIRANDE (*Compt. rend.*, 1925, 180, 1768—1769).—Only the positively birefringent phytosterol has been observed in 22 members of the *Lilium* genus investigated (cf. this vol., i, 618). The amount of sterol found increases with the age of the scales and finally seems almost to fill the cells. It is suggested that the function of the phytosterol is to protect the bulb from bacterial invasion and from too rapid drying.

L. F. H.

**Tannin of *Hevea braziliensis*.** W. H. ARISZ and J. SCHWEIZER (*Archief Rubbercultuur Nederl.-Indie*, 1924, **5**, 334—357; from *Chem. Zentr.*, 1924, ii, 2406).—The tannin isolated from the sap of *Hevea braziliensis* gives, besides general reactions for tannins, a red coloration with "butter-yellow" (benzeneazodimethylaniline) in the presence of hydrochloric acid. The mode of occurrence of the tannin in the different tissues of *Hevea* is described. G. W. R.

**Sodium Salts of the Nucleic Acid from Wheat Embryo.** A. THOMAS and A. W. DOX (*Z. physiol. Chem.*, 1925, **142**, 1—13).—Nucleic acid from wheat embryo forms sodium salts containing 4 to 8 sodium atoms. When potassium acetate is used to prevent emulsification of the salts during precipitation with alcohol, the sodium is partly replaced by potassium with the formation of a sodium potassium salt. Ammonium acetate, under similar conditions, converts the sodium salt of the nucleic acid into an acid sodium ammonium salt. This is due to the acetic acid liberated from the ammonium acetate by hydrolysis; the hydrolysis is greater in aqueous alcohol than in water. The formation of a nucleic acid salt containing 8 sodium atoms can only be explained on the theory of Jones that the mononucleotides are united by ether linkings between the carbohydrates. E. S.

**Nitrogenous Constituents of the Juice of the Alfalfa (Lucerne) Plant. III. Adenine in Alfalfa.** H. B. VICKERY and C. S. LEAVENWORTH (*J. Biol. Chem.*, 1925, **63**, 579—583).—The unidentified base, with a picrate melting at 298°, previously reported (A., 1924, i, 1393) as occurring in the juice of the alfalfa (lucerne), has been shown to be adenine. Adenine picrate, when perfectly pure and heated at the rate of 1° in 3 secs., has m. p. 298—299° (decomp.). The lower values previously recorded in the literature are due to retention of a minute amount of impurity and to variations in the rate of heating. C. R. H.

**Presence of Gitogenin in Digitalis Leaves.** A. WINDAUS and J. BRUNKEN (*Z. physiol. Chem.*, 1925, **145**, 37—39).—The substance reported by Merck (*Merck's Jahresb.*, 1922, **86**) as occurring in digitalis leaves has been identified with the gitogenin obtained by Windaus and Schneckenburger (A., 1913, i, 1213) by the hydrolysis of the gitonin of digitalis seeds. C. R. H.

**Presence of Nickel and Cobalt in Vegetables.** G. BERTRAND and M. MOKRAGNATZ (*Bull. Soc. chim.*, 1925, [iv], **37**, 554—558).—The 23 vegetables examined all contain nickel and cobalt. The former is present in greater amounts, which vary from 0.01 mg. (tomato) to 2 mg. (pea), whilst the quantities of cobalt range from 0.003 mg. (carrot) to 0.3 mg. (lentil) per kg. of fresh material. The nickel is weighed as nickel dimethylglyoxime and the cobalt determined as potassium cobaltinitrite or by a colour reaction. [Cf. B., 1925, 470.] F. M. H.

**Occurrence of Loroglossoside (Loroglossin) in *Listera ovata*, R. Br., and *Epipactis palustris*, Crantz, and its Reactions.** C. CHARAUX and P. DELAUNEY (*Compt. rend.*, 1925, 180, 1770—1771; cf. A., 1920, i, 801; 1921, i, 286; 1923, i, 1046).—Loroglossoside (loroglossin) has been extracted by ethyl alcohol from *Listera ovata*, R. Br., and *Epipactis palustris*, Crantz, in 0.5—0.77% yield. Hydrolysis with acids yields dextrose, and oxidation with chromic acid produces a red coloration and an odour of valeric acid. Fröhde's reagent gives a purple colour changing to red, and nitric acid produces a colourless solution giving a yellow coloration with alkalis.

L. F. H.

**Pedological Chemistry. I. Alkalinity of the Soil in Relation to its Lithological Constitution.** U. PRATOLONGO (*Atti R. Accad. Lincei*, 1925, [vi], 1, 238—243).—Aqueous solutions of calcite and aragonite saturated at the ordinary temperature have alkalinities expressed by  $p_H$  8.0—8.2, whereas for hydromagnesite the value is 9.2. Investigation of the solubility curve of the system  $\text{CaCO}_3\text{--Na}_2\text{CO}_3\text{--H}_2\text{O}$  at the ordinary temperature shows that the conditions for the formation and stability of gaylussite are the presence in the solution of about 5% of sodium carbonate and the presence of calcium carbonate; under such conditions the soil would be rendered completely sterile. For saturated solutions of brucite at the ordinary temperature, the value of  $p_H$  is 10. The conclusion is reached that the high degree of constitutional alkalinity ( $p_H$  8.8—9.2) exhibited by certain soils is attributable to the presence, not of aragonite or calcite, but of hydromagnesite.

T. H. P.

**Investigation of Soil Acidity by Means of Pot Experiments.** H. KAPPEN (*Z. Pflanz. Düng.*, 1925, 4A, 202—214).—Barley, turnips, clover, beans, lucerne, mustard, and, probably, wheat and rape are sensitive to "exchange acidity" (measured by interaction with a neutral salt), but oats, maize, potatoes, serradella, and, probably, rye are less sensitive. In pot experiments, with an acid soil, the first group of crops showed no response to the addition of ammonium sulphate, superphosphate, and "potash salts," unless calcium carbonate were added, whilst the second group showed a considerable response even in the absence of calcium carbonate. Physiologically alkaline manures are preferable for crops insensitive to "exchange acidity," but are of less value for the more sensitive crops. Superphosphate does not increase the "exchange acidity" of the soil and is not physiologically acid. A sufficient amount of superphosphate prevents the acidifying action of ammonium sulphates. [Cf. B., 1925, 465.]

E. M. C.

**Simple Apparatus for the Electrometric Measurement of Hydrogen-ion Concentration [of Soil Suspensions].** M. TRÉNEL (*Z. Pflanz. Düng.*, 1925, 4A, 239—241).—A standard quinhydrone electrode solution is contained in a porous cylinder, previously impregnated with saturated potassium chloride solution, and is introduced into a 1 : 2 suspension of soil in 0.1N-potassium

chloride solution. The addition of potassium chloride to the soil results in a measurement of the "exchange acidity."

E. M. C.

**Soil Acidity and its Determination.** B. TACKE (*Z. Pflanz. Düng.*, 1925, **4A**, 215—216).—The Daikuhara and the Tacke methods of determining soil acidity give discordant results. The addition of potassium chloride to the soil and calcium carbonate suspension in the Tacke method has no significant effect on the "exchange acidity."

E. M. C.

**Soil Acidity and its Determination.** E. RAMANN (*Z. Pflanz. Düng.*, 1925, **4A**, 217—221).—A general discussion of the analogies between acid "permutites" and acid soils, and the determination of the degree of saturation of the soil with respect to bases.

E. M. C.

**Soil Reaction. III. Determination of the Hydrogen-ion Concentration of Soil Suspensions by Means of the Hydrogen Electrode.** E. M. CROWTHER (*J. Agric. Sci.*, 1925, **15**, 201—221; cf. Fisher, A., 1921, i, 215; ii, 349).—A hydrogen electrode apparatus for use with soil suspensions is described. The buffering curves for a number of soils are given. These for any set of similar soils are parallel, although the individual  $p_H$  values may vary. In any set of related soils there is a good correlation between  $p_H$  and Hutchinson-McLennan "lime requirement." The results obtained for the effect of salts on  $p_H$  are in general agreement with current theory. The increase in acidity caused by neutral salts is greater with potassium, calcium, or barium salts than with sodium salts. Chlorides give lower  $p_H$  values than sulphates. Extraction with water increases the  $p_H$  value of soil suspensions. A soil-water ratio of 1:5 is recommended for water extractions. Methyl-red is shown to give untrustworthy values for the  $p_H$  of soils.

G. W. R.

**Soil Reaction. IV. Soil Reaction of Continuously Manured Plots at Rothamsted and Woburn.** E. M. CROWTHER (*J. Agric. Sci.*, 1925, **15**, 222—231; cf. preceding abstract).—The author gives data for the  $p_H$  values of the continuous barley plots at Woburn and the grass plots at Rothamsted. Ammonium sulphate has caused increased acidity, whilst sodium nitrate has exerted the reverse effect to a smaller extent. Mineral manures have in general exerted little effect. The change in  $p_H$  as the result of liming is less than might be expected from laboratory experiments, owing, in part, to subsoil acidity.

G. W. R.

**Soil Reaction. V. Depth Distribution of Reaction, and Flocculation in Continuously Manured Soils.** E. M. CROWTHER (*J. Agric. Sci.*, 1925, **15**, 232—236; cf. preceding abstract).—The  $p_H$  values of continuously manured barley plots at Woburn and grass plots at Rothamsted change with increasing depth and at 36 in. show the same relationships as in the surface soil. The difference in  $p_H$  between limed and unlimed soils at Rothamsted is substantially

constant down to 36 in. The reaction of the subsoil influences the effect obtained from liming. Complete flocculation of 1 : 5 suspensions is shown for the subsoils below 9 inches of plots treated with ammonium sulphate.

G. W. R.

**Soil Reaction. VI. Interaction of Acid Soils, Calcium Carbonate, and Water in Relation to the Determination of "Lime Requirements."** E. M. CROWTHER and W. S. MARTIN (*J. Agric. Sci.*, 1925, 15, 237—255; cf. preceding abstracts).—Variations in the results obtained by the Hutchinson-McLennan method for "lime requirement" are produced when the conditions of working are varied. From curves showing the relationship between the weight of soil originally used and the final equilibrium concentration of the calcium hydrogen carbonate solution, titration curves may be derived which, however, diverge from those obtained electrometrically owing to the varying calcium concentration in the equilibrium solutions. In the presence of calcium chloride, these divergences are masked. The Hutchinson-McLennan "lime requirement" is less than the equivalent of the amount of calcium hydroxide necessary to give a neutral soil suspension as determined by electrometric titration. "Lime requirements" should be given as corresponding with some determined final concentration of calcium hydrogen carbonate. This may be effected by interpolation. The results give no indication of the intensity of soil acidity, but show the amount of lime necessary to produce a considerable reduction in acidity. The decomposition of calcium carbonate by acid soils is greater in amount than that indicated by their "lime requirements."

G. W. R.

**Physical Properties of Soils. I. Mechanical Properties Concerned in Cultivation.** W. B. HAINES (*J. Agric. Sci.*, 1925, 15, 178—200).—The author discusses cohesion, plasticity, and surface friction in soils. Measurements of the cohesion of soils at different moisture contents are reported, using a modification of Atterberg's method (Atterberg, *Int. Mitt. Bodenkunde*, 1911, 1, 10; 1912, 2, 149; 1913, 3, 291; 1916, 6, 27). The curves obtained, whilst generally similar to those obtained by Atterberg, differ in some respects. Plasticity was examined by means of an apparatus in which the pressure required to extrude soil-water mixtures of varying composition through an orifice was measured. For low moisture contents a modification of the Brinell hardness test was used and the curves obtained were fitted to the curves obtained by the extrusion apparatus. Extrusion pressure is connected with moisture content by an exponential function. The physical properties of clays are not always deducible from their moisture content, previous treatment exerting an influence. Curves are given showing the relationship between surface friction and moisture content. In the case of a heavy soil two maxima were shown.

G. W. R.

## Organic Chemistry.

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**$\gamma\gamma$ -Diethylpentane (Tetraethylmethane).** G. T. MORGAN, S. R. CARTER, and A. E. DUCK (*J. Chem. Soc.*, 1925, **127**, 1252—1259).—*Triethylcarbinyl iodide*,  $\text{C}(\text{Et})_3\text{I}$ , b. p.  $71\cdot2^\circ/16$  mm.,  $153^\circ/737$  mm.,  $d_4^{20}$  1.42, is produced by the action of dry hydrogen iodide on triethylcarbinol. Interaction of zinc diethyl and triethylcarbinyl iodide, followed by successive treatment of the product with water and hydrochloric acid, yields an oil containing unsaturated compounds. When the latter are removed by treatment with concentrated sulphuric acid and the hydrocarbon is dried and repeatedly fractionated,  *$\gamma\gamma$ -diethylpentane* is obtained; this has b. p.  $45\text{—}47\cdot5^\circ/19$  mm.,  $139\cdot2^\circ$  (corr.)/760 mm., m. p.  $-41^\circ \pm 1^\circ$ ,  $d_4^{15}$  0.75651,  $V_m^{15} = 169\cdot4$ ,  $n_D^{18}$  1.42057. The hydrocarbon exhibits the chemical characteristics of a paraffin, and measurements of vapour density and surface tension indicate that it is not associated in the vapour or liquid states. C. J. S.

**Internal Oxidation Reactions with Additive Compounds of Nitrogen Tetroxide and Olefines.** A. SCHAARSCHMIDT and H. HOFMEIER (*Ber.*, 1925, **58**, [B], 1047—1054).—The action of nitrogen peroxide on *cyclohexene* dissolved in light petroleum is accompanied by feeble evolution of gas, mainly nitrogen, and spontaneous rise of temperature to about  $30^\circ$ ; if the product is warmed at  $60\text{—}70^\circ$ , a second exothermic change sets in which proceeds slowly at the atmospheric temperature, with copious evolution of nitrogen containing a considerable proportion of nitric oxide; at  $140\text{—}150^\circ$  a third, vigorous autodecomposition is observed. With amylene under similar conditions two phases of evolution of gas are observed, one dependent on spontaneous heating whereby temperatures of  $63\text{—}68^\circ$  are attained, and the second caused by heating the product at  $80^\circ$ ; the first gas contains a considerable proportion, the second about 33%, of nitric oxide. With cetene, the reaction is much less vigorous; the initial spontaneous evolution of heat causes the temperature to rise only to about  $30^\circ$  and very little gas is evolved, whereas at  $90^\circ$  a second change occurs accompanied by the evolution of nitrogen with about 10% of nitric oxide. The addition of nitrogen peroxide to olefines appears to be liable to considerable catalytic influences, since explosion occurs when carbon tetrachloride is used as diluent for *cyclohexene*. The experiments show that the additive change is accompanied by oxidation, whereby nitrogen is formed in considerable amount, and that the additive compounds undergo internal oxidations which lead to the reduction of nitric oxide residues mainly to nitrogen. It appears probable that the phases of the addition correspond with the production of two or three of the forms,  $\cdot\text{CH}(\text{NO})\cdot\text{CH}\cdot\text{O}\cdot\text{NO}_2$ ,  $\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}\cdot\text{O}\cdot\text{NO}$ ,  $\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}\cdot\text{NO}_2$ ,  $\cdot\text{CH}(\cdot\text{O}\cdot\text{NO})\cdot\text{CH}(\text{O}\cdot\text{NO})$ . The stability of the



additive products is greatly influenced by the temperature at which addition occurs. With *cyclohexene* at  $-30^{\circ}$  to  $-40^{\circ}$ , complicated oxidative reactions take place and unusually unstable liquids result; addition at  $-50^{\circ}$  yielded a product which exploded at  $-30^{\circ}$ . The change appears also to be influenced by the presence of traces of moisture, or of nitric acid or nitrogen trioxide in the nitrogen tetroxide.

H. W.

**$\alpha$ -Phenyl- $\Delta^{\gamma}$ -pentadi-inene.** C. PRÉVOST (*Compt. rend.*, 1925, **180**, 1851—1853).— $\alpha\beta\gamma\delta$ -Tetrabromo- $\alpha$ -phenylpentane, obtained from  $\alpha$ -phenyl- $\Delta^{\alpha}$ -penten- $\gamma$ -ol, yields, on treatment with alcoholic potassium hydroxide,  $\alpha$ -phenyl- $\Delta^{\gamma}$ -pentadi-inene, m. p.  $22\cdot3^{\circ}$ ,  $d_4^{21}$  0.9745,  $n_D^{21}$  1.6368, two stereoisomeric tetrabromides, m. p.  $97\cdot7^{\circ}$  and  $127$ — $131^{\circ}$ . The exaltation of the molecular refractivity of the diacetylenic hydrocarbon and its high refractive dispersion are notable.

L. F. H.

**Action of Free Thiocyanogen on Unsaturated Compounds.** E. SÖDERBÄCK.—(See i, 899.)

**Partial Dehalogenation of Polyhalogen Derivatives.** B. K. MEREJKOVSKI (*Bull. Soc. chim.*, 1925, [iv], **37**, 711—713).— $\alpha\beta\gamma$ -Tribromobutane (A., 1923, i, 527) on treatment with zinc in methyl-alcoholic solution in the presence of a little water and moderating the reaction by cooling gives, in 50% of the theoretical yield,  $\alpha$ -bromo- $\beta$ -methyl- $\Delta^{\beta}$ -propene, b. p.  $94\cdot2$ — $95\cdot2^{\circ}/774$  mm.,  $n_D^{20}$  1.46886,  $d_4^{20}$  1.31335, together with methyl  $\beta$ -methyl- $\Delta^{\beta}$ -propenyl ether, b. p.  $68^{\circ}/773$  mm.,  $d_4^{20}$  0.76975,  $n_D^{20}$  1.396412. In the absence of cooling, much isobutylene is formed. Replacement of the methyl alcohol by ethyl alcohol yields a mixture of the corresponding ethyl ether and bromobutylene which cannot be separated by fractional distillation.

R. B.

**Dehydrogenation and Dehydration of Alcohols over a Zinc Oxide Catalyst.** W. A. LAZIER and H. ADKINS (*J. Amer. Chem. Soc.*, 1925, **47**, 1719—1722).—The relative rates of reactivity of ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*.-butyl, and isobutyl alcohols over a zinc oxide catalyst (A., 1924, ii, 159) are approximately the same as over an alumina catalyst (this vol., i, 626), but the rate of reaction in the latter case is several times greater at any given temperature. With the four primary alcohols, the proportion of dehydration to dehydrogenation is apparently independent of the temperature. In the case of the secondary alcohols, temperature has a marked effect on the proportions of dehydration to dehydrogenation, the latter reaction being favoured by higher temperatures, and the temperature coefficient of reaction is much higher than with the primary alcohols. Over the temperature range  $340$ — $440^{\circ}$  the percentage of dehydration in the total reaction is as follows: ethyl alcohol, 10%, propyl alcohol, 16%, isopropyl alcohol, 89—71%, butyl alcohol, 15%, isobutyl alcohol, 31.5%, and *sec*.-butyl alcohol, 88—73%.

R. B.

**Alcohols Present in the Wax of American Cotton.** R. G. FARGHER and M. E. PROBERT (*J. Text. Inst.*, 1924, **15**, T 337—346).—It was previously reported (A., 1923, i, 278) that gossypyl alcohol appeared to exist in three forms which gave identical derivatives. This and other anomalies have now been explained as the result of closer examination, based chiefly on fractional crystallisation of the crude acetates. Small quantities of other alcohols and glycols were present in the so-called  $\beta$ - and  $\gamma$ -forms. The alcohols present in the wax of American cotton are chiefly (1) montanyl,  $C_{28}H_{58}O$ , m. p.  $83.5^\circ$ , and (2) gossypyl,  $C_{30}H_{62}O$ , m. p.  $85^\circ$ , and small quantities of (3) an alcohol,  $C_{32}H_{66}O$ , m. p.  $87-87.5^\circ$  (acetate, m. p.  $72.5^\circ$ ; benzoate, m. p.  $69-69.5^\circ$ ; corresponding acid,  $C_{32}H_{64}O_2$ , m. p.  $88^\circ$ ; its methyl ester, m. p.  $72.5-73^\circ$ ; and anilide, m. p.  $105-105.5^\circ$ ), (4) an alcohol,  $C_{34}H_{70}O$ , m. p.  $88.5-89^\circ$  (acetate, m. p.  $74.5^\circ$ ; benzoate, m. p.  $71.5-72.5^\circ$ ; corresponding acid,  $C_{32}H_{68}O_2$ , apparently that previously described), and (5) a glycol,  $C_{29}H_{60}O_2$  (possibly a mixture of  $C_{28}$  and  $C_{30}$  members), m. p.  $91.5-92.5^\circ$  (diacetate, m. p.  $58-59^\circ$ ; dibenzoate, m. p.  $46^\circ$ ). The data now assigned to the derivatives of montanyl and gossypyl alcohols are more trustworthy than those in the previous paper. J. C. W.

**Constituents of the Wax of American (Mississippi Delta) Cotton.** P. H. CLIFFORD and M. E. PROBERT (*J. Text. Inst.*, 1924, **15**, T 401—413).—The earlier method for the extraction of wax from cotton (A., 1924, i, 278) was open to some objections due to the use of crude benzene and live steam. An extract obtained by percolation with chloroform has now been examined and it is shown that the earlier results were erroneous only with regard to the hydrocarbon fraction. The ingredients isolated are as follows: Alcohols: montanyl, gossypyl,  $C_{32}$  and  $C_{34}$  alcohols,  $C_{28}$  and  $C_{30}$  glycols (mixed) (see preceding abstract), glycerol, amyryl, lupeol, sitosterol, and a sterol,  $C_{34}H_{58}O$ . Free acids:  $C_{32}H_{64}O_2$ ,  $C_{34}H_{68}O_2$ , gossypic, montanic, palmitic, stearic, oleic, carnaubic. Acids as esters: palmitic, stearic, oleic, carnaubic. Hydrocarbons: heptacosane(?), liquids, b. p.  $205-240^\circ/15$  mm., and b. p.  $225-275^\circ/2$  mm. Wax esters: mixtures, including esters of melissic acid and sterol esters of carnaubic acid. Also sitosterol glucoside and resinous matter.

Most of these compounds and their derivatives have been described previously, but the sterol,  $C_{34}H_{58}O$  (m. p.  $197-199^\circ$ ; acetate, m. p.  $213-213.5^\circ$ ), appears to be new. J. C. W.

**Constituents of the Wax of Egyptian Sakellaridis Cotton.** R. G. FARGHER and L. HIGGINBOTHAM (*J. Text. Inst.*, 1924, **15**, T 419—433).—The constituents of the wax of Egyptian cotton, obtained by percolation with chloroform, are similar to those of American cotton wax, many being identical. The chief difference is that the sitosterol and its glucoside in American cotton are replaced by another phytosterol and glucoside, whilst Egyptian cotton contains a greater proportion of wax esters. The substances isolated are as follows. Alcohols: gossypyl, montanyl, ceryl,

an alcohol  $C_{32}H_{66}O$ , a glycol,  $C_{30}H_{62}O_2$  (?), glycerol, amyirin, and a *phytosterol*,  $C_{29}H_{50}O$ , m. p.  $136^\circ$ ,  $[\alpha]_D^{20} -33.8^\circ$  (acetate, m. p.  $124.5-125.5^\circ$ , forming a *dibromide*, m. p.  $125-126^\circ$ ; *benzoate*, m. p.  $145-146^\circ$ ) which occurs also as the *glucoside*, m. p.  $295-300^\circ$  (acetate, m. p.  $168-169^\circ$ ,  $[\alpha]_D^{20} -21^\circ$ ). Free acids: palmitic, stearic, carnaubic, montanic, an acid  $C_{34}H_{68}O_2$ , *isobehenic* (?), oleic, and resin acids. Combined acids: palmitic, stearic, carnaubic, montanic, gossypic, lignoceric, and melissic. Hydrocarbons: triacontane and a mixture of unsaturated hydrocarbons contaminated with resins. Of the combined acids, the common fatty acids are present mainly in the form of glycerides, whilst the others occur as wax esters. The chief is *gossypyl carnaubate*,  $C_{54}H_{108}O_2$ , m. p.  $75-76^\circ$ , whilst *gossypyl gossypate*,  $C_{60}H_{120}O_2$ , m. p.  $86-87^\circ$ , and *montanyl montanate*,  $C_{56}H_{112}O_2$ , m. p.  $86-87^\circ$ , were isolated from other fractions of the crude wax.

J. C. W.

**Metallic Compounds of the Enolic Forms of Carbonyl Compounds and their Application to Syntheses. III. Action of Carbon Monoxide on Ketone- and Ester-enolates.** H. SCHEIBLER and O. SCHMIDT.—(See i, 917.)

**Metallic Compounds of the Enolic Forms of Carbonyl Compounds and their Application to Syntheses. IV. Reaction between Ester-enolates and Alkyl or Acyl Halides.** H. SCHEIBLER, E. MARHEUKEL, and D. BASSANOV.—(See i, 918.)

**Preparation of Esters.** A. WAHL (*Bull. Soc. chim.*, 1925, [iv], 37, 713—717; cf. Senderens, this vol., i, 113; Wuyts, *ibid.*, i, 501).—Yields of ethyl oxalate up to 75—80% of the theoretical are obtained by distilling the acid and alcohol in the presence of chloroform, which removes the water continuously as it is formed (cf. Hultman, Davis, and Clarke, A., 1921, ii, 325); with benzene the yield amounts to 80—85%. Esterification of glycerol with acetic acid, using toluene to remove water, yields diacetin, b. p.  $155-156^\circ/15$  mm., an azeotropic mixture, b. p.  $83-85^\circ$ , distilling during the reaction and separating into two layers. Formic acid (80%) similarly yields diformin (glyceryl diformate), b. p.  $158-160^\circ/18$  mm.

R. B.

**Esterification of Aliphatic Acids in Glycerol.** A. KAILAN and H. RAUPENSTRAUCH (*Monatsh.*, 1925, 45, 485—518).—The rates of esterification of heptioic acid in absolute glycerol, of *iso*- and *n*-valeric and hexoic acids in absolute and aqueous glycerol, in presence of hydrochloric acid, at  $25^\circ$ , have been measured. Contrary to esterification in mixtures rich in water, the unimolecular reaction constants are proportional to the total concentration of hydrogen chloride. In the case of *n*-valeric acid, a measurement was also made of the rate of esterification in presence of sulphuric acid in aqueous glycerol. Expressions are derived for the variation of the velocity constants with the water content of the system in the cases of the valeric acids. The velocity constants for the esterification of the above normal aliphatic acids have the same value, with the same catalyst, as that for *n*-butyric acid, whilst the

constant for *isovaleric* acid is much smaller. The retarding influence of water is also the same as in the case of *n*-butyric acid, and similarly much less in the case of glycerol than in that of ethyl alcohol. Thus, in presence of *N*/6-hydrogen chloride, the above aliphatic acids are esterified, with ethyl alcohol, in mixtures containing 0.03 mol. of water per litre, about four times as rapidly as with glycerol, whilst when the water concentration is  $\frac{4}{3}$  mols. per litre the rates are about the same. The rate of esterification at  $35^\circ$  is 2.7 times that at  $25^\circ$ . The rate of esterification of sulphuric acid with glycerol in presence of water is proportional to the  $\frac{3}{2}$  power of its concentration. *n*-Valeric acid is esterified with glycerol about 1.7 times as fast in presence of hydrochloric acid as in presence of sulphuric acid. Measurements of the rates of esterification of *iso*- and *n*-valeric, hexoic, and heptonic acids, in absence of catalyst, were made at  $183.5^\circ$ , both with absolute and aqueous glycerol, and showed that the rate of esterification under these conditions is proportional to the  $\frac{3}{2}$  power of the concentration of the acid present, indicating a catalysis by hydrogen ions. Water acts as an accelerator up to a concentration of 7 mols./litre, thereafter exerting a retarding influence.

F. G. W.

**"C<sub>4</sub>-Saccharinic Acids." III. Preparation of *dl*- $\alpha\beta$ -Dihydroxyisobutyric Acid and Some of its Derivatives.** J. W. E. GLATTFIELD and L. P. SHERMAN (*J. Amer. Chem. Soc.*, 1925, 47, 1742—1751; cf. A., 1921, i, 7; 1922, i, 318).—The saccharinic acids are now defined as the acids which would result from an hydroxyaldehyde,  $C_nH_{2n}O_n$ , in which one hydroxyl group is attached to each carbon atom except the aldehyde carbon atom, if the aldehyde group were oxidised to carboxyl at the expense of one of the  $:C\cdot OH$  groups, which would be reduced to a  $:CH$  group. Thus  $\alpha\beta$ -dihydroxyisobutyric acid is a saccharinic acid derived in this way from trihydroxyisobutaldehyde.  $\alpha\beta$ -Dihydroxyisobutyric acid, m. p.  $104^\circ$ , is obtained in 32% yield by the action of silver oxide on  $\beta$ -chloro- $\alpha$ -hydroxyisobutyric acid, as compared with 10—16% yields by Melikoff's method (A., 1886, 1009), the  $\beta$ -chloro- $\alpha$ -hydroxyisobutyric acid being obtained by Ultée's modification of Bischoff's method (A., 1909, i, 293). The dihydroxyisobutyric acid is also obtained from  $\beta$ -ketopropyl formate, prepared in 39.5% yield by a modification of Henry's method (A., 1902, i, 736), which with aqueous hydrogen cyanide is converted into  $\alpha\beta$ -dihydroxyisobutyronitrile. Hydrolysis with hydrochloric acid and crystallisation of the calcium salt ( $+7H_2O$ ) yield the  $\alpha\beta$ -dihydroxyisobutyric acid, m. p.  $104^\circ$ . The *phenylhydrazide*, m. p.  $107^\circ$ , and the *cupric* ( $+2H_2O$ ), *manganous* ( $+2H_2O$ ), *cadmium* ( $+1.5H_2O$ ), and *zinc* ( $+2H_2O$ ) salts are described. Attempts to resolve the acid with strychnine, quinine, and brucine were unsuccessful; brucine gave some evidence of resolution, but the active acid was apparently racemised in preparing its calcium salt.

R. B.

**Japanese Plants. IV. Saturated Fatty Acids in Camphor Seed Fat.** S. KOMATSU and S. YAMADA (*Mem. Coll. Sci. Kyōtō*, 1925, 8, 253—256).—The fat extracted from camphor seeds

(*Laurus camphora*) had  $d_{25}^{25}$  0.9308,  $n_D^{25}$  1.451, m. p.  $21^\circ$ , solidif. p.  $13.7^\circ$ , acid value 1.82, saponification value, 283.8, iodine value (Wijs) 4.56; it contains 1.1% of unsaponifiable matter. The saponifiable portion contains 21% of unsaturated acids and 79% of saturated acids, the latter being present as glycerides of octic and lauric acids. C. J. S.

**Oxidation of the Ammonium Salts of Normal Saturated Fatty Acids and its Biological Significance.** P. W. CLUTTERBUCK and H. S. RAPER (*Biochem. J.*, 1925, 19, 385—396).—The oxidation was carried out by heating the fatty acid with ammonia and hydrogen peroxide under a reflux condenser on the water-bath. Stearic acid yielded methyl pentadecyl ketone as a  $\beta$ -oxidation product and  $\gamma$ -ketostearic acid, m. p.  $97^\circ$ . Palmitic acid yielded  $\gamma$ -ketopalmitic acid, m. p.  $91$ — $92^\circ$ , myristic acid  $\gamma$ -ketomyristic acid, m. p.  $87^\circ$ . *n*-Hexoic, *n*-heptoic, and *n*-octoic acids yielded the respective  $\gamma$ -keto- and  $\delta$ -keto-acids, which were isolated as the semicarbazones and oximes.  $\gamma$ -Ketoheptoic acid semicarbazone, m. p.  $170^\circ$  (decomp.),  $\delta$ -ketoheptoic acid semicarbazone, m. p.  $173^\circ$ ,  $\gamma$ -ketoheptoic acid semicarbazone, m. p.  $152^\circ$  (decomp.),  $\delta$ -ketoheptoic acid semicarbazone, m. p.  $194^\circ$  (decomp.),  $\gamma$ -keto-octoic acid semicarbazone, m. p.  $153^\circ$  (decomp.), and  $\delta$ -keto-octoic acid semicarbazone, m. p.  $187^\circ$  (decomp.) are described. All the above  $\gamma$ - and  $\delta$ -acids have been synthesised for comparative purposes. No hydroxy-acids could be detected in the products of oxidation. The possibility of the occurrence of  $\gamma$ - and  $\delta$ -oxidation in the body is discussed.

S. S. Z.

**General Synthesis of  $\alpha$ -Unsaturated Acids from Malonic Acids.** S. DUTT (*J. Indian Chem. Soc.*, 1925, 1, 297—301).—Malonic acid readily condenses with aldehydes in the presence of piperidine in pyridine solution to yield alkylidene- and arylidene-malonic acids which, under the influence of pyridine at  $100^\circ$ , readily lose 1 mol. of carbon dioxide, yielding the  $\alpha$ -unsaturated monocarboxylic acids in good yields, the whole reaction being carried out in one stage in a few hours. Aromatic hydroxyaldehydes either do not condense or give very bad yields, this difficulty being overcome by employing their carbethoxy derivatives. Ketones also react, but the yields are smaller. J. W. B.

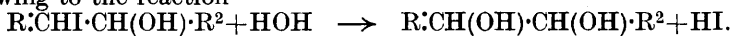
**Linoleic Acid and its Anhydride.** D. HOLDE and R. GENTNER (*Ber.*, 1925, 58, [B], 1067—1071).—Linoleic acid has m. p.  $-8^\circ$  to  $-7^\circ$ , b. p.  $202^\circ$  (corr.)/1.4 mm.,  $d_4^{18}$  0.9038,  $d_4^{22.8}$  0.9007,  $n_D^{11.5}$  1.4715,  $n_D^{21.5}$  1.4683. Linoleic anhydride, prepared by the action of acetic anhydride on the acid and purified by crystallisation from light petroleum in an atmosphere of carbon dioxide, has m. p.  $-3.5^\circ$  to  $-2.8^\circ$ ,  $d_4^{23.5}$  0.901,  $n_D^{11.5}$  1.4775,  $n_D^{21.5}$  1.4737. H. W.

**Additive Products of Iodine Monobromide and Hypoiodous Acid with Unsaturated Compounds. I.** D. HOLDE and A. GORGAS (*Ber.*, 1925, 58, [B], 1071—1074).—Determinations of the iodine number by the methods of Hanus and of Margosches, Hinner, and Friedmann (cf. A., 1924, i, 828) give concordant results

with erucic, oleic, and linoleic acids, whereas with cholesterol the latter method fails. The product obtained from erucic acid in the Hanus determination is *bromoiodobehenic acid*, m. p.  $38^{\circ}$ ,  $d_4^{20}$  1.2479,  $n_D^{20}$  1.4922, whereas linoleic acid gives *dibromodi-iodostearic acid*, m. p.  $77.8^{\circ}$ . Oleic, erucic, and linoleic acids are converted during the process of Margosches, Hinner, and Friedmann into *iodohydroxystearic acid*,  $d_4^{21}$  1.2070,  $n_D^{21}$  1.4962; *iodohydroxybehenic acid*,  $d_4^{18}$  1.1599,  $n_D^{18}$  1.4931, and *di-iododihydroxystearic acid*,  $d_4^{17.3}$  1.369,  $n_D^{17.3}$  1.5195, respectively.

H. W.

**Chemical Nature of Fats. II. Iodine Super-number of Fatty Oils and Unsaturated Fatty Acids of Similar Iodine Number.** B. M. MARGOSCHES, L. FRIEDMANN, E. SCHEINOST, and W. TSCHÖRNER (*Ber.*, 1925, **58**, [B], 1064—1067; cf. this vol., i, 629).—The possibility of utilising the iodine super-number for the discrimination of oils of similar iodine number is established by observations with poppy and sunflower oils, sesamé and cotton-seed oils, almond and rape-seed oils. Further, the compositions of mixtures of olive and castor oil can be determined through the iodine super-number with an accuracy of about 5%, the best results being obtained with mixtures rich in olive oil. The presence of hydroxyl groups in the oil appears to accelerate the reaction. With oleic acid, the absorption of iodine follows the same course as with oils (*loc. cit.*), whereas with elaidic acid the iodine number remains constant at the Hübl value, although the acidity increases probably owing to the reaction



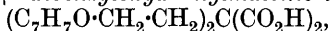
H. W.

**Hydrogenation of Triple Linkings; Formation of cis-Ethylenic Compounds.** M. BOURGUEL (*Compt. rend.*, 1925, **180**, 1753—1755).—By hydrogenation at the ordinary temperature in the presence of colloidal palladium, acetylenic compounds are converted almost entirely into *cis*-ethylenic compounds, in contradiction to some results of other workers. Phenylpropionic acid under these conditions yields only *isocinnamic acid* (cf. Paal and Hartmann, A., 1909, i, 926); tolane gives almost entirely *isostilbene* (Kelber and Schwarz, A., 1912, i, 617); tetrolic acid yields entirely *isocrotonic acid*;  $\beta\epsilon$ -dimethyl- $\Delta^7$ -hexinene- $\beta\epsilon$ -diol yields mainly one isomeride, m. p.  $67$ — $68^{\circ}$ , and a very small amount of a second isomeride, m. p.  $76.5^{\circ}$ , which has probably the *cis*-configuration (cf. Zalkind, A., 1914, ii, 257); acetylenedicarboxylic acid gives solely maleic acid.

L. F. H.

**Hepto- and Nono-dilactones.** G. M. BENNETT (*J. Chem. Soc.*, 1925, **127**, 1277—1282).—The dilactone of  $\beta\beta'$ -dihydroxydiethylmalonic acid (bis-7-butyrolactone- $\alpha\alpha$ -spiran) is easily formed by boiling ethyl  $\beta\beta'$ -dimethoxydiethylmalonate with concentrated hydriodic acid. The following method also yields the dilactone. *Benzyl  $\beta$ -hydroxyethyl ether*, b. p.  $138^{\circ}/15$  mm., is prepared by the action of benzyl chloride on a mixture of glycol and sodium ethoxide. *Benzyl chloroethyl ether*, b. p.  $124^{\circ}/20$  mm.,  $d_4^{20}$  1.109,

$n_D^{20}$  1.5204, is obtained when a mixture of benzyl hydroxymethyl ether and dimethylaniline is treated at  $30^\circ$  with thionyl chloride, the reaction product poured into dilute hydrochloric acid, washed, and distilled. When ethyl malonate, in alcoholic solution, is treated at  $100^\circ$  with two successive quantities of sodium (1 equiv.) and benzyl chloroethyl ether (1 equiv.), a crude ester is produced, from which, by hydrolysis with alcoholic potassium hydroxide, there is obtained  $\beta\beta'$ -dibenzyl oxydiethylmalonic acid,



m. p.  $120^\circ$ , which forms calcium and silver salts. By the action of fuming hydrobromic acid on the crude ester the corresponding dilactone is produced. By the action of alcoholic sodium ethoxide on di- $\beta$ -chloroethyl malonate, b. p.  $164^\circ/15$  mm., which is prepared from malonyl chloride and ethylene chlorohydrin, small yields of the dilactone are also obtained. The crystallographic characteristics of the heptodilactone are described.

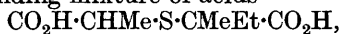
The dilactone of  $\beta\beta'$ -dihydroxy-di-*n*-propylmalonic acid (bis- $\gamma$ -valerolactone- $\alpha\alpha$ -spiran) is formed by boiling ethyl diallylmalonate with 70% sulphuric acid. Its crystallographic properties are recorded. C. J. S.

**Ring-chain Tautomerism. XIV. Structure of Balbiano's Acid.** E. ROTHSTEIN, A. STEVENSON, and J. F. THORPE (*J. Chem. Soc.*, 1925, **127**, 1072—1080).—The "oxide" formula for Balbiano's acid (cf. A., 1893, i, 174; 1894, i, 614) is untenable, and it is  $\alpha$ -keto- $\beta\beta$ -dimethylpentane- $\alpha\gamma$ -dicarboxylic acid; diethyl ester, b. p.  $148$ — $149^\circ/11.5$  mm. On reduction with hydrogen iodide and red phosphorus, the sole product is  $\alpha'$ -hydroxy- $\alpha\beta\beta$ -trimethylglutaric acid  $\gamma$ -lactone (I), m. p.  $162$ — $163^\circ$ . This differs from Blanc's synthetic lactonic acid (II) (A., 1901, i, 119), which is prepared as follows:  $\beta\beta$ -dimethylsuccinic anhydride  $\rightarrow$  chloride of  $\alpha$ -carbethoxy- $\beta$ -methylpropane- $\beta$ -carboxylic acid  $\rightarrow$  ethyl  $\beta\beta$ -dimethyl-lævulate  $\rightarrow$   $\beta\beta$ -dimethyl-lævulic acid  $\rightarrow$  nitrile  $\rightarrow$   $\alpha$ -hydroxy- $\alpha\beta\beta$ -trimethylglutaric acid  $\gamma$ -lactone (II), m. p.  $165.5^\circ$ . The structures assigned to the lactonic acids, m. p.  $165.5$ — $166^\circ$  and m. p.  $163^\circ$ , described by Pandya and Thorpe (T., 1923, **123**, 2852) must be interchanged, whilst the lactonic acid prepared by Chandrasena, Ingold, and Thorpe (T., 1922, **121**, 1550) has formula II, so that their proof of the existence of a bridged phase in  $\alpha$ -campholytic acid is invalid.

When a benzene solution of the diethyl ester of Balbiano's acid reacts with ethyl bromoacetate and zinc in presence of iodine, distillation yields the  $\gamma$ -lactone of  $\delta\epsilon$ -dicarbethoxy- $\delta$ -hydroxy- $\gamma\gamma$ -dimethylpentane- $\beta$ -carboxylic acid, which exists in two stereoisomeric modifications, m. p.  $86^\circ$  and m. p.  $115^\circ$ ; as their mixture has a considerably lower m. p., it is improbable that Balbiano isolated the two stereoisomerides of I. On hydrolysis both give the same lactonic acid, m. p.  $178^\circ$ , whilst the latter also yields an isomeric acid, m. p.  $140^\circ$  (decomp.). Ethyl methoxycarbonate, b. p.  $120^\circ/18$  mm. (prepared from ethyl  $\alpha\alpha'$ -dibromo- $\beta\beta$ -dimethylglutarate), is converted by hydrogen bromide into the hydrated form of  $\alpha$ -keto- $\beta\beta$ -dimethylglutaric acid, m. p.  $84^\circ$ ; its ethyl ester, b. p.  $140$ — $141^\circ/13$

mm., reacts with ethyl bromoacetate and zinc, and distillation of the product yields the lactone of  $\gamma\delta$ -dicarbethoxy- $\gamma$ -hydroxy- $\beta\beta$ -dimethylbutane- $\alpha$ -carboxylic acid. This is hydrolysed to the corresponding acid, m. p.  $132^\circ$  (decomp.), together with the anhydride, m. p.  $126-128^\circ$ , which is formed spontaneously from the acid. F. M. H.

**" $\alpha$ -Ethyl- $\alpha\alpha'$ -thiodilactic Acid."** R. AHLBERG (*Ber.*, 1925, 58, [B], 1061—1062).—The action of sodium  $\alpha$ -thiolpropionate on ethyl  $\alpha$ -bromo- $\alpha$ -methylbutyrate in the presence of sodium ethoxide in alcoholic solution leads to a mixture of ethyl hydrogen salts which cannot be separated from one another by fractional distillation. From the corresponding mixture of acids



a racemic form, m. p.  $133^\circ$ , is readily isolated by means of its sparingly soluble, non-resolvable *brucine* salt; the mother-liquors from this salt yield two further racemic acids, m. p.  $93^\circ$  and  $86-89^\circ$ , respectively, which are isolated through their *potassium hydrogen* salts and separated by taking advantage of the ability of the acid of lower m. p. to yield a crystalline *cinchonidine* salt. Possibly a fourth acid exists which resembles that of m. p.  $133^\circ$  in solubility and m. p. H. W.

**Autoxidation of Organic Compounds. IV. Autoxidation of Ketens.** H. STAUDINGER, K. DYCKERHOFF, H. W. KLEVER, and L. RUZICKA.—(See i, 933.)

**Ketenic Decomposition of Ketones: Acetylacetone, Diacetyl, and Pinacolin.** C. D. HURD and W. H. TALLYN (*J. Amer. Chem. Soc.*, 1925, 47, 1779—1782).—Acetylacetone undergoes pyrogenic decomposition giving keten in yields of more than 10% at temperatures between  $610-650^\circ$ , the maximum yield, 16.7%, being obtained at  $635^\circ$ . No acetylketen or carbon suboxide is formed and the decomposition is probably represented by  $\text{COMe}\cdot\text{CH}_2\cdot\text{COMe} \rightarrow 2\text{CH}_2\cdot\text{CO} + \text{CH}_4$ . Since the yield of keten from acetylacetone is very low at  $700^\circ$ , the optimum temperature for the production of keten from acetone (this vol., i, 785), it is improbable that acetone is a major product in this reaction or that acetylacetone is formed in the pyrogenic decomposition of acetone. Pinacolin gives less than 2% of keten and no dimethylketen, whilst at  $605-625^\circ$  diacetyl gives 10.8—14.5% of keten, probably according to the equation  $\text{COMe}\cdot\text{COMe} = \text{CH}_2\cdot\text{CO} + \text{CO} + \text{CH}_4$ . Acetone is possibly an intermediate product (cf. A., 1923, i, 312, 1060). R. B.

**Relative Reducing Powers of Some Common Sugars.** A. W. ROWE and B. S. WIENER (*J. Amer. Chem. Soc.*, 1925, 47, 1698—1701; cf. Greenwald, Gross, and Samet, this vol., i, 185).—Determinations of the reduction coefficients of dextrose, laevulose, galactose, mannose, lactose, and maltose by the Folin-Wu and the modified Lewis-Benedict methods show that all of these sugars in aqueous solution have different reaction velocities, and in consequence significant errors may be introduced into methods of blood analysis in which time is specified and reaction incomplete. In



mixtures of sugars, the reduction is proportional to the relative amounts of the various sugars and to their several reducing powers. The values obtained for the reduction coefficients in aqueous solution are valid in blood plasma. Examination of the time factor indicates that on longer boiling the disaccharides undergo hydrolysis.

R. B.

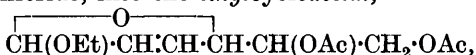
**Dynamic Isomerism. XVIII. Mechanism of Mutarotation.** T. M. LOWRY (*J. Chem. Soc.*, 1925, 127, 1371—1385).—Mainly polemical against the view of Baker, Ingold, and Thorpe that water “does not intervene” in the mutarotation of the sugars. The mechanism of mutarotation in reducing sugars is explained, on the basis of the electronic theory of valency, as a reversible isomeric change involving the intermediate formation of an aldehyde or its hydrate, water playing an essential part in the process. A definite rôle is assigned to those chemical reagents which appear to be necessary to enable the mutarotation to proceed. The initial stage of the conversion of the oxidic form of the sugar into the aldehydic form is regarded as involving the union of the sugar with base plus water or with acid plus water to form salts of the same bipolar molecule which differ only in the nature of the two “free ions” which are associated with the “bound ions” of the complex.

C. J. S.

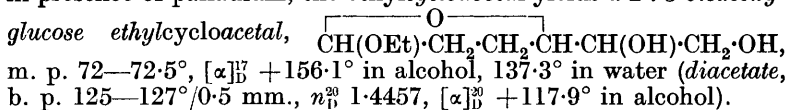
**Dynamic Isomerism. XIX. Arrest of Mutarotation of Tetramethylglucose.** T. M. LOWRY and E. M. RICHARDS (*J. Chem. Soc.*, 1925, 127, 1385—1401).—The mutarotation of tetramethylglucose in chloroform was found, in one instance, to be inhibited during a period of 10 days, this being attributed to the presence of carbonyl chloride, which eliminates traces of catalysts. In benzene, the velocity of mutarotation was reduced eightfold by careful drying, but the addition of water caused a very rapid mutarotation; this is attributed to the possible presence in the solvent of water-soluble impurities which develop strong catalytic properties only after association with water. The mutarotation in ethyl acetate was preceded by a period of induction of about a day, but in the presence of small quantities of water no period of inhibition was exhibited. No arrest or period of induction was observed in the mutarotation of dextrose in methyl alcohol or of tetramethylglucose in methyl or ethyl alcohol. In dry pyridine the velocity of mutarotation of dextrose was very small, but not arrested. The mutarotation of tetramethylglucose in pyridine was preceded by a short period of induction, the change appearing to depend on the presence of an auxiliary catalyst. Three types of solvent are recognised: (i) inactive solvents having no catalytic properties, such as chloroform; (ii) amphoteric solvents such as water, which can act as complete catalysts; (iii) solvents, such as pyridine, which only develop catalytic properties in the presence of an auxiliary catalyst, thus producing a mixed catalyst which is more efficient than a complete catalyst and can often produce very rapid mutarotation.

C. J. S.

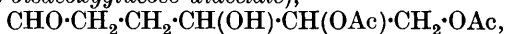
**Unsaturated Reduction Products of the Sugars. X.**  
 **$\psi$ -Glucal and Dihydro- $\psi$ -glucal.** M. BERGMANN (*Annalen*, 1925, **443**, 223—242).—Diacetyl- $\psi$ -glucal is converted, on treatment with ethyl orthoformate in alcohol in presence of a trace of ammonium chloride, into the *ethylcycloacetal*,



m. p. 81—82°, b. p. 130°/1 mm.,  $[\alpha]_D^{25} +102.8^\circ$ , which yields the free *acetal*, m. p. 100—101°,  $[\alpha]_D^{20} +100.3^\circ$  in alcohol,  $+71.26^\circ$  in water, on hydrolysis. This is hydrolysed by boiling water or cold 0.0001*N*-hydrochloric acid, to a product, not identical with  $\psi$ -glucal, which, on treatment with ethyl orthoformate, gives an *oil*, b. p. 80—90°/1 mm. On treatment with hydrogen in alcoholic solution in presence of palladium, the *ethylcycloacetal* yields  $\alpha$ -2 : 3-*bisdeoxyglucose ethylcycloacetal*,



Reduction of diacetyl- $\psi$ -glucal in aqueous methyl-alcoholic solution, with hydrogen in presence of palladium (cf. Willstätter and Waldschmidt-Leitz, A., 1921, ii, 185), affords *dihydro- $\psi$ -glucal diacetate* (2 : 3-*bisdeoxyglucose diacetate*),



m. p. 75—76°, b. p. 150°/0.6 mm.,  $[\alpha]_D^{20} +42.74^\circ$  in water,  $+116.7^\circ$  in freshly-prepared pyridine solution, falling in 12 hrs. to  $+77.5^\circ$ , the low (constant) value in aqueous solution being attributed to very rapid mutarotation. This yielded similarly the *ethylcycloacetal*,

$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH(OEt)} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH(OAc)} \cdot \text{CH}_2 \cdot \text{OAc} \end{array}$$

b. p. 121—123°/0.8 mm.,  $n_D^{20}$  1.4490,  $[\alpha]_D^{20} +47.6^\circ$  in alcohol, as a mixture of at least two isomerides. Hydrolysis with barium hydroxide yields the above  $\alpha$ -2 : 3-*bisdeoxyglucose ethylcycloacetal*, together with the  $\beta$ -*isomeride*, m. p. 95°,  $[\alpha]_D^{20} -29.5^\circ$  in water.

Reduction of the 2 : 3-*bisdeoxyglucose diacetate* in acetic acid, with hydrogen in presence of palladium (cf. Wieland, A., 1912, i, 247; Tausz and Putnoky, A., 1920, ii, 61), yields *tetrahydro- $\psi$ -glucal diacetate* (d-*hexan- $\alpha$ - $\epsilon$ -tetrol diacetate*), b. p. 160°/0.3 mm.,  $n_D^{20}$  1.4587,  $[\alpha]_D^{20} +2.2^\circ$  in alcohol.

Bis-(dihydro- $\psi$ -glucalyl)imine,  $\text{C}_{12}\text{H}_{26}\text{O}_6\text{N}$ , m. p. 142—143°, is obtained when dihydro- $\psi$ -glucal diacetate is treated with methyl-alcoholic ammonia.

F. G. W.

**Yield of  $\beta$ -Glucosan obtained from Low-pressure Distillation of Cellulose.** H. J. P. VENN (*J. Text. Inst.*, 1924, **15**, T 414—418).—The effect of the purity of the cotton on the yield of  $\beta$ -glucosan obtainable by Pictet and Sarasin's method (A., 1918, i, 59) has been investigated. Raw cotton did not give  $\beta$ -glucosan, but on removal of the impurities soluble in water and dilute acids the yield was 38%. Methods of purification designed for the removal of fats and waxes did not improve the yield, but this could possibly be raised to 50% by perfecting the distillation and

the means for determining the product, which at present depends on the isolation of the tribenzoate. The acidity of the aqueous distillate is lowest when the yield of  $\beta$ -glucosan is highest, which is at variance with Irvine and Oldham's view of the origin of the compound (T., 1921, 119, 1750). Slight differences between Egyptian and American cottons are recorded and thought to be due to a stereoisomeric change in the molecular complex of Egyptian cotton cellulose. Hydrocellulose and starch have also been distilled, with similar results.

J. C. W.

**Syntheses of Polysaccharides. I. Synthesis of an iso-Trehalose.** H. H. SCHLUBACH and K. MAURER (*Ber.*, 1925, 58, [B], 1178—1184).—In the hope of finding a method for the direct production of disaccharides of the  $\alpha$ -series, tetra-acetylglucose has been subjected to the action of hydrogen chloride dissolved in benzene under widely varied conditions of time and temperature and in the absence and presence of dehydrating agents and catalysts (sodium sulphate, aluminium chloride, zinc chloride, anhydrous copper sulphate, phosphoric oxide, calcium chloride). It has not been found possible to cause condensation to an extent greater than 10% as measured by diminution in the reducing power of the products, whereas the change in specific rotation appears to be quite irregular and to afford no clue to the course of the reaction. In many cases, protraction of the period of action involves fission of the disaccharide produced. Better results are not obtained with chloroform or ether as solvent. Treatment of tetra-acetylglucose with anhydrous zinc chloride at 140° gives a 50% yield of a disaccharide yielding an octamethyl derivative, b. p. 160°/0.015 mm.,  $n_D^{20}$  1.4626,  $[\alpha]_D^{20} +82.8^\circ$  in benzene, which could not be caused to crystallise. The substance differs appreciably from *trehalose octamethyl ether*, b. p. 170°/0.03 mm.,  $n_D^{20}$  1.4598,  $[\alpha]_D^{20} +199.8^\circ$  in benzene. Hydrolysis of the trehalose derivative with 5% hydrochloric acid yields crystalline  $\beta\gamma\epsilon\zeta$ -tetramethylglucose in 73% yield, thus proving that both glucose residues are present in the same form and that both contain the normal butylene oxide ring. Hydrolysis of the synthetic product under similar conditions gives only 17.5% of crystalline  $\beta\gamma\epsilon\zeta$ -tetramethylglucose, whereas the non-crystalline residue has  $[\alpha]_D^{20} +70.0^\circ$  in benzene and hence contains a product differing from the normal tetramethylglucose. Since acetic acid is evolved during the condensation, it is possible that union occurs in part at some position other than the terminal hydroxyl group or that the oxygen bridge becomes isomerised. The rotation of the disaccharide suggests that it is probably mainly  $\alpha\beta$ -trehalose.

H. W.

**Syntheses of Polysaccharides. II. The Galactosido-glucose of E. Fischer and E. F. Armstrong.** H. H. SCHLUBACH and W. RAUCHENBERGER (*Ber.*, 1925, 58, [B], 1184—1189).—The galactosido-glucose isolated by Fischer and Armstrong by the action of sodium alkoxide on acetochlorogalactose and dextrose has been considered to be identical with natural melobiose (cf. Armstrong, "The Carbohydrates and the Glucosides," 1924, pp.

123, 124; Pringsheim, "Die Polysaccharide," 1923, p. 34). In examination of this hypothesis, the product has been exhaustively methylated with methyl sulphate and alkali, thereby giving an octamethyl derivative, b. p.  $160^{\circ}/0.03$  mm.,  $n_D^{20}$  1.4660,  $[\alpha]_D^{20} +8.39^{\circ}$  in water,  $[\alpha]_D^{20} -6.15^{\circ}$  in alcohol, or (if residual monosaccharide is removed as completely as possible by fermentation),  $[\alpha]_D^{20} +12.92^{\circ}$  in alcohol. *Melibiose octamethyl ether*, on the other hand, has b. p.  $163^{\circ}/0.015$  mm., m. p.  $98.5^{\circ}$ ,  $n_D^{20}$  1.4662,  $[\alpha]_D^{20} +104.16^{\circ}$  in alcohol, so that the identity of the disaccharide with melibiose cannot be maintained. The physical constants of the synthetic ether approximate closely to those of lactose octamethyl ether, but comparative hydrolysis of these products with 5% hydrochloric acid shows that they are not identical. From the synthetic product  $\beta\gamma\delta\zeta$ -tetramethylgalactose is readily obtained as the crystalline anilide, thus proving the galactose components of lactose and galactosidoglucose to be identical. The glucose compound is isolated as a *trimethylglucose*,  $[\alpha]_D^{20} +35.8^{\circ}$  in methyl alcohol, which certainly differs from  $\beta\gamma\epsilon$ - and  $\beta\gamma\zeta$ -trimethylglucose. Since galactosidoglucose gives a phenylosazone, coupling cannot have occurred at the  $\alpha$ - or  $\beta$ -positions, and the non-identity of the new trimethylglucose with  $\beta\gamma\epsilon$ - or  $\beta\gamma\zeta$ -trimethylglucose excludes a homogeneous union at the  $\epsilon$ - or  $\zeta$ -positions. Assuming therefore that the glucose residue retains the butylene oxide structure, the methyl groups must be in the  $\beta\gamma\zeta$ -positions.

H. W.

**Composition of Starch Iodide.** H. D. MURRAY (*J. Chem. Soc.*, 1925, 127, 1288—1294).—Determinations of the concentration of the various substances formed when a solution of iodine in carbon tetrachloride is shaken with an aqueous solution of starch, with and without the addition of small amounts of potassium iodide, lead to the suggestion that the starch forms an additive compound, which in dilute solutions of potassium iodide forms an anion  $(C_6H_{10}O_5)_nI_5^-$ , where  $n$  is approximately 15.

C. J. S.

**Adsorption and Swelling of Cellulose Fibres.** C. G. SCHWALBE and G. TESCHNER (*Papier-Fabr.*, 1925, 23 [*Fest-u. Ausl.-Heft*], 144—148).—Pure cotton exhibits no specific adsorption for aluminium salts, but oxy- and hydro-cellulose adsorb strongly. The adsorbing power of wood pulp is greatly increased by milling, and it is suggested that the determination of the adsorption may be a useful method of measuring the degree of swelling of cellulose fibres. [Cf. *B.*, 1925, 585.]

A. G.

**Chemical Nature of Deciduous Woods.** E. HEUSER and A. BROTZ (*Papier-Fabr.*, 1925, 23 [*Fest-u. Ausl.-Heft*], 69—88).—Aspen wood is chiefly distinguished from pinewood by its high content of pentosan (17.61%) and by the larger yields of acetic acid (7.37% total acid calculated as acetic acid) and of methyl alcohol (1.48%) obtained by dry distillation. Aspen cellulose, pentosan, and lignin do not differ essentially from those of spruce; it is concluded that the different properties of deciduous and pine woods are due to different proportions of the constituents and to

physical variations. When hydrolysed with sulphuric acid, the yield of dextrose from aspen cellulose was 97.6% (reduction) or 99.7% (rotation), and by acetylation 28.5% cellobiose octa-acetate was obtained. The high yield of acetic acid from the wood is due to secondary reactions and more acid is obtained when mixtures of the constituents are distilled than when these are distilled separately. [Cf. *B.*, 1925, 585.] A. G.

**Sublimation of "Unsublimable" Substances.** K. KÜRSCHNER (*Mikrochem.*, 1925, 3, 1—20).—Micro-fractional sublimation of lignin from pinewood at about 200° yields vanillic acid and a residue having a caramel-like odour and reducing Fehling's solution. Formaldehyde and methoxyfurfuraldehyde are also probably formed. These, together with previously published results, indicate that in the main this lignin is a 1 : 3 : 4-benzene derivative bound to a glucoside residue. Other evidence is cited in support of this conclusion. S. K. T.

**Additive Compounds of Stannic Iodide and Organic Bases.** G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 582—586).—In chloroform solution, the interaction of stannic iodide and hexamethylenetetramine yields, according as one or the other reagent is in excess, either the colourless compound,  $\text{SnI}_4 \cdot 5\text{C}_6\text{H}_{12}\text{N}_4$ , or the deep violet compound,  $\text{SnI}_4 \cdot 4\text{C}_6\text{H}_{12}\text{N}_4 \cdot 2\text{CHCl}_3$ , which undergoes little change at 80° or in a vacuum over sulphuric acid, but is rapidly decolorised in moist air. Since both compounds are insoluble, their formulæ according to the co-ordination theory cannot be determined. T. H. P.

**Sphingosine. V. Synthesis of 1-Amino-2-hydroxy-n-heptadecane.** P. A. LEVENE and H. L. HALLER (*J. Biol. Chem.*, 1925, 63, 669—673).—In an attempt to throw light on the constitution of sphingine, the reduction product of sphingosine (A., 1916, i, 220)  $\alpha$ -amino- $\beta$ -hydroxy-*n*-heptadecane has been synthesised. *Ethyl palmitylacetoacetate*, m. p. 36—36.5°, was hydrolysed to *ethyl palmitylacetate*, m. p. 37—38°; by reduction with sodium amalgam in alcohol and subsequent hydrolysis this was converted into  $\beta$ -hydroxystearic acid, m. p. 90°. *Ethyl  $\beta$ -hydroxystearate* (m. p. 46°) when heated with hydrazine hydrate gave  $\beta$ -hydroxystearylhydrazide, m. p. 123—124°; from the hydrochloride of this base, by treatment with nitrous acid, was obtained  $\beta$ -hydroxyheptadecylcarbamide,  $[\text{C}_{15}\text{H}_{31} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{NH}]_2\text{CO}$ , m. p. 94°, which on hydrolysis with 20% sulphuric acid gave the desired hydroxyamine. C. R. H.

**Aldehydic Compounds of Amino-acids.** M. BERGMANN, N. EUSSLIN, and L. ZERVAS (*Ber.*, 1925, 58, [B], 1034—1043).—Alkylideneamino-acids are readily prepared by the action of aqueous solutions of salts of amino-acids and aldehydes. The method may be extended to peptides and promises to be successful in the separation and isolation of naturally occurring products of this class, since it permits considerable variation in the choice of aldehyde and base, which can subsequently be easily removed. The barium and calcium

salts have been mainly investigated and in those cases in which these salts have little ability to crystallise organic bases, notably brucine, render useful service. In certain cases, it is advantageous to replace the metallic hydroxide by the corresponding acetate. The following salts are described: *barium benzylideneaminoacetate* ( $+4\text{H}_2\text{O}$ ); *calcium benzylideneaminoacetate* [the barium salt is converted by acetic anhydride in the presence of pyridine into 3-acetyl-2-phenyl-5-oxazolidone,  $\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \diagup \\ \text{CH}_2 \cdot \text{N} \cdot \text{Ac} \end{array} > \text{CHPh}$ , m. p.  $103^\circ$  (corr.),

identical with the *N*-acetyl-*N*-benzylidenobetaine of Scheibler and Baumgarten (A., 1922, i, 656), and by benzoyl chloride in presence of carbon tetrachloride into 3-benzoyl-2-phenyl-5-oxazolidone, m. p.  $134.5\text{--}135^\circ$  (corr.)]; *barium o*-hydroxybenzylideneaminoacetate; *barium furfurylideneaminoacetate*; *barium dl*- $\alpha$ -*o*-hydroxybenzylideneamino- $\beta$ -phenylpropionate; *barium benzylideneglycylaminoacetate*; *barium o*-hydroxybenzylideneglycylaminoacetate; *barium o*-hydroxybenzylideneaminosuccinate, and the corresponding *brucine* salt, m. p. (anhydrous)  $145^\circ$  (decomp.); *brucine l*-*p*-nitrobenzylideneaminosuccinate, m. p. about  $116^\circ$  (decomp.) after softening at  $95^\circ$ ; *brucine trichloroethylideneaminosuccinate*; *barium*  $\alpha$ -*o*-hydroxybenzylideneaminoglutarate, and the corresponding *brucine* salt, m. p.  $148^\circ$  (decomp.).

H. W.

**Alkyl Derivatives of Hydroxyurethane and of Hydroxylamine.** L. NEUFFER and A. L. HOFFMAN (*J. Amer. Chem. Soc.*, 1925, 47, 1685—1687).— $\alpha$ -Alkylhydroxyurethanes are obtained by heating equivalent quantities of an alkyl halide, hydroxyurethane, and potassium hydroxide in alcoholic solution. The  $\beta$ -derivatives are similarly obtained by heating sodium ethoxide, an alkyl halide, and an  $\alpha$ -hydroxyurethane at  $60^\circ$ . The  $\alpha$ - or  $\alpha\beta$ -alkylhydroxylammonium chlorides are prepared by heating an  $\alpha$ -alkyl- or  $\alpha\beta$ -alkyl-hydroxyurethane with 2 mols. of potassium hydroxide in aqueous solution just below  $100^\circ$  in a sealed tube, and distilling the product into dilute hydrochloric acid. The  $\alpha$ - and  $\alpha\beta$ -alkylhydroxylamines are prepared by distilling a mixture of the corresponding hydroxylammonium chloride with 2 mols. of potassium hydroxide (cf. Jones and Neuffer, A., 1914, i, 1167; Bewad, A., 1900, i, 630). The following compounds are described:  $\alpha$ -*n*-Butylhydroxyurethane, b. p.  $98\text{--}102^\circ/18$  mm.;  $\alpha\beta$ -*di-n*-butylhydroxyurethane, b. p.  $77\text{--}83^\circ/17$  mm.;  $\alpha$ -ethyl- $\beta$ -*n*-butylhydroxyurethane, b. p.  $86\text{--}90^\circ/20$  mm.;  $\beta$ -ethyl- $\alpha$ -*n*-butylhydroxyurethane, b. p.  $89\text{--}92^\circ/18$  mm.;  $\alpha$ -*n*-butylhydroxylamine, b. p.  $89^\circ$  (hydrochloride, m. p.  $152\text{--}153^\circ$ );  $\alpha\beta$ -*di-n*-butylhydroxylamine, b. p.  $88^\circ$  (hydrochloride, m. p.  $143\text{--}144^\circ$ );  $\alpha$ -ethyl- $\beta$ -*n*-butylhydroxylamine, b. p.  $92\text{--}93.5^\circ$  (hydrochloride, m. p.  $120\text{--}121^\circ$ );  $\beta$ -ethyl- $\alpha$ -*n*-butylhydroxylamine, b. p.  $91^\circ$  (hydrochloride, m. p.  $152\text{--}153^\circ$ ).

R. B.

**Halogenation. XII. Derivatives of Carbamic Esters. Chlorine as a Simultaneous Oxidising and Chlorinating Agent. II.** R. L. DATTA and B. C. CHATTERJEE (*J. Indian Chem. Soc.*, 1925, 1, 311—313).—Further examples of the formation of

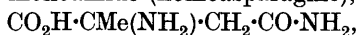
diurethanes when chlorine is passed into a solution of a carbamic ester in an alcohol (cf. Datta and Chatterjee, A., 1922; i, 815) are given. In the case of benzyl alcohol, the benzyl radical remains intact when an aliphatic urethane is employed, but with heavily substituted urethanes the phenyl group is detached and the methylene residue forms the diurethane. Two new urethanes were prepared: *isopropyl methylenedicarbamate*,  $\text{CH}_2(\text{NH}\cdot\text{CO}_2\text{Pr}^\beta)_2$ , m. p.  $110^\circ$ ; *methyl benzylidenedicarbamate*,  $\text{CHPh}(\text{NH}\cdot\text{CO}_2\text{Me})_2$ , m. p.  $175^\circ$ .

J. W. B.

**Alleged Dimeric Anils of Alkylglutaric Acids.** K. VON AUWERS (*Annalen*, 1925, 443, 310—314).—A re-examination of the "dimeric anils" of certain alkylated glutaric acids (cf. Auwers, A., 1895, i, 504; 1896, i, 639) has shown these to be actually the corresponding dianilides. The following dianilides are described:  *$\alpha$ -methylglutar-dianilide*, m. p.  $175^\circ$ ; *-di-p-toluidide*, m. p.  $174$ — $175^\circ$ , and *di- $\beta$ -naphthylide*, m. p.  $227$ — $228^\circ$ ; *mal.- $\alpha\alpha'$ -dimethylglutar-di-p-toluidide*, m. p.  $237^\circ$  after softening; *-di- $\alpha$ -naphthylide*, m. p.  $245$ — $246^\circ$ ; and *-di- $\beta$ -naphthylide*, m. p.  $232^\circ$ ;  *$\alpha\alpha'$ -diethylglutar-dianilide*, m. p.  $134^\circ$ ; and *-di-p-toluidide*, m. p.  $224$ — $225^\circ$ .

F. G. W.

**Action of Ammonia on the Esters of Citraconic, Mesaconic, and Itaconic Acids.** K. STOSIUS and E. PHILIPPI (*Monatsh.*, 1925, 45, 457—470).—The action of anhydrous liquid ammonia on ethyl citraconate at the ordinary temperature affords first the diethyl ester of homoaspartic acid, b. p.  $118$ — $119^\circ/12$  mm. (cf. Philippi and Spenner, A., 1915, i, 222; the b. p. there recorded should read  $125^\circ/18$  mm.), together with a trace of a substance, m. p.  $185^\circ$ . Continued action yields the diamide of homoaspartic acid, m. p.  $175^\circ$  (*oxalate*, m. p.  $237^\circ$ ), which is hydrolysed by boiling with water to the monoamide (homoasparagine),



m. p.  $242^\circ$  (cf. Piutti, A., 1898, i, 633), which was also obtained, together with  $\alpha$ -mesaconamic acid (cf. Anschütz, A., 1907, i, 468), by the action of ammonia on  $\alpha$ -ethyl mesaconate,



Citraconic diamide was not among the products (cf. Strecker, A., 1882, 1281), but the action of ammonia on methyl citraconate yielded *homoaspartimide*, m. p.  $185^\circ$ , together with the above diamide. Homoaspartic acid, prepared from homoasparagine (cf. Piutti, *loc. cit.*), crystallises anhydrous from water and does not lose weight at  $180^\circ$ , above which temperature it sublimes. The action of liquid ammonia on ethyl mesaconate afforded mesacon-diamide, whilst alcoholic ammonia at  $100^\circ$  yielded ethyl homoaspartate and the above homoaspartimide. Ethyl itaconate yielded similarly with liquid ammonia *2-ketopyrrolidine-4-carbamide*,  $\text{CO}\cdot\text{CH}_2\text{CH}\text{CH}_2\text{CONH}_2$ , m. p.  $217^\circ$ , hot alcoholic ammonia yielding again homoaspartimide.

F. G. W.

**Catalytic Action. XVI. Synthesis of Nitriles.** T. HARA and S. KOMATSU (*Mem. Coll. Sci. Kyoto*, 1925, **8**, 241—246).—When *isoamyl* alcohol and dry ammonia are passed over reduced copper at 300—350°, hydrogen is evolved, and *isovaleronitrile* is produced, together with *isovaleraldehyde*, hydrocarbons, and basic compounds; the yield varies according to the method of preparation of the catalyst. Similarly, from *benzyl* alcohol, *ethyl* alcohol, *n*-propyl alcohol, and *isobutyl* alcohol are prepared respectively *benzonitrile*, *acetonitrile*, *propionitrile*, and *isobutyronitrile*. The reaction is regarded as taking place in the stages:  $R \cdot CH_2 \cdot OH \rightarrow R \cdot CHO \rightarrow R \cdot CH : NH \rightarrow R \cdot CN$ , and this view of the mechanism is confirmed by the preparation of nitrile by passing *isovaleraldehyde* and ammonia over copper at 300°. F. M. H.

**Decomposition of Ethyl Diazoacetate by Copper Acetylide.** E. MÜLLER and C. GOTTFRIED (*J. pr. Chem.*, 1925, [ii], **110**, 40—41).—Ethyl diazoacetate gives ethyl fumarate, b. p. 98—100°/14 mm., in 68% yield (nitrogen evolved reaches 90% of theoretical) when treated in ethereal solution with one-tenth its weight of copper acetylide. In 50 c.c. of ether the decomposition of 0.1 g.-mol. of ester is complete in a few minutes; in 200 c.c. 10 hours are required. C. H.

**Laboratory Preparation of Zinc Diethyl and Lead Tetraethyl.** M. MEYER (*Chem. News*, 1925, **131**, 1—2).—Methods for the preparation of zinc diethyl by the action of zinc on ethyl iodide and for the reaction between the latter and lead chloride are described. The yield is quantitative in the first and 90% in the second. S. I. L.

**Does a Bismuth Cacodyl Exist?** D. GANASSINI and U. SANTI (*Boll. Chim. Farm.*, 1925, **64**, 289—293).—When a mixture of bismuth trioxide with anhydrous sodium acetate is strongly heated, a gas results which contains bismuth, has an alliaceous odour, exhibits marked resistance towards physical and chemical agents, and is very difficult to purify. Its chemical composition has not been determined, but it is probably a bismuth cacodyl or its oxide. T. H. P.

**Compounds of Tervalent Molybdenum III. Oxalates.** W. WARDLAW and W. H. PARKER (*J. Chem. Soc.*, 1925, **127**, 1311—1318).—Electrolytic reduction of a solution of molybdenum trihydroxide in oxalic acid and precipitation by acetone yields *molybdenum oxyoxalate*,  $Mo_2O(C_2O_4)_2 \cdot 6H_2O$ , which is readily soluble in cold water; the solution undergoes oxidation in the air, and possesses powerful reducing properties. Decomposition of this oxalate or prolonged boiling of a solution of the trihydroxide in oxalic acid gives an *insoluble molybdenum oxyoxalate*,  $Mo_4O_3(C_2O_4)_3 \cdot 12H_2O$ . These compounds, on exposure to air in the presence of water, yield a red solution from which, by treatment with acetone and alcohol, *molybdenyl oxalate*,  $MoO(C_2O_4) \cdot 3H_2O$ ,

is precipitated. A complex ion is present in these compounds since



the oxalate radical is not precipitated by calcium chloride or the molybdenum by alkalis in the cold. C. J. S.

**Spatial Structure of *cyclo*Paraffins. I. A New Aspect of Mohr's Theory and the Isomerism of Decahydronaphthalene.** W. A. WIGHTMAN (*J. Chem. Soc.*, 1925, 127, 1421—1424; cf. Sachse, A., 1890, 1386; Mohr, A., 1919, ii, 229; 1922, i, 243).—The author, reviewing Sachse's and Mohr's theories of the non-planar structure of *cyclohexane*, investigates the possibility of co-ordinated strain-free relative rotations about the single bonds and shows by construction of mechanical models that, whilst Sachse's first type of structure is rigid, the second is "loose" and can pass through a series of forms annihilating the isomeric possibilities which form the main objection to Sachse's theory. Two *cyclohexanes* are still to be expected, however, unless Mohr's postulate that the temporary strain of their interconversion is negligible or, alternatively, the author's theory that the rigid type tends to pass into the "loose" type as a result of molecular collision, is accepted. Decahydronaphthalene, if Mohr's postulate is accepted, must have two isomerides incapable of interconversion except by rupture of bonds, but the recent isolation of a third isomeride (cf. Zelinski, this vol., i, 123) may necessitate the abandonment of the postulate. M. J.

**Internal Oxidation Reactions with Additive Compounds of Nitrogen Tetroxide and Olefines.** A. SCHAARSCHMIDT and H. HOFMEIER.—(See i, 877).

**Structure of Benzene.** N. SCHOORL (*Chem. Weekblad*, 1925, 22, 343).—It is pointed out, with regard to the argument of von Laar (this vol., i, 799), that the molecular refraction was originally taken by Brühl as evidence in favour of Kekulé's formula, until the influence of conjugated double bonds was observed. S. I. L.

**Structure of Benzene. Reply to C. W. A. Lely.** J. J. VAN LAAR (*Chem. Weekblad*, 1925, 22, 357—358).—Polemical, pointing out that the agreement between the value of  $\sqrt{a}$  for benzene found by experiment and the value calculated assuming six ethylene linkings is not accidental (cf. Lely, A., 1924, i, 380). S. I. L.

**Polar Nature of the Benzene Nucleus, in Relation to the Theory of Induced Alternate Polarity.** H. J. PRINS (*Chem. Weekblad*, 1925, 22, 365—367).—An examination of the results of Duin (*ibid.*, 1925, 22, 146), in which it is pointed out that the tendency of the atom to conform to the inert gas configuration may not be the only force directing reaction, and that the conception of polarity must not be interpreted too narrowly; the reactions of diphenylketen, of phenyl- and diphenyl-ethylene, and of ethyl ethylenedicarboxylate with nitrosobenzene are considered. S. I. L.

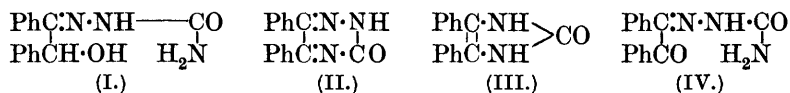
**Directing Influence of the Methanesulphonyl Group.** R. F. TWIST and S. SMILES (*J. Chem. Soc.*, 1925, 127, 1248—1252).—The methanesulphonyl group, like the benzenesulphonyl group

(Martinet and Haehl, A., 1921, i, 854), is solely meta-directive. The bromophenylmethylsulphone, described by Bourgeois and Abraham (A., 1912, i, 109) as the para-derivative, is now shown to be the meta-derivative.

Nitration of phenylmethylsulphone gives 3-nitrophenylmethylsulphone, m. p. 146°, identical with the methylation product of 3-nitrobenzenesulphinic acid. Nitration of phenylsulphoneacetic acid gives 3-nitrophenylsulphoneacetic acid, m. p. about 62° (dependent on rate of heating) (cf. Limpricht, A., 1897, i, 222, m. p. 57°). Chlorosulphonic acid reacts with phenylmethylsulphone, giving m-chlorosulphonylphenylmethylsulphone, m. p. 94°, converted through phenylmethylsulphone-m-disulphoxide, m. p. 200°, phenylmethylsulphone-m-disulphide, m. p. 120°, the corresponding mercaptan, m. p. 69°, and m-methylthiolphenylmethylsulphone, m. p. 53°, into m-phenylenedimethylsulphone, identical with the compound obtained from benzene-m-disulphonyl chloride by conversion into the sulphinic acid and subsequent methylation. Bromination of phenylmethylsulphone gives 3-bromophenylmethylsulphone, m. p. 103°, shown by a mixed m. p. to be identical with the compound prepared from 4-bromoaniline-2-sulphonic acid by elimination of the amino-group and conversion into the methylsulphone, and different from 4-bromophenylmethylsulphone, prepared by methylation of 4-bromobenzenesulphinic acid and also melting at 103°.

M. J.

**Semicarbazones of Benzoin.** I. I. V. HOPPER (*J. Chem. Soc.*, 1925, 127, 1282—1288; cf. Biltz, A., 1905, i, 673).—The interaction of benzoin and semicarbazide hydrochloride in aqueous alcoholic solution gives benzoinsemicarbazone (I) accompanied by diphenylhydroxytriazine (II; keto-form) and diphenylglyoxalone (III). Ammonia is also formed. The author suggests that the



secondary alcoholic group of the primary product is oxidised by semicarbazide giving a benzil derivative (IV) and carbamide. The latter condenses with more benzoin (acting as  $\alpha\beta$ -dihydroxystilbene). Thus: (I) +  $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \rightarrow$  (IV) +  $\text{NH}_3 + \text{CO}(\text{NH}_2)_2$ ; (IV)  $\rightarrow$  (II) +  $\text{H}_2\text{O}$ ;  $\text{CHPh}(\text{OH})\cdot\text{COPh} \rightleftharpoons \text{CPh}(\text{OH})\cdot\text{CPh}\cdot\text{OH} \xrightarrow{\text{CO}(\text{NH}_2)_2}$  (III) +  $2\text{H}_2\text{O}$  (cf. Anschütz, A., 1891, 725; 1895, i, 305; Biltz, *loc. cit.*). The formation of (II) precludes the formation of benzildisemicarbazone. Benzoin and  $\delta$ -benzylsemicarbazide hydrochloride react similarly. The presence of the benzyl radical in the  $\delta$ -position inhibits hydroxytriazine formation and the main product is now benzildi- $\delta$ -benzylsemicarbazone, m. p. 239—240°, accompanied by benzilmono- $\delta$ -benzylsemicarbazone, m. p. 198°, and benzoin- $\delta$ -benzylsemicarbazone, m. p. 115°. Similarly,  $\delta$ -phenylsemicarbazide gives benzildi- $\delta$ -phenylsemicarbazone, m. p. 253° (decomp.), and benzoin- $\delta$ -phenylsemicarbazone,  $\alpha$  form, m. p. 198° (decomp.),  $\beta$ -form, m. p. 169°.

Evidence is given for the supposition that oxidation of the :CH·OH group is dependent on the acid in the semicarbazide hydrochloride employed, a conclusion supported by the absence of benzil derivatives when benzoin and semicarbazide hydrochloride condense in pyridine solution. Condensation in this solvent has led to the isolation of isomerides in three cases, one already given, benzoinsemicarbazone [ $\alpha$ -form, m. p. 205—206°,  $\beta$ -form, m. p. 186—187° (decomp.)] and benzoin- $\delta\alpha$ -phenylethylsemicarbazone [ $\alpha$ -form, m. p. 174°,  $\beta$ -form, m. p. 154°,  $\gamma$ -form, m. p. 137°]. M. J.

**Disaccharins.** H. J. CHOUFOER (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 119—126; cf. A., 1924, i, 1070).—The product, m. p. 268—270°, obtained by oxidation of 1:3-xylene-4:6-disulphonamide, and previously regarded as a disaccharin, is now considered to be 4:6-disulphonamido-*m*-toluic acid (giving a soluble barium salt), which on further oxidation yields a substance, m. p. 112—114°. The diamide, m. p. 235°, from the by-product of sulphonation of *m*-xylene is considered to be 1:3-xylene-2:4-disulphonamide. Oxidation of 1:4-xylene-2:5-disulphonamide gives 2:5-disulphonamido-*p*-toluic acid, m. p. 320°. The chief product of the sulphonation of *p*-xylene yields a diamide, m. p. 297°, and is shown by the following synthesis to be 1:4-xylene-2:6-disulphonyl chloride. Partial reduction of the dinitration product of *p*-xylene yields 6-nitro-*p*-2-xylydine, m. p. 96°, which on diazotisation and treatment with sodium sulphide, followed by the action of heat, yields 6:6'-dinitro-di-*p*-xylyl 2:2'-disulphide, which is oxidised by warming with nitric acid to 2-nitro-*p*-xylene-6-sulphonic acid (chloride, m. p. 61°); replacement of the nitro group by the sulphonic group through the amino and diazo compounds completes the synthesis of *p*-xylene-2:6-disulphonamide, m. p. 297°. Attempts to synthesise *p*-xylene-2:3-disulphonyl chloride (*a*) from 3-nitro-*p*-2-xylydine and (*b*) by sulphonation of 6-nitro-*p*-2-xylydine have proved unsuccessful; sulphonation of nitro-*p*-xylene, followed by preparation of the sulphonyl chloride, gives two isomerides, namely, 2-nitro-*p*-xylene-6-sulphonyl chloride, m. p. 61°, and 2-nitro-*p*-xylene-5-sulphonyl chloride, m. p. 74·5°, which are characterised by reducing the mixture of potassium salts and converting to *p*-xylene-2:6-disulphonyl chloride, m. p. 72°, and *p*-xylene-2:5-disulphonyl chloride, m. p. 162°. When *p*-xylenesulphonic acid is treated with fuming nitric acid, the potassium salt of the product yields a nitro-*p*-xylene-sulphonyl chloride, m. p. 107°, which has not yet been identified. F. M. H.

**Salts of Aromatic Sulphonic Acids and their Solubilities [in Water].** F. EPHRAIM and A. PFISTER (*Helv. Chim. Acta*, 1925, **8**, 229—241).—The solubilities quoted are all at 20° except those of the naphthalene-2-sulphonates, which are at 16·5°. The figures are for grams per litre. The number of molecules of water of crystallisation, for the form stable at 20°, is given in brackets. Benzenesulphonate of calcium (1), 612·60; cadmium (7), 312·39; zinc (6), 143·10; manganese (6), 163·48; strontium (1), 154·93;

barium (1), 143.50; iron (ferrous) (6), 92.34; magnesium (6), 76.39; cobalt (6), 77.78. Naphthalene-2-sulphonate of ammonium (0), 131.44 (at 25°); potassium (0.5), 80.18 (at 16.5°, see above); sodium (0), 56.68 (at 25°); silver (0), 17.16; calcium (1), 19.87; copper (6), 10.53; strontium (1), 8.80; cadmium (6), 8.72; zinc (6), 4.62; lead (1), 5.41; nickel (6), 3.55; manganese (6), 3.34; barium (1), 3.84; cobalt (6), 2.56; iron (6), 2.40; magnesium (4), 2.00.  $\beta$ -Naphthol-6-sulphonate of barium (6), 17.420; cadmium (6—7), 16.510; lead (6), 18.140; magnesium (8), 9.640; copper (about 7), 12.485; manganese (8), 12.000; strontium (6), 11.112; zinc (8), 8.740; nickel (8), 5.290; cobalt (8), 5.004. 1-Chloronaphthalene-5-sulphonate of zinc (4), 12.05; copper (4), 10.88; silver (0), 5.51; manganese (1), 7.42; cobalt (4), 7.09; nickel (4), 6.18; strontium (3), 5.51; calcium (1.5), 3.73; barium (2), 2.75; lead (2), 2.00. Anthracene-1-sulphonate of strontium (3), 1.157; silver (0), 0.590; magnesium (4), 0.799; copper (6), 0.806; barium (3), 0.690; zinc (6), 0.500; manganese (6), 0.477; cobalt (6), 0.391; calcium (3), 0.269; nickel (6), 0.253. Anthracene-2-sulphonate of silver (0), 0.318; calcium (1), 0.157; manganese (6), 0.0575; cadmium (6), 0.0925; magnesium (4), 0.0770; copper (0), 0.0826; zinc (6), 0.0741; cobalt (6), 0.0519; nickel (6), 0.0463; barium (1), 0.0480. The colour, crystalline habit, and general behaviour of the above compounds are discussed. Certain other salts, either very sparingly or very freely soluble, are also briefly described. In the above lists the salts are arranged in order of decreasing "normality" of the saturated solution.

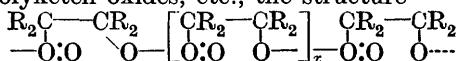
W. A. S.

**Autoxidation of Organic Compounds. V. Constitution of Ozonides.** H. STAUDINGER (*Ber.*, 1925, 58, [B], 1088—1096; cf. this vol., i, 898, 933).—The action of ozone on unsaturated substances can be explained readily if it be assumed that the primary product is an unstable mol-ozonide, analogous to the initial mol-oxide of autoxidative processes, which contains a four-membered ring; the extreme instability of these substances is probably the cause of the explosions observed occasionally during ozonisation.

The mol-ozonide,  $\text{CR}_2\text{<}\begin{smallmatrix} \text{CR}_2 \\ \text{O} \end{smallmatrix}\text{>O:O}$ , is assumed to become converted

into the isoozonide,  $\text{CR}_2\text{<}\begin{smallmatrix} \text{O:O} \\ \text{O} \end{smallmatrix}\text{>CR}_2$ , which on reduction yields  $2\text{CR}_2\text{:O}$ . The constitution now assigned to the isoozonides agrees

with their physical constants as well as the structure,  $\text{CR}_2\text{<}\begin{smallmatrix} \text{CR}_2\text{:O} \\ \text{O} \end{smallmatrix}\text{>O}$ , assigned by Harries, but gives a more rational explanation of their fission by reduction or hydrolysis. Like the mol-oxides, the mol-ozonides are capable of polymerisation, forming polyozonides to which, in conformity with the constitution of the polymeric malonic anhydrides, polyketen oxides, etc., the structure



is assigned. It is notable that the tendency towards polymerisation is most marked in those cases in which conversion into the

*isoozonide* may be expected to occur with unusual difficulty owing to the presence of the double bond in a ring. Further, the presence of glacial acetic acid appears to facilitate transformation, whereas that of carbon tetrachloride, which generally favours association, causes in most cases the production of highly polymerised substances. The mol-ozonides, like the mol-oxides, can also suffer fission of the four-membered ring,  $\text{CR}_2 \begin{smallmatrix} \text{CR}_2 \\ \text{O} \end{smallmatrix} \text{O} \cdot \text{O} \rightarrow \text{CR}_2 \cdot \text{O} + \text{R}_2\text{C} \cdot \text{O} \cdot \text{O} \rightarrow \text{CR}_2 \begin{smallmatrix} \text{O}-\text{O} \\ \text{O}-\text{O} \end{smallmatrix} \text{CR}_2$  or  $\text{R} \cdot \text{CO}_2\text{H}$  (where  $\text{R}=\text{H}$ ), or ozone may be lost with re-establishment of the ethylenic linking. For the oxozonides, the constitution  $\text{CR}_2 \begin{smallmatrix} \text{CR}_2 \\ \text{O}(\cdot\text{O}) \end{smallmatrix} \text{O} \cdot \text{O}$  is assumed; they become transformed into the *isooxozonides*,  $\text{CR}_2 \begin{smallmatrix} \text{O}-\text{O} \\ \text{O}-\text{O} \end{smallmatrix} \text{CR}_2$ , or become polymerised.

The following compounds are described incidentally: *isodicyclopentadiene diozonide*,  $\text{C}_{10}\text{H}_{12}\text{O}_6$ , m. p. 95–98° (decomp.), from dicyclopentadiene and ozone in glacial acetic acid solution; *dicyclopentadiene isooxodiozonide*,  $\text{C}_{10}\text{H}_{12}\text{O}_8$ , m. p. 105–108°, by the more protracted action of ozone under similar conditions; *polydicyclopentadiene diozonide*,  $\text{C}_{10}\text{H}_{12}\text{O}_7$ , m. p. 120–125° (decomp.) after softening at 114°, obtained in the presence of carbon tetrachloride; *polydihydrodicyclopentadiene ozonide*,  $(\text{C}_{10}\text{H}_{14}\text{O}_3)_x$ , m. p. 125–130°, from dihydrodicyclopentadiene and ozone in carbon tetrachloride.

H. W.

**Autoxidation of Organic Compounds. III. Autoxidation of *as*-Diphenylethylene.** H. STAUDINGER (*Ber.*, 1925, 58, [B], 1075–1079).—*as*-Diphenylethylene under the influence of light absorbs 1 mol. of oxygen with the formation of a *peroxide*, m. p. 131–132° (decomp.), in which active oxygen is indicated only faintly by titanous-sulphuric acid, which does not liberate iodine from potassium iodide or decolorise indigotin. It, however, catalytically accelerates processes of polymerisation such as that of isoprene. It decomposes when heated into benzophenone and formaldehyde, the process being quantitative in the presence of water. The insolubility of the peroxide in solvents, its gelatinisation in the presence of benzene, and its failure to affect the b. p. and m. p. of chloroform and benzene, respectively, indicate that it is a highly polymerised substance, probably of the type  $-\text{O} \cdot \text{CPh}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot [\text{O} \cdot \text{CPh}_2 \cdot \text{CH}_2 \cdot \text{O}]_x \cdot \text{O} \cdot \text{CPh}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot$ , and thus comparable with malonic anhydride, the polymeric salicylides, glycolides, and keten oxides. The peroxides hitherto isolated are not therefore the primary products of autoxidation. The mol-oxides formed initially (the term is used to denote the primary autoxidation products which are non-isolable or of unknown constitution, whereas mol-oxides of definite constitution are designated peroxides) are much more labile than the polymerides and either become polymerised, decompose spontaneously into two unsaturated compounds, or lose oxygen with the formation of a monoxide,

the formation of which does not necessarily involve the preformation of an asymmetric mol-oxide (cf. Staudinger, *Die Ketene*, p. 49). The invariable formation of benzophenone and formaldehyde during the autoxidation of *as*-diphenylethylene cannot be attributed to the peroxide, which is stable unless heated. Further, the violent explosion caused by the treatment of *as*-diphenylethylene with oxygen under 100 atm. pressure at 40—50° is readily explicable by the formation in quantity of an unstable, unimolecular mol-oxide.

H. W.

### Action of Free Thiocyanogen on Unsaturated Compounds.

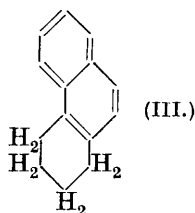
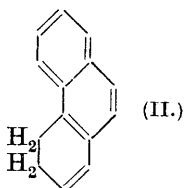
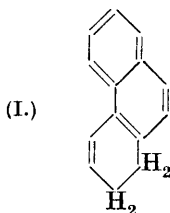
E. SÖDERBÄCK (*Annalen*, 1925, **443**, 142—161).—The addition of thiocyanogen to ethylenic hydrocarbons is very slow at the ordinary temperature, but goes smoothly when the reactants are exposed in dry (thiophen-free) benzene solution to the action of actinic light, yielding the dithiocyanoethanes of the type



The known ethylene and styrene compounds were prepared, and also *s*-dithiocyanodiphenylethane, m. p. 225—226° (decomp.). Only two thiocyanogen radicals will combine with acetylenic hydrocarbons, giving compounds of the type  $\text{CR}'(\text{CNS})\text{:CR}''(\text{CNS})$ . Whilst aromatic acetylene derivatives combine readily at the ordinary temperature in the dark, aliphatic acetylenes require intense photocatalysis to cause addition. Interconversion of *cis*- and *trans*-forms under the influence of ultra-violet light occurs with the compounds obtained from acetylenes, a 0.02*N*-solution of free thiocyanogen in benzene being an effective catalyst for the change. Acetylene itself yields a solid *s*-dithiocyanoethylene (80%), m. p. 97—98.5°, and a liquid form (20%), m. p. 15—17°,  $d_4^{25}$  1.332, which are interconvertible under the influence of light. Phenyl-acetylene yields  $\alpha\beta$ -dithiocyanophenylethylene,  $\text{CPh}(\text{CNS})\text{:CH}(\text{CNS})$ , m. p. 67—68°, which by the action of the above catalyst is converted into a thick oil of the same molecular weight, probably the stereoisomeride. Tolane yields *s*-dithiocyanodiphenylethylene, m. p. 194—195°, the  $\beta$ -form (m. p. 123—124°) not being obtained by the direct method. *s*-Dithiocyanoethylene combines with 2 atoms of bromine slowly in the dark to yield *s*-dibromodithiocyanoethane, the liquid (*cis*) form yielding the *meso*-compound, m. p. 83.5—84°, whilst the solid (*trans*) form yields the *racemic* compound, prisms, m. p. 110—111°, slowly at the ordinary temperature. In sunlight this reaction goes more readily, but the additive reaction now becomes a side reaction, the main reaction being the replacement of thiocyanogen by bromine to yield  $\beta$ -bromo- $\alpha$ -thiocyanoethylene, which then adds on bromine to yield tribromothiocyanoethane. All these bromo-additive products lose 2 atoms of bromine on treatment with zinc and alcohol. Thiocyanogen compounds of aromatic acetylenes show no tendency to combine with bromine. The action of thiocyanogen in benzene solution on  $\alpha\beta$ -dibromoethylene in bright sunlight causes the initial liberation of bromine, which is slowly reabsorbed, and from the complex mixture can be isolated  $\beta$ -bromo- $\alpha$ -thiocyanoethylene, the solid *s*-dithiocyanoethylene,

tetrabromoethane, tribromothiocyanoethane, and, with certain proportions of the reacting substances, *s*-dibromodithiocyanoethane (m. p. 110—111°).  $\beta$ -Tolane dibromide reacts with thiocyanogen in the presence of lead thiocyanate to produce  $\alpha$ - and  $\beta$ -tolane dithiocyanates. Thiocyanogen can also displace bromine from hydrogen bromide,  $2\text{HBr} + (\text{CNS})_2 = 2\text{HCNS} + \text{Br}_2$ . Thiocyanogen can readily replace iodine in acetylene di-iodide, only feeble photo-catalysis being necessary, the solid (*trans*) form yielding the solid dithiocyanoethylene, whilst the liquid yields a mixture of solid and liquid forms. J. W. B.

**Spectrochemistry and Structure of Polynuclear Aromatic Hydrocarbons.** K. VON AUWERS and R. KRAUL (*Annalen*, 1925, **443**, 181—191).—The authors have completed their investigation of the relation of spectrochemical data to the structure of naphthalene, anthracene, phenanthrene, and other polynuclear systems (cf. Auwers and Krollpfeiffer, A., 1923, ii, 101) by the investigation of phenanthrene derivatives, stilbene, di- and tetra-hydrophenanthrene, pyrene, and fluoranthrene, and previous results are summarised and some fresh measurements made. A comparison of the exaltations of refractive indices and dispersions of stilbene and phenanthrene and their alkyl and halogen derivatives shows that these values are considerably reduced when the olefinic double bond is replaced by a ring; also that the three rings in phenanthrene are similar. Dihydrophenanthrene exhibits a large exaltation and the optical evidence corresponds with the formula I or II (Schroeter, this vol., i, 130). Pure tetrahydrophenanthrene was prepared and some of its physical constants were redetermined: b. p. 165—167°/10 mm., 307°/760 mm., m. p. 14°, picrate, m. p. 110—111° (Schroeter, *loc. cit.*, gives 106—108°),  $d^{20}_D$  1.075,  $n^{20}_D$  1.628. The exaltation found corresponds with Schroeter's formula III.

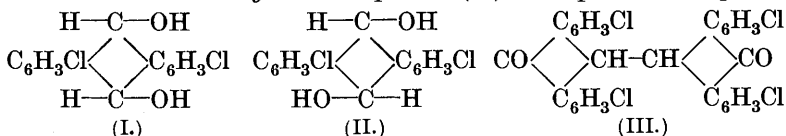


The value of the exaltation for pyrene is practically the same as that for anthracene, suggesting that the same ring systems are present in each. Fluoranthrene shows a much larger exaltation than fluorene, due to the introduction of a new double bond.

J. W. B.

**Mechanism of Substitution Reactions in the Aromatic Nucleus.** III. E. DE B. BARNETT, J. W. COOK, and M. A. MATTHEWS (*Rec. trav. chim.*, 1925, **44**, 728—739; cf. this vol., i, 18).—The dichloride and dibromide of 1:5-dichloroanthracene react in general as if they possessed the *cis*-configuration, but in some cases simultaneous partial conversion into a *trans*-compound seems

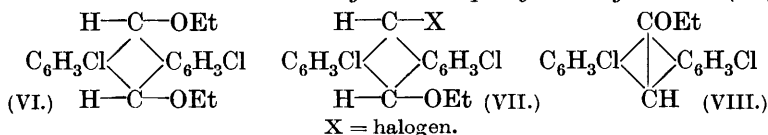
to take place, and this is particularly well marked in hydrolytic reactions. 1 : 5-Dichloroanthracene dibromide has been hydrolysed by boiling with aqueous acetone in the presence of excess of calcium or magnesium carbonate. The product consists of a mixture of 1 : 5-dichloro-*cis*-9 : 10-dihydroanthraquinol (I), m. p. 210°, 1 : 5-dichloro-*trans*-9 : 10-dihydroanthraquinol (II), m. p. 244°, together



with 1 : 5-dichloroanthracene, 1 : 5-dichloroanthraquinone, and 1 : 5 : 1' : 5'-tetrachlorodianthrone (III). 1 : 5-Dichloroanthracene dichloride gives similar results, but the reaction is much slower and less complete. If no basic substance is present to keep the solution neutral only the *cis*-isomeride is obtained; the *trans*-isomeride, being dehydrated by the acid produced during the hydrolysis, passes into the anthranol (IV) or its ketonic tautomeride (V). Similar



products are obtained by hydrolysing with moist silver oxide. The configuration of each isomeride is based on the ease with which one of them passes into the anthranol; this same isomeride, having the higher m. p. and a lower solubility, is considered to be the *trans*-compound. The *diacetate* of the *cis*-form,  $\text{C}_{18}\text{H}_{14}\text{O}_4\text{Cl}_2$ , has m. p. 246°, the *diacetate* of the *trans*-form, m. p. 259° (after first turning yellow and then red). The *bisphenylcarbamate* of the *cis*-compound has m. p. 222°, that of the *trans*-compound has m. p. 278—280°. Both the isomeric dihydroanthraquinols, when treated with hydrochloric or hydrobromic acid, give halides which are identical with those produced by the action of halogen on 1 : 5-dichloroanthracene, and on hydrolysis with aqueous acetone pass back into a mixture of the *cis*- and *trans*-dihydroanthraquinols. Boiling 1 : 5-dichloroanthracene dihalides with ethyl alcohol gives a mixture of *cis*-dichlorodihydroanthraquinyl diethyl ether (VI),



m. p. 184°, and (main product) dichloroanthranyl ethyl ether (VIII) (probably via the intermediary compound (VII), for reasons discussed). Other alcohols which brought about hydrolysis did not give dialkyl ethers, but the corresponding dichloroanthranyl alkyl ethers. Preparations of the following are described: 1 : 5-dichloroanthranyl *n*-propyl ether, m. p. 48°, 1 : 5-dichloroanthranyl *n*-butyl ether, m. p. 75° (rapid formation), 1 : 5-dichloro-



*anthranlyl isoamyl ether*, m. p. 77°. Others were obtained as viscous oils, but were identified by hydrolysis to 1 : 5-dichloroanthrone. No reaction took place with *tert.*-butyl alcohol after 6 hours' boiling. The action of phenol on 1 : 5-dichloranthracene dibromide leads to 1 : 5-dichloroanthracene, which is typical of the *cis*-configuration, but 1 : 5-dichloroanthracene dichloride yields 1 : 5-dichloroanthranlyl-phenyl ether, greenish-yellow needles from acetic acid, containing 1 mol. of acetic acid, m. p. 113—114°. It is considered that the replacement action in this case is accompanied by a change in configuration. Unlike the anthranlyl alkyl ethers, the aryl ethers are not hydrolysed by warming with mineral acids in acetic acid solution, although they readily decompose if hydriodic acid is present, giving 1 : 5-dichloroanthracene. The mechanism of the reaction must consist in the addition of hydrogen iodide to the "bridge" bond and subsequent hydrolysis and reduction of the resulting additive compound. 1 : 5-Dichloroanthranlyl *o*-tolyl ether has m. p. 114°, the *m*-tolyl ether, m. p. 166°, the *p*-tolyl ether, m. p. 124°. A. C.

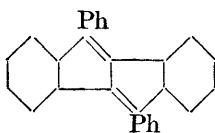
**Fluorene Compounds.** H. WIELAND and E. KRAUSE (*Annalen*, 1925, **443**, 129—141).—A simplified method for the preparation of diphenylene-ethylene (cf. Wieland, Reindel, and Ferrer, A., 1922, i, 1137) is described. Methylfluorenol (obtained by the action of magnesium methyl bromide on fluorenone) yields by the action of an ethereal solution of hydrochloric acid 9-chloro-9-methylfluorene, which, when warmed in alcohol, loses hydrogen chloride, giving the required hydrocarbon. On treatment with sodium methoxide, 9-chloro-9-methylfluorene yields 9-methoxy-9-methylfluorene; and with bromine loses hydrogen chloride to form diphenylene-ethylene dibromide, which on treatment with dimethylaniline loses 1 mol. of hydrogen bromide and 1 atom of bromine to yield bisdiphenylene-butadiene (cf. Wislicenus, A., 1915, i, 519), the base being partly converted into crystal-violet. The dibromide on treatment with methyl-alcoholic potassium hydroxide yields 9-methoxymethylene-fluorene,  $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}:\text{CH}(\text{OMe})$ , m. p. 106°, which on treatment in

methyl-alcoholic solution with 1 mol. of bromine is converted into the *monobromo-dimethoxy* compound,  $>\text{C}(\text{OMe})\cdot\text{CHBr}(\text{OMe})$  or  $>\text{CBr}\cdot\text{CH}(\text{OMe})_2$ , m. p. 131°. Sodium acetate acts on diphenylene-ethylene dibromide to form  $\omega$ -bromodiphenylene-ethylene, m. p. 78°, which with 1 mol. of bromine gives  $\alpha\beta\beta$ -tribromodiphenylene-ethane, m. p. 127°. Diphenylene-ethylene does not react with magnesium phenyl or methyl bromide; it yields a deep blue additive product (which cannot be isolated) with nitric acid, and reacts with 2 mols. of nitrogen peroxide to form  $\alpha\beta$ -dinitrodiphenylene-ethane, m. p. 117—118° (decomp.). This on treatment with ammonia loses 1 mol. of nitrous acid, yielding  $\omega$ -nitrodiphenylene-ethylene, m. p. 132°; *dibromide*, m. p. 110°. The 9-methylfluorenol obtained by the action of magnesium methyl bromide on fluorenone is identical with the compound, m. p. 176°, obtained by Ullmann and Wurster-berger (A., 1906, i, 76), whilst from the mother-liquor is isolated a

second form, m. p.  $84^{\circ}$ , which is proved to be the same as the compound,  $C_{14}H_{12}O$ , obtained by Daufresne (A., 1908, i, 165). The two forms are shown to be stereoisomerides, each giving the same chloride on treatment with hydrochloric acid. The explanation of the stereoisomerism of the diphenic acids (cf. Kenner, T., 1921, 119, 593; 1922, 121, 614) and the similarly constituted methylfluorenols is discussed; and the authors conclude that, taking strain conditions and the absence of optical isomerides into account, such stereoisomerism can only be represented as of the *cis-trans* type across the five-membered ring, the molecule not being regarded as uniplanar, but occupying a position intermediate between the uniplanar and Kauffler forms of diphenyl (cf. Mills, Palmer, and Tomkinson, J., 1924, 125, 2365). Similar examples have previously been noted (cf. Schmidt and Mezger, A., 1907, i, 43; Schmidt and Stützel, A., 1908, i, 415).  
J. W. B.

**Preparation of Symmetrical Polynitro Derivatives of the Dinaphthyls by the Action of Finely-divided Copper on Halogenated Nitronaphthalenes.** L. K. CHUDOŽILOV (*Chem. Listy*, 1925, 19, 187—190).—The above variant of Ullmann's reaction does not proceed smoothly unless the nitro group and the halogen are adjacent, and the naphthalene nucleus contains only one nitro group. The following are described: 2:2'-dinitro-1:1'-dinaphthyl, m. p.  $179-180^{\circ}$ ; 2:2'-diamino-1:1'-dinaphthyl, m. p.  $187^{\circ}$ ; 1:1'-dinitro-2:2'-dinaphthyl, m. p.  $264-265^{\circ}$ ; 1:1'-diamino-2:2'-dinaphthyl, m. p.  $253-259^{\circ}$ ; 4:4'-dinitro-1:1'-dinaphthyl, m. p.  $236-237^{\circ}$ ; 3:3'-dinitro-1:1'-dinaphthyl, m. p.  $142-143^{\circ}$ ; 2-iodo-5-nitronaphthalene, m. p.  $89-90^{\circ}$ ; 2-iodo-8-nitronaphthalene, m. p.  $128-129^{\circ}$ ; 2:2':4:4'-tetranitro-1:1'-dinaphthyl, m. p.  $291-292^{\circ}$ .  
B. F.

**9:12-Diaryl- $\Delta^{10}$ -diphensuccindenes and 9:12-Diaryldiphensuccindanes.** K. BRAND and W. MÜHL (*J. pr. Chem.*, 1925, [ii], 110, 1—9).—Reduction of 9:12-diphenyl- $\Delta^{9:11}$ -diphensuccindadiene (annexed formula) with zinc dust and acetic acid yields 9:12-diphenyl- $\Delta^{10}$ -diphensuccindene, m. p.  $285-286^{\circ}$ , the position of the double bond being shown by bromination to a dibromide which at once loses 2HBr to give the original succindadiene, and by oxidation with chromic-acetic acid to 2:2'-dibenzoylbenzil, m. p.  $188^{\circ}$ , and *o*-benzoylbenzoic acid, m. p.  $127^{\circ}$ . Reduction of the succindene or of the succindadiene with hydrogen and palladium yields 9:12-diphenyldiphensuccindane, m. p.  $207-208^{\circ}$ , which, together with a stereoisomeride, m. p.  $166-167^{\circ}$ , is also formed from the succindadiene by the action of sodium and amyl alcohol. 9:12-Di-*p*-tolyl- $\Delta^{10}$ -diphensuccindene, m. p.  $200^{\circ}$ , and two stereoisomeric di-*p*-tolyldiphensuccindanes, m. p.  $188-189^{\circ}$  and  $145-146^{\circ}$ , are similarly prepared from 9:12-di-*p*-tolyl- $\Delta^{9:11}$ -diphensuccindadiene. From the *m*-tolyl compound are obtained 9:12-di-*m*-tolyl- $\Delta^{10}$ -diphensuccindene, m. p.  $179-180^{\circ}$ , and only one 9:12-di-*m*-tolyldiphensuccindane, m. p.  $150^{\circ}$ .  
C. H.



**Coloured Phenol Ethers of the Diphensuccindene Group.**

K. BRAND and W. KREY (*J. pr. Chem.*, 1925, [ii], **110**, 10—25).—By the action of an ether solution of magnesium *o*-phenetyl bromide on diphensuccindan-9:12-dione in anhydrous benzene there is formed 9:12-di-*o*-phenetyldiphensuccindan-9:12-diol, m. p. 213—215° (darkens at 170—180°). 9:12-Di-*p*-phenetyldiphensuccindandiol, m. p. 208°, is similarly prepared. Both diols readily lose water to give the corresponding 9:12-diphenetyl- $\Delta^{9:11}$ -diphensuccindadienes, reddish-brown compounds melting at 204—205° and 223—224°, respectively, which are oxidised by chromic-acetic acid to *o*:*o'*-di(ethoxybenzoyl)benzils, m. p. 244—245° and 215—216°, respectively. *o*:*o'*-Di-(*o*-ethoxybenzoyl)benzil, owing to steric hindrance, will not condense with *o*-phenylenediamine, but from the *p*-ethoxybenzoyl compound a quinoxaline,  $C_{38}H_{30}O_4N_2$ , m. p. 227·5°, is readily obtained. The quinoxaline gives no oxime, but with hydroxylamine at 140—150° a small quantity of a compound, decomp. 170—180°, m. p. 202—203°. For the further oxidation of the benzils, chromic acid, permanganate, and nitric acid are useless, but with alkaline hydrogen peroxide in pyridine at water-bath temperature, 2-*o*-ethoxybenzoylbenzoic acid, m. p. 161—163°, and 2-*p*-ethoxybenzoylbenzoic acid, m. p. 135—136°, are obtained smoothly.

Di-*o*-phenetyldiphensuccindadiene is not reducible by the method used for the diphenyl compound (preceding abstract), but with activated aluminium in moist ether it gives 9:12-di-*o*-phenetyl- $\Delta^{10}$ -diphensuccindene, m. p. 250°, and with sodium and amyl alcohol a single 9:12-di-*o*-phenetyldiphensuccindane, m. p. 175—176°. 9:12-Di-*p*-phenetyl- $\Delta^{10}$ -diphensuccindene, m. p. 250—251°, and the related succindane, m. p. 240—241°, are similarly prepared. 9:12-Di-*o*-anisyl- $\Delta^{9:11}$ -diphensuccindadiene in the same way yields 9:12-di-*o*-anisyl- $\Delta^{10}$ -diphensuccindene, m. p. 254—255°, and the succindane, m. p. 250—251°. 9:12-Di-*p*-anisyldiphensuccindane melts at 244—244·5°.

C. H.

**Coloured Hydrocarbons of the Diphensuccindene Group.**

**An Abnormal Grignard Reaction.** K. BRAND, H. LUDWIG, and L. W. BERLIN (*J. pr. Chem.*, 1925, [ii], **110**, 26—36).—A 9:12-diaryldiphensuccindan-9:12-diol cannot be isolated from the product of reaction between magnesium *o*-tolyl, 2:4- or 2:5-xylyl halide and 9:12-diphensuccindandione, the diketone and hydrocarbon being recovered in each case, although from the oily product, by heating with formic acid, the corresponding 9:12-diaryl- $\Delta^{9:11}$ -diphensuccindadiene may be obtained, showing that the diol has been formed. With anthraquinone, a normal reaction is observed.

9:12-Di-*o*-tolyl- $\Delta^{9:11}$ -diphensuccindadiene, m. p. 240°, is oxidised by chromic-acetic acid in the cold to *o*:*o'*-di-*o*-toluoylbenzil, m. p. 154° (which does not condense with *o*-phenylenediamine), and in the hot to 2-*o*-toluoylbenzoic acid, m. p. 84° (+H<sub>2</sub>)O.

9:12-Di-*m*-tolyldiphensuccindan-9:12-diol, m. p. 180°, is formed in normal manner. Boiled with formic acid it gives 9:12-di-*m*-

*tolyl- $\Delta^{9:11}$ -diphensuccindadiene*, m. p. 184—185°, which is oxidised to *o*:*o'*-*di-m-toluoylbenzil*, m. p. 159°, and *2-m-toluoylbenzoic acid*, m. p. 162° (+H<sub>2</sub>O).

*9:12-Di-3':4'-xylyldiphensuccindan-9:12-diol*, m. p. 252°, is dehydrated to *9:12-di-3':4'-xylyl- $\Delta^{9:11}$ -diphensuccindadiene*, m. p. 212°.

From anthraquinone are obtained *9:10-dihydroxy-9:10-di-o-tolyldihydroanthracene*, m. p. 285° (decomp.), the corresponding *di-2':4'-xylyl* compound, m. p. 331—332° (decomp.), and the *di-2':5'-xylyl* compound, m. p. 260° (decomp.). C. H.

**Catalytic Action. XIV. Comparative Study of the Catalytic Activity of Reduced Copper, Reduced Nickel, and Thoria. II.** S. KOMATSU and C. TANAKA (*Mem. Coll. Sci. Kyoto*, 1925, **8**, 135—145).—*cyclo*Hexylamine is unaffected by thoria even at 300°, but with nickel or copper at 200° or 300° decomposition occurs, giving ammonia, benzene, aniline, *cyclo*-hexylimine, *dicyclo*hexylamine, phenyl*cyclo*hexylamine, diphenylamine, and carbazole, the amounts of which products are determined. At 200°, copper promotes only deamination, yielding chiefly *dicyclo*hexylamine, but copper at 300°, or nickel at 200°, causes both deamination and oxidation; with nickel at 300°, the yield of oxidation products is greater and of deamination products less than at 200°. It is supposed that the oxidation occurs in the stages: *cyclo*hexylamine  $\rightarrow$  *dicyclo*hexylamine  $\rightarrow$  phenyl*cyclo*hexylamine  $\rightarrow$  diphenylamine  $\rightarrow$  carbazole, and this is confirmed by oxidising *dicyclo*hexylamine in presence of copper to phenyl*cyclo*hexylamine and, in presence of nickel, to diphenylamine and carbazole. Differences in the behaviour of copper towards *cyclo*hexylamine and *cyclo*hexanol are attributed to its varying absorptive power towards reactants or resultants. On reducing aniline with hydrogen in presence of nickel at 190°, the yield of *cyclo*hexylamine is 30%, which corresponds with the amount of *cyclo*hexylamine recovered unchanged when it is passed over heated nickel.

F. M. H.

**Nitration of Symmetrical Arylalkylcarbamides.** L. C. E. KNIPHORST (*Rec. trav. chim.*, 1925, **44**, 693—727; cf. Thiele and Lachmann, A., 1896, i, 207; Scholl and Holdermann, A., 1906, i, 767; Rendler, A., 1914, i, 521).—*s*-Arylalkylcarbamides have been prepared by coupling ethylcarbimide with aniline and some of its derivatives. On nitrating these products with excess of 100% nitric acid, two nitro groups enter the ring, whilst a third enters the amino group which contains the alkyl radical. The group  $\text{-N(alk.)NO}_2$  is mobile and can be replaced by the groups  $\text{-OH}$ ,  $\text{-OMe}$ ,  $\text{-OEt}$ ,  $\text{-NH}_2$ ,  $\text{-NHMe}$ ,  $\text{-NHPh}$ , etc., giving in each case an alkylnitroamine or its salt.  $\alpha$ -Phenyl- $\beta$ -ethylcarbamide with excess of nitric acid at  $-15^\circ$  gives  $\alpha$ -2:4-dinitrophenyl- $\beta\beta$ -ethyl-nitrocarbamide, decomp.  $64^\circ$ , a yellow powder which (like most of the analogous compounds described below) gives the nitroamine reactions of Franchimont and Bamberger and of Thiele and Lach-

mann. On warming with water, the compound evolves carbon dioxide, forming 2:4-dinitroaniline and ethylnitroamine. Absolute alcoholic ammonia gives 2:4-dinitrophenylcarbamide in the cold and 2:4-dinitroaniline at 100°. All the arylcarbamides described are unstable towards aqueous ammonia, and many, like this one, are decomposed with the formation of the corresponding aniline derivative by heating with absolute alcoholic ammonia at 100°. Ethyl and methyl alcohols when warmed with the nitrocarbamide give the corresponding carbamates. Nitration with a mixture of nitric and sulphuric acids yields  $\alpha$ -2:4:6-trinitrophenyl- $\beta$ -ethylnitrocarbamide, decomp. 100—105°; on keeping in a desiccator, 60—65°. Rendler (*loc. cit.*) with phenylcarbamide found that only two nitro groups entered the ring under these conditions, hence the alkyl group attached to the  $\beta$ -nitrogen atom exerts an influence on substitution in the phenyl group. Water or aqueous sodium hydroxide converts it into 2:4:6-trinitroaniline. With cold alcoholic ammonia, 2:4:6-trinitrophenylcarbamide, m. p. 196—199° (decomp.), is formed. Ethyl 2:4:6-trinitrophenylcarbamate has m. p. 144.5° (van Romburgh gives 144°; Crocker and Lowe, 147°). The methyl compound has m. p. 194—196° (van Romburgh gives 192°);  $\alpha$ -*p*-tolyl- $\beta$ -ethylcarbamide, m. p. 143.5 on nitration (as above), gives  $\alpha$ -2:6-dinitro-*p*-tolyl- $\beta$ -ethylnitrocarbamide,  $C_{10}H_{11}O_7N_5$ , m. p. 95—99°, decomp. about 110°. With alcoholic ammonia (hot or cold), 2:6-dinitro-*p*-tolylcarbamide, m. p. 209°, is obtained. Boiling with absolute ethyl alcohol gives ethyl 2:6-dinitro-*p*-tolylcarbamate, m. p. 136°; the methyl analogue has m. p. 153°.  $\alpha$ -4-Chlorophenyl- $\beta$ -ethylcarbamide, m. p. 200°, prepared by the action of ethylcarbimide on *p*-chloroaniline, on nitration gives  $\alpha$ -4-chloro-2:6-dinitrophenyl- $\beta$ -ethylnitrocarbamide, decomp. about 60°. Cold alcoholic ammonia converts it into 4-chloro-2:6-dinitrophenylcarbamide, m. p. 214° (decomp.), warm ammonia into 4-chloro-2:6-dinitroaniline. Ethyl 4-chloro-2:6-dinitrophenylcarbamate has m. p. 168°, the methyl analogue, m. p. 153°.  $\alpha$ -4-Bromophenyl- $\beta$ -ethylcarbamide, m. p. 211—212° (decomp.), gives  $\alpha$ -4-bromo-2:6-dinitrophenyl- $\beta$ -ethylnitrocarbamide, decomp. 100—105°, on nitration. With cold alcoholic ammonia, 4-bromo-2:6-dinitrophenylcarbamide, m. p. 230—231° (decomp.), is formed. Ethyl 4-bromo-2:6-dinitrophenylethylcarbamate has m. p. 175.5—176.5°, the methyl compound, m. p. 189°.  $\alpha$ -*o*-Tolyl- $\beta$ -ethylcarbamide (from ethylcarbimide and *o*-toluidine), m. p. 165°, on nitration gives  $\alpha$ -4:6-dinitro-*o*-tolyl- $\beta$ -ethylnitrocarbamide, m. p. about 90° (decomp.). The nitration was not complete even with the addition of sulphuric acid, and the substance tended to decompose during the preparation. Boiling with water gave 4:6-dinitro-*o*-toluidine as chief product, together with a mixture (probably) of mononitrotolyl compounds. Cold alcoholic ammonia converts the nitroamide into 4:6-dinitro-*o*-tolylcarbamide, m. p. about 210° (decomp.). Ethyl 4:6-dinitro-*o*-tolylcarbamate has m. p. 155—157° (Ryan and Cullinane give 159—160°). Methyl 4:6-dinitro-*o*-tolylcarbamate has m. p. 192°.  $\alpha$ -2-Chlorophenyl- $\beta$ -ethylcarbamide, m. p. 134°, nitrates more readily than the corre-

sponding 2-methyl derivative, giving  $\alpha$ -2-chloro-4 : 6-dinitrophenyl- $\beta\beta$ -ethylnitrocarbamide; the crude substance decomp. at  $90^\circ$ , purified at  $50$ – $60^\circ$  (strikingly contrary to this, 2-chloro-4 : 6-dinitroacetanilide cannot be obtained on nitration of *o*-chloroacetanilide even with mixed concentrated nitric and sulphuric acids). Heating with water converted the carbamide into 2-chloro-4 : 6-dinitroaniline. Cold alcoholic ammonia converts the nitroamide into 2-chloro-4 : 6-dinitrophenylcarbamide, m. p.  $212$ – $213^\circ$  (decomp.). This substance or the original nitroamide passes into ethyl 2-chloro-4 : 6-dinitrophenylcarbamate, m. p.  $160^\circ$  (decomp.), on warming with alcohol. The methyl ester has m. p.  $183.5^\circ$ .  $\alpha$ -Phenyl- $\beta$ -methylcarbamide (cf. Dixon, T., 1895, 560) on nitration gives  $\alpha$ -2 : 4-dinitrophenyl- $\beta\beta$ -methylnitrocarbamide, decomp.  $70^\circ$ , having similar properties to the ethyl derivative, and giving the same decomposition products with water and alcoholic ammonia so far as the  $\alpha$ -portion of the molecule is concerned. Nitration with a mixture of nitric and sulphuric acids gives a tetranitro compound, decomp. about  $110^\circ$  (see ethyl analogue above). Nitration by means of Scholl and Holdermann's method (*loc. cit.*), using 3 mols. of ethyl nitrate, did not cause a nitro group to enter the  $\beta$ -position, but gave  $\alpha$ -2 : 4-dinitrophenyl- $\beta$ -methylcarbamide.  $\alpha$ -2 : 6-Dinitro-*p*-tolyl- $\beta\beta$ -methylnitrocarbamide has m. p.  $112^\circ$  (decomp.). Nitration of  $\alpha$ -phenyl- $\beta$ -ethylthiocarbamide with 100% nitric acid gives the same nitro compound as  $\alpha$ -phenyl- $\beta$ -ethylcarbamide. The nitration of  $\alpha$ -*p*-tolyl- $\beta$ -methylthiocarbamide gave a similar result. The group  $-\text{CO}\cdot\text{NR}(\text{NO}_2)$ , ( $\text{R}=\text{Me}$  or  $\text{Et}$ ) contained in  $(\text{NO}_2)_2\text{C}_6\text{H}_3\cdot\text{NH}\cdot\text{CO}\cdot\text{NR}(\text{NO}_2)$  is also eliminated as a nitroamine by the action of aniline, *p*-toluidine, hydrazine, and phenylhydrazine in exactly the same way as by ammonia, the residue of the amine taking the place of the  $-\text{NR}(\text{NO}_2)$  group. This occurs in the cold in ethereal solution, but may be carried out in alcohol, since the secondary reaction with alcohol itself is much slower. The reactions take place smoothly and give nearly quantitative results.  $\alpha$ -2 : 4-Dinitrophenyl- $\beta$ -phenylcarbamide, m. p.  $186$ – $187^\circ$  (decomp.), is obtained from aniline and  $\alpha$ -2 : 4-dinitrophenyl- $\beta\beta$ -ethylnitrocarbamide, or from the corresponding  $\beta$ -methyl analogue.  $\alpha$ -2 : 4-Dinitrophenyl- $\beta$ -*p*-tolylcarbamide has m. p.  $210^\circ$  (decomp.).  $\alpha$ -2 : 6-Dinitro-*p*-tolyl- $\beta$ -phenylcarbamide has m. p.  $190$ – $193^\circ$  (or  $202^\circ$ ) (decomp.),  $\alpha$ -4-chloro-2 : 6-dinitrophenyl- $\beta$ -phenylcarbamide, m. p.  $197$ – $201^\circ$  (decomp.),  $\alpha$ -2-chloro-4 : 6-dinitrophenyl- $\beta$ -phenylcarbamide, m. p.  $168.5^\circ$  (decomp.). Phenylhydrazine and  $\alpha$ -2 : 4-dinitrophenyl- $\beta\beta$ -ethylnitrocarbamide give 1-phenyl-4(2 : 4-dinitrophenyl)-semicarbazide, m. p.  $162$ – $162.5^\circ$  (decomp.).  $\alpha$ -2 : 4-Dinitrophenyl- $\beta$ -nitrocarbamide appeared to give an additive product with phenylhydrazine, probably owing to the more strongly acidic character of the group  $-\text{CO}\cdot\text{NH}(\text{NO}_2)$  making further reaction difficult. Hydrazine condenses with  $\alpha$ -2 : 4-dinitrophenyl- $\beta\beta$ -ethylnitrocarbamide to form 4(2 : 4-dinitrophenyl)-semicarbazone, m. p.  $195^\circ$ , decomp.  $197^\circ$ , which gives with acetone the semicarbazone,  $\text{C}_{10}\text{H}_{11}\text{O}_5\text{N}_5$ , m. p.  $205$ – $210^\circ$  (decomp.), and with benzaldehyde the semicarbazone,  $\text{C}_{14}\text{H}_{11}\text{O}_5\text{N}_5$ , m. p.  $241^\circ$  (decomp.). A. C.

**Substituted Ammonium Molybdates and Tungstates.**

A. C. KRAUSE and F. C. KRAUSKOPF (*J. Amer. Chem. Soc.*, 1925, **47**, 1689—1694).—By digestion of molybdic acid with amines, or of ammonium molybdate with the amine hydrochloride, a number of organic salts of molybdic acid have been prepared. Analogous tungstates were similarly prepared from tungstic acid. Salts are formed most readily with the basic alkylamines, the stability of the salts in water and the constancy of composition increasing with the basicity of the amine. Similarly, the apparent ease of formation of molybdates and tungstates varies with the basicity of the aromatic amine used. The *o*-toluidine molybdate is more readily prepared than the *p*-toluidine salt, the latter than the aniline salt. Salts of *o*- and *m*-nitroanilines, and of *o*- and *p*-bromoanilines could not be prepared successfully. The weakly basic mixed tertiary aromatic amines, *e.g.*, dimethyl- and diethyl-aniline, give similar salts to aniline, these salts from weak bases having the general composition  $X \cdot H_2MoO_4 \cdot MoO_3$  (where  $X=1$  mol. of a mono-acid base). The stronger bases yield salts of the general formula  $X \cdot 2H_2MoO_4$ , which are more crystalline and more readily soluble in water than those from the aromatic amines. Similar relationships appeared with tungstic acid. The following ammonium molybdates are described: *phenyl*-, *p*-*tolyl*-, *o*-*tolyl*-, *phenyldimethyl*-, *phenyldiethyl*-, *dimethyl*-, and *picolyl*. *Piperidinium molybdate*,  $(C_5H_{11}N)_2 \cdot H_2MoO_4 \cdot MoO_3$ ; *ethylenediammonium molybdate*,  $C_2H_8N_2 \cdot 2H_2MoO_4 \cdot 2MoO_3 \cdot H_2O$ ;

*methylammonium tungstate*,  $(MeNH_3)_6W_7O_{24} \cdot 4H_2O$ ; *piperidinium tungstate*,  $(C_5H_{11}N)_6W_7O_{24} \cdot 4H_2O$ , and *o*-*tolylammonium tungstate*,  $(C_7H_7NH_2)_2H_2W_5O_{16}$ , are also described. R. B.

**Toluidine Derivatives. I. Quantitative Preparation of 5-Iodo-*o*-toluidine and Some of its Derivatives.** R. M. HANN and J. F. T. BERLINER (*J. Amer. Chem. Soc.*, 1925, **47**, 1709—1712).

—By trituration of *o*-toluidine hydrochloride, instead of the free amine, with iodine and calcium carbonate, yields of 5-iodo-*o*-toluidine, m. p.  $87.2^\circ$ , amounting to 98% of the theoretical can be obtained. The following derivatives are described: *hydrochloride*, m. p.  $214^\circ$ ; *hydrobromide*, m. p.  $196^\circ$ ; *hydriodide*, m. p.  $190^\circ$  (decomp. at  $105^\circ$ , more slowly at  $70-90^\circ$ ); *hydrofluoride*,

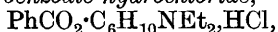
$NH_2 \cdot C_6H_3MeI \cdot 4HF$ , m. p.  $105^\circ$ ; *perchlorate*, m. p.  $209^\circ$ ; *picrate*, yellow needles, m. p.  $188.5^\circ$ ; *picrolonate*, yellow needles, m. p.  $189.5^\circ$ ; *oxalate*, m. p.  $158^\circ$ ; *mercurichloride*,  $[NH_2 \cdot C_6H_3MeI]_2 \cdot HgCl_2$ , m. p.  $134.5^\circ$ . 5-Iodo-*o*-tolylcarbamide has m. p.  $273^\circ$  (*hydrochloride* sublimes), *s*-phenyl-5-iodo-*o*-tolylcarbamide,  $C_6H_3MeI \cdot NH \cdot CO \cdot NHPh$ , m. p.  $232^\circ$ , *s*-5-iodo-*o*-tolyl- $\alpha$ -naphthylcarbamide,  $C_6H_3MeI \cdot NH \cdot CO \cdot NHC_{10}H_7$ , m. p.  $214^\circ$ , and 5-iodo-*o*-tolylcarbylamine, yellow needles, m. p.  $83-84^\circ$ . R. B.

**Reduction of Anethole Nitrosochloride by Stannous Chloride and Hydrochloric Acid.** J. B. SHOESMITH and R. H. SLATER (*J. Chem. Soc.*, 1925, **127**, 1490).—Anethole nitrosochloride in chloroform solution is reduced by stannous chloride and hydrochloric acid to the double compound of *anisylideneazine hydrochloride*

and stannic chloride,  $(\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} : \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}, \text{HCl})_2, \text{SnCl}_4$ , m. p.  $259^\circ$  (decomp.), decomposed by water into stannic oxide and anisylideneazine, m. p.  $168^\circ$  (to a liquid crystal converted into the isotropic liquid at  $180^\circ$ ). The latter yields the free hydrochloride, m. p.  $172^\circ$  (decomp. at  $177^\circ$ ), converted by nitrous acid into anisaldehyde. M. J.

**Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. X. Reduction of Aminophenols to Cyclic Amino-alcohols.** H. HECKEL and R. ADAMS (*J. Amer. Chem. Soc.*, 1925, 47, 1712—1718).—On reduction with the platinum oxide-platinum-black catalyst and hydrogen under 2—3 atm. pressure by the methods previously described (cf. A., 1923, ii, 773; 1924, i, 968) the hydrochlorides of aminophenols yield the corresponding cyclohexylamine and cyclic amino-alcohol in proportions depending on the aminophenol reduced. Of the unsubstituted aminophenols only the *m*-aminophenol was reduced readily, *o*-aminophenol causing immediate poisoning of the catalyst. The *N*-alkyl-substituted aminophenols were reduced more readily and the presence of an *N*-alkyl group appears to increase the stability of the amino-alcohol formed. *o*-Dimethylaminophenol undergoes reduction to the extent of 25% before the catalyst becomes inactive, probably through its precipitation by the large quantities of cyclohexane produced. The presence of small quantities of impurities considerably affects the activity of the catalyst. Platinum catalyst made from Merck's "U.S.P." sodium nitrate is superior to that made from chemically pure sodium nitrate, and addition of ferrous or ferric salts to the reduction mixture when using a catalyst obtained in the latter case had no accelerating effect. Oxygen has no reactivating influence on the spent catalyst in the reduction of aminophenols.

*p*-Dimethylaminophenol hydrochloride yields cyclohexyldimethylamine and a fraction, b. p.  $99\text{--}100^\circ/7\text{ mm.}$ ,  $228\text{--}229^\circ/740\text{ mm.}$ ,  $d_{25}^{25} 0.9830$ ,  $n_D^{25} 1.4859$ , apparently a mixture of *cis*- and *trans*-forms of *p*-dimethylaminocyclohexanol, since with benzoyl chloride it yields two *p*-dimethylaminocyclohexyl benzoate hydrochlorides; the  $\alpha$ -form has m. p.  $243\text{--}244^\circ$ ; the  $\beta$ -form, m. p.  $212.5\text{--}213.5^\circ$ . Similarly, *p*-nitrobenzoyl chloride yields both an  $\alpha$ -, m. p.  $250\text{--}252^\circ$ , and a  $\beta$ -form, m. p.  $233\text{--}234^\circ$ , of the *p*-nitrobenzoate. *m*-Diethylaminophenol hydrochloride yields cyclohexyldiethylamine and a fraction, b. p.  $132\text{--}133^\circ/19\text{--}20\text{ mm.}$ ,  $245^\circ/740\text{ mm.}$ ,  $d_{25}^{25} 0.9503$ ,  $n_D^{25} 1.4850$ , yielding a benzoate hydrochloride,



m. p.  $148\text{--}150^\circ$ , and a *p*-nitrobenzoate, m. p.  $161\text{--}163^\circ$ . Similarly, *m*-dimethylaminophenol hydrochloride yields cyclohexyldimethylamine and a fraction, b. p.  $231^\circ/740\text{ mm.}$ ,  $d_{25}^{25} 0.9766$ ,  $n_D^{25} 1.4846$ ; the *m*-dimethylaminocyclohexyl benzoate hydrochloride obtained from this has m. p.  $229\text{--}230^\circ$ , the *p*-nitrobenzoate, m. p.  $224\text{--}225^\circ$ . *p*-Methylaminophenol hydrochloride yields methylaminocyclohexane and a fraction, b. p.  $134\text{--}135^\circ/23\text{--}24\text{ mm.}$ ,  $229\text{--}230^\circ/740\text{ mm.}$ , m. p.  $78^\circ$  (hydrochloride, m. p.  $121\text{--}135^\circ$ ). *m*-Amino-



phenol hydrochloride yields *cyclohexylamine*, *dicyclohexylamine*, and *m-cyclohexylaminocyclohexanol* but no *m-aminocyclohexanol*.

R. B.

**Arylamino-naphtholsulphonic Acids.** R. LANTZ and A. WAHL (*Compt. rend.*, 1925, **180**, 1668—1670; cf. this vol., i, 413). —By the action of sodium hydrogen sulphite on 1-phenylimino- $\beta$ -naphthaquinone, simultaneous sulphonation and reduction are effected, and 1-phenylamino- $\beta$ -naphthol-4-sulphonic acid is obtained; similarly 1-*p*-tolylamino- $\beta$ -naphthol-4-sulphonic acid is obtained from 1-*p*-tolylimino- $\beta$ -naphthaquinone. Treatment of the arylamino-naphthols with sulphuric acid results in the formation of isomeric sulphonic acids.

L. F. H.

**Hydroaromatic 1:2-Oxides and 3-Keto-1:2-oxides.** A. KÖTZ and W. HOFFMANN (*J. pr. Chem.*, 1925, [ii], **110**, 101—122). —Certain reactions of 1:2-cyclohexene oxide, 1-methyl- $\Delta^1$ -cyclohexene oxide (prepared by the action of potassium hydrogen sulphate or dilute sulphuric acid on 1-methyl-2-cyclohexanol, followed by treatment of 1-methyl- $\Delta^1$ -cyclohexene with perbenzoic acid), 1-methyl- $\Delta^2$ -cyclohexene oxide (1-methyl-3-cyclohexanol being converted into 1-methyl- $\Delta^2$ -cyclohexene by means of phosphorus pentoxide), and 1-methyl- $\Delta^3$ -cyclohexene oxide have been studied. By catalytic reduction of the methylcyclohexene oxides, it appears that the methyl group tends to repel the oxygen atom; thus when 1-methyl- $\Delta^1$ -cyclohexene oxide in acetic acid solution is treated with hydrogen in presence of platinum-black, it gives 1-methyl-2-cyclohexanol, b. p. 165—168° (phenylurethane, m. p. 104—105°), whilst 1-methyl- $\Delta^2$ -cyclohexene oxide gives chiefly 1-methyl-3-cyclohexanol, b. p. 170—173° (phenylurethane, m. p. 95—96°), together with 1-methyl-2-cyclohexanol, and 1-methyl- $\Delta^3$ -cyclohexene gives chiefly 1-methyl-4-cyclohexanol, b. p. 173—175° (phenylurethane, m. p. 125°), together with 1-methyl-3-cyclohexanol. Catalytic reduction of 1:2:3:4-tetrahydronaphthalene 1:2-oxide yields solely tetrahydro- $\beta$ -naphthol. By the action of dry hydrogen chloride on an ethereal solution of 1-methyl- $\Delta^3$ -cyclohexene oxide, the chief product is 4-chloro-1-methyl-3-cyclohexanol, b. p. 93—97°/15 mm. (with 3-chloro-1-methyl-4-cyclohexanol), and by treatment of this with potassium cyanide, followed by heating with hydrochloric acid, there is obtained 1-methyl- $\Delta^3$ -cyclohexene-4-carboxylic acid, m. p. 134° (cf. Reyle, *Diss.*, Göttingen, 1925), together with *r*-1-methyl-4-cyclohexanol-3-carboxylic acid, m. p. 113°. When cyclohexene oxide is heated with alcohol at 150°, or by boiling the alcoholic solution with sodium ethoxide, 2-ethoxy-1-cyclohexanol, b. p. 85—87°/11 mm., is formed (and may be oxidised to 2-ethoxy-1-cyclohexanone, m. p. 137—138°, by means of potassium dichromate and sulphuric acid), but it is only obtained in low yield by heating 2-chloro-1-cyclohexanol with alcoholic sodium ethoxide at 140—150°. Addition of alcohol to 1-methyl- $\Delta^3$ -cyclohexene oxide occurs similarly, yielding a monoethyl ether, b. p. 90—93°/15 mm., of 1-methyl-3:4-cyclohexandiol.

cycloHexene oxide with ethyl sodiomalonate in alcoholic solution

forms the lactone of *ethyl 1-cyclohexanol-2-malonate*, b. p. 175—190°/14—15 mm., whilst only a poor yield of impure substance is obtained from 2-chloro-1-cyclohexanol and ethyl sodiomalonate even at 140—150°. 1 : 2 : 3 : 4-Tetrahydronaphthalene-1 : 2-oxide with alcoholic ethyl sodiomalonate at 140—150° gives ethyl phloroglucintricarboxylate and  $\beta$ -tetralone, but styryl methyl ketone oxide reacts spontaneously, giving the lactone ester, b. p. 140—150°/20 mm. 3-Keto- $\Delta^1$ -*p*-menthene oxide, b. p. 138—145°,  $d^{15}$  0.9992 (prepared in small yield by the action of hydrogen peroxide on 3-keto- $\Delta^1$ -*p*-menthene in methyl alcohol and sodium hydroxide), when melted with ethyl sodiomalonate yields a lactone of *ethyl 1-methyl-4-isopropylcyclohexanolmalonate*, b. p. 164—166°,  $d^{17}$  1.085. From ethyl sodiomalonate and 1-methyl- $\Delta^3$ -cyclohexene oxide is obtained the lactone of *ethyl 1-methyl-3-cyclohexanol-4-malonate*, b. p. 183—185°/15 mm.,  $d^{17}$  1.0853; 1-methyl-3-cyclohexanol-4-malondiamide, m. p. 225—226°, is converted by alcoholic potassium hydroxide into the *potassium* salt, from which (a) hydrochloric acid liberates 1-methyl-3-cyclohexanol-4-malonic acid, m. p. 96—99°, which by heating at 90° is converted into the lactone of 1-methyl-3-cyclohexanol-4-acetic acid, m. p. 143—149°, whilst (b) oxidation with permanganate and subsequent heating yields 1-methyl-3-cyclohexanone-4-acetic acid (ester semicarbazone, m. p. 114—115°). When an alcoholic solution of cyclohexene oxide and ethyl sodioacetoacetate is heated, it is partly decomposed to dehydracetic acid and the lactone of 1-cyclohexanol-2-acetoacetic acid, b. p. 142—147°/15 mm.

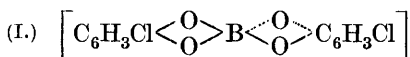
F. M. H.

**Association of Polyhydric Phenols.** E. ROUYER (*Compt. rend.*, 1925, **180**, 1934—1936).—The equilibria between simple and associated molecules in aqueous solutions of polyhydric phenols have been studied by ebullioscopic methods. The results show that all the polyhydroxybenzenes (with the exception of phloroglucinol) are associated; at low concentrations ( $< 1.25M$ ) the equilibrium is between single and double molecules, between 1.25 and  $2M$  single and triple molecules seem to be in equilibrium.

The trihydroxybenzenes are less associated than the dihydroxy derivatives. The degree of association is higher for *ortho* than for *para* and *meta* isomerides. Phenol cannot be examined by ebullioscopic methods, but osmotic pressure measurements indicate an equilibrium between single and double molecules at concentrations  $< 0.9M$  in water.

R. A. M.

**Asymmetric Derivatives of Boron.** J. BÖESEKEN and J. A. MIJS (*Rec. trav. chim.*, 1925, **44**, 758—762; cf. A., 1923, i, 557; ii, 406; Böeseken and Meulenhoff, A., 1924, i, 776).—4-Chloropyrocatechol, m. p. 91°, prepared by the action of sulphuryl chloride on pyrocatechol in ethereal solution, combines with boric acid to



form di(4-chloropyrocatechol)boric acid. The composition of the anion (I) was determined by the preparation of its salts (all found

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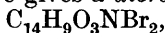
crystalline) with *potassium, ammonium, aniline, p-chloroaniline, p-iodoaniline, and o-toluidine*, using 2 mols. of the chloropyrocatechol to 1 mol. each of boric acid and the base. Successive crops of the *brucine* salt,  $+6\text{H}_2\text{O}$  (losing  $2\text{H}_2\text{O}$  after a time), when allowed to separate slowly from the solvent (alcohol and water) all had the same  $[\alpha]_D^{20} -12.5^\circ$  to  $-13.5^\circ$  and were racemic. By rapidly fractionating the freshly-prepared dry salt by precipitation from chloroform with ligroin, fractions were obtained having  $[\alpha]_D -5.9^\circ$  to  $-19.7^\circ$ , all changing to  $[\alpha]_D -13.7^\circ$  in 10 days. The asymmetric character of the anion is therefore established, as was done for the salicylic acid-boric acid compound (A., 1924, i, 776) although the salts quickly racemise. Pyrocatechol on nitration by a modification of Dakin's method gives a 25% yield of 3-nitro- and 45% of 4-nitro-pyrocatechol, separable by means of ligroin, in which the 3-form is soluble with a deep yellow colour. 3-Nitropyrocatechol-boric acid salts of aniline, *p-chloroaniline*, and of various alkaloids were prepared. The *strychnine* salt, whether viscous or micro-crystalline, is racemic and has  $[\alpha]_D -59^\circ$  to  $-61^\circ$ . Rapidly prepared and fractionated as above, the first fraction had  $[\alpha]_D -68.7^\circ$ , the seventh  $-55.2^\circ$ . The *ll*-isomeride is the least soluble and is concentrated in the early fractions, whilst the last fraction is richest in the *dl*-form. A. C.

**Partial Valency of the Hydroxyl Group. IV. Aquo- and Pyrido-tripyrrocatechyl-arsenic and -antimonic Acids.** H. REIHLEN, A. SAPPER, and G. A. KALL (*Z. anorg. Chem.*, 1925, **144**, 218—224; cf. A., 1924, ii, 384).—The formula of Weinland and Scholder (A., 1923, i, 1196) for the potassium salt of tripyrocatechyl-antimonic acid,  $[\text{O}=\text{Sb}(\equiv(\text{OC}_6\text{H}_4\text{O})_3)\text{K}, 0.5\text{H}_2\text{O}$ , has the disadvantage that the acid would be expected to be tribasic instead of monobasic; the formula  $[(\text{C}_6\text{H}_4\text{O}_2)_2\equiv\text{Sb}-(\text{OC}_6\text{H}_4\text{O}) \dots \text{OH}_2]\text{K}, 0.5\text{H}_2\text{O}$  is therefore proposed and is supported by the examination of *sodium* and *potassium pyridotripyrocatechylantimonate* and *sodium pyridotripyrocatechylarsenate*. The sexavalency of the central atom in these substances accounts for the absence of similar phosphorus compounds. A. G.

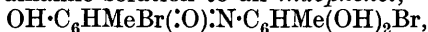
**Co-ordination Valency of two Hydroxyl Groups in the Ortho Position. I. Complexes of Pyrocatechol and Pyrogallol with Acids of the Molybdenum Group.** L. FERNANDES (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 439—443).—Treatment of molybdic, tungstic, or uranic anhydride with pyrocatechol or pyrogallol gives, according to the conditions and proportions employed, compounds of one of the two series,  $\left[ \begin{smallmatrix} \text{Z} \\ \text{XO}_3\text{H}_2\text{O} \end{smallmatrix} \right]_R$  and  $\left[ \begin{smallmatrix} \text{Z} \\ \text{XO}_2\text{Z} \end{smallmatrix} \right]_R$ , where  $\text{X}=\text{Mo, W, or Ur}$ ,  $\text{R}=\text{H, K, Na, Tl, guanidine, pyridine, etc.}$ , and  $\text{Z}$  is the *o*-dihydroxy compound. The compounds of both classes are intense red, and the free acids are unstable, but the corresponding salts, which are mostly acid salts, are markedly stable; the salts with organic bases are crystallisable. The colour is ascribed to weakening of the primary linkings by intervention of

the secondary linkings, and is thus the more pronounced with compounds of the second type. Compounds of neither type are formed by either di- or tri-hydroxylated compounds unless at least two hydroxyl groups occupy ortho-positions to one another, such relationship being apparently necessary for the development of a co-ordination valency. The two classes of compounds appear to be formed together and to exist in the solution in equilibrium :  $\left[ \begin{smallmatrix} \text{Z} \\ \text{XO}_3\text{H}_2\text{O} \end{smallmatrix} \right] \text{R} + \text{Z} \rightleftharpoons \left[ \begin{smallmatrix} \text{Z} \\ \text{XO}_2\text{Z} \end{smallmatrix} \right] \text{R} + 2\text{H}_2\text{O}$ ; in aqueous, but not in alcoholic, solution excess of the dihydroxy compound is required for the isolation of the compound of the second class. T. H. P.

**Dyes and other Derivatives of Cresorcinol.** F. HENRICH and F. Götz (*Ber.*, 1925, 58, [B], 1055—1060).—5-Amino-2:4-dihydroxytoluene undergoes autoxidation in faintly alkaline solution, yielding 6:4':6'-*trihydroxy-3:3'-dimethylindophenol*, which gradually darkens above 100° and is converted by acids or alkalis into the fluorescent 7-hydroxy-3:6-dimethyl-2:10-phenoxazone,  $\text{C}_6\text{H}_2\text{Me}(\text{:O}) \leq \text{N} > \text{C}_6\text{H}_2\text{Me}(\text{OH})$  (apparently isolated as a *monohydrate*, which yields the above compound at 150°); the *monoacetyl* derivative, m. p. 216—218°, is described. Bromination of the phenoxazone derivative gives a *dibromo* compound,

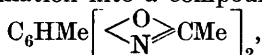


which blackens above 230° but does not melt below 310°. The action of bromine on 5-amino-2:4-dihydroxytoluene in glacial acetic acid solution affords *bromo-4:6-dihydroxy-m-toluidine hydrobromide*, which evolves bromine copiously when warmed with manganese dioxide and concentrated sulphuric acid; it is autoxidised in alkaline solution to an *indophenol*,



the *acetyl* derivative,  $\text{C}_{20}\text{H}_{17}\text{O}_7\text{NBr}_2$ , of which is described. Ring closure of the brominated indophenol takes place with comparative difficulty and leads to the production of a bromo compound identical with that derived by the action of bromine on 7-hydroxy-3:6-dimethyl-2:10-phenoxazone (see above); the corresponding *acetyl* derivative is described.

3:5-Dinitroso-2:4-dihydroxytoluene is reduced by stannous chloride and concentrated hydrochloric acid to 3:5-diamino-2:4-dihydroxytoluene *hydrochloride*, decomp. 286—288° after darkening at 220°. 3:5-Diacetamido-2:4-diacetoxytoluene, m. p. 134°, is converted by dry distillation into a compound,



m. p. 144°.

H. W.

**Synthesis of β-Phenylethyl Alcohol.** C. S. LEONARD (*J. Amer. Chem. Soc.*, 1925, 47, 1774—1779).—A modified form of Bouveault and Blanc's method (*A.*, 1903, i, 673; 1904, i, 213) is recommended. Benzyl chloride, when heated with alcoholic sodium cyanide, with efficient agitation, gives a 76% yield of phenylacetonitrile, recovery of the phenylacetamide simultaneously pro-

duced giving a total yield of 93%. The phenylacetonitrile is hydrolysed and esterified with alcoholic sulphuric acid and the ethyl  $\beta$ -phenylacetate (yield 78%) is dissolved in alcohol and toluene and reduced by adding the solution to a well-agitated emulsion of sodium in toluene. The yield of  $\beta$ -phenylethyl alcohol is 47%, which is increased to 85% by recovery of the phenylacetic acid also produced.

R. B.

**Dependence of Rotatory Power on Chemical Constitution. XXV. Three Optically Active Alcohols containing a Phenyl Group and Some Esters derived therefrom.** L. F. HEWITT and J. KENYON (*J. Chem. Soc.*, 1925, 127, 1094–1104; cf. T., 1911, 99, 49; 1913, 103, 1933; 1914, 105, 1123).—In the optically active alcohols examined, the rotatory power is enhanced by the presence of a phenyl group, but the effect diminishes the farther this group is removed from the asymmetric carbon atom. Whilst for alcohols of the aliphatic series the values of the rotatory dispersion,  $\alpha_{4358}^{20}/\alpha_{5461}^{20}$ , lie between 1.63 and 1.66, for the aromatic alcohols they vary between 1.53 and 1.83 and are very susceptible to temperature changes. The aromatic alcohols show complex rotatory dispersion. The dispersion ratio in the case of seven aromatic secondary alcohols lies below 1.85 (cf. Baly, T., 1908, 93, 1902). In the case of the esters now prepared, the dispersion ratio varies from 1.78 to 2.51, except in one instance.

After passing propionic and  $\beta$ -phenylpropionic acids over thoria at 420°, reduction of the phenylpentanone yields  $\alpha$ -phenyl- $\gamma$ -pentanol, which on heating with phthalic anhydride at 110° is converted into dl- $\alpha$ -phenyl- $\gamma$ -amyl hydrogen phthalate, m. p. 74°; the strychnine salt l-B, d-A, m. p. 158°,  $[\alpha]_{5461} -38.7^\circ$  in chloroform, and cinchonidine salt l-B, l-A, m. p. 154°,  $[\alpha]_{5461} -54.2^\circ$  in ethyl alcohol, are isolated, and from them are obtained the d- and l- $\alpha$ -phenyl- $\gamma$ -amyl hydrogen phthalates as gums,  $[\alpha]_{5461} \pm 42.9^\circ$  in ethyl alcohol. By hydrolysis with sodium hydroxide are produced, respectively, (a) d- $\alpha$ -phenyl- $\gamma$ -pentanol, b. p. 143°/19 mm., m. p. 38°,  $d_4^{20}$  0.9687,  $[\alpha]_{5461}^{30} +23.00^\circ$  (formate, b. p. 135°/15 mm.,  $d_4^{20}$  0.9980,  $[M]_{5461}^{20} -52.59^\circ$ ; acetate, b. p. 147°/19 mm.,  $d_4^{20}$  0.9829,  $[M]_{5461}^{20} -46.76^\circ$ ; propionate,  $d_4^{17.8}$  0.9997), and (b) l- $\alpha$ -phenyl- $\gamma$ -pentanol, b. p. 143°/19 mm., m. p. 38° (propionate, b. p. 150°/14 mm.,  $d_4^{20}$  0.9731,  $[M]_{5461}^{20} +55.31^\circ$ ). By passing n-butyric and  $\beta$ -phenylpropionic acids over thoria at 425°, followed by reduction, is obtained  $\alpha$ -phenyl- $\gamma$ -hexanol; dl- $\alpha$ -phenyl- $\gamma$ -hexyl hydrogen phthalate has m. p. 108°; by fractional crystallisation are obtained the brucine salts, l-B, l-A, m. p. 95°,  $[\alpha]_{5893} -2.1^\circ$  in ethyl alcohol, and l-B, d-A, m. p. 75°,  $[\alpha]_{5893} -12.5^\circ$  in ethyl alcohol; the d- and l- $\alpha$ -phenyl- $\gamma$ -hexyl hydrogen phthalates have m. p. 75°,  $[\alpha]_{5893} \pm 25.5^\circ$ . They yield (a) d- $\alpha$ -phenyl- $\gamma$ -hexanol, b. p. 146°/16 mm., m. p. 34°,  $[\alpha]_{5461}^{20} +20.7^\circ$  in ethyl alcohol (propionate, b. p. 163°/18 mm.,  $d_4^{20}$  0.9629,  $[M]_{5461}^{20} -46.80^\circ$ ), and (b) l- $\alpha$ -phenyl- $\gamma$ -hexanol, b. p. 146°/16 mm., m. p. 34°,  $d_4^{20}$  0.9565,  $[\alpha]_{5461}^{20} -15.06^\circ$ ,  $n_{5461}^{20}$  1.5118 (formate, b. p. 147°/18 mm.,  $d_4^{20}$  0.9872,  $[M]_{5461}^{30} +55.64^\circ$ ; acetate, b. p. 154°/20 mm.,  $d_4^{20}$  0.9725,  $[M]_{5461}^{20} +43.34^\circ$ ). Reduction of phenyl styryl ketone

with sodium amalgam yields  $\alpha\delta$ -diphenyl- $\alpha$ -propanol (m. p.  $45.5^\circ$ , as obtained from a mixture of the *d*- and *l*-isomerides); *dl*- $\alpha\delta$ -diphenyl- $\alpha$ -propyl hydrogen phthalate has m. p.  $110^\circ$ ; the *brucine* salt, *l*-B, *l*-A, has m. p.  $121^\circ$ ,  $[\alpha]_{5893} -8.8^\circ$  in ethyl alcohol, and the *strychnine* salt, *l*-B, *d*-A, has m. p.  $189^\circ$ . The *d*- and *l*- $\alpha\delta$ -diphenyl- $\alpha$ -propyl hydrogen phthalates are obtained as gums,  $[\alpha]_{5893} \pm 8.9^\circ$ . They yield (a) *d*- $\alpha\delta$ -diphenyl- $\alpha$ -propanol, b. p.  $195^\circ/15$  mm., m. p.  $54^\circ$ ,  $d_4^{20}$  1.0661,  $[\alpha]_{5461}^{20} +18.95^\circ$  (formate, b. p.  $195^\circ/15$  mm.,  $d_4^{20}$  1.0790,  $[M]_{5461}^{20} +110.76^\circ$ ; acetate, b. p.  $165^\circ/2$  mm.,  $d_4^{20}$  1.0670,  $[M]_{5461}^{20} +166.8^\circ$ ), and (b) *l*- $\alpha\delta$ -diphenyl- $\alpha$ -propanol, b. p.  $195^\circ/15$  mm., m. p.  $54^\circ$ ,  $[\alpha]_{5461}^{20} -17.9^\circ$  in ethyl alcohol (formate,  $d_4^{164}$  1.0821). From *d*- $\alpha$ -phenyl- $\gamma$ -butanol are prepared the formate, b. p.  $120^\circ/15$  mm.,  $d_4^{20}$  1.0083,  $[M]_{5461}^{20} -42.90^\circ$ , acetate, b. p.  $130^\circ/15$  mm.,  $d_4^{20}$  0.9854,  $[M]_{5461}^{20} +3.30$ ,  $\alpha_{4358}/\alpha_{5461}$ , 0.2 at  $20^\circ$ , and propionate, b. p.  $141^\circ/16$  mm.,  $d_4^{20}$  0.9790,  $[M]_{5461}^{20} -8.08^\circ$ . Hydrolysis of each ester gives the corresponding alcohol unchanged in rotatory power. Tables of densities and of specific and molecular rotations are given.

F. M. H.

**True Derivatives of Diphenylstyrylmethane. VI. Polyaryl-substituted Vinylcarbinols and their Derivatives.** K. ZIEGLER, K. RICHTER, and B. SCHNELL (*Annalen*, 1925, **443**, 161—180; cf. Meyer and Schuster, A., 1922, i, 540; Ziegler, Grabbe, and Ulrich, this vol., i, 131; Straus and Ehrenstein, this vol., i, 534).—By a synthesis which leaves no doubt as to their structure, the authors have shown that the two methyl ethers, m. p.  $97-98^\circ$  and  $78.5-79^\circ$ , respectively, obtained by Straus and Ehrenstein (*loc. cit.*) by the action of sodium methoxide on  $\gamma$ -chloro- $\alpha\gamma$ -triphenyl- $\Delta\beta$ -propylene,  $\text{CHPh}_2\cdot\text{CH}:\text{CClPh}$ , are not stereoisomerides as supposed, but structural isomerides. The higher melting isomeride is obtained by the application of Lipp's method (cf. A., 1923, i, 319) for the preparation of  $\beta$ -bromo- $\alpha\alpha$ -diphenylethyl methyl ether.  $\alpha\alpha\gamma$ -Triphenyl- $\Delta\alpha$ -propylene (Ziegler and others, *loc. cit.*) combines with two atoms of bromine to produce  $\alpha\beta$ -dibromo- $\alpha\alpha\gamma$ -triphenylpropane, m. p.  $94-95^\circ$  (when heated above its melting point this loses 1 mol. of hydrogen bromide, forming  $\beta$ -bromo- $\alpha\alpha\gamma$ -triphenylpropylene), which with boiling methyl alcohol yields the solid  $\beta$ -bromo- $\alpha\gamma\gamma$ -triphenylpropyl methyl ether. This, on further treatment with sodium hydroxide in amyl alcohol, yields the true methyl ether of diphenylstyrylcarbinol,  $\text{OMe}\cdot\text{CPh}_2\cdot\text{CH}:\text{CHPh}$ , m. p.  $78-79^\circ$ , which is proved to be identical with the compound obtained by Straus and Ehrenstein (*loc. cit.*). On oxidation, it gives no trace of the products (methyl ether of mandelic acid and methyl benzoate) obtained from the higher melting  $\alpha\alpha\gamma$ -triphenylallyl methyl ether, but yields the expected products, benzoic acid and the methyl ether of benzilic acid, the latter being isolated as benzilic acid. The same isomeride can also easily be isolated from the crude mixed ethers obtained by the action of sodium methoxide on  $\alpha\alpha\gamma$ -triphenylallyl chloride. The action of magnesium styryl bromide on benzophenone is quite normal, since if the quantity of bromostyrene used is such that there is a 50%

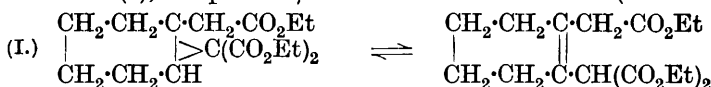
excess of the magnesium compound, a double magnesium compound separates out, and from it pure diphenylstyrylcarbinol, m. p. 109.5—110.5°, is obtained. This carbinol is transformed with extreme ease by methyl alcohol in the presence of minute traces of mineral acids into the methyl ether of the isomeric triphenylallyl alcohol,  $\text{CPh}_3\cdot\text{CH}\cdot\text{CHPh}(\text{OMe})$  (m. p. 97—98°), and this explains the results of Straus and Ehrenstein. By the action of methyl iodide on the potassium derivative of diphenylstyrylcarbinol, its true methyl ether (m. p. 78—79°) is obtained. *Diphenylstyrylmethane*, m. p. 97—98°, b. p. 230°/15 mm., 180°/0.2 mm., is obtained by the action of an excess of magnesium phenyl bromide on cinnamylidene chloride ( $\text{CHPh}\cdot\text{CH}\cdot\text{CHCl}_2$ ) and its structure proved by its reduction to  $\alpha\gamma$ -triphenylpropane, and oxidation to benzoic and diphenylacetic acids. By the addition of alkali to the halochromic solution of the two isomeric carbinols in sulphuric acid, diphenylindene is obtained in quantitative yield and the halochromism is therefore probably not due to the presence of the hypothetical triphenylallene.

J. W. B.

**Condensations of Chloroform, Carbon Tetrachloride, and Iodoform with Resorcinol and Similar Other Hydroxy Aromatic Compounds.** R. N. SEN, N. N. SINHA, and N. N. SARKAR (*J. Indian Chem. Soc.*, 1925, **1**, 303—306).—Resorcinol and other phenols condense with chloroform, carbon tetrachloride, and iodoform in the presence of fused zinc chloride at 180—200° to yield benzeins. *Resorcinol-op-dihydroxybenzein*, orange-yellow, micro-crystalline powder, not melting below 290° (tetra-bromo derivative which dyes wool and silk red), is obtained thus from chloroform, carbon tetrachloride or iodoform and resorcinol; and from the requisite phenols are obtained *pyrogallol-omp-trihydroxybenzein*, not melting below 250°, and *quinol-om-dihydroxybenzein*, not melting below 250°.

J. W. B.

**Ring-chain Tautomerism. XIII. Three-carbon Ring-chain Tautomerism in a Bridged Ring System.** J. W. BAKER (*J. Chem. Soc.*, 1925, **127**, 985—990; cf. T., 1922, **121**, 1765).—Ethyl  $\Delta^1$ -cyclohexeneacetate, b. p. 118—125°/20 mm., combines with bromine, giving *ethyl 1:2-dibromocyclohexane-1-acetate*, which reacts with ethyl sodiomalonate to form *ethyl 2-bromo- $\Delta^1$ -cyclohexene-1-acetate*, b. p. 128—135°/8 mm., which, reacting further with ethyl sodiomalonate, yields *ethyl  $\Delta^1$ -cyclohexene-1-acetate-2-malonate* (I), b. p. 210°/10 mm. This substance (in which the



*cyclopropane* ring is stabilised by the *cyclohexane* ring) exhibits ring-chain tautomerism, as is shown by the preparation of products derived from each form. Thus hydrolysis with alcoholic potassium hydroxide gives  $\Delta^1$ -cyclohexene-1-acetic-2-malonic acid m. p. 210°, in 69% yield; oxidation of the acid with alkaline potassium permanganate gives the lactone of 1:2-dihydroxycyclo-

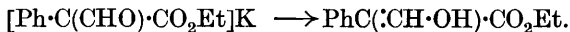
*hexane-1 : 2-diacetic acid* (II), m. p. 187°, and this is also obtained in small yield by hydrolysis of the ozonide of ethyl  $\Delta^1$ -cyclohexene-1-acetate-2-malonate. On the other hand, hydrolysis of (I) with 20% hydrochloric acid gives 2-carboxydicyclo-[3, 1, 0]heptane-1-acetic acid (III), m. p. 186°, in 34% yield; it behaves on titration as a monobasic acid and is stable to potassium permanganate. By 20% hydrochloric acid (II) is converted into (III), whilst by heating at 215° (II) yields  $\Delta^1$ -cyclohexene-1 : 2-diacetic acid, m. p. 122°.

F. M. H.

**Condensation of Nitriles with Thioamides. IV. Thioamides with Phenylimidoacetyl Chlorides.** S. ISHIKAWA (*Sci. Papers, Inst. Phys. Chem. Res.*, 1925, 2, (27), 299—304; cf. A., 1923, i, 926; 1924, i, 639).—Thioacetanilide and acetonitrile react only in presence of a high concentration of hydrochloric acid and give phenylimidoacetyl chloride, and thioacetamide. This is shown to be a reversible reaction,  $\text{CMe}(\text{SH})\cdot\text{NPh} + \text{MeCN} + \text{HCl} \rightleftharpoons \text{CMeCl}\cdot\text{NPh} + \text{CMe}(\text{SH})\cdot\text{NH}$ , by mixing ethereal solutions of the latter two substances in molecular proportions when a 96% yield of thioacetanilide is obtained. Similarly, thioacetamide and phenylimidobenzoyl chloride gave 94% of the theoretical amount of thiobenzanilide. Thiobenzamide and phenylimidoacetyl chloride gave 46% of thioacetanilide, whilst thiobenzamide and phenylimidobenzoyl chloride gave 50% of the theoretical amount of benzonitrile.

F. R.

**Metallic Compounds of the Enolic Forms of Carbonyl Compounds and their Application to Syntheses. III. Action of Carbon Monoxide on Ketone- and Ester-enolates.** H. SCHEIBLER and O. SCHMIDT (*Ber.*, 1925, 58, [B], 1189—1197; cf. A., 1920, i, 366; 1922, i, 426).—Hydrogen is not evolved during the action of potassium on the esters of acetic, butyric,  $\beta$ -phenylpropionic, or  $\beta$ -phenyl- $\alpha$ -benzylpropionic acids, the generated gas being used in the partial hydrogenation of the ester-enolates. On the other hand, ethyl phenylacetate yields about 67.6% of the calculated quantity of gaseous hydrogen, and the ethyl potassio-phenylacetate is therefore more suitable for synthetic application than the other metallic derivatives. All the enolates, with the exception of that derived from  $\beta$ -phenyl- $\alpha$ -benzylpropionic ester, absorb carbon monoxide. Ethyl potassio-phenylacetate yields thereby ethyl formylphenylacetate, which is readily separated from ethyl  $\alpha\gamma$ -diphenylacetoacetate produced simultaneously. The reaction is represented by the scheme:  $[\text{CHPh}\cdot\text{C}(\text{OEt})\cdot\text{O}\cdot]\text{K} + >\text{C}\cdot\text{O} \rightarrow [\text{Ph}\cdot\text{CH}\cdot\text{C}(\text{OEt})\cdot\text{O}\cdot]\text{K} \rightarrow [\text{Ph}\cdot\text{CH}\cdot\text{CO}_2\text{Et}]\text{K} \rightarrow$

$$\left[ \begin{array}{c} \text{Ph}\cdot\text{CH}\cdot\text{C}(\text{OEt})\cdot\text{O}\cdot \\ \text{>>C=O} \end{array} \right] \text{K} \rightarrow \left[ \begin{array}{c} \text{Ph}\cdot\text{CH}\cdot\text{CO}_2\text{Et} \\ \text{>>CO} \end{array} \right] \text{K} \rightarrow$$


With metallic derivatives of the simple fatty esters the separation of the products of the action from the compounds formed by the interaction of metal and ester is extremely difficult and cannot be accomplished satisfactorily even after conversion of the  $\alpha$ -hydroxymethylene compounds which are presumably

*k k\**



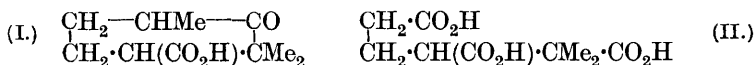
formed into their *O*-acetyl derivatives. Carbon monoxide is also absorbed by the sodio derivative of acetone and the potassio compound from acetophenone with formation in the latter case of hydroxymethyleneacetophenone. To avoid the formation of hydrogen, attempts are described to prepare the enolates by the action of sodium triphenylmethyl on aliphatic esters; the product obtained in this manner from ethyl acetate does not, however, absorb carbon monoxide. H. W.

**Metallic Compounds of the Enolic Forms of Carbonyl Compounds and their Application to Syntheses. IV. Reaction between Ester-enolates and Alkyl or Acyl Halides.** H. SCHEIBLER, E. MARBENKEL, and D. BASSANOV (*Ber.*, 1925, 58, [B], 1198—1204; cf. A., 1920, i, 366; 1922, i, 426, and preceding abstract).—The action of ethyl bromide on ethyl potassioacetate suspended in ether yields ethyl *n*-butyrate so that *C*-substitution appears to be the normal course of the alkylation of esters and not to depend on the presence of any activating group. Under similar conditions, ethyl potassio-phenylacetate and ethyl bromide give ethyl  $\alpha$ -phenyl-*n*-butyrate. With acetyl chloride and ethyl potassio-phenylacetate, both *C*- and *O*-derivatives are formed, the products being ethyl  $\alpha$ -phenylacetoacetate (characterised as 1 : 4-diphenyl-3-methyl-5-pyrazolone) and the acetate of the enolic form of ethyl phenylacetate, which is hydrolysed by dilute aqueous potassium hydroxide to potassium acetate and ethyl phenylacetate. Ethyl chloroformate and ethyl potassio-phenylacetate yield exclusively the compound  $\text{CHPh}\cdot\text{C}(\text{OEt})\cdot\text{O}\cdot\text{CO}_2\text{Et}$ , b. p. 155—160°/18 mm.,  $d_{20}^{20}$  1.0970,  $d_4^{20}$  1.0950,  $n_D^{20}$  1.49766, which is readily hydrolysed to ethyl phenylacetate and potassium ethyl carbonate. Attempts to reduce the substance by sodium or aluminium amalgam or in the presence of platinum or palladium were unsuccessful. H. W.

**Isomerisation of *O*-Acyl into *C*-Acyl Compounds under the Catalytic Influence of Noble Metals. I.** H. SCHEIBLER (*Ber.*, 1925, 58, [B], 1205—1208).—Attempts to hydrogenate the product  $\text{CHPh}\cdot\text{C}(\text{OEt})\cdot\text{O}\cdot\text{CO}_2\text{Et}$  (obtained by the action of ethyl chloroformate on ethyl potassio-phenylacetate) in the presence of palladised charcoal gave considerable quantities of ethyl phenylmalonate. The presence of hydrogen is not essential to the change, which is more efficiently catalysed by spongy platinum. Attempts to effect a similar transformation with phenyl ethyl carbonate were unsuccessful. H. W.

**Action of Ammonia on Ethyl Cinnamate.** K. STOSIUS and E. PHILIPPI (*Monatsh.*, 1925, 45, 569—572).—By keeping a mixture of ethyl cinnamate (14 g.) and liquid ammonia (5 c.c.) in a sealed tube at the ordinary temperature for 4 months, the following products were obtained: cinnamamide, m. p. 142°;  $\beta$ -amino- $\beta$ -phenylpropionic acid, m. p. 221—222° (slow heating) or 231° (rapid heating); and  $\beta$ -amino- $\beta$ -phenylpropionamide, m. p. 88—110° [oxalate (+2H<sub>2</sub>O)], m. p. 193° (anhydrous)], which loses ammonia when boiled with water, yielding cinnamamide. F. G. W.

**Formation of *d*-2 : 2 : 4-Trimethylcyclohexan-3-one-1-carboxylic Acid from *d*-Camphorquinone.** C. S. GIBSON and J. L. SIMONSEN (*J. Chem. Soc.*, 1925, **127**, 1294—1303; cf. Manasse and Samuel, A., 1898, i, 147; 1903, i, 45).—The keto-acid formed by the action of sulphuric acid on camphorquinone has the structure (I) since oxidation with nitric acid gives  $\beta$ -methylpentane-



$\beta\gamma\epsilon$ -tricarboxylic acid (II). The hydroxy-acid (III) formed by reduction with sodium amalgam gives no lactone and must therefore be the *trans*-form. The unsaturated ester obtained, in addition to a chloro-ester, by treatment of the methyl ester of the hydroxy-acid with phosphorus pentachloride is given the formula (IV), the acid obtained on hydrolysis being an oil, laevorotatory in alcoholic solution.

The keto-acid, *d*-2 : 2 : 4-trimethylcyclohexan-3-one-1-carboxylic acid, tending to separate as an oil, was purified through the methyl ester (*oxime*, m. p. 110—111°). The crystalline form of the latter is always accompanied by a liquid ester, the whole distilling as a homogeneous substance. The latter is assumed to consist of an equilibrium mixture of the keto and enol forms, since a mixture of the same two  $\alpha$ - and  $\beta$ -semicarbazones is obtained from either form of the methyl ester. The crystalline form has  $[\alpha]_{5461}^{15} + 64.33^\circ$  in alcohol. Hydrolysis of the ester yields an acid showing non-homogeneity, owing to racemisation in alkaline solution accompanying enol-keto change which involves one of the two asymmetric carbon atoms. The two main fractions give the following constants : (1) m. p. 71—72°,  $[\alpha]_{5461}^{15} + 47.4^\circ$  in alcohol; in slight excess of aqueous sodium hydroxide  $+ 22.2^\circ$ , changing to the constant value  $+ 15.1^\circ$  in 48 hrs.; (2) m. p. 67—69°,  $[\alpha]_{5461}^{15} + 18.7^\circ$  in alcohol; in alkali  $+ 8.1^\circ$ , changing to constant value  $+ 5.1^\circ$ . The  $\alpha$ -oxime, prepared in alkaline solution, has m. p. 164—165°. The  $\beta$ -oxime, prepared in alcoholic solution, has m. p. 226°.

The  $\alpha$ -semicarbazone of the methyl ester, leaflets sintering at 229—230°, decomp. at 231°, shows slight mutarotation in acetic acid solution, changing from  $[\alpha]_{5461}^{15} - 55.8^\circ$  to the constant value  $- 50.5^\circ$  in 48 hrs. The  $\beta$ -semicarbazone, m. p. 161—162°, is unstable and tends to pass into the  $\alpha$ -form in presence of acetic acid (cf. Forster, T., 1905, **87**, 237). It gives considerable mutarotation (absent in alcohol), passing from a lower to a higher constant value representing the rotation of the equilibrium mixture :  $[\alpha]_{5461}^{15} - 38.2^\circ$ ,  $- 53.5^\circ$ ,  $- 50.2^\circ$  (after 60 hrs.). Mixtures of the two forms give an initial rotation higher than any recorded for the pure forms separately, afterwards falling to the constant value. The formation of an intermediate compound (? salt formation) in the conversion of the  $\beta$ - into the  $\alpha$ -form is tentatively suggested. Hydrolysis of

the semicarbazones gives a mixture of crystalline and liquid methyl ester.

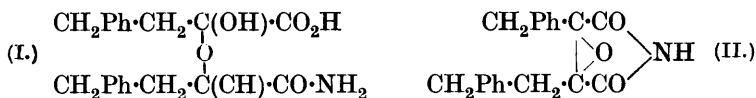
The *trans*-hydroxy-acid (III) gives  $[\alpha]_{5461}^{15} +43.6^\circ$  in alcohol (methyl ester, b. p.  $150-152^\circ/12$  mm.). The unsaturated ester (IV), methyl 1-2 : 2 : 4-trimethyl- $\Delta^3$ -cyclohexene-1-carboxylate, b. p.  $105-107^\circ/14$  mm., gives the acid, b. p.  $150-152^\circ/16$  mm.,  $[\alpha]_{5461}^{15} -38.5^\circ$  in alcohol (ammonium salt, decomp.  $147-148^\circ$ ; calcium, barium, and silver salts, sparingly soluble in water). M. J.

**Optically Active Boron.** J. MEULENHOF (Z. anorg. Chem., 1925, **142**, 373—382; cf. A., 1924, i, 776).—The auto-racemisation of the strychnine salt of borodisalcyclic acid in chloroform solution is due to hydrolysis resulting from the small quantity of water remaining in the solution. L. J. H.

**Tervalent Vanadium.** G. SCAGLIARINI and A. AIROLDI (Gazzetta, 1925, **55**, 44—48).—The following complex compounds of trivalent vanadium are described: *vanadicamphoryl camphorate*,  $\{V_3(OH)[C_8H_{14}(CO_2)_2]_3\}C_8H_{14}(CO_2)_2 \cdot 2H_2O$ , prepared from vanadous sulphate and ammonium camphorate, a greenish-grey precipitate corresponding in composition with Weinland and Paschen's ferri-camphoryl camphorate (cf. A., 1916, i, 315); *vanadicinnamyl cinnamate*,  $[V_3(OH)_4(CHPh \cdot CH \cdot CO_2)_4]CHPh \cdot CH \cdot CO_2$ , greenish-yellow; *vanadisalcyclic acid*,  $[V(C_6H_4 \cdot \overset{O}{\underset{CO_2}{\text{C}}})_2]H \cdot 3H_2O$ , greenish-yellow, turning green and then black in the light; *vanadium pyridine sulphate*,  $V(C_5H_5N)_2(H_2O)_3SO_4 \cdot HSO_4$ , emerald-green crystals; vanadium trifluoride,  $VF_3 \cdot 3H_2O$ , obtained by reducing a suspension of vanadic anhydride in hydrofluoric acid by means of sulphur dioxide and submitting the resulting oily vanadyl fluoride to electrolytic reduction (cf. Petersen, A., 1889, 107, 1123). T. H. P.

**Halogen Compounds of Tyrosine.** R. ZEYNEK (Z. physiol. Chem., 1925, **144**, 246—254).—Cautious treatment with chlorine at low temperatures of tyrosine in aqueous suspension or, much better, in acetic acid solution leads to the formation of colourless halogen compounds. By repeated recrystallisation a small yield of monochlorotyrosine was obtained. When tyrosine is suspended in acetic acid and sulphuryl chloride added, a good yield (81—82%) of monochlorotyrosine hydrochloride is obtained, giving monochlorotyrosine in 90—95% yield. *Chlorotyrosine*, m. p.  $256-257^\circ$ , forms a *benzoyl* derivative, m. p.  $195^\circ$ ; *formyl* derivative, m. p.  $198^\circ$ . With bromine in acetic acid, it gives *chlorobromotyrosine*, m. p.  $252-4^\circ$ ; with nitric acid in acetic acid, *chloronitrotirosine*, m. p.  $208-210^\circ$ . Similarly, *p*-hydroxyphenylethylamine in acetic acid with sulphuryl chloride gives *chloro-p-hydroxyphenylethylamine hydrochloride*, m. p.  $210^\circ$ ; free base, m. p.  $125^\circ$ . Bromotyrosine, prepared by adding bromine very gradually to a well-cooled suspension of finely-powdered tyrosine in formic acid, has m. p.  $246-249^\circ$  (decomp.) (cf. Rosenmund, A., 1923, i, 1095); *bromo-nitrotirosine* has m. p.  $204-206^\circ$ . P. W. C.

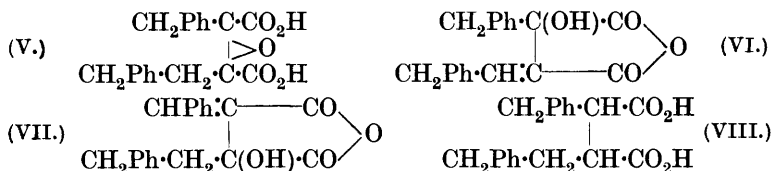
**$\alpha$ -Hydroxy- $\gamma$ -phenylcrotonamide.** J. BOUGAULT (*Compt. rend.*, 1925, **180**, 1944—1946).—The acid amide (I) previously obtained (A., 1913, i, 269), on oxidation with potassium permanganate, yields the imide (II), and not the symmetrical compound previously described (A., 1913, i, 366). Treated with sodium



hydroxide the imide (II) yields  $\alpha$ -keto- $\gamma$ -phenyl-*n*-butyric acid and  $\beta$ -phenylpropionic acid, and with sodium carbonate the *acid amide* (III) or (IV), m. p.  $170^\circ$ , and the corresponding *dibasic acid* (V),

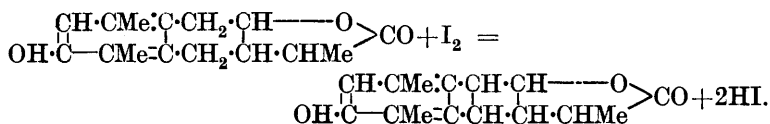


m. p.  $204^\circ$ , giving an *anhydride*, m. p.  $104^\circ$ , and on long treatment with acetic anhydride an *anhydride*, m. p.  $75^\circ$ , to which the constitution (VI) or (VII) has been ascribed. This anhydride gives a

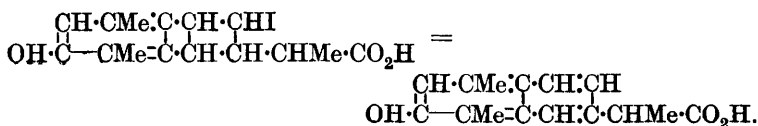


*methyl ester*, m. p.  $53^\circ$ , and on reduction  $\alpha$ -benzyl- $\beta$ -phenylethylsuccinic acid (VIII), m. p.  $170^\circ$ .  
L. F. H.

**Genesis of Artemisic Acid from Desmotroposantonin.** P. BERTOLO (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 436—439).—In the formation of artemisic acid from desmotroposantonin by the action of iodine in acetic acid solution (cf. this vol., i, 546), the iodine probably acts first on the tetrahydrogenated ring containing the lactonic grouping,



The action of the hydrogen iodide formed would then rupture the lactonic linking with formation of an unstable iodinated compound, which would yield artemisic acid by loss of hydrogen iodide:



That the genesis of artemisic acid from santonin derivatives requires the formation of an intermediate compound resulting from the opening of the lactonic linking, as with desmotroposantonin, explains the non-formation of artemisic acid from santonous acid under similar treatment.

T. H. P.

**Attempts to Prepare a Methylhydroxyethylmaleic Acid.**

**I. Derivatives of cycloPropanedicarboxylic Acid.** W. KÜSTER and F. GRASSNER. **II. Derivatives of Acetylcyclopropanedicarboxylic Acid.** W. KÜSTER (*Z. physiol. Chem.*, 1925, **145**, 45—52; 53—68).—I. With a view to determine by synthesis the constitution of the methylmethoxyethylmaleimide obtained by the oxidation of hæmatoporphyrin dimethyl ether (A., 1915, i, 853), an attempt was made to prepare methyl- $\beta$ -methoxyethylmaleic acid, by substitution of the bromine of ethyl bromoethylmalonate by the methoxyl group, making the acetyl derivative, converting the latter into the cyanohydrin, hydrolysing and eliminating the elements of water. The object was not attained because the bromine of ethyl bromoethylmalonate could not be displaced without regeneration of a cyclopropane derivative. Condensation of ethyl acetylmalonate with ethylene dibromide gave ethyl cyclopropanedicarboxylate, which was also obtained after the action of sodium ethoxide, acetyl chloride, and ammonia on ethyl bromoethylmalonate; in the case of ammonia, there were further isolated *ethyl cyclopropanedicarboxymonoamide*, m. p. 125°, and *cyclopropanedicarboxylamide*, needles, m. p. 189—190°; the latter, on boiling with mercuric oxide, gave a characteristic *mercury* compound. On heating ethyl bromoethylmalonate with aniline, there was obtained the *dianilide* of cyclopropanedicarboxylic acid, m. p. 196°, which, on hydrolysis with hydrobromic acid, gave *cyclopropanedicarboxylic acid* and *1-phenyl-5-pyrrolidone-4-carboxylic acid*, m. p. 64—65°.

II. On treating acetylcyclopropanedicarboxylic acid in ethereal solution with potassium cyanide and concentrated hydrochloric acid there was obtained the *cyanohydrin* in a state of 80% purity; on heating this product at 130—140° with hydrobromic acid, there resulted a mixture of about 70% of *methylbromoethylmaleic anhydride* and 30% of *methylvinylmaleic anhydride* which could not be separated, together with a small amount of the *lactone* of *methylhydroxyethylfumaric acid*, m. p. 202—203°; the last substance, which was not obtained quite free from bromine, gave, on treatment with ammonia in ethereal solution, a *substance*,  $C_7H_{14}O_4N_2$ , m. p. 216°, which in turn, on subjection to steam distillation, yielded a non-volatile residue of the *monoamide* of *methylhydroxyethylfumaric acid*, m. p. 210°. On hydrolysis of the above cyanohydrin with hydriodic acid, there were identified among the products of the reaction *trans*-methylethylsuccinic acid and methyl- $\beta$ -iodoethylmaleic anhydride. The product of the hydrobromic acid hydrolysis was saturated with hydrogen bromide in ethereal solution and the product, containing almost the theoretical bromine for methylbromoethylmaleic anhydride, was heated with sodium methoxide;

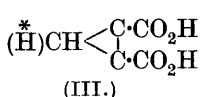
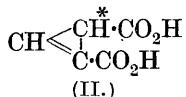
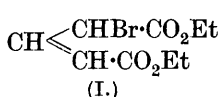
by fractional distillation of the products of this reaction there were obtained two fractions, both giving figures on analysis in close agreement with those required by methylmethoxyethylmaleic anhydride, but differing from the latter substance in boiling point and in giving no precipitate with ammonia in ethereal solution.

Ethyl bromoethylacetoacetate, prepared by treating ethyl acetyl-cyclopropanecarboxylate with hydrobromic acid at 0°, gave with ammonia the *acetylcyclopropanecarboxylamide*, m. p. 89°. With phenylhydrazine, this gave a *phenylhydrazone*, m. p. 137°, which on heating with hydrochloric acid lost ammonia to give a mixture of the keto form (needles, m. p. 98°) and the enol form (rhombohedra, m. p. 138°) of 1-*phenyl-3-dimethylene-4-methylpyrazolone hydrochloride*; the free base has m. p. 72—73°. Ethyl acetylcyclopropanecarboxylate forms a *semicarbazone*, m. p. 126—127°, and an *oxime*, needles, m. p. 77—78°.

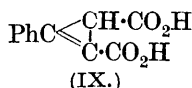
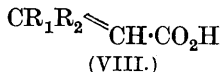
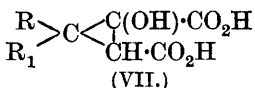
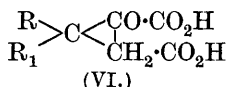
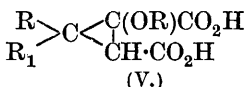
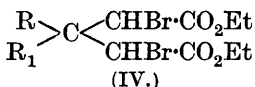
C. R. H.

### Conditions underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives.

**VII. Influence of the Phenyl Group on the Formation of the *cycloPropene* Ring.** W. HAERDI and J. F. THORPE (*J. Chem. Soc.*, 1925, 127, 1237—1248; cf. T., 1923, 123, 330).—*cycloPropene* ring formation occurs only when the ring produced is of the glutaconic type, containing a mobile hydrogen atom, enabling it to pass into the semi-aromatic form. Thus, the acid (II) (semi-aromatic form (III)—mobile hydrogen \*) is readily obtained from ethyl  $\alpha$ -bromoglutaconate (I). Should conditions prohibit the

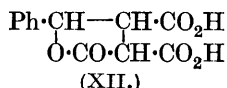
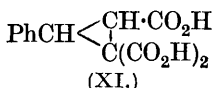
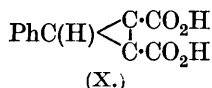


existence of this mobile hydrogen, the unsaturated bond cannot be introduced into the *cyclopropane* ring. Hence dibromo-esters of type (IV), losing hydrogen bromide (2 mols.) give either the alkoxy derivative (V), the keto-acid (VI), or the hydroxy-ring acid (VII) depending on the value of the group  $\text{RR}'$  (reaction I) or else undergo fission to an acid of type (VIII) and oxalic acid (reaction II).



The authors attempted to obtain further evidence of the structure of the aromatic ring type by preparation of an acid (IX) [semi-aromatic form (X)], since the phenyl group in the  $\beta$ -position

might be expected to stabilise the latter form. The acid was not obtained, as abnormal reaction took place in every case.



*Methyl αα'-dibromo-β-phenylglutarate*, m. p. 82.5—83.5°, b. p. 215—220°/20 mm. (free acid, m. p. 192—193°) undergoes both reactions (I) and (II), yielding 2-ethoxy-3-phenylcyclopropane-1:2-dicarboxylic acid, m. p. 198—199° (methyl ester, b. p. 175—179°/13 mm.; ethyl ester, b. p. 184—190°/14 mm.), cinnamic acid, and oxalic acid. The lactone of ethyl α-bromo-α'-hydroxy-β-phenylglutarate, b. p. 230—234°/21 mm., gives the same hydrolysis products. *Methyl α-bromo-β-phenylglutarate*, m. p. 83—83.5°, on treatment with potassium hydroxide, does not yield 3-phenylcyclopropane-1:2-dicarboxylic acid, but is quantitatively converted into β-phenylglutaric acid. The bromine atom is similarly removed by hot pyridine. By bromination of the cyclopropane acid, prepared by Kötze and Stalman's method (A., 1907, i, 707), the authors obtain monomethyl 1-bromo-3-phenylcyclopropane-1:2-dicarboxylate, m. p. 175—176°; the dimethyl ester, an oil decomposing on distillation, and a compound, m. p. 227—228°, believed to be a monobromo or a bromolactonic acid. Hydrolysis of either ester, however, instead of eliminating hydrogen bromide, replaces bromine, regenerating the original acid. An attempt to prepare the acid (XI), preparatory to obtaining its bromo derivative, showed that the compound thus described (Buchner, A., 1892, 849) prepared by hydrolysis of the triethyl ester, is actually carboxyphenylparaconic acid (XII). The acid (IX) is not obtained by hydrolysis of the product formed by elimination of hydrogen bromide from ethyl α-carbethoxy-α'-bromo-β-phenylglutamate, but deep-seated decomposition gives benzoylisosuccinic acid.

An acid,  $\text{C}_{14}\text{H}_{12}\text{O}_6$ , m. p. 171—172°, obtained from ethyl dibromocinnamate and ethyl sodiomalonate is described. It is converted, on boiling with hydrochloric acid, into phenylparaconic acid, and probably contains a lactone ring. M. J.

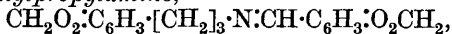
**Action of Magnesium Methyl Iodide on Esters of Camphoric Acid α-Mononitrile.** A. HALLER and F. S. LEGAGNEUR (*Compt. rend.*, 1925, 180, 1621—1624; cf. this vol., i, 683).—Magnesium methyl iodide in anhydrous ethereal solution reacts with the o-tolyl ester of camphoric acid α-mononitrile, yielding a mixture of o-cresol, β-3-cyano-2:2:3-trimethylcyclopentylisopropyl alcohol (large, flat prisms, m. p. 93—94°,  $[\alpha]_D^{20} + 78.3^\circ$ , benzyl derivative, m. p. 169—170°), and a substance,  $\text{C}_{11}\text{H}_{17}\text{ON}$ , tetrahedra, subliming without fusion at 100°. Under the same conditions, magnesium methyl iodide reacts with the methyl ester of camphoric acid α-mononitrile, yielding the two last-named products; in boiling toluene solution, however, the Grignard reagent reacts with the nitrile group as well as the ester group, giving a ketonic tertiary alcohol, β-3-acetyl-2:2-dimethylcyclopentylisopropyl alcohol, m. p.

95—96°, *semicarbazone*, m. p. 221—222°. On heating the toluene solution of this ketonic alcohol very strongly, or on treating it with phenylcarbimide, it is dehydrated, giving  $\beta$ -3-*acetyl*-2 : 2-*dimethylcyclopentylpropylene*, liquid,  $[\alpha]_D^{25} + 40.7^\circ$ , *oxime*, m. p. 103—104°, *semicarbazone*, m. p. 229—230°, which, on oxidation with potassium permanganate, yields the diketone, 1 : 3-*diacetyl*-2 : 2-*dimethylcyclopentane*, b. p. 154—156°/19 mm., *disemicarbazone*, m. p. 305—307° (decomp.).

The following new esters of camphoric acid  $\alpha$ -mononitrile have been prepared in the same way as the methyl ester (*loc. cit.*) from benzyl alcohol, and the sodium derivatives of phenol and *o*- and *p*-cresol: *phenyl* ester, m. p. 76—77°,  $[\alpha]_D^{25} + 30.5^\circ$  in benzene, *o*-*tolyl* ester, m. p. 99—100°,  $[\alpha]_D^{25} + 25.1^\circ$  in benzene, *p*-*tolyl* ester, m. p. 96—97°,  $[\alpha]_D^{25} + 28.9^\circ$  in benzene, *benzyl* ester, b. p. 223°/17 mm.,  $[\alpha]_D^{25} + 56.5^\circ$  in benzene,  $[\alpha]_D^{30} + 59.4^\circ$  in alcohol. L. F. H.

### $\beta$ -Piperonylpropionitrile and Some Derived Substances.

W. BAKER and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 1424—1433).— $\beta$ -*Piperonylpropionitrile* is formed by thermal decomposition of  $\alpha$ -cyano- $\beta$ -piperonylpropionic acid in presence of copper powder; it has m. p. 33°, b. p. 186—187°/18—20 mm., and on treatment with a warm, alkaline solution of hydrogen peroxide is converted into  $\beta$ -piperonylpropionamide. By nitration of  $\beta$ -piperonylpropionitrile in acetic acid solution there is produced  $\beta$ -6-*nitropiperonylpropionitrile*, m. p. 113°, which on boiling with concentrated hydrochloric acid gives  $\beta$ -6-*nitropiperonylpropionic acid*, m. p. 153—153.5°. Reduction of  $\beta$ -6-*nitropiperonylpropionitrile* with tin and a mixture of acetic and hydrochloric acids yields a feebly basic substance, m. p. 230°, which appears to be identical with the ethylamidopiperonyl- $\omega$ -carboxylic anhydride, m. p. 235°, prepared by F. M. Perkin (*T.*, 1891, 59, 159) by reduction of ethyl 6-nitropiperonylacrylate. When  $\beta$ -piperonylpropionitrile in alcoholic solution is treated with sodium, there is obtained, in 85% yield,  $\gamma$ -*piperonylpropylamine*, b. p. 160—161°/14 mm.,  $d_4^{16} 1.141$ , which on exposure to air gives a *carbonate*, m. p. 92—94°; the *hydrochloride* has m. p. 206—208°, and the *acetyl* derivative, m. p. 89°. *Piperonylidene- $\gamma$ -piperonylpropylamine*,

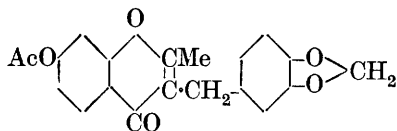


m. p. 79.5°, is produced by heating a mixture of the amide and piperonal. On treatment of  $\gamma$ -piperonylpropylamine with methyl iodide and alcoholic sodium ethoxide, there is formed a quaternary compound,  $\gamma$ -*piperonylpropyltrimethylammonium iodide*, m. p. 146°, which can be converted into its corresponding hydroxide, and this, on decomposition by heating at 160°, yields *isosafrole* (yield 60% on weight of iodide).

*Homopiperonylresacetophenone* (2 : 4-*dihydroxyphenyl*  $\beta$ -*piperonyl-ethyl ketone*), m. p. 130°, is prepared by saturating an ethereal solution of  $\beta$ -piperonylpropionitrile and resorcinol with hydrogen chloride at 0° and keeping at this temperature for 48 hrs., the mixture being somewhat diluted with ether during this period. Methyl sulphate converts it into its *monomethyl ether* (homopiperonyl-



pæanol), m. p. 89—90° (cf. Tognazzi, A., 1924, i, 1324, who gives the m. p. 85—87°). Acetylation of homopiperonylresacetophenone by boiling acetic anhydride in presence of sodium acetate gives an excellent yield of 7-acetoxy-3-homopiperonyl-2-methylchromone (annexed formula). This occurs



in two forms, the  $\alpha$ -variety, as prepared above, having m. p. 101·5°, then solidifying, and melting at 119·5° ( $\beta$ -form). When the acetyl derivative is hydrolysed with dilute sodium carbonate solution it is converted into 7-hydroxy-3-homopiperonyl-2-methylchromone; this also occurs in  $\alpha$ - and  $\beta$ -forms having m. p. 214—215° and 222—223°, respectively. This phenol forms a methyl ether, m. p. 124—125°, giving a dibromide, of indefinite m. p., which on boiling with alcohol yields a compound, m. p. 206—207°, which may be a bromo-derivative of the methyl ether.

By an application of the method of Lapworth and McRae (T., 1922, **121**, 1699), a quantitative yield of  $\alpha$ -cyano- $\beta$ -veratrylacrylic acid is obtained from veratraldehyde; it has m. p. 201—202°, and when crystallised from methyl alcohol contains 1 mol. of solvent of crystallisation; on reduction, it is converted into  $\alpha$ -cyano- $\beta$ -veratrylpropionic acid, m. p. 139°. The following substances are prepared by the methods used for the piperonyl analogues:  $\beta$ -veratrylpropionitrile, b. p. 194—195°/17 mm., m. p. 46·5°; homoveratrylresacetophenone, m. p. 146—147°; 7-acetoxy-3-homoveratryl-2-methylchromone, m. p. 140·5°; 7-hydroxy-3-homoveratryl-2-methylchromone, m. p. 183—184°; 7-methoxy-3-homoveratryl-2-methylchromone, m. p. 108°. C. J. S.

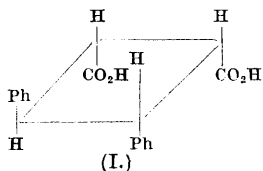
**Synthesis of 3:5-Dihydroxycinnamic Acid.** F. MAUTHNER (*J. pr. Chem.*, 1925, [ii], **110**, 125—128).—3:5-Dihydroxycinnamic acid, m. p. 245—246°, is obtained by heating an alcoholic solution of 3:5-dihydroxybenzaldehyde and malonic acid in presence of piperidine, and after distillation of the alcohol, warming to complete the evolution of carbon dioxide. Similarly, from 3:5-dimethoxybenzaldehyde is prepared 3:5-dimethoxycinnamic acid, m. p. 175—176°. By warming 3:5-dimethoxybenzaldehyde and hippuric acid with acetic acid and sodium acetate, there is formed an azlactone, m. p. 156—157°, which on treatment with sodium hydroxide, followed by hydrogen peroxide, gives benzoic acid and 3:5-dimethoxyphenylacetic acid, m. p. 99—100°. By melting together 2:6-dimethoxyphenol and chloral hydrate, with addition of potassium carbonate, there may be isolated, after 2 months, a 2-hydroxy-1:3-dimethoxyphenyltrichloromethylcarbinol, m. p. 162—163°. F. M. H.

**[So-called] 2:7:9:9-Tetrahydroxyfluorene.** C. COURTOT and R. GEOFFROY (*Compt. rend.*, 1925, **180**, 1665—1667; cf. A., 1924, i, 956).—The constitution 2:7:9:9-tetrahydroxyfluorene has been assigned by Schmidt, Retzlaff, and Haid (A., 1912, i, 695) to the product of alkaline fusion of sodium fluorene-2:7-disulphon-

ate, but this substance is identical with 4:4'-dihydroxydiphenyl-2-carboxylic acid. It forms a tribenzoyl derivative, not a tetrabenzoyl compound as stated by the previous investigators. When decomposed by lime it yields 4:4'-dihydroxydiphenyl, and 2:7:9:9-tetrachlorofluorene by the action of phosphorus pentachloride. 2:7-Dihydroxyfluorenone, m. p. 338°, dibenzoate, yellow, m. p. 241°, oxime, m. p. 300°, is obtained by treating the substance with zinc chloride. Fluorenemonosulphonic acid when fused with alkalis gives, in an analogous manner, 4-hydroxydiphenyl-2-carboxylic acid, m. p. 180°, which, on treatment with dehydrating agents, gives 2-hydroxyfluorenone, m. p. 211°.

L. F. H.

**$\zeta$ -Truxinic Acid. IX.** R. STOERMER and P. KLOCKMANN (*Ber.*, 1925, 58, [B], 1164—1178).—The resolution of  $\zeta$ -truxinic acid into its optical antipodes (Stoermer and Scholtz, A., 1921, i, 180) has led to assigning to it the constitution (I) since among *cis*-acids of this series this is the only configuration with which optical isomerism is theoretically possible. Similarly, only an acid of this constitution can give rise to isomeric alkyl hydrogen esters, semi-amides, etc., and the

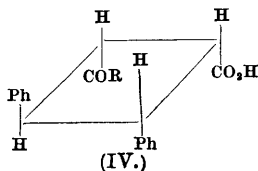
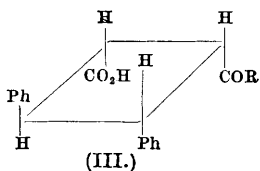
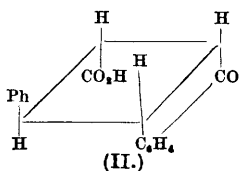


conception of the constitution of  $\zeta$ -truxinic acid is therefore confirmed by the isolation of such a series of compounds from it.

Methyl hydrogen *a*- $\zeta$ -truxinate, m. p. 198° [instead of 168° recorded previously (*loc. cit.*)], is obtained as by-product of the esterification of  $\zeta$ -truxinic acid by methyl alcohol and hydrogen chloride or by boiling  $\zeta$ -truxinic anhydride with methyl alcohol. *a*- $\zeta$ -Truxinanilic acid from the  $\zeta$ -anhydride and aniline has m. p. 214° (instead of 209°). The product obtained by the action of alcoholic potassium hydroxide on  $\zeta$ -truxinphenylimide is a mixture of  $\delta$ -truxinanilic acid, m. p. 225°, and *b*- $\zeta$ -truxinanilic acid, m. p. 237°; protracted action of alcoholic potassium hydroxide converts the latter acid quantitatively into  $\delta$ -truxinanilic acid, which is itself unchanged under these conditions. The two  $\zeta$ -truxinanilic acids are sharply differentiated from one another, since the *a*-acid in contrast to the *b*-acid yields a freely-soluble *sodium* salt, and is not isomerised to the  $\delta$ -anilic acid by cold alcoholic potassium hydroxide. Esterification of the *b*-anilic acid with methyl alcohol and hydrogen chloride, diazomethane, or methyl sulphate and alkali leads without configurational change to *a*-methyl *b*- $\zeta$ -truxinanilate, m. p. 244°. If the *a*-anilic acid is esterified with diazomethane or methyl sulphate, the corresponding *b*-methyl *a*- $\zeta$ -truxinanilate, m. p. 234°, is obtained. If, however, methyl alcohol and hydrogen chloride are employed, a mixture of esters results from which only the isomeric *a*-methyl *b*- $\zeta$ -truxinanilate, m. p. 244°, can be isolated; doubtless,  $\zeta$ -truxinanil is formed intermediately, since it also yields this ester when treated with methyl alcohol and hydrogen chloride. Hydrolysis of either ester by alcoholic potassium hydroxide yields a mixture of  $\delta$ -truxinanilic acid and *b*- $\zeta$ -truxinanilic acid, m. p. 237°,  $\zeta$ -truxinanil being probably pro-

duced intermediately. Hydrolysis of the esters in such a manner as to remove the anilic group only without causing isomerisation can be effected by use of their nitroso derivatives (the method has been worked out for the  $\gamma$ -acids by Fretwurst, *Diss.*, Rostock, 1923). Thus the stable *nitroso* derivative of *b*- $\zeta$ -truxinanilic acid loses mainly nitrous acid when heated and gives  $\zeta$ -truxinanyl, whereas it is transformed by cold potassium hydroxide into  $\zeta$ -truxinic acid. *a*- $\zeta$ -Truxinanilic acid gives a very unstable *nitroso* compound, which is converted by alkali hydroxide or warm water into benzenediazonium hydroxide and homogeneous  $\zeta$ -truxinic acid. The *nitroso* compounds from *b*-methyl *a*- $\zeta$ -truxinanilate and *a*-methyl *b*- $\zeta$ -truxinanilate are smoothly converted by hot sodium carbonate solution (10%) into methyl hydrogen *a*- $\zeta$ -truxinate, m. p. 198°, and methyl hydrogen *b*- $\zeta$ -truxinate, m. p. 201°, respectively. If the esters are treated successively with thionyl chloride and aniline they re-form *b*-methyl *a*- $\zeta$ -truxinanilate and *a*-methyl *b*- $\zeta$ -truxinanilate, respectively, thus proving that hydrolysis of the ester group has not occurred during the cycle. Treatment of the chlorides obtained from the isomeric hydrogen esters with ammonia gives respectively *b*-methyl *a*- $\zeta$ -truxinamate, m. p. 212°, and *a*-methyl *b*- $\zeta$ -truxinamate, m. p. 195°. The latter compound can also be obtained from *b*- $\zeta$ -truxinamic acid by esterification with diazomethane or by the action of methyl iodide on the silver salt, but not by means of methyl alcohol and hydrogen chloride or methyl sulphate and alkali. *a*- $\zeta$ -Truxinamic acid, m. p. 204°, is prepared by the action of dry gaseous ammonia on a solution of  $\zeta$ -truxinic anhydride in benzene; it is readily hydrolysed by boiling 50% acetic acid to  $\zeta$ -truxinic acid, whereas the isomeric *b*-acid is much more slowly and, probably, not quantitatively converted into  $\zeta$ -truxinic acid under these conditions. Both amic acids are smoothly converted into  $\zeta$ -truxinic acid by the action of nitrous fumes in the presence of glacial acetic acid. In contrast to the *b*-acid, the *a*-acid is readily esterified by methyl sulphate and alkali to *b*-methyl *a*- $\zeta$ -truxinamate, m. p. 212°. Either ester dissolved in glacial acetic acid is smoothly converted by nitrous fumes into the corresponding methyl hydrogen  $\zeta$ -truxinate.

The constitutions of the pairs of isomeric derivatives is elucidated in the following manner.  $\zeta$ -Truxinyl chloride is converted by successive treatment with aluminium chloride and sodium carbonate into " *$\zeta$ -semitruxinonic acid*," m. p. 158°, to which the constitution (II) must be ascribed, since it behaves as a saturated, monobasic



acid and yields an *oxime*, m. p. 220° and a *methyl* ester, m. p. 88°; it could not be converted into  $\zeta$ - or  $\delta$ -truxinic acid by molten

potassium hydroxide. If the same series of reactions is applied to the chlorides derived from the isomeric methyl hydrogen  $\zeta$ -truxinates, it is found that the *b*-methyl compound yields methyl  $\zeta$ -semitruxionate, m. p.  $88^\circ$ , whereas a homogeneous compound cannot be obtained from the *a*-methyl ester. The *a*-carboxyl group must therefore be directly vicinal to the phenyl group, to which the *b*-carboxyl group is in the diagonal position. The constitutions (III) and (IV) are therefore assigned to the *a*-hydrogen esters, semi-amides, etc., and to the corresponding *b*-derivatives, respectively. H. W.

**Action of Phosphorus Pentachloride on 2-Oximino-1-hydrindones.** R. D. HAWORTH and H. S. PINK (*J. Chem. Soc.*, 1925, 127, 1368—1371; cf. Perkin and Robinson, T., 1907, 91, 1082).—The authors show that the intermediate product in the preparation of 4 : 5-dimethoxyhomophthalic acid from an ethereal suspension of 2-oximino-5 : 6-dimethoxy-1-hydrindone and phosphorus pentachloride is not 4 : 5-dimethoxyhomophthalimide, but 2-carboxy-4 : 5-dimethoxyphenylacetoneitrile, m. p.  $164\text{--}165^\circ$  (decomp.), readily hydrolysed to 4 : 5-dimethoxyhomophthalic acid, m. p.  $223\text{--}224^\circ$  (cf. Perkin and Robinson, *loc. cit.*, m. p.  $215^\circ$ ), and converted by alkaline hydrogen peroxide into 4 : 5-dimethoxyhomophthalamic acid, m. p.  $204^\circ$  (decomp.), which gives on heating 4 : 5-dimethoxyhomophthalimide, m. p.  $245^\circ$ , identical with the compound obtained by heating ammonium 4 : 5-dimethoxyhomophthalate.

Similar reactions were carried out with 2-oximino-1-hydrindone and 2-oximino-5 : 6-methylenedioxy-1-hydrindone : 2-carboxy-4 : 5-methylenedioxyphenylacetoneitrile, m. p.  $195\text{--}196^\circ$  (decomp.), gives 4 : 5-methylenedioxyhomophthalamic acid, softening at  $230^\circ$ , darkening at  $280^\circ$  and melting at  $295^\circ$ , the m. p. of 4 : 5-methylenedioxyhomophthalimide. M. J.

**Compounds Formed by the Action of Bromine on Benzaldehydephenylhydrazone.** F. D. CHATAWAY and A. J. WALKER (*J. Chem. Soc.*, 1925, 127, 975—984).—When benzaldehydephenylhydrazone is treated with bromine in acetic acid solution, and the precipitated additive product is washed with water, the resultant tribromo derivative (I), m. p.  $114^\circ$ , is  $\omega$ -bromobenzaldehyde-2 : 4-dibromophenylhydrazone (cf. Humphries, Bloom, and Evans, T., 1923, 123, 1771); it is also obtained by warming  $\beta$ -benzoyl-2 : 4-dibromophenylhydrazine with phosphorus pentabromide and phosphorus tribromide. By the preparation of *p*-bromobenzaldehyde-2 : 4-dibromophenylhydrazone, m. p.  $126^\circ$ , from *p*-bromobenzaldehyde and 2 : 4-dibromophenylhydrazine, the possibility of (I) having this constitution (cf. Ciusa and Vecchiotti, A., 1916, i, 437) is disproved. When (I) is boiled with acetic acid and sodium acetate, it gives  $\alpha$ -acetyl- $\beta$ -benzoyl-2 : 4-dibromophenylhydrazine, m. p.  $158\text{--}159^\circ$  (hydrolysable to acetic acid, benzoic acid, and 2 : 4-dibromophenylhydrazine), and the formation of this compound is attributed to acetylation of the imino group, followed by replacement of the methine bromine atom by hydroxyl; the

substance is synthesised by benzoylation of 2:4-dibromophenylhydrazine, yielding  $\beta$ -benzoyl- $\alpha$ -2:4-dibromophenylhydrazine, m. p. 172°, and subsequent acetylation. By ammonia, (I) is converted into benzaldehyde-2:4-dibromophenylhydrazidine, m. p. 115° [hydrochloride, m. p. 260° (decomp.)], which is also formed by the action of ammonia on  $\omega$ -chlorobenzaldehyde-2:4-dibromophenylhydrazone, m. p. 109° (prepared by bromination of  $\omega$ -chlorobenzaldehydephenylhydrazone). When (I) is treated with potassium cyanide it gives  $\omega$ -cyanobenzaldehyde-2:4-dibromophenylhydrazone, m. p. 139°, which is dimorphic; with phenylhydrazine, (I) yields dibromoformazylbenzene, m. p. 173—174°, whilst the bright colour produced on heating the hydrazone with alcoholic potassium hydroxide is attributed to formation of a tetrabromoformazyl compound.

When bromination of benzaldehydephenylhydrazone is carried out in presence of sodium acetate, the product is 3:6-diphenyl-1:4-di-*p*-bromophenyl-1:4-dihydro-1:2:4:5-tetrazine, m. p. 265° (yielding benzonitrile on distillation, either alone or with zinc dust, and on reduction giving *p*-bromoaniline), which is also obtained by similar bromination of benzaldehyde-*p*-bromophenylhydrazone or  $\omega$ -chlorobenzaldehydephenylhydrazone. But by bromination of benzaldehyde-2:4-dibromophenylhydrazone in presence of sodium acetate, the chief product is  $\omega$ -bromobenzaldehyde-2:4-dibromophenylhydrazone, with only a little 3:6-diphenyl-1:4-di(2:4-dibromophenyl)-1:4-dihydro-1:2:4:5-tetrazine, m. p. 255°, by treating benzaldehydephenylhydrazone in presence of sodium acetate with an increased amount of bromine, a mixture of these tetrazines is produced. It is suggested that in the presence of sodium acetate 1 mol. of the tetrazine is formed by elimination of 2HBr from 2 mols. of the  $\omega$ -bromo compound. In the production of a tetrazine, the substituting action of the bromine and the formation of the heterocyclic ring cannot be regarded as separate and independent processes.

F. M. H.

**Isomerism of the Oximes. XXII. Configuration of the Aldoximes.** O. L. BRADY and G. BISHOP (*J. Chem. Soc.*, 1925, 127, 1357—1362).—The generally accepted configuration of the aldoximes is based on Hantzsch's assumption that *cis*-elimination of acetic acid takes place from the acetyl derivatives of the aldoximes. The case for *trans*-elimination in ethylenic compounds is reviewed and Meisenheimer's view that the Beckmann change in ketoximes takes place in a *trans* and not a *cis* sense is discussed. The authors investigate the action of alkalis on the isomeric 2-chloro-5-nitrobenzaldoximes, and show that the so-called *syn*-isomeride is more readily converted through the unstable benzoisooxazole into the hydroxynitrile than the *anti*-isomeride. 2-Chloro-5-nitrobenzanti-aldoxime, m. p. 110°, gives no ionised chlorine when heated at 50° for 4 hrs. with 0.25*N*-sodium hydroxide, whilst 2-chloro-5-nitrobenzsyn-aldoxime, m. p. 176°, yields 27% of its chlorine in an ionised form after 1 hr., 45% after 2 hrs., 53% after 4 hrs. Boiled with *N*-alkali for 30 mins., the *anti*-aldoxime gives a small amount of 5-nitrosalicylic acid on acidification. The *syn*-aldoxime is completely

converted into the nitrile. Assuming that ring formation occurs more readily when the hydroxyl group is vicinal to the halogenated benzene ring, this result involves the reversal of the Hantzsch configuration of the oximes in accordance with the views of Meisenheimer, Beckmann, and von Auwers. The authors suggest that, pending further confirmation, the oximes should be termed  $\alpha$ - and  $\beta$ - instead of *syn* and *anti*, that of which the acetyl derivative yields the nitrile on hydrolysis being designated the  $\beta$ -compound.

M. J.

**Catalytic Hydrogenation of Nitriles under Reduced Pressure. Synthesis of Aldimines.** V. GRIGNARD and R. ESCOURROU (*Compt. rend.*, 1925, **180**, 1883—1887).— $\alpha$ -Phenyl- $\beta$ -iminomethane ( $\beta$ -phenylacetalimine), b. p. 212—214°/750 mm., is prepared by hydrogenation of phenylacetonitrile under reduced pressure in presence of platinum oxide or reduced nickel, and on hydrolysis with potassium hydroxide yields ammonia and phenylacetaldehyde. The imine hydrochloride, m. p. 180° (with sublimation), on exposure to air deposits colourless leaflets of phenylacetaldehyde-ammonia, m. p. 83—85° (sublimes). Benzaldimine, an unstable liquid,  $d^{13}_4$  1.009,  $n^{12}_D$  1.5725, obtained by hydrogenation in a vacuum of benzonitrile in presence of reduced nickel, yields an unstable hydrochloride described by Busch (A., 1896, i, 677).

L. F. H.

**Nitration of the Carbonate and Ethyl Carbonate of *m*-Hydroxybenzaldehyde.** F. A. MASON [with H. JENKINSON] (*J. Chem. Soc.*, 1925, **127**, 1195—1199).—*m*-Aldehydophenyl carbonate, m. p. 132—134°, is obtained in 90% yield by the action of carbonyl chloride on a solution of *m*-hydroxybenzaldehyde, in presence of the calculated amount of sodium hydroxide, together with sodium carbonate and sodium chloride. Nitration gives 4-nitro-3-aldehydophenyl carbonate, m. p. 194—198° (decomp.) with previous softening (yield 97%). On hydrolysis with sodium hydroxide, it is converted into 6-nitro-3-hydroxybenzaldehyde, m. p. 167°; methyl ether, m. p. 83°; monoacetyl derivative, m. p. 74°; triacetyl derivative, m. p. 120°; benzoyl derivative, m. p. 104—105°; phenylhydrazone, m. p. 185—195° (decomp.), giving a sodium salt, m. p. above 270°; oxime, m. p. 179—180°; semicarbazone, decomp. 245—260°. *m*-Aldehydophenyl ethyl carbonate, b. p. 289—292°/760 mm. (with slight decomposition), 165—167°/20 mm.,  $d$  1.42, is obtained in 95% yield by the action of ethyl chloroformate on *m*-hydroxybenzaldehyde in presence of sodium hydroxide. Nitration yields a mixture containing 50% of 4-nitro-3-aldehydophenyl ethyl carbonate, m. p. 63—65°, which is hydrolysed to 6-nitro-3-hydroxybenzaldehyde.

F. M. H.

**Conversion of Trimethylgallic Acid into Trimethylgallic aldehyde [3 : 4 : 5-Trimethoxybenzaldehyde].** A. SONN and W. MEYER (*Ber.*, 1925, **58**, [B], 1096—1103; cf. Sonn and Müller, A., 1920, i, 58).—3 : 4 : 5-Trimethoxybenz-p-toluidide, m. p. 154°, is converted by phosphorus pentachloride into the corresponding iminohydrochloride, m. p. 108—109°, which by reduction with stannous

chloride and hydrogen chloride in ethereal solution affords the tin salt of the Schiff's base, m. p. 122—124° (decomp.), convertible by sodium hydroxide into *p*-toluidino-3 : 4 : 5-trimethoxyphenylcarbinol (or 3 : 4 : 5-trimethoxybenzylidene-*p*-toluidine), m. p. 100—101° (hydrochloride, m. p. 90—91°). The latter substance is also obtained from 3 : 4 : 5-trimethoxybenzaldehyde and *p*-toluidine in the presence of hydrochloric acid; it is converted by warm hydrochloric acid into 3 : 4 : 5-trimethoxybenzaldehyde. Similarly, 3 : 4 : 5-trimethoxybenz-*p*-anisidide, m. p. 158·5°, gives successively the iminochloride, m. p. 105—106°, tin salt, m. p. 192°, and *p*-anisidino-3 : 4 : 5-trimethoxyphenylcarbinol, m. p. 111—112° (hydrochloride, m. p. 153—154°); the base is decomposed with some difficulty by 2*N*-sulphuric acid. Anilino-3 : 4 : 5-trimethoxyphenylcarbinol (hydrochloride, m. p. about 165°) has m. p. 91·5—92°. The difficulties attendant on the preparation of 3 : 4 : 5-trimethoxybenzaldehyde (cf. *loc. cit.*) owing to the stability of the carbinols can be avoided by the use of the benzyl- or methyl-amide of 3 : 4 : 5-trimethoxybenzoic acid. Thus, 3 : 4 : 5-trimethoxybenzbenzylamide, m. p. 140·5°, is converted through the iminochloride and tin salt, m. p. 180° (decomp.), into 3 : 4 : 5-trimethoxybenzaldehyde in 51% yield. 3 : 4 : 5-Trimethoxybenz-methylamide, m. p. 135°, yields an iminochloride and a tin salt, m. p. 125° after softening. 3 : 4 : 5-Tribenzoyloxybenzanilide, m. p. 178—179°, when similarly treated, gives a difficultly decomposable product in which the benzyl groups have been partly displaced. On the other hand, the iminochloride derived from 3 : 4 : 5-tribenzoyloxybenzanilide is reduced by ethereal stannous chloride to a Schiff's base which readily yields 3 : 4 : 5-tribenzoyloxybenzaldehyde, m. p. 127—128° (decomp.).

Reduction of benzhydroxymyl chloride by stannous chloride and hydrogen chloride in ethereal solution yields benzylideneimine chlorostannate,  $(\text{CHPh}\cdot\text{NH})_2\cdot\text{H}_2\text{SnCl}_6$ , decomp. 240—260°, which is also obtained from benzaldoxime under similar conditions. Acetoxime gives the chlorostannate,  $(\text{CMe}_2\cdot\text{NH})_2\cdot\text{H}_2\text{SnCl}_6$ , m. p. 219—220° (decomp.), whereas benzophenoneoxime yields the chlorostannate,  $(\text{CPh}_2\cdot\text{N}\cdot\text{OH})_2\cdot\text{H}_2\text{SnCl}_6$ , m. p. about 140°. Dibenzoylhydrazinochloride is reduced to benzaldimine chlorostannate. H. W.

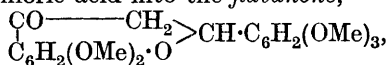
**Syntheses with 3 : 4 : 5-Trimethoxybenzaldehyde.** A. SONN [with E. MÜLLER, W. BÜLOW, and W. MEYER] (*Ber.*, 1925, 58, [B], 1103—1110).—3 : 4 : 5-Trimethoxybenzaldehyde condenses with methylamine in alcoholic solution, yielding 3 : 4 : 5-trimethoxybenzylidenemethylamine, b. p. 181—192°/14 mm., which is catalytically hydrogenated in the presence of colloidal palladium to 3 : 4 : 5-trimethoxybenzylmethylamine, b. p. 192°/17 mm. (hydrochloride, m. p. 178°; benzoyl derivative, m. p. 102°). 3 : 4 : 5-Trimethoxyacetophenoneoxime, m. p. 102°, is reduced by sodium amalgam to  $\alpha$ -3 : 4 : 5-trimethoxyphenylethylamine, b. p. 173—174°/17 mm. (hydrochloride, m. p. 214°; benzoyl derivative, m. p. 152°).  $\omega$ -Oximino-3 : 4 : 5-trimethoxyacetophenone, m. p. 95° (the sodium salt is described), is converted by stannous chloride and fuming

hydrochloric acid into  $\omega$ -amino-3:4:5-trimethoxyacetophenone hydrochloride, m. p. 256° (decomp.).

3:4:5-Trimethoxybenzaldehyde condenses with hippuric acid in the presence of acetic anhydride and anhydrous sodium acetate at 100° to form 4(3':4':5'-trimethoxybenzylidene)-2-phenyl-5-oxazolone,  $\text{CO}\cdot\text{C}(\text{O})\cdot\text{CH}\cdot\text{C}_6\text{H}_2(\text{OMe})_3 \gg \text{N}$ , m. p. 194—195° after

softening, which passes in alkaline solution into  $\alpha$ -benzoylamino- $\beta$ -3:4:5-trimethoxyphenylacrylic acid, m. p. 184°. The latter substance could not be reduced; when treated with sodium hydroxide and methyl sulphate it is converted into  $\alpha$ -benzoylmethylamino- $\beta$ -3:4:5-trimethoxyphenylacrylic acid, m. p. 164°, which is reduced by sodium amalgam to  $\alpha$ -benzoylmethylamino- $\beta$ -3:4:5-trimethoxyphenylpropionic acid, m. p. 116° after softening. 5-Nitrovanillin and hippuric acid yield 4(3'-nitro-5'-methoxy-4'-acetoxybenzylidene)-2-phenyl-5-oxazolone, m. p. 230°, which when heated in alkaline solution affords  $\alpha$ -benzoylamino- $\beta$ -3-nitro-4-hydroxy-5-methoxyphenylacrylic acid, m. p. 233°. 3-Nitro-4:5-dimethoxybenzaldehyde, sodium acetate and acetic anhydride at 180° yield  $\beta$ -3-nitro-4:5-dimethoxyphenylacrylic acid, m. p. 161°, which is converted by ferrous sulphate and ammonia and subsequently by hydrochloric acid into  $\beta$ -3-amino-4:5-dimethoxyphenylacrylic acid hydrochloride, m. p. 204° (decomp.). 3:4:5-Trimethoxybenzaldehyde, glycine anhydride, sodium acetate, and acetic anhydride afford 3:6-di-(3':4':5'-trimethoxybenzylidene)-2:5-diketopiperazine, m. p. 255—256°, which is reduced to 3:6-di(3':4':5'-trimethoxybenzyl)-2:5-diketopiperazine, m. p. 230—231° after softening; the latter substance affords  $\beta$ -3:4:5-trimethoxyphenyl- $\alpha$ -alanine when heated with sodium or barium hydroxide.

2-Hydroxy-4:6-dimethoxyacetophenone and 3:4:5-trimethoxybenzaldehyde afford 2-hydroxy-4:6-dimethoxyphenyl 3:4:5-trimethoxystyryl ketone, m. p. 183°, which is converted by aqueous-alcoholic hydrochloric acid into the flavanone,



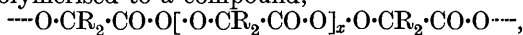
m. p. 173—174°, the oximino derivative, m. p. 210—211° (decomp.), of which is transformed by sulphuric and acetic acids into myricetin-5:7:3':4':5'-pentamethyl ether, m. p. 230°. H. W.

**Autoxidation of Organic Compounds. IV. Autoxidation of Ketens.** H. STAUDINGER, K. DYCKERHOFF, H. W. KLEVER, and L. RUZICKA (*Ber.*, 1925, 58, [B], 1079—1087; cf. this vol., i, 897, 898).—Dimethylketen is converted by oxygen at a low temperature into an exceedingly unstable peroxide which, as judged from its physical properties, appears to be highly polymerised. In the presence of ether or ethyl acetate it decomposes slowly at the atmospheric temperature mainly into carbon dioxide and acetone with small amounts of polymerised substances. The formation of a monoxide could not be established. Diethylketen behaves similarly to its lower homologue, but the peroxide is still less stable; the isolation of peroxides of the higher aliphatic ketens is frequently



impossible, since their rate of decomposition exceeds that of formation. Phenylmethylketen yields a *peroxide* at  $-80^\circ$  which is too unstable to permit investigation; autoxidation of phenylmethylketen at the atmospheric temperature gives acetophenone, carbon dioxide, and *phenylmethylketen monoxide*, decomp.  $140-160^\circ$ , which is probably a mixture of polymerides. A peroxide could not be obtained from diphenylketen at  $-80^\circ$ ; at the atmospheric temperature the production of benzophenone and carbon dioxide (the fission products of the mol-oxide) and, mainly, of keten oxides is observed, whilst, under particular conditions of autoxidation at a

higher temperature, *benzilide*,  $\text{O} \begin{smallmatrix} \text{CPh}_2 \cdot \text{CO} \\ \text{CPh}_2 \cdot \text{CO} \end{smallmatrix} \text{O}$ , m. p.  $192-193.5^\circ$ , is formed; the latter substance may be prepared by heating sodium diphenylchloroacetate in a vacuum at  $125^\circ$ . It is considered that the initial step in the change consists in the production primarily of a unimolecular, symmetrical mol-oxide,  $\text{R}_2\text{C} \begin{smallmatrix} \text{CO} \\ \text{O} \end{smallmatrix} \text{O}$ , which immediately undergoes fission into carbon dioxide and ketone or becomes polymerised to a compound,



the stability of which decreases as the weight of the alkyl group R increases or is replaced by phenyl; the same influence of groups on the stability of the product is observed with the polymeric malonic anhydrides. In addition, the unimolecular mol-oxides can lose oxygen with the formation of monoxides; the tendency towards decomposition in this direction increases in the order dimethyl-, phenylmethyl-, diphenyl-keten. The *keten oxides* obtained by the autoxidation of diphenylketen are mixtures of amorphous compounds which can be separated into a fraction of high m. p. (above  $210^\circ$ ) insoluble in ether or acetone but giving a colloidal solution in benzene or chloroform, a fraction, m. p.  $170^\circ$ , soluble in ether or acetone, and a mixture of keten oxides soluble to some extent in light petroleum. All these products are converted by water or acetic acid into benzoic acid, by methyl alcohol into *methoxy-diphenylacetic acid*, m. p.  $120-121^\circ$ , and by aniline into anilino-diphenylacetic acid. When heated at  $150-200^\circ$ , they are converted in part into benzilide, the formation of which must be preceded by depolymerisation, since benzilide is itself stable below  $250^\circ$ . The less highly polymerised substances of lower m. p. and greater solubility are distinguished from the more highly polymerised products only by their greater reactivity. H. W.

**Beckmann Rearrangement. XIV. Distillation of the Sodium Salts of Oximes under Reduced Pressure.** S. KOMATSU and T. HIRADZUMI (*Mem. Coll. Sci. Kyoto*, 1925, 8, 273-282).—When the sodium salt of a ketoxime is distilled under reduced pressure, some of it undergoes decomposition, yielding a nitrile and ammonia, sometimes accompanied by the ketone and by the acid corresponding with the nitrile. Thus the sodium salt of benzophenoneoxime gives benzonitrile and ammonia; the sodium salt of acetophenone oxime ( $+\text{H}_2\text{O}$ ) gives benzonitrile, ammonia, aceto-

phenone, benzoic acid, a nitrogenous *substance*, m. p. 186—196°, and a basic *substance*; the sodium salt of  $\alpha$ -camphoroxime gives  $\alpha$ -campholenitrile, a trace of ammonia, and  $\alpha$ -campholenic acid. Similarly, the sodium salt of isovaleraldoxime gives isovaleronitrile and ammonia, but the sodium salt of  $\alpha$ -benzaloxime (+H<sub>2</sub>O) gives benzonitrile, ammonia, benzoic acid, benzamide, and a substance, m. p. 78—80°, *i.e.*, the same products as are produced by the contact action of reduced copper. It is considered that in this decomposition of ketoximes the acid amide is formed intermediately, and owes its conversion into nitrile to the power of sodium to give up electrons. The following stages are postulated:  $\text{R.R}'\text{C:NO}\cdot\text{Na} \rightarrow \text{RC(ONa):NH} \rightarrow \text{RC:N}$  and also  $\text{RC(ONa):NH} \rightarrow \text{HC(ONa):NR} \rightarrow \text{C:NR} \rightarrow \text{RC:N}$ . In confirmation of this view, it is shown that the sodium salt of benzamide when heated under reduced pressure is converted into benzonitrile and ammonia.

F. M. H.

**Derivatives of Semioxamazide. III.** F. J. WILSON and E. C. PICKERING (*J. Chem. Soc.*, 1925, **127**, 965—967).—It is considered that on heating a ketonic semioxamazone there are first produced oxamide and the ketonic oxalyldihydrazone, which subsequently yields *cyclooxalyldihydrazide* and a ketazine. Thus acetophenonesemioxamazone at 215° is converted into oxamide, *acetophenoneoxalyldihydrazone*, m. p. 250° (also prepared by boiling an alcoholic solution of acetophenone and oxalyldihydrazide in presence of iodine), *cyclooxalyldihydrazide*, and phenylmethylketazine. By heating ethyl acetoacetate semioxamazone at 130—135° are formed oxamide, *cyclooxalyldihydrazide*, and 3:4-dimethyl-1:2-pyrazo-6:7-pyrone, m. p. 247°, which would be expected on the theory that the intermediate product is ethyl oxalyldihydrazone-acetoacetate (cf. Bülow and Lobeck, A., 1907, i, 301; Bülow and Schaub, A., 1908, i, 579; Wolff and Schreiner, A., 1908, i, 291). The action of heat on the semioxamazones of dibenzyl ketone, acetone, and methyl ethyl ketone, leads respectively to dibenzylketazine, dimethylketazine, and methylethylketazine, together with oxamide and *cyclooxalyldihydrazide*.

F. M. H.

**Action of Diazomethane on Some Aromatic Acyl Chlorides. III. Mechanism of the Reaction.** H. H. LEWIS, M. NIERENSTEIN, and E. M. RICH (*J. Amer. Chem. Soc.*, 1925, **47**, 1728—1732).—The low yield of  $\omega$ -bromoacetophenone obtained by the action of diazomethane on benzoyl bromide (Clibbens and Nierenstein, T., 1915, **107**, 1492) is due to the formation of 3:6-dibromo-3:6-diphenyl-1:4-dioxane,  $\text{CPhBr}\cdot\text{O}\cdot\text{CH}_2$   
 $\text{CH}_2\text{—O—CPhBr}$ , m. p. 159° (*picrate*, m. p. 217°), in 62% of the theoretical yield. The constitution of this substance is shown by its conversion into 3:6-diphenyl-1:4-dioxane, m. p. 103° (*picrate*, m. p. 227°), which yields phenylethylene glycol on hydrolysis, and by its resemblance to dioxane (diethylene ether, Faworsky, A., 1907, i, 274). The high yields of  $\omega$ -chloroacetophenones obtained from acyl chlorides are attributed to the greater mobility of the chlorine as compared with the corresponding

bromine atom. Thus triphenylacetyl chloride, in which the chlorine atom is very immobile (cf. Schmidlin and Hodgson, A., 1908, i, 170), gives a 92% yield of 3 : 6-dichloro-3 : 6-di[triphenylmethyl]-1 : 4-dioxane, whilst phenylacetyl chloride gives an 87% yield of benzyl chloromethyl ketone (*acetate*, m. p. 131°) and diphenylacetyl chloride an 82% yield of *diphenylmethyl chloromethyl ketone* (m. p. 91—92°, *acetate*, m. p. 147°), results which agree with the relative mobilities of the chlorine atom in these three compounds as measured by their reactivity with 5% potassium hydroxide solution (cf. Schmidlin and Hodgson, *loc. cit.*). These results favour the Oliveri-Mandalà interpretation (A., 1922, i, 994) of the action of diazomethane on acyl chlorides and are opposed to Staudinger's theory (A., 1922, i, 238).

3 : 6-Dichloro-3 : 6-di[triphenylmethyl]-1 : 4-dioxane, yellow needles, has m. p. 167° (*picrate*, m. p. 249—251°); 3 : 6-di[triphenylmethyl]-1 : 4-dioxane, has m. p. 133° (decomp.) (*picrate*, m. p. 259—263°), and on hydrolysis gives (71% yield)  $\alpha$ -triphenylmethyl-ethylene glycol, m. p. 116° (*di-p-nitrobenzoate*, m. p. 192—194° [decomp.]).

R. B.

**Action of Organo-magnesium Compounds on Nitriles.** M. JASPERS (*Bull. Soc. chim. Belg.*, 1925, **34**, 182—187; cf. A., 1924, i, 853).—Magnesium ethyl bromide reacts with *o*-toluonitrile to yield *o*-tolyl ethyl ketone and *o*-tolylethylketimine, b. p. 105°/15 mm.,  $d_4^{20}$  0.974,  $n_D^{20}$  1.5103, *hydrochloride*, m. p. 175—177°. If the product of the reaction is treated directly with gaseous hydrogen chloride in ether solution, the yield of ketimine (as its hydrochloride) is 94%, but distillation of the product causes a large amount of polymerisation. When heated at 180°/30—50 mm. (Moureu and Mignonac, A., 1914, i, 1076), the ketimine is converted into its dimeride, 3 : 6-di-tolyl-4 : 5-dimethylhexahydro-1 : 2-diazine, m. p. 120°. Magnesium methyl bromide similarly yields *o*-tolylmethylketimine (35%), b. p. 95°/15 mm.,  $d_4^{20}$  0.959 (*hydrochloride*, m. p. 183—185°), *o*-tolyl methyl ketone (20%), and some unchanged nitrile (8%). Magnesium benzyl chloride yields *o*-tolylbenzylketimine (87%), b. p. 185°/12 mm.,  $d_4^{20}$  1.0719 (*hydrochloride*, m. p. 230—233°), toluene, some unchanged nitrile (27%), and a little dibenzyl; whilst magnesium phenyl bromide yields *o*-tolylphenylketimine (85%), b. p. 165°/12 mm.,  $d_4^{20}$  1.073 (*hydrochloride*, m. p. 215—218°), benzene, unchanged nitrile (15%), and a small quantity of diphenyl. On heating at 185°/35 mm., the ketimine is converted into the *ketisoketimine*, b. p. 250—260°/1 mm.

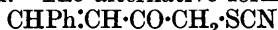
J. W. B.

**Interaction of Thiocyanogen with Unsaturated Compounds.** F. CHALLENGER and T. H. BOTT (*J. Chem. Soc.*, 1925, **127**, 1039—1042; cf. *ibid.*, 1923, **123**, 1055).—When thiocyanogen reacts with styryl methyl ketone in dry ethereal solution in the dark (or by reaction of styryl methyl ketone, iodine, and mercuric thiocyanate in ethereal solution) the product is  $\alpha$ -thiocyanostyryl methyl ketone, m. p. 119°; a probable intermediate compound is



It is reduced by zinc dust and water to benzylacetone, together with

traces of a *substance*, m. p.  $157^{\circ}$ ; with bromine in carbon disulphide, it yields a *dibromide*, m. p.  $138^{\circ}$  (decomp.); it is oxidised by potassium permanganate to potassium sulphate, benzoic acid, and traces of a fatty acid, whilst with bromine and potassium hydroxide it gives cinnamic acid. The alternative formula



is improbable and is further discountenanced by preparation from distyryl ketone of a *substance*, m. p.  $151^{\circ}$ , containing two thiocyno groups. The bromostyryl methyl ketone of Ruhemann and Watson (T., 1904, 85, 456) probably possesses the  $\alpha$ -structure. Carvone and thiocyanogen yield a *compound*, m. p.  $254^{\circ}$ , with only one thiocyno group. When styryl methyl ketone dibromide is boiled with alcoholic potassium thiocyanate, the ketone is regenerated.

F. M. H.

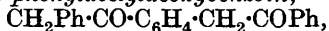
**$\alpha\gamma$ -Diphenylpropan- $\alpha\beta$ -dione (Phenylbenzylglyoxal).** C. DUFRAISSE and H. MOUREU (*Compt. rend.*, 1925, 180, 1946—1949; cf. Widman, A., 1916, i, 406).— $\alpha\gamma$ -Diphenylpropan- $\alpha\beta$ -dione, which is dimorphous, m. p.  $67^{\circ}$  and  $90^{\circ}$ , undergoes auto-oxidation in air, yielding benzoic acid and two *substances*, m. p.  $194^{\circ}$  and  $236^{\circ}$ , respectively, and yields coloured *sodium, copper, zinc, uranium, antimony, and lead* derivatives. On treatment with antimony trichloride the diketone yields a yellow salt, m. p.  $179$ — $180^{\circ}$ , to which the constitution  $\text{COPh}\cdot\text{C}(\text{OSbCl}_2)_2\cdot\text{CHPh}$  is assigned. With hydroxylamine the diketone gives a *dioxime*, m. p.  $220^{\circ}$ , a known monoxime, oximinobenzylacetophenone,  $\text{COPh}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\text{Ph}$ , and an *isomeride* of the latter, m. p.  $114$ — $115^{\circ}$ . On slow distillation crystalline  $\alpha\gamma$ -diphenylpropane- $\alpha\beta$ -dione passes into a liquid *isomeride*, b. p.  $191$ — $192^{\circ}/15$  mm., giving the same metallic derivatives as the crystalline diketone, which is regenerated on treating these metallic derivatives with acids. It is suggested, on the basis of experiments with the Grignard reagent, that the crystalline isomeride is the enolic form whereas the liquid isomeride consists entirely or in part of the diketonic form. Stereoisomerism might also account for the phenomenon.

L. F. H.

**Organo-metallic Compounds of Aluminium. IV. Action of Acid Chlorides.** P. LEONE (*Atti R. Accad. Lincei*, 1925, [vi], 1, 443—445; cf. this vol., i, 677).—The action of benzoyl chloride on aluminium ethyl iodide in ethereal solution yields  $\alpha\alpha$ -dibenzoylthane, a small proportion of propiophenone, and ethane, the last probably resulting from decomposition of some of the aluminium ethyl iodide by the hydrochloric acid formed during the condensation.

T. H. P.

***o*-Phenylacetyldeoxybenzoin, its Conversion into Substituted Naphthalenes and Attempted Preparation of further *o*-Phenylene Derivatives.** R. WEISS and L. SONNENSCHNEIN (*Ber.*, 1925, 58, [B], 1043—1047).—The action of magnesium benzyl chloride in ethereal solution on *isobenzylidenephthalide* leads to the production of *o*-phenylacetyldeoxybenzoin,



m. p.  $146$ — $150^{\circ}$ , which is converted by the protracted action of

sodium ethoxide into 2 : 3-diphenyl- $\alpha$ -naphthol, m. p. 128—131° (acetyl derivative, m. p. 161—163°). The naphthol is oxidised by sodium dichromate in the presence of acetic acid to 2 : 3-diphenyl- $\alpha$ -naphthaquinone, m. p. 140—142°. The action of amyl nitrite on *o*-phenylacetyldeoxybenzoin in the presence of sodium ethoxide yields 4-hydroxy-1-benzoyl-3-phenylisoquinoline, m. p. 193° (decomp.). The constitution of the latter compound rests on its ability to yield an acetyl derivative (+0.5H<sub>2</sub>O), m. p. 138—141°, from which it is regenerated by alcoholic potassium hydroxide and on its conversion by warm amyl nitrite into a compound which is regarded as 2 : 5-dibenzoyl-3 : 4-benzofuran, m. p. 233—234° (decomp.), since it is transformed by alcoholic potassium hydroxide (by a type of benzilic acid transformation) into *o*-phenylenediphenyldiglycollomonolactone, 
$$\text{C}_6\text{H}_4 \begin{array}{l} \text{CPh}(\text{CO}_2\text{H})-\text{O} \\ \text{CPh}(\text{OH})-\text{CO} \end{array}$$
, m. p. 206—207° (decomp.) [monomethyl ester, m. p. 204—206°].

H. W.

**Laboratory Preparation of *p*-Benzoquinone.** R. CRAVEN and W. A. T. DUNCAN (*J. Chem. Soc.*, 1925, 127, 1489).—Pure *p*-benzoquinone is conveniently prepared by oxidation of quinol (66 g.) in ice-cold 60% acetic acid solution (300 c.c.) by slow addition of chromic anhydride (84 g.) in 30% acetic acid (200 c.c.), keeping the temperature below 10°.

M. J.

**4 : 5-Diamino-*o*-benzoquinone and Derivatives.** E. HOEHN (*Helv. Chim. Acta*, 1925, 8, 275—280).—Triacetamidopyrocatechol (Kehrmann and Hoehn, this vol., i, 560) is partly hydrolysed by the action of cold dilute sodium hydroxide and when the soluble product, without isolation, is treated with potassium nitrite and acetic acid at 0°, 5-nitroso-4-acetamidopyrocatechol (decomp. 230°) is obtained. This is reduced by stannous chloride in alcoholic solution to 4 : 5-diaminopyrocatechol, an easily oxidised substance, the hydrochloride and tetra-acetyl derivative (m. p. 224—225°) of which are described. When the base, in weakly ammoniacal solution, is oxidised by air, brown needles of 4 : 5-diamino-*o*-benzoquinone (decomp. 290—295°) are precipitated. A table is given showing how this compound compares with its two known isomerides. It interacts with phenyl-*o*-phenylenediamine in alcoholic solution containing hydrochloric acid to give 2 : 3-isophenosafranine (2 : 3-diamino-5-phenylphenazonium), the orange nitrate and perchlorate and the chloroplatinate of which are described.

When 4-acetamido-*o*-benzoquinone (Kehrmann and Hoehn, *loc. cit.*) is treated with aniline in alcoholic solution at 50°, dianilinoquinoneanil (Jackson and Koch, A., 1898, i, 518) is produced, the acetamido group also being displaced.

W. A. S.

**Derivatives of 2 : 3-Diamino-1 : 4-naphthaquinone.** K. FRIES and K. BILLIG (*Ber.*, 1925, 58, [B], 1128—1138).—The activity of the halogen atom of 3-chloro-2-amino-1 : 4-naphthaquinone or its *N*-aryl or alkyl derivatives is so greatly enhanced by acetylation of the basic group that derivatives of 2 : 3-diamino-

1 : 4-naphthaquinone are readily prepared from the chloro compound (cf. Fries and Ochwat, A., 1923, i, 842).

2-Acetamido-3-anilino-1 : 4-naphthaquinone, m. p. 200°, prepared from 3-chloro-2-acetamido-1 : 4-naphthaquinone and aniline in boiling alcoholic solution, is converted when melted, when boiled with alcoholic ammonia or potassium hydroxide or with concentrated acids, into 3-phenyl-2-methyl-lin-naphthiminazole-4 : 9-quinone,  $C_{10}H_4O_2 \left\langle \begin{smallmatrix} NPh \\ \text{---} N \end{smallmatrix} \right\rangle CMe$ , m. p. 239°. The same change is effected

by sodium nitrite in the presence of boiling glacial acetic acid, whereas in cold solution 2-acetamido-3-N-nitrosoanilino-1 : 4-naphthaquinone, m. p. 129°, is produced. 3-Chloro-2-acetanilido-1 : 4-naphthaquinone, m. p. 135°, and ammonia in the presence of boiling benzene afford 3-amino-2-acetanilido-1 : 4-naphthaquinone, m. p. 187°; removal of the acetyl group from this compound by acids or alkalis leads very readily to the production of 3-phenyl-2-methyl-lin-naphthiminazole-4 : 9-quinone. 2-Anilino-3-acetanilido-1 : 4-naphthaquinone, m. p. 157°, on the other hand, is hydrolysed by cautious treatment with alcoholic potassium hydroxide to 2 : 3-dianilino-1 : 4-naphthaquinone.

3-Phenyl-2-methyl-lin-naphthiminazole-4 : 9-quinone is reduced by zinc dust and acetic acid to 4 : 9-dihydroxy-3-phenyl-2-methyl-lin-naphthiminazole, m. p. 157° (decomp.) after softening at 100° (diacetyl derivative, m. p. 182°). 3-β-Naphthyl-2-methyl-lin-naphthiminazole-4 : 9-quinone has m. p. 222°. 3-Chloro-2-N-nitrosoanilino-1 : 4-naphthaquinone, m. p. 126°, is conveniently prepared by addition of sodium nitrite to a suspension of 3-chloro-2-anilino-1 : 4-naphthaquinone in glacial acetic acid. The nitroso group is removed with re-formation of the parent material when the compound is treated with *o*- or *m*-toluidine, mono- or di-methylaniline, *p*-nitro- or *p*-chloro-aniline, β-naphthylamine or phenylhydrazine whereas with aniline, *p*-toluidine, *p*-phenylenediamine, or *p*-anisidine the chlorine atom is almost exclusively replaced. With α-naphthylamine and *o*-phenylenediamine both reactions occur, the former preponderating. 3-Chloro-2-N-nitroso-*p*-toluidino-1 : 4-naphthaquinone, m. p. 140° after softening and darkening at 115°, 3-chloro-2-N-nitroso-*p*-anisidino-1 : 4-naphthaquinone, m. p. 177° (decomp.) after softening, and 3-chloro-2-N-nitroso-β-naphthylamino-1 : 4-naphthaquinone, m. p. about 180° after blackening at 150°, are also described. 3-Chloro-2-N-nitrosoanilino-1 : 4-naphthaquinone and alcoholic sodium hydroxide yield 2-anilino-3-hydroxy-1 : 4-naphthaquinone, m. p. 212° after softening, which is also obtained from 2-amino-3-anilino-1 : 4-naphthaquinone and concentrated sulphuric acid and from 2-amino-3-N-nitrosoanilino-1 : 4-naphthaquinone or the 2-anilino-3-N-nitrosoanilino derivative and alcoholic sodium hydroxide. 2-β-Naphthylamino-3-hydroxy-1 : 4-naphthaquinone has m. p. 228° after much softening. 3-Amino-2-N-nitrosoanilino-1 : 4-naphthaquinone, m. p. 138° (decomp.), is reduced by stannous chloride and glacial acetic acid to 2-amino-3-anilino-1 : 4-naphthaquinone, m. p. 197°, and is transformed by boiling glacial acetic acid into 1-phenyl-lin-naphthatriazole-4 : 9-

quinone,  $C_8H_4O_2 < \begin{smallmatrix} NPh \\ \text{---} N \end{smallmatrix} > N$ , m. p. 241°. 1-*p*-Tolyl-lin-naphthatriazole-4 : 9-quinone has m. p. 212°. 3-Chloro-2-*N*-nitrosoanilino-1 : 4-naphthaquinone and aniline yield 2 : 3-dianilino-1 : 4-naphthaquinone (see above); the *diacetyl* derivative, decomp. above 240°, is described. The quinone is converted by cautious treatment with zinc dust and acetic anhydride into 2 : 3-dianilino-1 : 4-diacetoxynaphthalene, m. p. 243° (decomp.), and by more protracted treatment with the same reagents into 2 : 3-diacetanilido-1 : 4-diacetoxynaphthalene, m. p. 245° (decomp.) after darkening at 220°; either compound is readily hydrolysed in the presence of air to dianilidonaphthaquinone. The latter compound is converted by concentrated sulphuric acid into *phenyl*-di-3(2-anilino-1 : 4-naphthaquinonyl)-amine,  $(C_8H_4O_2 \cdot NPh)_2NPh$ , m. p. 268°. 2-Anilino-3-*p*-anisidino-1 : 4-naphthaquinone, m. p. 180°, *p*-toluidino-*p*-anisidino-1 : 4-naphthaquinone, m. p. 170°, *p*-toluidino-*m*-toluidino-1 : 4-naphthaquinone, m. p. 155°, *di-p*-toluidino-1 : 4-naphthaquinone, m. p. 179°, and anilino-*p*-aminoanilino-1 : 4-naphthaquinone, m. p. 197°, are described incidentally. 3-Chloro-2-acetanilido-1 : 4-naphthaquinone and ethyl sodioacetate yield ethyl  $\alpha$ -2-acetanilido-1 : 4-naphthaquinonyl-3-acetoacetate,  $CH_3 \cdot CO \cdot CH(C_8H_4O_2 \cdot NPhAc) \cdot CO_2Et$ , m. p. 160°, whereas 3-chloro-2-acetamido-1 : 4-naphthaquinone gives ethyl  $\alpha$ -2-acetamido-1 : 4-naphthaquinonyl-3-acetoacetate, m. p. 143°.

H. W.

**Reduction of the Bromoanthraquinones.** E. DE B. BARNETT and J. W. COOK (*J. Chem. Soc.*, 1925, 127, 1489—1490).—Reduction of the chloroanthraquinones with zinc dust and ammonia gives the corresponding chloroanthracenes, except in the case of 1 : 2 : 3 : 4-tetrachloroanthraquinone, which gives 2 : 3-dichloroanthracene. 1- and 2-Bromo- and 2 : 3-dibromoanthraquinone give only anthracene. 2 : 3-Dibromoanthraquinone, m. p. 283° (cf. Meyer and Zahn, *Annalen*, 1913, 396, 174, m. p. 269—270°), is obtained by oxidation of 2 : 3 : 9 : 10-tetrabromoanthracene, m. p. 274° (cf. Meyer and Zahn, *loc. cit.*, m. p. 265—266°). This compound is obtained by the action of alcoholic potassium hydroxide on 9 : 10-dibromoanthracene tetrabromide which, when suspended in cold pyridine, gives 2 : 9 : 10-tribromo- and 2 : 3 : 9 : 10-tetrabromo-anthracene. M. J.

**Constitution and Molecular Magnitude of the Hydroxycamphors.** P. KARRER and N. TAKASHIMA (*Helv. Chim. Acta*, 1925, 8, 242—244).—The methyl ether of  $\alpha$ -hydroxycamphor has no pronounced odour and might therefore be expected to have an abnormal molecular weight. That both it and its parent (cf. Manasse, A., 1903, i, 42) are, in fact, associated is shown by the following determinations carried out by the cryoscopic method in various solvents. The methyl ether ( $C_{11}H_{18}O_2=182.1$ ) has M.W. about 348 in bromoform, 322 in benzene, and 358 in camphor.  $\alpha$ -Hydroxycamphor ( $C_{10}H_{16}O_2=168.1$ ) has M.W. about 350 in bromoform and 199 in benzene. The corresponding figures for  $\beta$ -hydroxycamphor are 380 and 223 and those for "*para*"-hydroxycamphor (Bredt and Goeb, A., 1921, i, 257) are 457 and 169. These

three compounds are too sparingly soluble in camphor for determinations to be made in that solvent. It will be observed that "para"-hydroxycamphor is associated only in bromoform. The above methyl ether yields neither semicarbazone nor phenylhydrazone. For this reason it is considered to have a *cycloacetal* formula (annexed). Its parents (both the  $\alpha$ - and  $\beta$ -hydroxy compounds yield the same ether) are to be formulated in a similar fashion. Their behaviour is compared with that of the simpler compounds described by Bergmann (A., 1924, i, 1042).

W. A. S.

**Camphor Oils. II. Reaction of Japanese Acid Clay to Camphor White Oil.** K. ONO (*Mem. Coll. Sci. Kyoto*, 1924, A., 7, 349—360).—The distillate obtained by heating camphor white oil with Japanese clay was washed and fractionated. Condensates were obtained from below 100° to above 350°, showing steady rises in specific gravity and refractive index with the boiling point. Benzene, *p*-menthane, and *p*-cymene were identified in the fractions, the largest of which was obtained at 170—180°. The largest fraction obtained by distillation of the product of the action of the clay on *d*-limonene also boiled at 170—180°; it contained a hydrocarbon, C<sub>10</sub>H<sub>20</sub>, presumably *p*-menthane, and by nitration and oxidation yielded *o*-nitro-*p*-hydroxyisopropylbenzoic acid. The action of the clay on cineole also gave an oil of which the largest fraction distilled at 170—180°; this fraction also contained *p*-cymene and *p*-menthane.

S. I. L.

**Alcohols of the Hydroaromatic and Terpene Series. IV.  $\alpha$ - and  $\beta$ -Fenchyl Alcohols and Derived Esters.** J. KENYON and H. E. M. PRISTON (*J. Chem. Soc.*, 1925, 127, 1472—1487).—Reduction of *d*-fenchone yields two stereoisomeric *l*-rotatory fenchyl alcohols, separated through their hydrogen phthalates and *p*-nitrobenzoates. Although of the same sign, their rotatory effects are, in some degree, opposite in character. The  $\alpha$ -neutral esters are of considerably higher *l*-rotatory power than the parent alcohol; in the  $\beta$ -series, the esterification effect is in the reverse direction. The effect of solvents on the rotatory power of the alcohols and their derivatives is also in opposite directions in the two cases. In the temperature-rotation curves, the value for the  $\beta$ -alcohol reaches a maximum and falls slowly, whilst that for the  $\alpha$ -alcohol reaches a minimum and rises.

Because of the similarity in structure of the camphor and fenchone molecules, simple esters of borneol and isoborneol have been studied in parallel with the  $\alpha$ - and  $\beta$ -fenchyl esters. Tables are given showing the specific rotatory powers of the four alcohols and their derivatives in the homogeneous state over a wide range of temperature and in solution. Under the conditions employed, all four series show simple rotatory dispersion. Refractive indices and densities are also given. The curve connecting the specific rotatory powers of the bornyl esters with the number of carbon atoms in



the acyl chain is similar in character to that for the corresponding  $\alpha$ -fenchyl esters. Those for the *isobornyl* and  $\beta$ -fenchyl esters show a similar correspondence. The temperature-rotation curves are similarly related, the rotatory powers in all cases decreasing regularly with rise of temperature. Thus, in general, the *bornyl* and *isobornyl* esters bear the same relation to each other as do the  $\alpha$ - and  $\beta$ -fenchyl esters.

The authors give further evidence for regarding *isoborneol* as a geometrical isomeride of *borneol* rather than as a tertiary alcohol, as in the accepted formula, adducing its ready esterification with phthalic anhydride and its easy resolution as contributory evidence.

Physical constants are given for the following esters of  $\alpha$ -fenchyl alcohol: *formate*, b. p.  $97^{\circ}/21$  mm.; *acetate*, b. p.  $99^{\circ}/19$  mm.; *propionate*, b. p.  $115^{\circ}/21$  mm.; *n-butyrate*, b. p.  $127^{\circ}/21$  mm.; *n-valerate*, b. p.  $135^{\circ}/15$  mm.; *n-hexoate*, b. p.  $152^{\circ}/17$  mm.; *n-heptoate*, b. p.  $160^{\circ}/16$  mm.; *n-octoate*, b. p.  $176^{\circ}/25$  mm.; *n-nonate*, b. p.  $185^{\circ}/16$  mm.; *laurate*, b. p.  $207-209^{\circ}/14$  mm.; *myristate*, b. p.  $190-195^{\circ}/2$  mm.; and of  $\beta$ -fenchyl alcohol: *formate*, b. p.  $83.5^{\circ}/11$  mm.; *acetate*, b. p.  $90^{\circ}/12$  mm.; *propionate*, b. p.  $102^{\circ}/11$  mm.; *n-butyrate*, b. p.  $112^{\circ}/16$  mm.; of *l-borneol*, *formate*, b. p.  $94^{\circ}/14$  mm.; *acetate*, b. p.  $103^{\circ}/14$  mm.; *propionate*, b. p.  $114^{\circ}/12$  mm.; *n-butyrate*, b. p.  $125^{\circ}/15$  mm.; *n-valerate*, b. p.  $136^{\circ}/12$  mm.; of *d-isoborneol*, *formate*, b. p.  $94^{\circ}/15$  mm.; *propionate*, b. p.  $119^{\circ}/16$  mm.; *n-valerate*, b. p.  $138^{\circ}/14$  mm.; and of *l-isoborneol*, *acetate*, b. p.  $112^{\circ}/17$  mm.; *n-butyrate*, b. p.  $125^{\circ}/14$  mm.

Rotatory powers are also given for  $\alpha$ -fenchyl hydrogen phthalate, (*magnesium* salt, m. p.  $290-295^{\circ}$ ),  $\beta$ -fenchyl hydrogen phthalate, m. p.  $153^{\circ}$ ,  $\alpha$ -fenchyl *p*-nitrobenzoate, m. p.  $108-109^{\circ}$ ,  $\beta$ -fenchyl *p*-nitrobenzoate.  $\alpha$ -Fenchyl *p*-chlorobenzoate has m. p.  $73-74^{\circ}$ . M. J.

**Catalytic Action. XV. Catalytic Activity of Reduced Copper. II.** S. KOMATSU and M. KURATA (*Mem. Coll. Sci. Kyōtō*, 1925, 8, 147-153).—After passing menthol over reduced copper at  $200^{\circ}$  or  $300^{\circ}$ , the product was fractionally distilled and the volume of evolved hydrogen measured. The amounts of cymene and menthene in the fraction boiling up to  $180^{\circ}$  were determined by refractive index measurements; the fraction, b. p.  $200-220^{\circ}$ , consisted of menthol together with menthone, which was converted into its oxime, which varied in rotatory power according to the conditions of the experiment (cf. following abstract). The fraction, b. p.  $>220^{\circ}$ , is regarded as thymol. When cupric oxide is prepared from cupric nitrate or basic cupric nitrate, the reduced copper acts principally as an oxidising agent, but that obtained from cupric sulphate gives copper which behaves as an oxidising and dehydrating agent, or as a dehydrating agent only, according to the method of preparation. Thus menthene is prepared by using, at  $300^{\circ}$ , copper which has been obtained from cupric oxide produced by the action of an equivalent of sodium hydroxide on cupric sulphate, whilst menthone is prepared by using, at  $200^{\circ}$ , copper which has been obtained from cupric oxide produced by the action of an excess of sodium hydroxide on cupric nitrate or sulphate. Ketone formation

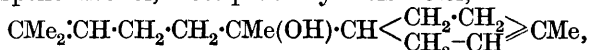
is favoured by a temperature of 200—245° and thymol formation occurs at 300°.

F. M. H.

**Camphor Series. VII. Catalytic Formation of Menthols and Menthones from *l*-Menthol.** S. KOMATSU and M. KURATA (*Mem. Coll. Sci. Kyōtō*, 1925, 8, 247—252).—When *l*-menthol is passed over reduced copper, it gives menthone, the oxime of which varies in rotatory power according to the method of preparation of the catalyst and the reaction temperature. When the copper is prepared by reduction at 200° of cupric oxide obtained from cupric nitrate and ammonia, and the reaction temperature is 250—260°, the menthone in the distillate gives (a) a solid oxime, m. p. 84°, hydrolysable to *r*-menthone (characterised by its semicarbazone and by reduction to menthol) and (b) a liquid oxime, described as yielding semicarbazones, separable by fractional crystallisation, of *d*-isomenthone, *l*-menthone, and *r*-isomenthone. To explain the production of these isomerides, it is supposed that piperitone is produced intermediately. After treatment of the menthones with hydroxylamine, the residual menthols in the distillate are converted into their hydrogen phthalates and fractional crystallisation of these esters and purification through their magnesium salts leads to the conclusion that, besides *l*-menthol, there are present *r*-menthol, *r*-neomenthol, and *d*-neomenthol, although these were not actually identified.

F. M. H.

**Higher Terpene Compounds. XXIV. Ring Formation in Sesquiterpenes. Complete Synthesis of Bisabolene and of a Hexahydrocadaline.** L. RUZICKA and E. CAPATO (*Helv. Chim. Acta*, 1925, 8, 259—274).—The analogy between nerolidol and linalool, already emphasised (cf. VIII, A., 1923, i, 691), suggests that the former should undergo intramolecular condensation to a monocyclic sesquiterpene under appropriate conditions. Such condensation does, in fact, take place, as the results described below show, and nerolidol may justly be termed the “linalool of the sesquiterpene series.” Already it has been found (*loc. cit.*, IX) that synthetic *dl*-nerolidol is converted, like its naturally occurring prototype, into farnesol and (probably) farnesene by the action of hot acetic anhydride. When the aliphatic sesquiterpene (farnesene) so obtained is treated with cold acetic acid and a little sulphuric acid for 15 hrs., a large proportion is transformed into the acetate (b. p. 120°/5 mm.,  $d_4^{16}$  0.9221,  $n_D^{16}$  1.4781) of a monocyclic sesquiterpene alcohol, most probably  $\alpha$ -bisabolol,

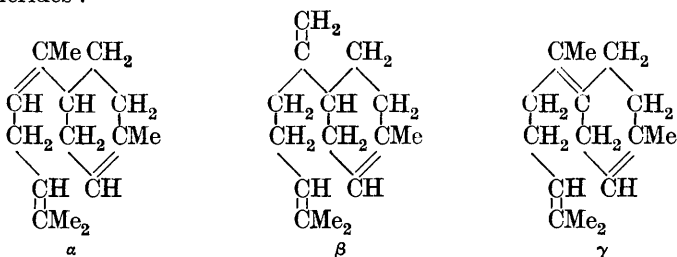


b. p. 105—110°/0.5 mm.,  $d_4^{17}$  0.9093,  $n_D^{17}$  1.4871. When this compound is treated in ethereal solution with hydrogen chloride, it affords bisabolene trihydrochloride, m. p. 79—80°, identical with that formed from natural bisabolene (see below).

Moreover, when synthetic *dl*-nerolidol (*loc. cit.*) is treated directly with acetic and sulphuric acids (as above) it yields farnesene and a mixture of farnesol and bisabolol, eventually separated by treating the appropriate hydrolysed fractions with phthalic

anhydride (cf. Ruzicka and Stoll, A., 1924, i, 531). The latter does not react with phthalic anhydride; from it bisabolene trihydrochloride was again obtained.

A similar conversion is brought about by the action of cold 90% formic acid. From the product on this occasion farnesene containing a little bisabolene, farnesol (b. p. 156°/12 mm.,  $d_4^{18}$  0.8945,  $n_D^{18}$  1.4897; it yielded a farnesol which afforded a semicarbazone, m. p. 132°, identical with that prepared from musk kernel oil), and bisabolol (b. p. 154—156°/12 mm.,  $d_4^{18}$  0.9216,  $n_D^{18}$  1.4939) were eventually isolated. This specimen of bisabolol likewise gave bisabolene trihydrochloride. When this synthetic bisabolene trihydrochloride is heated with acetic acid and sodium acetate it affords a monocyclic sesquiterpene the constants of which (b. p. 133—134°/12 mm.,  $d_4^{21}$  0.8717,  $n_D^{21}$  1.4923) compare satisfactorily with those of natural bisabolene. The bisabolene trihydrochloride isolated for comparison with that obtained synthetically was prepared from an appropriate fraction (b. p. 110—140°/12 mm.) of opopanax oil. As bisabolene may contain three ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) isomerides :



it is not easy to make a more rigorous comparison of the synthetic and natural products.

It would be expected that more drastic treatment of nerolidol would convert it into a dicyclic sesquiterpene. Actually when synthetic *dl*-nerolidol is treated with formic acid, at first as above and later at the b. p., there is obtained, besides a large amount of polymerised products, a mixture of dicyclic sesquiterpenes, one fraction of which (b. p. 125—126°/12 mm.,  $d_4^{15}$  0.9160,  $n_D^{15}$  1.5089) possesses properties very similar to those of naturally occurring hexahydrocadalene. The product gave no crystalline hydrochloride, but when dehydrogenated by heating with sulphur it afforded an oil (b. p. 120—165°/12 mm.) which on redistillation gave three fractions, all of which yielded cadalene picrate (m. p. 115°) and styphnate (m. p. 139°), identical with authentic specimens obtained *via* natural cadinene and synthetic cadalene (Ruzicka and Seidel, A., 1922, i, 562). When synthetic nerolidol is treated with hydrogen chloride in ether at 0° farnesene tetrahydrochloride is produced. This proves that no ring formation takes place under these conditions and that when bisabolene trihydrochloride is obtained by this means from a natural product it is derived from bisabolene already present. The above farnesene tetrahydrochloride is converted by the action of alcoholic potassium hydroxide into an oil which,

however, contains chlorine. The above results support Ruzicka and Stoll's hypothesis (A., 1923, i, 119) of the formation of sesquiterpenes in nature by condensation of isoprene. W. A. S.

**Travancore Essential Oils. V. Essential Oil from *Ageratum conyzoides*, Linn. (Appa Grass).** K. L. MOUDGILL (*J. Indian Chem. Soc.*, 1925, 1, 273—276).—Appa grass (*Ageratum conyzoides*) on steam distillation yields a heavy essential oil of nauseating odour (yield 0.16% of the dried grass) which on fractionation is found to consist mainly of a compound,  $C_{12}H_{16}O_2$ , b. p. 204—206°/756 mm., 130—135°/19 mm.,  $d_4^{25}$  1.019,  $n_D^{25}$  1.5298, which is under investigation. J. W. B.

**$\beta$ -Amyrin from Manila Elemi Resin. III.** A. ROLLETT and A. SCHMIDT (*Monatsh.*, 1925, 45, 519—523; cf. A., 1923, i, 588).—Oxidation of mixed amyryns with persulphate yields oxy- $\alpha$ - and - $\beta$ -amyrin acetates as mixed crystals, m. p. 215—216°, from which neither isomeride can be separated. When the mixed benzoates are oxidised with chromic acid in acetic acid, oxy- $\alpha$ -amyrin benzoate, m. p. 263°, can be isolated from the product first precipitated by the addition of water, but the  $\beta$ -isomeride could not be isolated from subsequent precipitates. Treatment of the mixed amyryns with bromine in acetic acid afforded bromo-amyrin acetates as mixed crystals, m. p. 215—216°. When a larger proportion of bromine was applied, bromo- $\alpha$ -amyrin acetate, m. p. 263°, could be isolated, but the more soluble  $\beta$ -isomeride could not be crystallised. Bromination of the mixed acetates gave similar results. F. G. W.

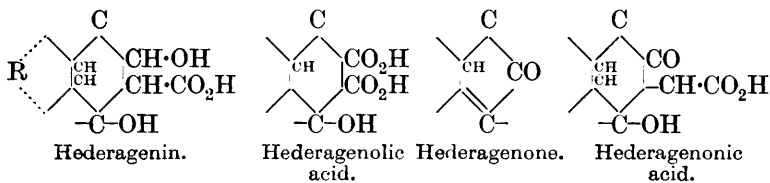
**Siam Benzoin. IV.** F. REINITZER (*Arch. Pharm.*, 1925, 263, 347—358; cf. A., 1921, i, 351, 352).—The amorphous substance precipitated by light petroleum from an ethereal solution of Siam benzoin (cf. A., 1915, i, 431) is not homogeneous; when purified by repeated solution and reprecipitation it eventually forms a viscous mass containing ether and miscible with more ether, but part is precipitated when much ether is added. This insoluble portion will be described later; it is also obtained when the original benzoin is dissolved in a little ether and the solution is diluted with more of the solvent. The remainder of the amorphous material, namely, that retained in solution in the ether, is eventually obtained as a yellow or reddish-yellow, vitreous mass. It gradually becomes discoloured and at the same time insoluble in ether. Similarly, when freshly-prepared, it is readily soluble in carbon disulphide, but becomes insoluble in that solvent even more rapidly than in ether. A better solvent for effecting the above separation on a small scale is cedar-wood oil or turpentine.

This amorphous product has, when fresh, m. p. 72°, but on keeping the m. p. rises; thus, after 6 months in a dry atmosphere it is 110°. In chemical properties, it closely resembles lubanyl benzoate (*loc. cit.*); thus, it decomposes, yielding benzoic acid, at 120—140°; it is hydrolysed by alcoholic potassium hydroxide, affording

an amorphous compound, m. p. 70—73°, apparently coniferyl alcohol; it yields a dibenzoate, m. p. 83—85°. It is a methoxy derivative, but the determination of the methoxy group, like the other quantitative analyses, gave only approximate results, doubtless because of the ready way in which the compound decomposes, oxidises, and polymerises. However, by cautious oxidation of the substance with mercuric oxide vanillin is obtained, and by prolonged reduction with zinc dust and sulphuric acid some eugenol is produced. It is concluded that the substance is amorphous coniferyl benzoate. Hofmann's objections to this supposition ("Siambenzoe," Zürich, 1920) are shown to have no satisfactory basis, Hofmann's own results, in fact, confirming Reinitzer's conclusions.  
W. A. S.

**Saponins and Related Substances. XIV. Structure of Hederagenin: an Example of Steric Hindrance.** A. W. VAN DER HAAR (*Rec. trav. chim.*, 1925, **44**, 740—757; cf. A., 1922, i, 160, 565, 1169).—Chromic acid oxidises only one of the hydroxyl groups in hederagenin, the other one being protected by the adjacent carboxyl group. Steric hindrance of this kind appears general amongst the saponinins. When hederagenin is boiled for 3 hrs. with 3% hydrogen chloride in methyl alcohol, only 1.2% is esterified; with 20% alcoholic acid the amount is 15% after 5.5 hrs. Esters obtained in this way are difficult to hydrolyse. On heating the ethyl ester for 1 hr. at 100° with *N*-potassium ethoxide, 93% of it was recovered and 78% after 7 hrs.' heating. On account of these and other reasons, the two hydroxyl groups in hederagenin are considered to be in *ortho* positions to the carboxyl group. Hederagenin has been converted into a monohydroxydicarboxylic acid, *hederagenolic acid*,  $\text{OH}\cdot\text{C}_{28}\text{H}_{45}(\text{CO}_2\text{H})_2$ , m. p. about 230°, by slow oxidation (several weeks) with permanganate in aqueous potassium hydroxide, yield about 80%. The acid and its *sodium* salt froth strongly on shaking with water, and in pharmacological action are similar to the acids obtained by the oxidation of cholesterol and allied substances (cf. Diels and Abderhalden, A., 1903, i, 819). Hederagenolic acid still contains an alcoholic hydroxyl group (proved by Tschugaev and Zerewitinov's method) which cannot be acetylated by ordinary methods and is clearly that which in the parent substance is influenced by the vicinal carboxyl group. No aldehydic or ketonic grouping could be detected. The methyl ester of hederagenin under the above conditions is more slowly oxidised, but gives the same dicarboxylic acid. Hederagenolic acid when heated with acetic anhydride (Blanc's method, cf. A., 1907, i, 710) loses 1 mol. of carbon dioxide and 2 mols. of water and gives the cyclic ketone, *hederagenone*,  $\text{C}_{29}\text{H}_{44}\text{O}$ , m. p. 179—180°. Although this is not dissolved by potassium hydroxide (excluding the possibility of its being an anhydride) no semicarbazone could be obtained. Its unsaturated nature is indicated by instantaneous decolorisation of permanganate and addition of bromine. The presence of a secondary alcoholic group in hederagenin is shown by oxidation with chromic acid in acetic acid solution, when 2 atoms of

hydrogen are removed, giving *hederagenonic acid*,  $C_{31}H_{45}O_4$ , m. p.  $292^\circ$ , in almost theoretical yield, *semicarbazone*, m. p. about  $260^\circ$ . The *sodium* and *potassium* salts give strongly foaming solutions in water. The *methyl* ester, m. p.  $192^\circ$ , is obtained by treating the acid with an ether solution of diazomethane, or from the sodium salt and methyl iodide. The same ester is obtained by oxidising the methyl ester of hederagenin with chromic acid. The *ethyl* ester has m. p.  $182^\circ$ . Evidence is given to show that hederagenonic acid is a  $\beta$ -ketonic acid; when heated with hydrogen chloride in acetic acid solution it loses 1 mol. of carbon dioxide whilst its esters are unattacked under these conditions. It was not found possible to reduce the  $-CO$  group back to  $-CH\cdot OH$  by the Fokin and Willstätter method. Energetic oxidation of hederagenin with concentrated nitric acid resulted in the formation of a small quantity of dimethylsuccinic acid from which the presence of the dimethylsuccinic acid skeleton is inferred (cf. Rosenthaler and Strom, A., 1912, i, 640), but no evidence of an *isopropyl* group was obtained. Hederagenin, hederagenolic acid, and hederagenone all give the fluorescein reaction with resorcinol. The four oxygen atoms of hederagenin are divided amongst three carbon atoms in vicinal position in the same ring. From the results of distilling hederagenin with zinc dust it is thought probable that two hydrogenated naphthalene nuclei are present and not two condensed rings as in dinaphthyl, or perylene. The relations between the above described compounds are expressed in the formulæ :



A. C.

**Saponins. I. Sapogenin from Soapnuts.** W. A. JACOBS (*J. Biol. Chem.*, 1925, **63**, 621—629).—By extraction with alcohol and hydrolysis with aqueous-alcoholic hydrochloric acid there was isolated from the nuts of *Sapindus saponaria*, L. (?) a *sapogenin*,  $C_{31}H_{50}O_4$ , m. p.  $327$ — $329^\circ$  with sintering,  $[\alpha]_D^{25} + 80^\circ$  in pyridine; the substance titrated as a monobasic acid to phenolphthalein. This was identified by direct comparison with the hederagenin obtained by van der Haar (A., 1912, i, 885) from ivy leaves. On boiling in glacial acetic acid, the substance gives a *monoacetate*, m. p.  $270$ — $275^\circ$  after softening at  $240^\circ$ ; on longer boiling in glacial acetic acid or on treatment with acetic anhydride, there was obtained a *diacetate*, sintering at  $156$ — $159^\circ$ , m. p.  $170$ — $175^\circ$ ; the latter was a stable substance, differing therein from the corresponding derivative described by van der Haar. The *dibenzoate*, obtained by benzylation in pyridine, has m. p.  $290$ — $291^\circ$ ; the *di-o-bromobenzoate* sinters at  $165^\circ$ , m. p.  $203$ — $205^\circ$ . The *methyl* ester ( $+1H_2O$ ) has m. p.  $238$ — $240^\circ$ ,  $[\alpha]_D^{25} + 75^\circ$  in alcohol, and was identified with

the methyl ester of hederagenin; it could not be hydrolysed with 10% alcoholic potassium hydroxide, nor could it be reduced with hydrogen and palladium. The *diacetate* of the methyl ester has m. p. 190—193° and the *di-o-bromobenzoate* m. p. 205—206°.

C. R. H.

**Saponins. II. Structure of Hederagenin.** W. A. JACOBS (*J. Biol. Chem.*, 1925, **63**, 631—640; cf. preceding abstract).—On treatment of hederagenin with thionyl chloride there was obtained the *sulphite* of *hederagenin chloride*,  $C_{31}H_{47}O_4ClS$ , m. p. 251—253°; on boiling with methyl alcohol this gave the *sulphite* of hederagenin methyl ester, m. p. 238—239°, and, on treatment with ammonia, the *sulphite* of *hederagenin amide* ( $+1H_2O$ ), m. p. 285°. These compounds appear to correspond with the chloride, methyl ester, and amide of hederagenin described by van der Haar and Tamburello (A., 1922, i, 160), who failed to recognise the formation of a neutral sulphite; the esterification of the hydroxyl groups and simultaneous bridge-formation between them is evidence of their proximity; this assumption is further supported by the ease with which hederagenin methyl ester gives an *acetonyl* derivative,  $C_{35}H_{56}O_4$ , m. p. 250—252°. *Hederagenin amide* ( $+3H_2O$ ), prepared by boiling the sulphite with alcoholic sodium hydroxide, has m. p. 300—303°. On oxidation of hederagenin methyl ester with potassium permanganate in acetone, there was obtained from the acetone solution *hederagenic acid methyl ester*,  $C_{32}H_{50}O_4$ , m. p. 217—218°,  $[\alpha]_D^{25} + 97^\circ$  in acetone; this gave an *oxime*, m. p. 211—213° with effervescence, and an *o-bromobenzoate*, m. p. 236—238°; by boiling out the precipitate of manganese dioxide with 70% alcohol, there was obtained the potassium salt of an *acid*,  $C_{64}H_{102}O_9$  ( $+2H_2O$ ), softening at 242°, m. p. 249—255°,  $[\alpha]_D^{25} + 84.6^\circ$  in 95% alcohol. On dissolving this acid in acetone and treating the solution with concentrated hydrochloric acid there was obtained a precipitate of the *acetonyl* derivative of hederagenin methyl ester; the mother-liquor yielded a compound,  $C_{32}H_{50}O_5$ , m. p. 274—276°,  $[\alpha]_D^{25} + 89.5^\circ$  in 95% alcohol, which titrated as a monobasic acid and still contained the ester group of hederagenin methyl ester; it was therefore the monomethyl ester of a dibasic acid designated *hederagic acid*, and the acid,  $C_{64}H_{102}O_9$ , was a molecular additive compound of this ester with hederagenin methyl ester. *Hederagic acid* monomethyl ester with methyl sulphate gave a *dimethyl* ester, m. p. 244—246°, and this in turn yielded an *o-bromobenzoate*, m. p. 194—197°. It did not form an oxime. The oxidation experiments lead to the conclusion that hederagenin is a dihydroxy-acid having a primary and a secondary alcoholic group, these groups being removed from one another by one carbon atom.

C. R. H.

**[Composition of] Chrysarobin.** R. EDER and F. HAUSER (*Arch. Pharm.*, 1925, **203**, 321—347; cf. A., 1917, i, 464; Hesse, A., 1917, i, 276, etc.).—The composition ascribed by Hesse (*loc. cit.*) to commercial chrysarobin differed in several respects from that arrived at by earlier workers. The authors have therefore examined

the product again, taking three different samples, m. p. 147—148° (two samples), 151—156°, respectively, for investigation.

When chrysarobin is oxidised, with or without previous reduction, in acetic acid solution with chromic acid, crystalline products are obtained in less satisfactory yield than when it is oxidised in alkaline solution by air. Moreover, no better results are obtained by oxidising acetylated chrysarobin, the yield of crystalline acetyl derivatives being meagre, although triacetylemodinanthranol monomethyl ether is almost quantitatively converted by this chromic acetic acid oxidation into diacetylemodin monomethyl ether.

The chrysarobin was therefore mixed with an excess of 1% sodium hydroxide solution and air was passed through until no further colour change was observed (cf. Hesse, *loc. cit.*). The solution, decanted and filtered, contained emodin, chrysophanol, emodin monomethyl ether, and amorphous substances (see below). That emodin is present as such in the original chrysarobin, and is not produced from an anthrone or anthranol by oxidation, is shown by the fact that it is extracted from a benzene solution of the drug by dilute sodium carbonate solution; that no reduced derivatives of emodin are present is shown by the fact that this extracted chrysarobin gives no more emodin on oxidation (cf. Tutin and Clewer, T., 1912, 101, 290). The composition of the amorphous substances from the solution above was not determined, but they are considered to arise from side-reaction (cf. Eder, A., 1915, i, 823). The chrysophanol and emodin monomethyl ether isolated above evidently represent material present in the chrysarobin as such, together with that formed by the "autoxidation." The compounds that have suffered oxidation have hitherto been considered to be the corresponding anthranols, but the work of Meyer (A., 1920, i, 745) suggests that this conclusion is incorrect. Direct tests, based on the fluorescence exhibited by the anthranols, but not by the tautomeric anthrones, in alkaline solution, show that the compounds present in chrysarobin are the latter, namely, chrysophanolanthrone (I) and emodinanthrone monomethyl ether (II), respectively. The anthranols do not exist in the free state, but only in alkaline solution. For reasons based on partial valency considerations the formulæ below are attributed to these compounds.



From the products of the air-oxidation treatment that remained undissolved by the sodium hydroxide solution there were isolated, after an exhaustive separation by fractional crystallisation from and extraction with acetic acid and petroleum, dehydroemodinanthranol monomethyl ether, emodinanthrone monomethyl ether, and, eventually, what appears to be ararobinol (m. p. 224—225°, cf. Tutin and Clewer, *loc. cit.*). The supposition that it is ararobinol



is to be accepted for the present, but the compound is still under investigation. Further, dehydro-emodinanthranol monomethyl ether was proved to be present as such in the original chrysarobin by direct extraction of the drug with petroleum. Hesse's "chrysarobol" is considered to be simply impure dehydro-emodinanthranol monomethyl ether.

For an approximately quantitative determination of the emodin present in the original material, it was separated as above and the quantity determined colorimetrically. The emodin-free chrysarobin was then shaken with sodium hydroxide in the absence of air. A rough colorimetric determination of the emodin monomethyl ether and chrysophanol (together) was made; the solution was precipitated with hydrochloric acid, redissolved (again in absence of air) and reprecipitated. The product was a mixture (m. p. 162—165°) of almost pure emodin monomethyl ether and chrysophanol ("methoxyl-containing chrysophanic acid").

From the above the authors arrive at the following for the composition of chrysarobin: chrysophanolanthrone, 29.3—38.8%; emodinanthrone monomethyl ether, 18.7—19.4%; dehydroemodinanthranol monomethyl ether, 22—35%; ararobinol (found only in two samples) 4%; "methoxy-containing chrysophanic acid," 2.5—3.5%; emodin, 2—3%; ash, 0.4—0.5%; the remainder is represented by unidentified amorphous substances and experimental losses.

The above results agree qualitatively with those of Tutin and Clewer. It is noteworthy that no reduction product of emodin is present. The botanical significance of these results is discussed.

W. A. S.

**Kakishibu. III. Constitution of Shibuol. II.** S. KOMATSU and N. MATSUNAMI (*Mem. Coll. Sci. Kyōtō*, 1925, 8, 231—240).—The insoluble shibuol isolated from kakishibu by precipitation with alcohol and ether (cf. A., 1923, i., 1197) is converted into a soluble form when heated with water at 125—130°. One portion of the soluble product dissolves in cold water, and appears to be a calcium salt, the portion insoluble in cold water being regarded as the free hydroxy-acid. Insoluble shibuol is considered to be an anhydride formed by elimination of 1 mol. of water from a carboxyl and a hydroxyl group. The anhydride form contains at least four hydroxyl groups, since it yields a tetra-acetyl derivative. When shibuol is hydrolysed, it yields phlobaphen and gallic acid, the former being assumed to be produced by removal of 1 mol. of water from two of the hydroxyl groups in the shibuol, forming an oxonium compound.

Phlobaphen when acetylated under pressure gives a triacetyl derivative. Acetylshibuol and acetylphlobaphen are completely hydrolysed when heated with water in a sealed tube. C. J. S.

**Synthesis of Androsin.** F. MAUTHNER (*J. pr. Chem.*, 1925, [ii], 110, 123—124).—Moore's preparation of androsin from the rhizome of *Apocynum androsaemifolium*, Linné (T., 1909, 95, 734), has been repeated, and the glucoside ( $C_{15}H_{20}O_8 \cdot 2H_2O$  and anhydrous)

is found to have m. p. 223—224°, identical with that of the author's synthetic *d*-glucoacetovanillone (A., 1918, i, 544) and of a mixture of the two, whilst their tetra-acetyl derivatives likewise have identical m. p. F. M. H.

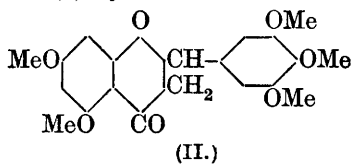
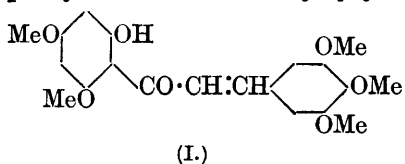
**Sphingosine. V. Synthesis of 1-Amino-2-hydroxy-*n*-heptadecane.** P. A. LEVENE and H. L. HALLER.—(See i, 890.)

**Gallotannin. XIV. Action of Yeast on Gallotannin.** M. NIERENSTEIN, C. W. SPIERS, and A. C. HADLEY (*J. Amer. Chem. Soc.*, 1925, **47**, 1726—1728).—By the action of *Saccharomyces cerevisiae*, cultivated to maximum intensity (yeast X) in gallotannin solutions, on purified Chinese gallotannin a gallotannin is obtained in 65% yield which is optically inactive and yields no dextrose on hydrolysis (cf. Biddle and Kelley, A., 1912, i, 713). No *m*-digallic acid is produced in the fermentation and only a little gallic acid. These results do not agree with the pentadigalloylglucose structure for gallotannin proposed by Fischer and Freudenberg (A., 1912, i, 471), but support the polydigalloyl-leucodigallic acid anhydride structure

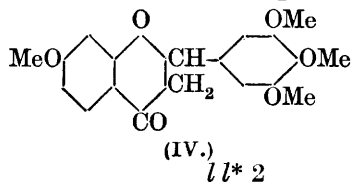
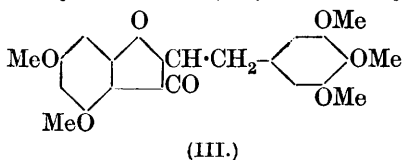
$$\begin{array}{c} [\text{CO} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{O}]_x \cdot \text{CO} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_2(\text{OH})_3 \\ \text{O} \cdot \text{C}_6\text{H}_2(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OH})_2 \\ \text{O} \text{-----} \alpha \text{-----} \text{CO} \end{array}$$

of Nierenstein (A., 1912, i, 468), on the assumption that the dextrose in the gallotannin-glucoside is attached to the  $\alpha$ -hydroxyl group of the formula, on the asymmetric carbon atom of the leucodigallic acid radical. On this assumption, the production of the optically inactive gallotannin is due to racemisation of the leucodigallic acid radical and fermentation of the dextrose. R. B.

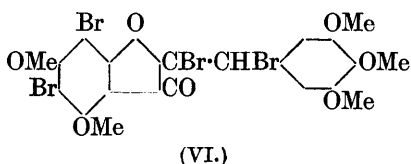
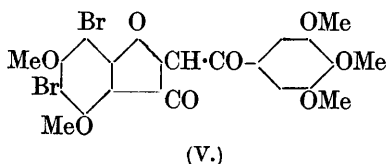
**Attempts to Synthesise Myricetin.** H. F. DEAN and M. NIERENSTEIN (*J. Amer. Chem. Soc.*, 1925, **47**, 1676—1684).—Although the product obtained from 2-hydroxy-4 : 6-dimethoxyphenyl 3 : 4 : 5-trimethoxystyryl ketone (I) by the usual methods



for the formation of flavanones yields no *isonitroso* derivative and cannot therefore be converted into myricetin it is regarded as the 4 : 6 : 3' : 4' : 5'-pentamethoxyflavanone (II) for the following reasons. (1) It is not identical with the 1 : 3 : 3' : 4' : 5'-pentamethoxybenzylcoumarone (III) obtained by reduction of 1 : 3 : 3' : 4' : 5'-penta-



methoxybenzylidenecoumaranone; (2) it is neither the *cis* nor *trans* form of the original phenyl styryl ketone since only the latter undergoes reduction to 2-hydroxy-4:6-dimethoxyphenyl 3:4:5-trimethoxyphenylethyl ketone; (3) the possibility of bimolecular condensation of the phenyl styryl ketone is excluded by molecular-weight determinations on the flavanone. The failure of the new flavanone to form an isonitroso derivative is not, however, due to steric hindrance of the pyrogallol nucleus, since 4:3:4':5'-tetramethoxyflavanone (IV) yields an isonitroso derivative. Attempts to obtain myricetin by Auwers' method (A., 1909, i, 45; 1920, i, 866) from 1:3:3':4':5'-pentamethoxybenzylidenecoumaranone were also unsuccessful, 2:4-dibromo-1:3:3':4':5'-pentamethoxybenzoylcoumaranone (V) being obtained. Similar results were obtained on application of the method to 3:3':4':5'-tetramethoxybenzylidenecoumaranone.



Phloracetophenone dimethyl ether and gallaldehyde trimethyl ether (obtained in 75.5% yield by a modification of Rosenmund's method, A., 1918, i, 300) with 50% aqueous potassium hydroxide at 60—70° yield 2-hydroxy-4:6-dimethoxyphenyl 3:4:5-trimethoxystyryl ketone, yellow, m. p. 180° (acetyl derivative, m. p. 146—147°), which on reduction in alcoholic solution with hydrogen in the presence of palladium yields 2-hydroxy-4:6-dimethoxyphenyl 3:4:5-trimethoxyphenylethyl ketone, m. p. 123°. When boiled with phosphoric acid in alcoholic solution, the phenyl styryl ketone is converted (yield 25%) into 1:3:3':4':5'-pentamethoxyflavanone (II), m. p. 177—178°, which on treatment in alcoholic solution with 10% potassium hydroxide is reconverted into the phenyl styryl ketone. Boiling with acetic anhydride converts the flavanone into the acetyl derivative of the phenyl styryl ketone, m. p. 146—147°.

Resacetophenone monomethyl ether and gallaldehyde trimethyl ether in alcoholic solution with 50% potassium hydroxide similarly yield 2-hydroxy-4:6-methoxyphenyl 3:4:5-trimethoxystyryl ketone, yellow, m. p. 132—133° (acetyl derivative, m. p. 125—127°), which with alcoholic phosphoric acid gives a 60% yield of 4:3':4':5'-tetramethoxyflavanone (IV), m. p. 148—149°. Alcoholic potassium hydroxide converts this into the original phenyl styryl ketone, but acetic anhydride is without action; amyl nitrite and hydrochloric acid yield the isonitroso derivative, yellow, m. p. 193°.

1:3-Dimethoxycoumaranone (Dumont and Tambor, A., 1910, i, 579) and gallaldehyde trimethyl ether with 10% sodium hydroxide give (yield 50%) 1:3:3':4':5'-pentamethoxybenzylidenecoumaranone, yellow, m. p. 214—216°, reduced by hydrogen and palladium in alcoholic solution to 1:3:3':4':5'-pentamethoxybenzylcoumaranone (III), m. p. 138—139°. On bromination in

chloroform solution the pentamethoxybenzylidenecoumaranone is converted into 2:4-dibromo-1:3:3':4':5'-pentamethoxybenzylidenecoumaranone dibromide (VI), white, m. p. 204—205° (decomp.). Bromination of the phloroglucinol nucleus precedes the addition of bromine to the  $-C:CH-$  group, yielding a dark red dibromocoumaranone, m. p. 217—219°. On treatment with aqueous potassium hydroxide in alcoholic solution, the tetrabromo-compound (VI) is converted into 2:4-dibromo-1:3:3':4':5'-pentamethoxybenzylidenecoumaranone (V), yellow, m. p. 260—261°.

3-Methoxycoumaranone (Blom and Tambor, A., 1905, i, 916) and gallaldehyde similarly yield 3:3':4':5'-tetramethoxybenzylidenecoumaranone, yellow, m. p. 187—188°, which on bromination in chloroform solution yields successively bromo-3:3':4':5'-tetramethoxybenzylidenecoumaranone, yellow, m. p. 163—164°, and bromo-3:3':4':5'-tetramethoxybenzylidenecoumaranone dibromide, white needles, m. p. 180° (decomp.). The latter compound on treatment with 0.1N-potassium hydroxide in alcoholic solution yields bromo-3:3':4':5'-tetramethoxybenzylidenecoumaranone, yellow, m. p. 162°.

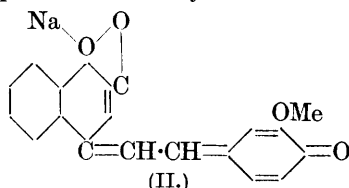
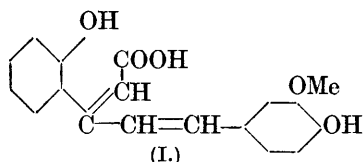
R. B.

**Furfuryl Furfuroate.** J. E. ZANETTI (*J. Amer. Chem. Soc.*, 1925, 47, 1452—1453).—Furfuryl furfuroate was obtained by the action of furfuroyl chloride on furfuryl alcohol in presence of sodium hydroxide. It forms prisms, m. p. 19.5°,  $d_{20}^{20}$  1.2443 (liquid), b. p. 122°/2 mm., or above 350° (decomp.) at atmospheric pressure. On keeping it passes into short prisms or thick, hexagonal plates, m. p. 27.5°.

F. G. W.

**Reactivity of the Methylene Group in Coumarin-4-acetic Acids.** II. B. B. DEY and K. K. ROW (*J. Indian Chem. Soc.*, 1925, 1, 277—287; cf. this vol. i, 149).—Coumarin-4-acetic acids condense with many aldehydes to form compounds of the stilbene type in which one of the phenyl groups is replaced by the coumarin residue, the carboxylic acids formed as the initial condensation products frequently eliminating carbon dioxide to yield ethylene derivatives, this tendency being greater in piperidine condensations than in Perkin reactions. The temperature of the reaction must be maintained as far as possible below the melting point of the substituted acetic acid in order to reduce the formation of 4-methylpyrones to a minimum. This tendency cannot be eliminated by previous esterification of the acid, since the esters fail to condense. By condensation of the appropriate coumarin-4-acetic acid and aldehyde the following compounds are obtained: 7-methyl-4-coumaryl-p-methoxyphenylethylene, pale yellow needles, m. p. 180°; 7-methyl-4-coumaryl-p-dimethylaminophenylethylene, orange, m. p. 190° (picrate, m. p. 204°, mercurichloride, dichromate, chloroplatinate, and ferrocyanide are prepared); 7-methyl-4-coumaryl-3'-methoxy-4'-hydroxyphenylethylene, golden needles, m. p. 222°. This compound dissolves in dilute solutions of alkali hydroxides to a deep red solution (immediate acidification reprecipitates the original substance) the colour of which disappears slowly on keeping or rapidly on heating on a water-bath, and acidification now precipitates a

white solid soluble in sodium carbonate solution, which the authors suggest is the unstable acid of the coumaric type (I), the deep red colour in alkaline solution being due to a doubly quinonoid form (II), the pyrone oxygen being quadrivalent.



of  $\alpha$ -naphthapyrone-4-acetic acid with anisaldehyde is obtained  $\alpha$ -naphthapyrone-4-*p*-methoxyphenylethylene, yellow needles, m. p. 182—183°;  $\alpha$ -naphthacoumarinacetic acid and *p*-dimethylaminobenzaldehyde yield  $\alpha$ -naphthapyrone-4-*p*-dimethylaminophenylethylene, deep red, m. p. 215—216° (hydrochloride, colourless). Similar compounds are obtained by the condensation of phenylacetic acid and aromatic aldehydes, 4-hydroxy-3-methoxystilbene- $\alpha'$ -carboxylic acid, colourless, m. p. 186—187°, being obtained from vanillin by Perkin's method, whilst condensation by means of piperidine at 140—150° yields only 4-hydroxy-3-methoxystilbene (m. p. 134°), which on methylation yields 3:4-dimethoxystilbene, colourless needles, m. p. 111°; 5-bromo-4-methoxystilbene- $\alpha'$ -carboxylic acid, colourless, has m. p. 222°; *p*-dimethylaminostilbene has m. p. 150° (cf. Sachs, A., 1905, i, 202, gives 147—148°); methylene ether of 3:4-dihydroxystilbene- $\alpha'$ -carboxylic acid, colourless, m. p. 231—232° (silver salt; ethyl ester, m. p. 104°, described) results from piperonal by Perkin's method, whilst condensation using piperidine at 170° yields the methylene ether of 3:4-dihydroxystilbene (cf. Hell and Wiegandt, A., 1904, i, 490) in addition. *m*-Dinitrotoluene condenses with vanillin to yield 2':4'-dinitro-4-hydroxy-3-methoxystilbene, red, m. p. 193°, and with piperonal to yield the methylene ether of 2':4'-dinitro-3:4-dihydroxystilbene, reddish-brown, m. p. 183°.

J. W. B.

**Bz-Hydroxycoumarone Compounds.** K. FRIES and M. NÖHREU (*Ber.*, 1925, 58, [B], 1027—1034; cf. Sonn and Patschke, this vol., i, 282).—7-Hydroxy-4-methylcoumarin is converted by ethyl chloroformate and sodium hydroxide into 7-ethylcarbonato-4-methylcoumarin, m. p. 102°, which is slowly converted by bromine in chloroform solution at the atmospheric temperature into 3-bromo-7-ethylcarbonato-4-methylcoumarin, m. p. 144°. The latter substance is transformed by ammonia into 3-bromo-7-hydroxy-4-methylcoumarin, m. p. 215°, by alcoholic potassium hydroxide into 6-hydroxy-3-methyl-2-coumarilic acid, m. p. 226° (ethylcarbonato derivative, m. p. 189°), and by aqueous sodium carbonate solution into 6-hydroxy-3-methylcoumarone, m. p. 103° (ethylcarbonato derivative, m. p. 54°; benzoyl compound, m. p. 102°). 6-Hydroxy-3-methylcoumarone gives dark blue salts when treated in ethereal solution with hydrogen chloride or perchloric acid from which the original material cannot be regenerated; the perchlorate appears to have

the composition  $C_{18}H_{16}O_4.HClO_4$ . Treatment of 6-hydroxy-3-methylcoumarone dissolved in chloroform with bromine and chlorine yields the compounds  $C_{18}H_{13}O_4Br$ , m. p.  $218^\circ$  (decomp.), and  $C_{18}H_{13}O_4Cl$ , m. p. about  $190^\circ$  (decomp.), in which the halogen is replaced by hydrogen under the influence of boiling acetone, thus giving the dicoumarone derivative,  $C_{18}H_{14}O_4$ , m. p.  $254^\circ$  after darkening at  $240^\circ$  (diacetyl compound, m. p.  $222^\circ$ ; dimethyl ether, m. p.  $191^\circ$ ). The dihydroxydicoumarone is converted by ferric chloride in glacial acetic acid solution into the compound  $(C_{18}H_{14}O_4)_2O$ . 7-Ethylcarbonatocoumarin, m. p.  $98^\circ$ , is much less readily brominated than the methyl derivative described above. 3-Bromo-7-ethylcarbonatocoumarin, m. p.  $132^\circ$ , is transformed by alcoholic potassium hydroxide into 6-hydroxycoumarilic acid, decomp.  $264^\circ$  (Karrer, Glattfelder and Widmer, A., 1920, i, 628, record m. p.  $234-236^\circ$ ), and by boiling sodium acetate solution into 3-bromo-7-hydroxycoumarin, m. p.  $242^\circ$  (decomp.). 6-Ethylcarbonato-4-methylcoumarin, m. p.  $134^\circ$ , is resistant towards bromine, which, under drastic conditions, causes substitution in the benzenoid nucleus.

H. W.

### Dissociation into Free Radicals of Substituted Dixanthyls.

**I. Dibenzyl- and Dibutyl-dixanthyl.** J. B. CONANT and A. W. SLOAN (*J. Amer. Chem. Soc.*, 1925, **47**, 572—580).—When benzylxanthidrol, benzylidenexanthone, or benzylxanthyl perchlorate, m. p.  $226-227^\circ$ , is reduced in concentrated hydrochloric acid solution with vanadous chloride (cf. A., 1924, i, 304), dibenzyl-dixanthyl, m. p.  $146.5-148.5^\circ$ , is obtained. This is undissociated in benzene at the freezing point of the latter, but the solution is yellow at  $20^\circ$  and reddish-brown at  $100^\circ$ . At  $108^\circ$ , the colour fades rapidly, and the solution then contains benzylidenexanthone and probably benzylxanthone, m. p.  $60-62^\circ$  (cf. Ziegler, A., 1924, i, 850). The dibenzyl-dixanthyl absorbs oxygen with formation of dibenzyl-dixanthyl peroxide, m. p.  $131^\circ$ , which decomposes when heated in benzene solution, yielding xanthone and other products. *n*-Butylxanthidrol, m. p.  $109-112^\circ$ , obtained from xanthone and *n*-butyl magnesium bromide, undergoes auto-oxidation, forming unidentified products, and loses water when stored over sulphuric acid. *n*-Butylxanthyl perchlorate, orange, m. p.  $187-189^\circ$ , is more stable than the above xanthidrol. It yields dibutyl-dixanthyl, m. p.  $158-158.5^\circ$ , when reduced with vanadous chloride. This exists in the undissociated form in benzene solution, and absorbs oxygen slowly with formation of di-*n*-butyl-dixanthyl peroxide, m. p.  $182-183.5^\circ$  (decomp.). The effect of non-aromatic groups on the dissociation of ethanes is discussed, and it is pointed out that the existence of the free radical benzylxanthyl is contrary to Werner's theory of valency (cf. Schlenk and Mark, A., 1922, i, 1002) and to theories involving alternate strong and weak affinities and alternating polarities.

F. G. W.

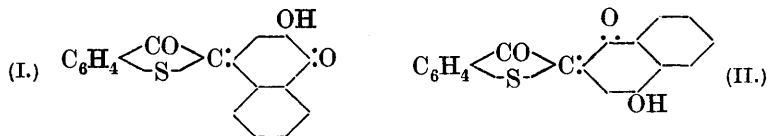
**Dyes of the Pyrone Series.** FARBENFABRIKEN VORM. F. BAYER & Co. (Brit. Pat. 223596).—Fluorescein chloride is condensed at  $200-210^\circ$  with 2 mols. of *vic*-*m*-xylidine in presence of

zinc oxide and zinc chloride and the product sulphonated. The resulting dye, isolated as *sodium* salt, dyes wool a yellowish-red shade, extraordinarily fast to light. [Cf. *B.*, 1925, 624.] E. H. R.

**The Thiophens and Intermediate Products for their Synthesis.** [MISS] A. CHRZASZCZEWSKA (*Roczniki Chemji*, 1925, 5, [1—3], 33—76).—Various thiophen derivatives have been synthesised by Paal's method from salts of homologues of succinic acid. The yield is greatly increased by the addition of sand to the reaction mixture, in quantity equal to that of the phosphorus trisulphide used, the violence of the reaction being thereby considerably diminished. Better yields of 2-substituted thiophens are obtained where the latter are more volatile, this being explained by the greater tendency to charring of the higher  $\gamma$ -keto-acids. An excess of phosphorus trisulphide has a deleterious effect on the reaction. The nitration of thiophens has been investigated, and it is shown that the yield is quadrupled if acetyl chloride be added to the nitrating mixture of acetic anhydride and nitric acid. 3-Phenylthiophen, m. p. 91—92°, was synthesised in the above way from sodium phenylsuccinate, and from it *nitro-3-phenylthiophen*, pale yellow, m. p. 141°, was prepared, the nitro group being shown to be in the thiophen ring, and this on reduction gave *amino-3-phenylthiophen hydrochloride*. Platinum-black and hydrogen have practically no reducing action on 3-phenylthiophen. 3-*p-Anisylthiophen*, m. p. 129°, was prepared from *p-anisylsuccinic acid*, pale yellow, m. p. 189—190°, prepared from *ethyl p-methoxybenzylidenemalonate*, m. p. 38—40°, obtained from the condensation of anisaldehyde with ethyl malonate. In the same way, *ethyl p-tolylidenemalonate*, m. p. 46—47°, is prepared, giving on hydrolysis *p-tolylidenemalononic acid*, m. p. 184°, and from which *p-tolylsuccinic acid*, m. p. 192°, is prepared. From this, 3-*p-tolylthiophen*, m. p. 111—112°, is obtained by the modified Paal's method. 2-Methylthiophen is obtained in 62% yield in this way from sodium laevulate, as compared with 15% yield from the unmodified method; its *nitro* derivative, yellow oil, b. p. 147·7°/38·5 mm., is described. Similarly, 2-phenylthiophen is prepared from sodium benzoylpropionate in 30% yield, giving on nitration *nitro-2-phenylthiophen*, yellow, m. p. 74°, and on treatment with iodine *iodo-2-phenylthiophen*, pale yellow, m. p. 76—77°. 2-*p-Tolylthiophen*, m. p. 63—64°, is obtained from *p-toluypropionic acid*, and *p-hydroxyphenylsuccinic acid* (+1H<sub>2</sub>O), m. p. 159°, from *ethyl p-hydroxybenzylidenemalonate*, m. p. 93°. R. T.

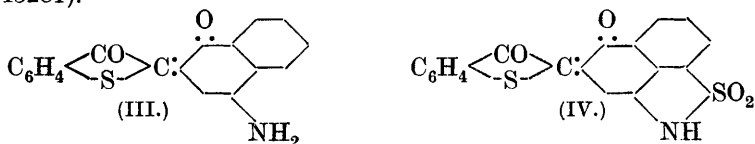
**Indigoid Dyes of the Naphthalene Series.** P. FRIEDLÄNDER (*Annalen*, 1925, 443, 211—223).—Indigoid dyes of the naphthalene-thionaphthen or naphthalene-indole groups can be obtained by the condensation of  $\alpha$ - and  $\beta$ -naphthaquinones (in dilute alcoholic solution) or their sulphonic acids (in aqueous solution) with 3-oxythionaphthen or indoxyl, respectively. The primary reaction products are leuco compounds formed by addition of the thionaphthen or indole to the  $\cdot\text{C}:\text{C}\cdot$  linking of the diketone, which are

then oxidised, either by air or by an added oxidising agent, or by excess of the quinone itself, to the dyes. For example, 3-hydroxy-4-keto-1-oxythionaphthenylidene-1:4-dihydronaphthalene (I), brownish-



violet (*acetyl* derivative, brownish-red), is obtained when air is bubbled through a mixture of equivalents of  $\beta$ -naphthaquinone and 3-oxythionaphthen in dilute alcoholic solution in presence of sodium carbonate. It reacts with primary aromatic amines in acetic acid solution, the hydroxyl group being replaced by the corresponding arylamino residue. The products obtained in this way from aniline, anthranilic acid, methyl anthranilate, and aminoazobenzene, are described. 1-Hydroxy-4-keto-3-oxythionaphthenylidene-3:4-dihydronaphthalene (II) is obtained similarly from  $\alpha$ -naphthaquinone.

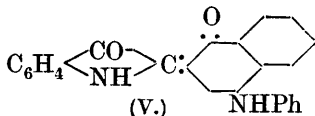
Compounds of the same series can also be obtained by the interaction of  $\alpha$ -naphthol-*p*-azo compounds with 3-hydroxythionaphthen or indoxyl, or their substitution products (cf. Kalle u. Co., D.R.-PP. 229267 and 282890). Thus, 1-amino-4-keto-3-oxythionaphthenylidene-3:4-dihydronaphthalene (III) is produced when equivalents of "orange I" (benzeneazo- $\alpha$ -naphthol-4-sulphonic acid) are boiled in aqueous solution in presence of borax. It is separated from accompanying thioindigotin by extracting the nitrobenzene solution of the crude product at 70° with sulphuric acid (*d* 1.712), the pure dye being precipitated by hydrolysis on dilution of the acid extract. The amino group of this series cannot be diazotised, but the indigoid azo dyes can be synthesised by the action of isatinanilide on benzeneazo- $\alpha$ -naphthols (cf. Kalle u. Co., D.R.-P. 245281).



*N*-Derivatives of  $\alpha$ -naphthaquinoneimine can also be condensed with 3-oxythionaphthen. For example, the dye (IV) is obtained by condensing 1:8-naphthasultam-4-quinone (cf. Zincke and Schürmann, A., 1917, i, 38) with 3-oxythionaphthen. The naphthaquinoneanils (cf. Euler, A., 1906, i, 369) can be obtained by oxidation of the corresponding 4-arylamino- $\alpha$ -naphthols, which are readily prepared by boiling  $\alpha$ -naphthaquinol with primary aromatic amines. 4-Anilino- $\alpha$ -naphthol, m. p. 89—90° (*O*-methyl ether, m. p. 189°), and 4-*p*-chloroanilino- $\alpha$ -naphthol, m. p. 96° (*O*-methyl ether, m. p. 125°), are described, as well as the preparation of 4-anilino-1-keto-3-oxythionaphthenylidenedihydronaphthalene (cf. Fries and Ehlers, A.,

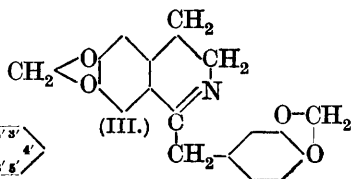
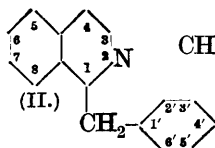
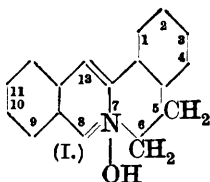


1923, i, 829), from 3-oxythionaphthen and  $\alpha$ -naphthaquinoneanil. For the preparation of corresponding compounds of the naphthalene-indole series, replacement of 3-oxythionaphthen by indoxyl in the above reaction is unsatisfactory, as large proportions of indigo are formed. The condensation of isatinanilide with 4-arylamino- $\alpha$ -naphthols offers a convenient alternative. Thus 4-anilino-1-keto-3-oxindolidene-3:4-dihydronaphthalene (V), blue, is obtained when equivalents of isatinanilide and 4-anilino- $\alpha$ -naphthol are warmed in acetic anhydride solution. The corresponding *p*-chloro-anilino compound, obtained similarly, is described. [Cf. *B.*, 1925, 582.] F. G. W.



**Vasicine—An Alkaloid Present in *Adhatoda vasica*, Nees.** J. N. SEN and T. P. GHOSE (*J. Indian Chem. Soc.*, 1925, **1**, 315—320).—*Vasicine*,  $C_{11}H_{12}ON_2$ , extracted from the leaves of *Adhatoda vasica* by means of alcohol or a mixture of ammonia and chloroform, forms needles, m. p. 190—191° (decomp.), is optically inactive, and contains no methoxyl groups. It gives characteristic precipitates with the alkaloid reagents; the following derivatives are described: *picrate*, m. p. 199° (decomp.); *hydrochloride* (+2H<sub>2</sub>O), m. p. 204° (anhydrous salt); *chloroaurate*, B<sub>2</sub>H<sub>2</sub>AuCl<sub>4</sub>, orange; *chloroplatinate*, yellowish-brown, B<sub>2</sub>H<sub>2</sub>PtCl<sub>6</sub>; *hydriodide* (+2H<sub>2</sub>O), m. p. 195° (anhydrous salt); *sulphate*, B<sub>2</sub>H<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O; *methiodide*, m. p. 187°, converted by aqueous barium hydroxide into “*hydroxymethylvasicine*,” m. p. 100°. J. W. B.

**Synthesis of 2:3:10:11-Bismethylenedioxyprotoberberine and 6:7:3':4'-Bismethylenedioxyprotopapaverine.** J. S. BUCK, W. H. PERKIN, jun., and T. S. STEVENS (*J. Chem. Soc.*, 1925, **127**, 1462—1472).—The names “protoberberine” and “protopapaverine” are suggested for the parent substances (I and II) of berberine and papaverine, respectively.



Homopiperonylhomopiperonylamine, prepared by a modification of Decker's method (Decker, Kropp, Hoyer, and Becker, A., 1913, i, 289), is converted by phosphoryl chloride in toluene into 6:7:3':4'-bismethylenedioxy-3:4-dihydroprotopapaverine, m. p. 92—96° [*phosphate* and *picrate*, m. p. 220° (decomp.), described], which is reduced by zinc and dilute sulphuric acid to the *tetrahydro* compound, m. p. 84—85° [*hydriodide*, m. p. 250—254°; *picrate*, m. p. 210° (decomp., softens 190°)]. By condensation of the *tetrahydro* base with formaldehyde there is obtained 2:3:10:11-*bis*-

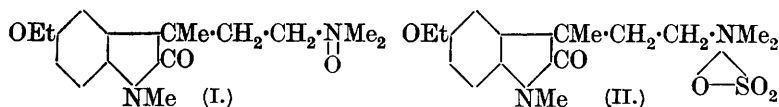
*methylendioxytetrahydroprotoberberine*, m. p. 214° (*hydrochloride* described), the 6'- probably reacting in preference to the 2'-carbon atom (cf. this vol., i, 969). 2:3:10:11-*Bismethylendioxyprotoberberinium iodide*, decomp. >300° [*chloride* (+2H<sub>2</sub>O), decomp. >300°; *picrate* darkens 260°, explodes 310°], results from the action of iodine on the tetrahydro compound. The quaternary chloride, heated at 100° with 40% aqueous potassium hydroxide, gives 2:3:10:11-*bismethylendioxyoxyprotoberberine*, m. p. >270°, and the corresponding *bismethylendioxy-7:8-dihydroprotoberberine*, m. p. 161—164° (*picrate*, decomp. >240°).

The 6:7:3':4'-*Bismethylendioxy-3:4-dihydroprotopapaverine* of m. p. 92—96° is rapidly oxidised by air to the 9-keto derivative, m. p. 136° [*hydriodide*, m. p. 216—219° (decomp.); *picrate*, m. p. 202° (decomp., softens 180°); *oxime*, m. p. 235° (decomp.)], which is most probably identical with the by-product, m. p. 136—137°, obtained by Decker, Kropp, Hoyer, and Becker (*loc. cit.*) from the action of phosphoryl chloride on homopiperonylhomopiperonylamine, and to which they wrongly assigned the structure (III). This compound is converted by hot methyl-alcoholic potassium hydroxide into 6:7:3':4'-*bismethylendioxy-9-ketoprotopapaverine*, m. p. 186° [*hydriodide*, m. p. about 230° (decomp.); *picrate*, m. p. 240° (decomp.); *oxime*, m. p. 275° (decomp.)]. The latter base is reduced with zinc and acetic acid to the corresponding 9-*hydroxy* compound, m. p. 169—170°, which is converted into 6:7:3':4'-*bismethylendioxyprotopapaverine*, m. p. 170—172° [*picrate*, m. p. 199—202° (decomp.)], by dissolving in acetic acid, saturating for 12 hrs. with hydrogen bromide, and reducing the 9-bromo compound so formed by adding zinc powder at 25—50°. Papaverine is readily obtained from papaverinol in a similar manner, but the yield by reduction of papaveraldine with zinc dust and acetic anhydride (Stuchlik, A., 1901, i, 41) is not satisfactory.

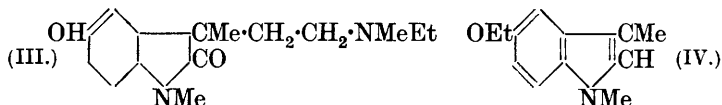
When tetrahydropapaverine is oxidised with iodine, the product is 6:7:3':4'-tetramethoxy-9-keto-3:4-dihydroprotopapaverine [identical with the substance prepared by Buck, Haworth, and Perkin (T., 1924, 125, 2176) by air-oxidation of the corresponding benzyldihydroisoquinoline], together with two feebly basic *substances*, m. p. 300° and 163—167°. C. H.

**Alkaloids of the Calabar Bean. XIV. Constitution of Eserine and Oxyeserine Derivatives.** M. POLONOVSKI and M. POLONOVSKI (*Bull. Soc. chim.*, 1925, [iv], 37, 744—759).—Results already published (this vol., i, 151, 293) are discussed in relation to the work of Stedman and Barger (this vol., i, 292). The low yields of oxyeseretholemethine (Stedman and Barger's dehydro-eseretholemethine) obtained in oxidising eseretholemethine with hydrogen peroxide are partly due to the formation of a *N-oxide*, C<sub>16</sub>H<sub>24</sub>O<sub>3</sub>N<sub>2</sub>, m. p. 60°,  $\alpha_D$  -38°, which is readily soluble in water but nearly insoluble in ether. The oxide yields a *hydrochloride*, m. p. 198°, and is converted into oxyeseretholemethine when reduced with zinc and hydrochloric acid. The structure (I) is suggested for this oxide, whilst the *sulphone ether*, m. p. 193—194° (decomp.), precipi-

tated by passing sulphur dioxide into its aqueous solution is probably (II).

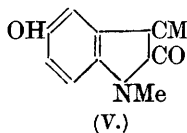


The amine oxide is obtained by the action of hydrogen peroxide on oxyseretholemethine itself, whilst analogous amine oxides are similarly obtained from oxyserolemethine and oxyserimethine. The *N-oxide* of oxyserolemethine has m. p.  $180^{\circ}$ ,  $\alpha_D -29^{\circ}$ . Oxyserolemethine, m. p.  $171^{\circ}$ , is readily obtained by oxidising eserine nitromethiodide with hydrogen peroxide, a reaction which shows that the presence of iodine is not essential for the passage from the eserine to the oxyserine series. The passage from the geneserine to the oxyseroline series can be achieved in the absence of oxidising agents in the methylation of geneserine with methyl sulphate and methyl alcohol, the product consisting of oxyserimethine and oxyserolemethine. Geneserine is converted by alcoholic ethyl bromide into eserine and *oxyseriethine*,  $[\alpha]_D -72^{\circ}$ , this substance, when hydrolysed, yielding the corresponding phenolic derivatives. *Oxyserole-ethine* (III) has m. p.  $166-167^{\circ}$ . Ethyl-



physostigmol (IV), m. p.  $86^{\circ}$ , is obtained by the distillation of eserethole or of eserethole hydrochloride at  $200-220^{\circ}$  in a vacuum, when methylamine is eliminated, whereas eserethole methiodide yields only dimethylamine. Geneserine, when heated in absolute alcohol with sodium ethoxide and methyl iodide yields a *hydriodide*,  $C_{15}H_{23}O_2N_2I$ , m. p.  $244^{\circ}$ , of *O-methyloxyserolemethine*. This salt is converted by potassium carbonate into an ether-soluble base. Geneseroline yields the same hydriodide, but with a larger excess of methyl iodide, or on starting from oxyserimethine, besides an iodo derivative, m. p.  $200^{\circ}$ , a methiodide,  $C_{16}H_{27}O_2N_2I$ , m. p.  $153^{\circ}$  (not decomposed by potassium carbonate), is almost exclusively formed.

Oxyserolemethine methiodide, m. p.  $278^{\circ}$ , when heated in a vacuum at  $280-290^{\circ}$  decomposes in two ways, the first reaction yielding methyl iodide and oxyserolemethine, m. p.  $171^{\circ}$ , whilst the second yields trimethylamine and oxyserolene, m. p.  $224^{\circ}$ ,  $[\alpha]_D -85^{\circ}$  (*picrate*, m. p.  $215^{\circ}$ ),  $OH \cdot C_{12}H_{13}ON \cdot NMe_3I \rightarrow NMe_3, HI + OH \cdot C_{12}H_{12}ON$ . When reduced with hydrogen in the presence of colloidal platinum, oxyserolene is converted into hydro-oxyserolene (V), m. p.  $199-200^{\circ}$ .



Ethyloxyserolene (oxyetheserolene) is also obtained by direct ethylation of oxyserimethine with ethyl *p*-toluenesulphonate. Oxyseretholemethine when heated

at 275° in a vacuum similarly decomposes in two ways, yielding trimethylamine and ethyloxyeserolene, and methyl iodide and oxy-eseretholemethine.

R. B.

**Preparation of Monobromo- and Monochloro-codeine and their Behaviour on Catalytic Reduction.** E. SPEYER and H. ROSENFELD (*Ber.*, 1925, 58, [B], 1110—1113).—Codeine hydrochloride is converted when warmed with hydrogen peroxide in formic acid solution into chlorocodeine, m. p. 175—176°,  $[\alpha]_D^{16}$  —147.21° in alcohol. Codeine hydrobromide is transformed similarly into bromocodeine. Catalytic hydrogenation of the latter substance in the presence of palladised charcoal gives in well-defined stages, successively *bromodihydrocodeine*, m. p. 190°, and *dihydrocodeine*, whereas chlorocodeine is reduced only to *chlorodihydrocodeine*, m. p. 196°.

H. W.

**Action of Thionyl Chloride on Codeine and its Isomerides.** E. SPEYER and H. ROSENFELD (*Ber.*, 1925, 58, [B], 1113—1116).— $\beta$ -Chlorocodeide, m. p. 153°, is readily obtained by boiling a solution of  $\alpha$ -chlorocodeide in tetrahydronaphthalene or, preferably, bromobenzene, the yield being 70—75%. The action of thionyl chloride on  $\psi$ -codeine at 0° gives  $\alpha$ -chlorocodeide, m. p. 148°,  $[\alpha]_D^{15}$  —385.2° in alcohol, whereas  $\beta$ -chlorocodeide is obtained exclusively under similar conditions from *allo-ψ*-codeine and *isocodeine*. The conversions of  $\psi$ -codeine and codeine into  $\beta$ -chlorocodeide by fuming hydrochloric acid under pressure is probably due to secondary change of the  $\alpha$ -chlorocodeide produced initially.

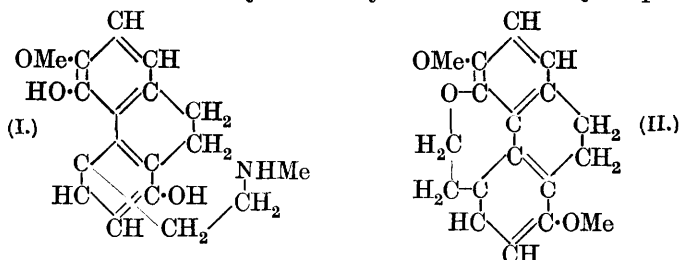
H. W.

**Action of Sodium Hyposulphite on Bromocodeinone.** E. SPEYER and H. ROSENFELD (*Ber.*, 1925, 58, [B], 1117—1119).—Reduction of bromocodeinone with warm sodium hyposulphite solution followed by treatment of the ice-cold solution with sodium hydroxide gives a colourless, amorphous, halogen-free base which gives non-crystalline salts. It is converted by warm sodium hydroxide solution into a crystalline substance,  $C_{18}H_{21}O_3N$ , m. p. 240—241° (decomp.) [*picrate*, decomp. about 210°]. The presence of a tertiary nitrogen atom is established by the production of an amorphous *methiodide* and of the ketonic group by the isolation of the *oxime*,  $C_{18}H_{22}O_3N_2$ , decomp. 266—270°. The insolubility of the base in sodium hydroxide solution shows the oxygen bridge of the original material to remain intact, whereas it is ruptured by reduction at prepared lead electrodes, giving amorphous products which yielded only amorphous salts. It is suggested that the new base is dehydro- $\psi$ -codeinone.

H. W.

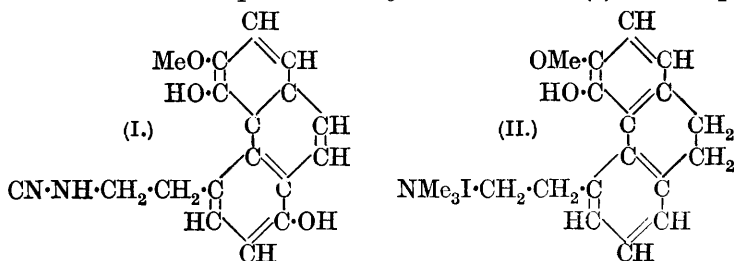
**Dihydrothebenine and its Degradation.** E. SPEYER and H. ROSENFELD (*Ber.*, 1925, 58, [B], 1120—1124).—Thebenine hydrochloride is converted by boiling aqueous sodium hyposulphite solution into *dihydrothebenine thiosulphate*, m. p. 194—195°, which with ammonia yields *dihydrothebenine* (I) (+H<sub>2</sub>O), decomp. 147—148° (*hydrochloride*, decomp. 237—238°; *N-methyl**dihydrothebenine hydriodide*, m. p. 130—131°). Attempts to methylate the compound

exhaustively failed, owing to the presence of the phenolic hydroxy groups, but it is converted by sodium hydroxide and methyl sulphate



into *dimethoxydihydrothebeninmethine methosulphate*, decomp. 270—271°, from which the corresponding quaternary *iodide*, decomp. 245°, is derived. Silver oxide converts the iodide into the hydroxide, which is decomposed by boiling potassium hydroxide solution into trimethylamine and "*methoxydihydrothebenol*" (II), m. p. 133—134°. Reduction of the latter substance with red phosphorus and hydriodic acid (*d* 1.7) at 220° gives an oil, b. p. 300—310°, which yields a *picrate*, decomp. 212—214°. H. W.

**Action of Cyanogen Bromide on Thebaine.** E. SPEYER and H. ROSENFELD (*Ber.*, 1925, 58, [B], 1125—1128).—The action of cyanogen bromide on thebaine in the presence of chloroform has yielded a small amount of a substance to which von Braun (A., 1914, i, 1138) has assigned the composition  $C_{20}H_{20}O_3N_2$ . The compound, m. p. 146—147°, is much more readily produced if glacial acetic acid is used as solvent; it has the composition  $C_{18}H_{16}O_3N_2$ . The changes in colour observed during the reaction and, particularly, the presence of only one methoxyl group in the molecule show the compound to be *cyanonorthebenine* (I). Attempts



to obtain the substance from cyanogen bromide and thebaine and to hydrolyse it to northebenine were unsuccessful. In dilute acetic acid solution in the presence of palladised charcoal it absorbs 4 mols. of hydrogen, and the oily base thus obtained is converted by methyl iodide into the *compound* (II), m. p. 298—299°. H. W.

**Dissociation of Salts of Narcotine and optimum Conditions for its Extraction.** R. FABRE and E. PARINAUD (*Compt. rend.*, 1925, 180, 2077—2079; cf. Otto, A., 1896, ii, 508).—Narcotine hydrochloride is dissociated more in aqueous solution than the

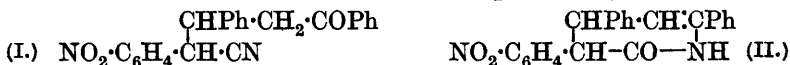
sulphate. All the narcotine present in solutions of the hydrochloride, sulphate, or tartrate may be extracted by a continuous process by means of chloroform, ethyl alcohol, or benzene. Extraction of solutions of the hydrochloride with chloroform is the most rapid method.  
L. F. H.

**Synthesis of 1-Aryl-2-pyrrolidones.** P. LIPP and F. CASPERS (*Ber.*, 1925, 58, [B], 1011—1014).— $\gamma$ -Chloro-*n*-butyryl chloride, b. p. 59—60°/11 mm., conveniently prepared by the action of thionyl chloride on  $\gamma$ -chloro-*n*-butyric acid in the presence of light petroleum, is transformed by aniline into the corresponding *anilide*, m. p. 69—70°, and thence by cautious treatment with molten potassium hydroxide into 1-phenyl-2-pyrrolidone, m. p. 68—69°. Similarly,  $\gamma$ -chloro-*n*-butyro-*p*-toluidide, m. p. 91—92·5° (corr.) after softening, affords 1-*p*-tolyl-2-pyrrolidone, m. p. 88—89° (corr.) [*picrate*, m. p. 121—122° (corr.)].  
H. W.

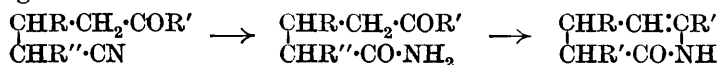
**Colour Reactions of Tryptophan with Aldehydes.** A. BLANCHETIÈRE (*Compt. rend.*, 1925, 180, 2072—2074; cf. A., 1907, ii, 320; 1908, ii, 76; 1910, ii, 559; 1912, i, 401; 1920, ii, 786).—Pure tryptophan does not give the colour reaction with phosphoric acid described by Romieu (this vol., i, 607), the presence of an aldehyde being necessary. Sulphuric acid yields the same reaction as phosphoric acid. The substitution of phosphoric acid for sulphuric acid in the condensation of tryptophan with vanillin (Steensma, A., 1906, ii, 315) results in an increased sensitivity, and the reaction may be used for the determination of tryptophan.

L. F. H.

**Reactions of  $\delta$ -Ketonic Nitriles.** C. F. H. ALLEN (*J. Amer. Chem. Soc.*, 1925, 47, 1733—1741).—*p*-Nitrophenylacetone nitrile yields two stereoisomeric additive products (I) with phenyl styryl ketone, the addition taking place more readily than with the cyanoacetic acid derivatives. Both additive products yield the same



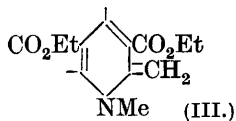
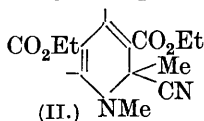
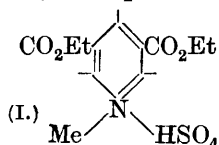
tetrahydropyridine derivative (I), but the reaction is no more rapid than with the unsubstituted nitriles (Kohler and Allen, A., 1924, i, 855), differences being more probably due to limited solubilities than to activity of the  $\alpha$ -hydrogen atom. Although this transformation does not take place in the presence of acetyl chloride to exclude traces of water, the cyanoacetamide additive product,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CH}(\text{CN}) \cdot \text{CO} \cdot \text{NH}_2$  (Kohler and Souther, A., 1923, i, 243), undergoes transformation to the tetrahydropyridine derivative either in the presence of acetyl chloride or in dimethylaniline. It is therefore concluded that in the formation of tetrahydropyridine derivatives from  $\delta$ -ketone nitriles the first stage of the reaction is the addition of water, forming an amide which then undergoes ring closure:



*p*-Nitrobenzyl cyanide and phenyl styryl ketone in methyl alcoholic solution and the presence of a trace of alkali give a mixture of  $\gamma$ -benzoyl- $\beta$ -phenyl- $\alpha$ -*p*-nitrophenylbutyronitrile, m. p. 144° (yield 65%), with its stereoisomeride, m. p. 126° (yield 19%). Hydrogen bromide in glacial acetic acid converts both isomerides (yield 92%) into 2-keto-4 : 6-diphenyl-3-*p*-nitrophenyltetrahydropyridine, m. p. 236°, which with sodium nitrite in glacial acetic acid yields 2-hydroxy-4 : 6-diphenyl-3-*p*-nitrophenylpyridine (II), yellow prisms, m. p. 311—312° (decomp.). In hot carbon tetrachloride, hydrogen bromide gives a yellow precipitate (yield 90%) of the "amide bromide." That from the nitrile, m. p. 126°, had m. p. 118—119° and the composition  $C_{23}H_{18}O_3N_2 \cdot 2HBr$ . The intermediately formed  $\gamma$ -benzoyl- $\beta$ -phenyl- $\alpha$ -*p*-nitrophenylbutyramide, m. p. 214—215°, is formed in practically quantitative yield on dissolving either nitrile in sulphuric acid and diluting with water or alcohol. On treatment with benzoyl chloride, acetyl chloride, or hydrogen bromide-acetic acid, it yields the tetrahydropyridine derivative (II), m. p. 236°, whilst its structure is confirmed by its synthesis by condensing *p*-nitrophenylacetamide and phenyl styryl ketone in the presence of sodium methoxide. Both nitriles react readily with bromine in acetic acid, yielding the types of bromine compound previously obtained from unsaturated nitriles (Kohler and Allen, *loc. cit.*).

The isomeride, m. p. 126°, yields 2-bromo-4 : 6-diphenyl-3-*p*-nitrophenylpyridine, m. p. 191°; the nitrile, m. p. 144°, yields a mixture of two isomeric  $\alpha$ -bromo- $\gamma$ -benzoyl- $\alpha$ -*p*-nitrophenylbutyronitriles, m. p. 151° and 191°. Both isomerides are converted into the pyridine derivative by hydrogen bromide in acetic acid. In warm pyridine or with potassium acetate in acetic acid, both isomerides yield a mixture of three isomerides which do not react with bromine or permanganate and in which the cyano group cannot be hydrolysed. They melt at 170°, 144°, and 151°, the former predominating from the higher melting bromo-nitrile, the two latter from the lower melting bromo-nitrile, and are provisionally regarded as 1-cyano-3-benzoyl-2-phenyl-1-*p*-nitrophenylcyclopropanes. R. B.

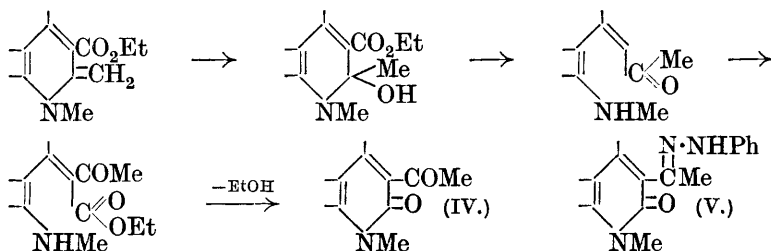
**Pyridonemethides [Methylenedihydropyridines].** O. MUMM [with K. BEHRENS, A. VON FISCHER-TREUENFELD, G. HINGST, W. LUND, O. MROZEK, J. SÖNKSEN, and O. TONN] (*Annalen*, 1925, **443**, 272—309; cf. A., 1924, i, 83).—A study of pyridonemethides, synthesised by the reactions previously described, derived from a series of pyridine derivatives. The *methosulphates* (I) of *ethyl* 4-*ethyl*-, m. p. 130.5°, 4-*isobutyl*-, m. p. 115° after sintering at 103°,



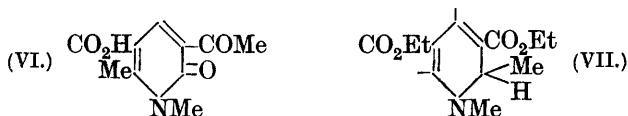
4-*furyl*-, m. p. 152—153°, and 4-*phenyl*-1 : 6-dimethylpyridine-3 : 5-dicarboxylate, m. p. 150—152°, are described, as well as the

$\psi$ -cyanides (2-cyano derivatives) (II) of the following *ethyl 1-methyl-2:3-dihydropyridine-3:5-dicarboxylates*: 2:6-dimethyl-, m. p. 131°; 2:6-dimethyl-4-ethyl-, m. p. 92°; 2:6-dimethyl-4-isobutyl-, m. p. 67°; 4-p-anisyl-2:6-dimethyl-, m. p. 117—118°; and 4-m-nitrophenyl-2:6-dimethyl-, m. p. 151.5°. From these the following *pyridonemethides* (III) were prepared: 1:6-dimethyl-, m. p. 110° (impure); 1:4:6-trimethyl- (*loc. cit.*); 1:6-dimethyl-4-ethyl-, yellow, m. p. 78° (*perchlorate*, m. p. 111.5°); 1:6-dimethyl-4-isobutyl-, yellow, m. p. 47° (*perchlorate*, m. p. 140—141°; *picrate*, m. p. 117—118°); 4-furyl-1:6-dimethyl-, reddish-brown, m. p. 81° (*perchlorate*, m. p. 156—157°; *picrate*, m. p. 119—120°), rapidly oxidising on exposure to air or oxygen to a *peroxide*,  $C_{18}H_{21}O_7N$ , dark brown, hygroscopic; 4-phenyl-1:6-dimethyl-, red, m. p. 110—111° (decomp.) (*perchlorate*, m. p. 191—192°); 4-p-anisyl-1:6-dimethyl-, yellowish-red, m. p. 94—95°; and 4-m-nitrophenyl-1:6-dimethyl-, dark red, m. p. 76—78° (*perchlorate*, m. p. 158—159°):

When suspended in water, the methides undergo a transformation according to the scheme:



Phenylhydrazine in absolute ether effects an analogous change, the products being the corresponding phenylhydrazones (V). *Ethyl 3-acetyl-1:6-dimethyl- $\alpha$ -pyridone-5-carboxylate*, m. p. 131°, see (IV) (*phenylhydrazone*, m. p. 194°), and its following 4-substitution products are described: 4-methyl- (*phenylhydrazone*, m. p. 191—192°); 4-isobutyl-, m. p. 87°; 4-furyl-, m. p. 137° (*phenylhydrazone*, m. p. 204—205°); 4-phenyl-, m. p. 141—142°; 4-p-anisyl-, m. p. 126—127° (*phenylhydrazone*, m. p. 231—232°); and 4-m-nitrophenyl-, m. p. 137—138° (*phenylhydrazone*, m. p. 188—189°). The above pyridones, when boiled with alkali, are hydrolysed to the corresponding 3-acetyl-1:6-dimethyl- $\alpha$ -pyridone-5-carboxylic acids (VI), of which (VI), m. p. 255°, is described, and its 4-ethyl-, m. p. 201°; 4-isobutyl-, m. p. 209—210°; 4-furyl-, m. p. 220—222° (decomp.), and 4-p-anisyl derivative, m. p. 237°. The carboxyl group of the



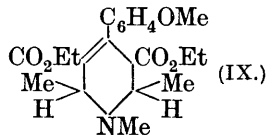
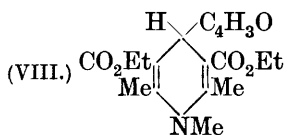
above acids is eliminated, by treatment with concentrated hydrochloric acid, with production of the corresponding 3-acetyl-1:6-di-



*methyl- $\alpha$ -pyridones*, whilst concentrated sulphuric acid also eliminates the acetyl group, with formation of  $\alpha$ -pyridones, of which 1:6-dimethyl- $\alpha$ -pyridone, m. p. about 352°, and 4-furyl-1:6-dimethyl- $\alpha$ -pyridone, m. p. 153.5°, are described.

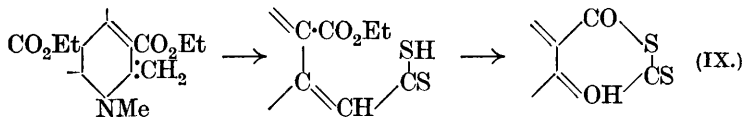
Reduction of the corresponding methides with hydrogen, in alcohol, ethyl acetate, or hexane, in presence of platinum sponge, affords the following products (VII): ethyl 1:2:6-trimethyl-4-ethyl-2:3-dihydropyridine-3:5-dicarboxylate, m. p. 52°, and the corresponding 4-isobutyl, yellow, b. p. 140°/0.1 mm., 4-furyl, yellow, m. p. 98°, 4-phenyl, yellow, m. p. 127—128°, 4-p-anisyl, m. p. 106—107°, and 4-m-nitrophenyl derivative, yellow, m. p. 112—113°.

Reduction of the methosulphate of ethyl 4-furyl-2:6-dimethylpyridine-3:5-dicarboxylate with sodium amalgam and water under continuous neutralisation with acetic acid affords ethyl 4-furyl-1:2:6-trimethyl-1:4-dihydropyridine-3:5-dicarboxylate, (VIII), m. p. 96°, an analogous 1:4-dihydro compound, m. p. 89°, also accompanying the above 2:3-dihydro compound of m. p. 52°, whilst further reduction of the above 4-anisyl-2:3-dihydro compound yields ethyl 4-anisyl-1:2:6-trimethyl-1:2:3:6-tetrahydropyridine-3:5-dicarboxylate (IX), yellow, b. p. 200—201°/1.2 mm.



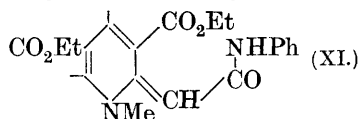
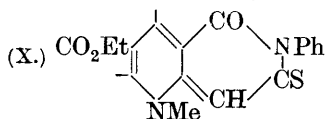
The above 4-phenylpyridonemethide yields, on treatment with methyl iodide and methyl sulphate, respectively, the *methiodide*, m. p. 167° (decomp.), and *methosulphate*, m. p. 160—161°, of ethyl 4-phenyl-6-methyl-2-ethylpyridine-3:5-dicarboxylate. The methiodide of the corresponding 2:6-dimethyl derivative has m. p. 173—174° (decomp.). The action of cold sodium hydroxide on the above methosulphate affords a *compound*, m. p. 108—110° (decomp.) (*perchlorate*, m. p. 173°), closely resembling the methide of which it is a homologue. This affords in turn a *methosulphate*, m. p. 160—161°, from which a further homologous *methide*, m. p. 107—108°, was obtained.

The methides combine with carbon disulphide (cf. Schneider, Gaertner, and Jordan, A., 1924, i, 551; Rosenhauer, *ibid.*, 1236), probably according to the scheme:



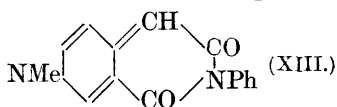
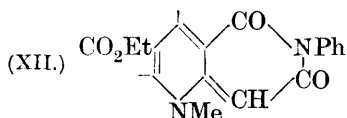
Compounds of this series (IX) were prepared from the above 4-ethyl-, red, m. p. 181° (*hydrochloride* and *perchlorate*); 4-isobutyl-, reddish-violet, m. p. 198—200° (*hydrochloride*); and 4-p-anisyl-methide, violet, m. p. 229—230°. Phenylthiocarbimide reacts similarly and derivatives (X) from ethyl 1:6-dimethylpyridonemethide-3:5-dicarb-

oxylate, dark red, m. p. 261° (*hydrochloride*), and from the corresponding 1 : 4 : 6-*trimethyl*-, carmine-red, m. p. 264—265° (*hydrochloride*), the 1 : 6-*dimethyl*-4-*ethyl*-, m. p. 239° (*hydrochloride*, *dihydrochloride*,



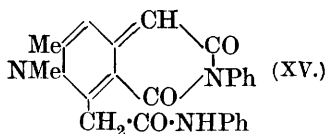
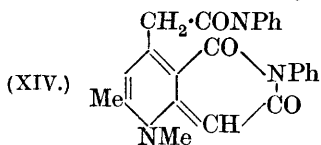
and *perchlorate*), the 1 : 6-*dimethyl*-4-*isobutyl*-, red, m. p. 221° (*dihydrochloride*), the 4-*furyl*-1 : 6-*dimethyl*-, dark red, m. p. 233—235° (decomp.), the 4-*p-anisyl*-1 : 6-*dimethyl*-, similar, m. p. 273° (decomp.), and the 4-*m-nitrophenyl*-1 : 6-*dimethyl*-*pyridone methide*, similar, m. p. 247° (decomp.), are described.

Reaction of the methides with phenylcarbimide proceeds similarly, but the primary additive compounds (XI) can be isolated. These are converted, by boiling in alcoholic solution, into the dicyclic derivatives (XII) or (XIII). The following are described : from the 1 : 6-*dimethylpyridonemethide*, the *additive product* (XI), yellow, m. p. 251°; from the 1 : 4-*dimethylpyridonemethide*, *additive product*



(XI), golden-yellow, m. p. 137—139°, with loss of alcohol and conversion into the *dicyclic* derivative (XII), m. p. 212—213°; from the 4-*ethyl*-1 : 6-*dimethylpyridonemethide*, the *additive product* (XI), reddish-yellow, m. p. about 131°, and the *dicyclic* derivative, m. p. 217° (*hydrochloride*, yellow); from the 1 : 6-*dimethyl*-4-*isobutyl*-*pyridonemethide*, *additive product*, brown, m. p. 117—119°, the *dicyclic* derivative (XII), m. p. 227—228° (*hydrochloride*), and its *isomeride* (XIII), m. p. 161°; from the 4-*furyl*-1 : 6-*dimethylpyridonemethide*, *additive product*, brown, m. p. 157—158°, and the *dicyclic* derivative, brick-red, m. p. 257—258°; from the 4-*p-anisyl*-1 : 6-*dimethylpyridonemethide*, *additive product*, m. p. 169°, and the *dicyclic* derivative, m. p. 295—300°; and from the 4-*m-nitrophenyl*-1 : 6-*dimethylpyridonemethide*, the *additive product*, yellow, m. p. 151—152°, and the *dicyclic* derivative, eosin-red, m. p. 283°.

In addition, the 1 : 4 : 6-*trimethylpyridonemethide* forms an *additive product* with 2 mols. of phenylcarbimide, m. p. 135° after sintering at 122°, which yields two isomeric *dicyclic* compounds,



(XIV), yellow, m. p. 228—229°, and (XV), brownish-red, m. p. 158—160° after sintering at 145°, the allotment of the two formulæ being uncertain.

F. G. W.

**Synthetical Experiments in the isoQuinoline Group. I.**

R. D. HAWORTH and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1925, **127**, 1434—1444).—In the preparation of 2 : 3-dimethoxybenzaldehyde by the methylation of *o*-vanillin a small quantity of 2 : 3-dimethoxybenzaldehyde dimethylacetal, b. p. 134—136°/11 mm., is formed. 2 : 3-Dimethoxybenzyl bromide, m. p. 27—29°, prepared from the alcohol in dry benzene saturated with hydrogen bromide, has strong lachrymatory and sternutatory effects. It combines with 6 : 7-dimethoxyisoquinoline to form an isoquinolinium bromide, m. p. 114° [softens 109°; iodide, m. p. 204—205°; periodide, m. p. 159—160°], which with excess of alkali gives the  $\psi$ -base, 1-hydroxy-6 : 7 : 2' : 3'-tetramethoxy-2-benzyl-1 : 2-dihydroisoquinoline (stannous chloride derivative, m. p. 163—164°). The corresponding 1-cyano compound, m. p. 120—122°, is formed by adding potassium cyanide to the isoquinolinium bromide. 6 : 7 : 2' : 3'-Tetramethoxy-2-benzyl-1-isoquinoline, m. p. 171°, is prepared from the isoquinolinium bromide by the action of aqueous alkaline ferri cyanide or of alcoholic potassium hydroxide. Reduction of the isoquinolinium bromide with tin and hydrochloric acid yields 6 : 7 : 2' : 3'-tetramethoxy-2-benzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, m. p. 112—113° (stannous chloride derivative, m. p. 109—110°), which is converted by iodine and potassium acetate into 6 : 7 : 2' : 3'-tetramethoxy-2-benzyl-3 : 4-dihydroisoquinolinium iodide, m. p. 200°. From a solution of the corresponding chloride sodium hydroxide precipitates the  $\psi$ -base, 1-hydroxy-6 : 7 : 2' : 3'-tetramethoxy-2-benzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline (picrate, m. p. 135°; zinc chloride double salt, m. p. 158—160°). From the dihydroisoquinolinium iodide there is obtained, by boiling with aqueous-alcoholic potassium hydroxide, 6 : 7 : 2' : 3'-tetramethoxy-2-benzyl-3 : 4-dihydro-1-isoquinoline, m. p. 160°, or by condensation with nitromethane, the tetramethoxybenzyl-1-nitromethyltetrahydroisoquinoline, m. p. 111—112°, from which, by reduction, only methylamine and the  $\psi$ -base are obtainable.

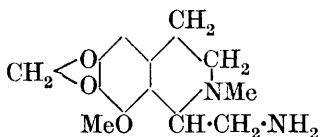
2 : 3-Dimethoxybenzyl bromide reacts with norhydrohydrastinine to form a quaternary ammonium bromide, which, condensed with nitromethane, yields 6 : 7-methylenedioxy-2' : 3'-dimethoxy-2-benzyl-1-nitromethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, m. p. 135—136°, from which also no oxime is obtained by reduction.

1-Cyano-6 : 7 : 2' : 3'-tetramethoxy-2-benzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, m. p. 125°, the  $\psi$ -cyanide prepared from the above dihydroisoquinolinium iodide (m. p. 200°) reacts with magnesium methyl iodide in anisole to give tetramethoxybenzyl-1-methyltetrahydroisoquinoline (picrate, m. p. 157—158°), but attempts to oxidise this to a dihydro compound and thence to an aldehyde by condensation with nitrosodimethylaniline were unsuccessful.

1-Cyano-6 : 7-dimethoxy-2-benzoyl-1 : 2-dihydroisoquinoline, m. p. 164°, is obtained from 6 : 7-dimethoxyisoquinoline, potassium cyanide, and benzoyl chloride. 2 : 3-Dimethoxybenzoyl chloride, prepared from the acid by heating with thionyl chloride, similarly gives 1-cyano-6 : 7 : 2' : 3'-tetramethoxy-2-benzoyl-1 : 2-dihydroisoquinoline, m. p. 181°. Either of these cyano-benzoyl compounds is converted by hydrogen chloride in dry chloroform into 6 : 7-di-

*methoxyisoquinoline-1-carboxylamide*, m. p. 168—169° (*mercuric chloride* additive compound described), together with a small amount of the 1-carboxylic acid (Goldschmiedt, A., 1886, 478; 1888, 302), which also forms a crystalline *mercuric chloride* compound. The amide reacts with 2:3-dimethoxybenzyl bromide to give an *ammonium bromide*, m. p. above 250°, which is reduced by tin and hydrochloric acid to 6:7:2':3'-*tetramethoxy-2-benzyl-1:2:3:4-tetrahydroisoquinoline-1-carboxylamide*, m. p. 192°, obtainable less satisfactorily by treating the  $\psi$ -cyanide of m. p. 125° (see above) with hydrogen chloride and zinc chloride in anisole. It is not hydrolysed by boiling concentrated hydrochloric acid or alcoholic potassium hydroxide.

Anhydrocotarnine-nitromethane is reduced by zinc dust and alkali or by stannous chloride and hydrochloric acid to *anhydrocotarnine-methylamine* (annexed formula), which gives a *dihydrochloride*, m. p. 227°, and a *picrate*, m. p. 200° (decomp.).



The above compounds were prepared in an unsuccessful attempt to synthesise berberine alkaloids from tetramethoxybenzylisoquinoline and its derivatives. C. H.

### Synthetical Experiments in the *isoQuinoline* Group. II.

R. D. HAWORTH, W. H. PERKIN, jun., and J. RANKIN (*J. Chem. Soc.*, 1925, 127, 1444—1448).—The following substances correspond with those of the preceding abstract, but are derived from vanillin in place of *o*-vanillin. The methods used are exactly similar.

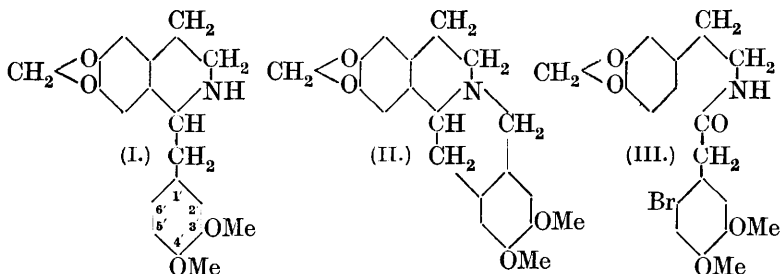
3:4-*Dimethoxybenzyl bromide* has only feeble lachrymatory properties; it could not be distilled without decomposition.

6:7:3':4'-*Tetramethoxy-2-benzylisoquinolinium bromide*, m. p. 137—138° (*iodide*, m. p. 203—204°). 1-*Hydroxy-6:7:3':4'-tetramethoxy-2-benzyl-1:2-dihydroisoquinoline* could not be recrystallised. 6:7:3':4'-*Tetramethoxy-2-benzyl-1-isoquinoline*, m. p. 128—129°; the corresponding *tetrahydro* compound, m. p. 93°, does not react with methylal, acetal, or sulphoacetic acid. 1-*Cyano-6:7:3':4'-tetramethoxy-2-benzyl-1:2-dihydroisoquinoline*, m. p. 117° (decomp., darkens 115°). 6:7:3':4'-*Tetramethoxy-2-benzyl-3:4-dihydroisoquinolinium iodide*, m. p. 184—185° [*periodide*, m. p. 160°; *chloride* (+Aq.), m. p. 52—56°]. 1-*Hydroxy-6:7:3':4'-tetramethoxy-2-benzyl-1:2:3:4-tetrahydroisoquinoline* was not obtained crystalline; the corresponding *isoquinolone* melts at 116°, the 1-*cyano* compound ( $\psi$ -cyanide) at 98°. 6:7:3':4'-*Tetramethoxy-2-benzyl-1-nitromethyl-1:2:3:4-tetrahydroisoquinoline*, m. p. 148—149°, like its isomeride could not be reduced to an oxime. C. H.

### Synthetical Experiments in the *isoQuinoline* Group. III.

R. D. HAWORTH and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1925, 127, 1448—1453).—In the attempted synthesis of tetrahydroberberine from veratrylnorhydrodrastinine (I) with formaldehyde and hydrochloric acid (Haworth, Perkin, and Rankin, T., 1924, 125, 1685), condensation occurs in the 6'-position, giving tetra-

hydro- $\psi$ -berberine (II). Attempts have now been made without success to force the 2'-carbon atom to react by blocking the 6'-position with a substituent.



6'-Nitroveratrylnorhydrohydrastinine, m. p. 149—150°, prepared by nitration of (I) in acetic acid at 0°, gave with formaldehyde a gummy *additive* compound, which could not be converted into nitrotetrahydroberberine. 6'-Nitrotetrahydroberberine, m. p. 185°, from tetrahydroberberine, is reduced by zinc dust and hydrochloric acid to an *amine*, which gives a greenish-blue coloration with ferric chloride. The ease of nitration of tetrahydroberberine and its derivatives distinguishes them readily from compounds of the tetrahydro- $\psi$ -berberine type, which give no nitro derivatives but are oxidised.

6-Bromohomoveratric acid, m. p. 115°, obtained by bromination of homoveratric acid in acetic acid, was identical with Pschorr's product (Pschorr, Koch, Selle, Stoof, and Treidel, A., 1912, i, 775), prepared differently. It condenses with homopiperonylamine at 180° to give 6'-bromohomoveratrylhomo-piperonylamine (III), m. p. 159—160°, from which, by the action of phosphoryl chloride in toluene, the dihydroisoquinoline was readily obtained. Reduction of this with zinc dust and dilute sulphuric acid yielded 6'-bromoveratrylnorhydrohydrastinine, m. p. 159—160° [*hydrochloride*, m. p. 260—262° (softens 250°); *picrate*, m. p. 174—175°; *formate* also described]. The *N*-hydroxymethyl derivative (*picrate*, m. p. 154—155°), obtained by the action of formaldehyde, could not be converted into bromotetrahydroberberine. The *N*-formyl derivative, prepared by heating the formate of the base, reacted with phosphoryl chloride in benzene, but the product, m. p. 177°, contained no bromine and was shown to be tetrahydro- $\psi$ -berberine (*hydrochloride*, m. p. 220°; *picrate*, m. p. 176°). From *N*-formylveratrylnorhydrohydrastinine by the same method was obtained dihydroanhydro- $\psi$ -berberine, m. p. and mixed m. p. 154—155° [not 165—167° as previously reported (T., 1924, 125, 1699); *hydrochloride*, m. p. 253—255° (decomp.)].

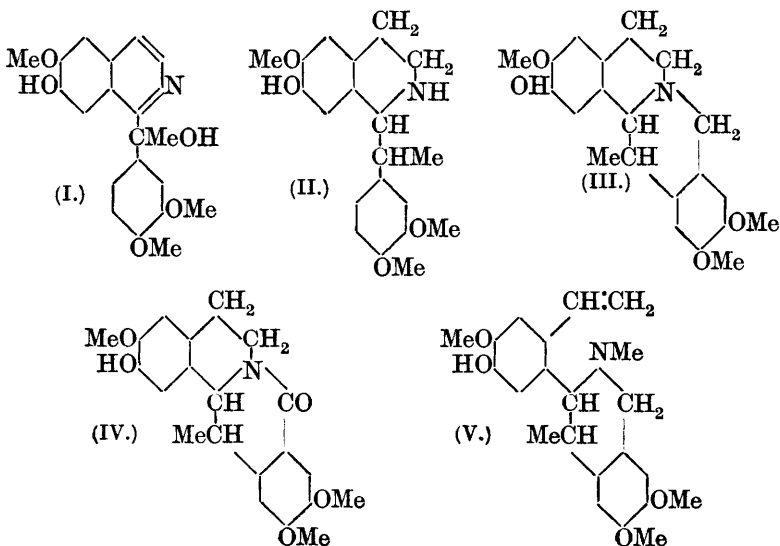
The correct m. p. of *N*-*o*-nitrobenzoylnorhydrohydrastinine (*loc. cit.*) is 160—161°, not 154°. C. H.

#### Synthetical Experiments in the isoQuinoline Group. IV.

R. D. HAWORTH and W. H. PERKIN, jun. (*J. Chem. Soc.*, 1925, 127, 1453—1462).—As in the tetrahydroberberine series (preceding

abstract), attempts to convert a 9-methyltetrahydropapaverine derivative by means of methylal and hydrochloric acid into a corydaline derivative give the isomeric base, the 6'-carbon atom reacting in preference to the 2'-carbon atom.

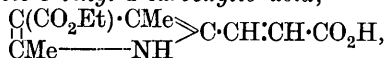
Papaveraldine reacts with magnesium methyl iodide to form 7-demethylomethylpapaverinol (I), one methoxyl group being demethylated. Like all the other demethylo-compounds here described, this substance exhibits no phenolic properties although it must contain a free phenolic group [cf. methylnoroxyberberine (Faltis, A., 1910, i, 698; Bland, Perkin, and Robinson, T., 1912, 101, 262; 1925, 127, 744)]. By the action of acetic anhydride, phenylcarbimide, or concentrated acids it is converted into the corresponding *anhydro* derivative ( $>\text{CMeOH} \rightarrow >\text{C}:\text{CH}_2$ ), m. p.  $151^\circ$  [*picrate*, m. p.  $110$ – $112^\circ$  (decomp.); *perchlorate*, m. p.  $150^\circ$ ]. Reduction of the tertiary alcohol (I) or its anhydro derivative with tin and hydrochloric acid gives 7-demethylomethylpapaverine, m. p.  $148^\circ$  (*picrate*, *chromate*, *chloroplatinate*, and *chloroaurate* described), and eventually 7-demethylomethyltetrahydropapaverine (II), m. p.  $64$ – $65^\circ$  [*picrate*, m. p.  $225^\circ$  (decomp.); *nitrosoamine*, m. p.  $124^\circ$ ]. Condensation of the tetrahydro base with methylal yields 7-demethylo- $\psi$ -corydaline (III), m. p.  $150$ – $151^\circ$  (*methiodide*, m. p.  $250^\circ$ ; *methochloride*, m. p.  $253^\circ$ ; *hydriodide*, m. p.  $242^\circ$ ; *periodide*, m. p.  $210^\circ$ ). From the periodide, suspended in hot water and treated with sulphur dioxide, there is obtained *dihydro*-7-demethylo- $\psi$ -dehydrocorydalinium iodide, m. p.  $250^\circ$ , which may also be prepared by oxidation of nor- $\psi$ -corydaline with mercuric acetate. The *chloride*, m. p.  $235^\circ$  (decomp.), is converted by 50% potassium hydroxide into *ketonor*-7-demethylo- $\psi$ -corydaline (IV), m. p.  $210^\circ$ , and 7-demethylo- $\psi$ -corydaline (III).



On boiling 7-demethylo- $\psi$ -corydaline methochloride with potassium hydroxide, there is formed *anhydro-7-demethylomethyl- $\psi$ -corydaline* (V) [*hydrochloride*, m. p. 228° (decomp.); *hydriodide*, m. p. 232°; *picrate* (+2EtOH), m. p. 165° after partial melting at 130°].

Attempts to obtain corydaline from the two isomeric 4-methyl-tetrahydroberberines (Freund and Fleischer, A., 1915, i, 982) by replacing the methylenedioxy group by two methoxyl groups were unsuccessful. C. H.

**3-Carbethoxy-2:4-dimethylpyrrole-5-vinyl- $\omega\omega$ -dicarboxylic Acid and -5-vinyl- $\omega$ -carboxylic Acid.** W. KÜSTER, E. BRUDI, and S. KOPPENHÖFER (*Ber.*, 1925, 58, [B], 1014—1021).—Ethyl 2:4-dimethyl-5-aldehydopyrrole-3-carboxylate (cf. Fischer and Zerweck, A., 1923, i, 758) condenses with malonic acid in the presence of alcoholic ammonia, yielding a mixture of 3-carbethoxy-2:4-dimethylpyrrole-5-vinyl- $\omega$ -carboxylic acid,



m. p. (indef.) 265° (decomp.) (*silver salt*; *ethyl ester*, m. p. 155—157°; *methyl ester*, m. p. 179—181°) and 3-carbethoxy-2:4-dimethylpyrrole-5-vinyl- $\omega\omega$ -dicarboxylic acid, m. p. 199—200°, decomp. 202°, which are separated from one another by taking advantage of the differing solubilities of their potassium salts in alcohol. The dicarboxylic acid is obtained more conveniently if ammonia is replaced by diethylamine as condensing agent. The normal *silver salt* is transformed by ethyl bromide in the presence of benzene into *ethyl 3-carbethoxy-2:4-dimethylpyrrole-5-vinyl- $\omega\omega$ -dicarboxylate*, m. p. 86—87°. The *silver hydrogen salt* is converted by methyl iodide into *methyl hydrogen 3-carbethoxy-2:4-dimethylpyrrole-5-vinyl- $\omega\omega$ -dicarboxylate*, m. p. 161°, decomp. 163°, which immediately yields an *ammonium salt* when treated with ammonia in benzene; with ethyl bromide an *ethyl hydrogen ester*, m. p. 114°, decomp. 174°, is produced which does not immediately give an ammonium salt under similar conditions and in which the carboxyl group is therefore considered to have reacted with the NH group of the pyrrole. Protracted treatment with boiling ethyl alcohol converts the dicarboxylic acid into an isomeric *ethyl hydrogen ester*, m. p. 183°, which does not decompose below 280°, whilst methyl alcohol gives an isomeric *methyl hydrogen ester* darkening at 260°. The action of hydrogen bromide and glacial acetic acid on 3-carbethoxy-2:4-dimethylpyrrole-5-vinyl- $\omega\omega$ -dicarboxylic acid leads mainly to elimination of carbon dioxide and production of 3-carbethoxy-2:4-dimethylpyrrole-5-vinyl- $\omega$ -carboxylic acid, whereas the latter acid becomes resinified by these reagents. The monocarboxylic acid absorbs bromine vapour with production of (?) 3-carbethoxy-2:4-dimethylpyrrole-5- $\alpha\omega$ -dibromoethyl- $\omega$ -carboxylic acid, which could not be obtained homogeneous; a similar behaviour is shown by ethyl 3-carbethoxy-2:4-dimethylpyrrole-5-vinyl- $\omega\omega$ -dicarboxylate. With iodine in ethereal solution, the latter ester affords *ethyl 3-carbethoxy-2:4-dimethylpyrrole-5- $\alpha\omega$ -di-iodoethyl- $\omega\omega$ -dicarb-*

*oxylate*, m. p. 175°. Reduction of 3-carbethoxy-2:4-dimethylpyrrole-5-vinyl- $\omega$ -dicarboxylic acid with sodium amalgam appears to yield 3-carbethoxy-2:4-dimethylpyrrole-5-ethyl- $\omega$ -dicarboxylic acid, decomp. 232°, which could not be purified completely and when thermally decomposed gives only a 28% yield of 3-carbethoxy-2:4-dimethylpyrrole-5-propionic acid, m. p. 119°, which is therefore more conveniently obtained by reduction of 3-carbethoxy-2:4-dimethylpyrrole-5-vinyl- $\omega$ -carboxylic acid (cf. Küster and Maurer, A., 1924, i, 202). H. W.

**Synthesis of Indole.** C. NENITZESCU (*Ber.*, 1925, 58, [B], 1063—1064).— $\omega$ -Dinitrostyrene is reduced by iron filings and dilute acetic acid to indole in 30% yield; probably *o*-aminophenyl-acetaldoxime is intermediately formed. If sodium hyposulphite is used as reducing agent indigotin is formed owing to the atmospheric oxidation of indole accelerated by the presence of sodium hydrogen sulphite. H. W.

**Catalysts for the Fischer Synthesis of Indoles.** A. KORCZYŃSKI and L. KIERZEK (*Roczniki Chemji*, 1925, 5, [1—3], 23—32).—The catalytic action of powdered nickel, cobalt, and copper, and of salts such as cobaltous, nickelous, chromous, and cupric chlorides, and uranium hexachloride on the Fischer synthesis of indoles from phenylhydrazones has been investigated. Using nickelous chloride or metallic nickel, copper, or cobalt, the yields are respectively 65% and 60%. Two red *picryl* derivatives of 2-methylindole are described, m. p. 110° and 225°. Using nickelous chloride as catalyst 2-*p*-anisylindole, silver, m. p. 228—229°, is prepared from the *p*-methoxyacetophenonephenylhydrazone, pale yellow, m. p. 142°. *p*-Methoxyacetophenone-*p*-bromophenylhydrazone, pink, m. p. 154°, with nickel chloride as catalyst, gives no identifiable product, profound decomposition taking place. *Acetophenone-p*-methoxyphenylhydrazone, yellow, m. p. 63—64°, yields small quantities of 5-methoxy-2-phenylindole, not isolated pure. *p*-Methoxyacetophenone-*p*-methoxyphenylhydrazone, yellow, m. p. 162—163°, yields 5-methoxy-2-*p*-anisylindole, yellow, m. p. 213—214°. 2-*p*-Hydroxyphenylindole, yellow leaves, m. p. 70°, is obtained from *p*-hydroxyacetophenonephenylhydrazone, using nickel as catalyst, and its condensation product with diphenylchlorocarbamide, an amorphous, colourless powder, m. p. 65°, is described. 3-Amylindole, colourless, m. p. 54°, is given by heptaldehydephenylhydrazone, and its *picrate*, red, m. p. 91—92°, prepared. *p*-Hydroxydibromoacetophenone-*p*-bromophenylhydrazone, yellow, m. p. 180°, gives no indole on treatment in the above manner. R. T.

**Arsenyl Tartrates of Pyridine, Quinoline, and Some Alkaloids.** L. DEBUCQUET (*J. Pharm. Chim.*, 1925, 1, 571—574).—The compounds  $C_4H_3O_6AsR$ , where R is an organic base, are prepared by boiling arsenious oxide with an aqueous solution of the tartrate of the base. They are colourless, sparingly soluble in cold water, readily soluble in hot water, separating anhydrous on cooling. The *pyridine* compound,  $[\alpha]_{21}^D +18.5^\circ$ , and the *quinoline* compound,  $[\alpha]_{21}^D +15.83^\circ$ , are described. S. I. L.



**Nitro- and Amino-ethoxylutidine.** J. N. COLLIE and G. BISHOP (*J. Chem. Soc.*, 1925, **127**, 962—964; cf. T., 1898, **73**, 229, 235).—Nitration of 4-ethoxy-2:6-dimethylpyridine, b. p. 208° (prepared from dimethylpyrone), yields 3-nitro-4-ethoxy-2:6-dimethylpyridine, m. p. 99°, which is reduced by tin and hydrochloric acid to 3-amino-4-ethoxy-2:6-dimethylpyridine, and the latter, after purification through the chlorostannate and chloroplatinate has m. p. 62°, b. p. 267°. Oxidation of nitroethoxylutidine with potassium permanganate gives nitro-4-ethoxy-2-methylpyridine-6-carboxylic acid, m. p. 147° (silver salt described). Moderated oxidation of ethoxylutidine yields impure 4-ethoxy-2-methylpyridine-6-carboxylic acid, m. p. 138° (characterised as its silver salt and chloroplatinate), which is completely decomposed by further treatment with potassium permanganate, but with boiling nitric acid yields the nitrate, m. p. 125°; it is converted by heat into ethoxypicoline, b. p. about 220° (chloroplatinate, m. p. 207°), and by hydrogen iodide into 4-hydroxy-2-methylpyridine-6-carboxylic acid (+H<sub>2</sub>O), m. p. 295°. More extensive oxidation of ethoxylutidine with permanganate gives 4-ethoxy-2-methylpyridine-6-carboxylic acid and 4-ethoxypyridine-2:6-dicarboxylic acid, m. p. 200° (silver salt and chloroplatinate described) [giving 4-ethoxypyridine, b. p. 200—202° (chloroplatinate, m. p. 215°), on distillation], together with 4-hydroxy-2-methylpyridine, b. p. 350—360° (chloroplatinate described). F. M. H.

**Condensation of *m*- and *o*-Nitrobenzaldehyde with 8-Methoxy-2-methylquinoline.** J. TRÖGER and J. DANEHL (*J. pr. Chem.*, 1925, [ii], **110**, 86—100; cf. this vol., i, 432).—When an aqueous solution of the methiodide, m. p. 184°, or the ethiodide, m. p. 208—209°, of 8-methoxy-2-methylquinoline is shaken with silver oxide, the alkaline filtrate contains an ammonium base, and in each case the corresponding chloride yields double salts with auric chloride and mercuric chloride. By heating 8-methoxy-2-methylquinoline with *m*-nitrobenzaldehyde at 100° or 180°, is formed 8-methoxy-2-*m*-nitrostyrylquinoline, m. p. 154°; the hydrochloride gives a chloroplatinate and double salts with mercuric chloride and stannic chloride; the methiodide, m. p. 205°, or ethiodide, m. p. 210°, on treatment with alcoholic potassium hydroxide regenerates 8-methoxy-2-*m*-nitrostyrylquinoline; attempts to reduce the base have proved unsuccessful. When equivalent amounts of 8-methoxy-2-methylquinoline and *m*-nitrobenzaldehyde are heated with water in a sealed tube at 100°, the product is 8-methoxy-2- $\beta$ -hydroxy- $\beta$ -*m*-nitrophenylethylquinoline, m. p. 164°, which is dimorphous (hydrochloride, chloroplatinate, and gold chloride double salt are described); the ethiodide, m. p. 214°, is converted by silver oxide into 8-methoxy-2-*m*-nitrostyrylquinoline. On heating 8-methoxy-2-methylquinoline and *o*-nitrobenzaldehyde at 180°, or at 100° in presence of zinc chloride, the product is 8-methoxy-2- $\beta$ -hydroxy- $\beta$ -*o*-nitrophenylethylquinoline, m. p. 97—98° (hydrochloride, chloroplatinate, and mercuric chloride and stannic chloride double salts described), whilst heating at 180—190° with zinc chloride causes decomposition, but gives no stilbazole derivative; with methyl iodide 8-methoxy-2- $\beta$ -hydroxy- $\beta$ -*o*-nitro-

phenylethylquinoline gives a *product* (not the methiodide), whilst a similar *substance*, together with the *ethiodide*, m. p. 203°, is obtained through ethyl iodide; with silver oxide the ethiodide regenerates the original compound. 8-Methoxy-2-methylquinoline and cinnamaldehyde at 180° produce 8-methoxy-2- $\alpha$ -hydroxycinnamyl-methylquinoline, characterised as its hydrochloride. F. M. H.

[Condensation of Hydroxy- and Methoxy-2-methylquinolines, and 2-Hydroxylepidine with Aromatic Aldehydes.]

**Correction.** J. TRÖGER and E. DUNKER (*J. pr. Chem.*, 1925, [ii], 110, 64).—Analytical results for 8-methoxy-2- $\beta$ -hydroxy- $\beta$ -p-methoxyphenylethylquinoline and its platinum salt were transposed in the original paper (cf. this vol., i, 432). C. H.

**$\alpha$ -Acenaphthaquinoline.** (MISS) J. STEWART (*J. Chem. Soc.*, 1925, 127, 1331—1332).—By the Skraup reaction, with nitrobenzene as oxidant, 5-aminoacenaphthene is converted into  $\alpha$ -acenaphthaquinoline, m. p. 61—62° (chromate, hydrochloride, and picrate, m. p. 234°, prepared). Oxidation of the base with chromic-acetic acid gives  $\alpha$ -naphthaquinoline-6 : 7-dicarboxylic acid (anhydrides at 150°), from which by distillation with soda-lime,  $\alpha$ -naphthaquinoline (m. p. 49—50°) may be obtained. C. H.

**Hydantoins. XLVI. Nitropyruvic Ureide.** D. DAVIDSON (*J. Amer. Chem. Soc.*, 1925, 47, 1722—1726).—Nitropyruvic ureide (m. p. 204°, decomp.) is most conveniently obtained by nitrating dipyruvic ureide (this vol., i, 584). Since nitropyruvic ureide does not give V. Meyer's nitrolic acid test and undergoes rapid hydrolysis into nitromethane and parabanic acid when boiled with water, its formula is probably  $\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}\cdot\text{CH}\cdot\text{NO}_2$  and not

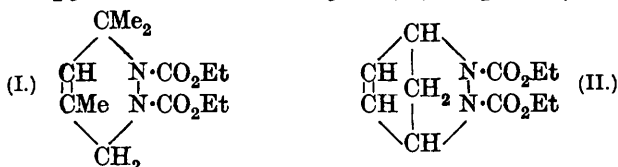
$\text{NH}\cdot\text{CO}\cdot\text{N}\begin{smallmatrix} \text{CO}\cdot\text{N} \\ \text{CO}\cdot\text{C}\cdot\text{CH}_2\cdot\text{NO}_2 \end{smallmatrix}$ . Thus, bromine yields bromonitropyruvic ureide,  $\text{NH}\cdot\text{CO}\cdot\text{N}\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{C}\cdot\text{CBrNO}_2 \end{smallmatrix}$  (cf. this vol., i, 583), which is even

more readily hydrolysed than the parent substance; whilst acetic anhydride affords a *diacetyl* derivative, yellow leaflets, m. p. 150° (decomp.). When reduced with hydrogen in the presence of platinum oxide, nitropyruvic ureide yields the oxime of hydantoin-5-aldehyde (cf. Kohler and Drake, A., 1923, i, 666). *Bromonitropyruvic ureide*, yellow plates, decomp. 225°, is converted by boiling water into bromonitromethane and parabanic acid. R. B.

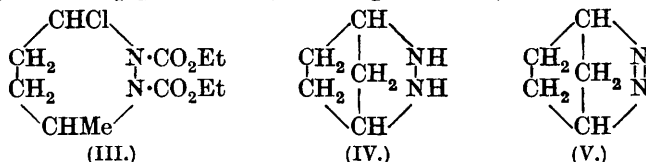
**Compounds of Amino-acids with Piperazines.** E. ABDERHALDEN and E. ROSSNER (*Z. physiol. Chem.*, 1925, 144, 219—233).—Condensation of piperazine with  $\alpha$ -bromopropionyl bromide gave 1 : 4-di- $\alpha$ -bromopropionylpiperazine, m. p. 162°, which with ammonia gave 1 : 4-dialanilpiperazine dihydrobromide. The free base liberated by means of silver sulphate and barium hydroxide gave a dibenzoyl derivative, m. p. 237°. Condensation of  $\alpha$ -bromo- $\gamma$ -methylvaleryl chloride with piperazine gave 1 : 4-dibromo- $\gamma$ -methylvalerylpiperazine, m. p. 141—142°, which with ammonia gave 1 : 4-dileucylpiperazine dihydrobromide. The free base, m. p. 118—121°, gave a dibenzoyl derivative, m. p. 244°. 1 : 4-Dileucylpiper-

azine was condensed with chloroacetyl chloride giving *dichloroacetyldileucylpiperazine*, m. p. 233° (decomp.), which with alcoholic ammonia gave *diglycyldileucylpiperazine*, m. p. 182—184°. Dileucylpiperazine and  $\alpha$ -bromopropionyl bromide similarly gave *dibromopropionyldileucylpiperazine*, m. p. 205°, which with alcoholic ammonia gave *dialanyldileucylpiperazine*, m. p. 142—149°. The above compounds were hydrolysed by acids but not by enzymes. Piperazine and chloroacetyl chloride gave 1:4-*dichloroacetyl*piperazine, m. p. 137°, which with ammonia gave an insoluble product of unknown constitution together with 1:4-diglycylpiperazine [dibenzoyl derivative, m. p. 266°, and picrate, m. p. 221° (decomp.)].  
P. W. C.

**Formation of *endo*Methylenepiperidazine from cyclo-Pentadiene and Azo-esters, and its Conversion into 1:3-Diaminocyclopentane.** O. DIELS, J. H. BLOM, and W. KOLL (*Annalen*, 1925, 443, 242—262).—Dimethylisoprene ( $\beta\delta$ -dimethyl- $\Delta^{\gamma}$ -pentadiene) reacts energetically with ethyl azodicarboxylate with formation of *ethyl 3:3:5t-rimethyl- $\Delta^4$ -tetrahydro-1:2-pyridazine-1:2-dicarboxylate* (I), b. p. 136°/0.4—0.5 mm. *cyclo*Pentadiene affords similarly *ethyl 3:6-endomethylene-1:2:3:6-tetrahydro-1:2-pyridazine-1:2-dicarboxylate* (II), b. p. 121°/0.5 mm. to

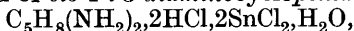


133°/1.5 mm., in 90—95% yield. This is stable when kept, and is soluble in acids, from which it is recovered unchanged by precipitation with alkali. It combines vigorously with bromine in chloroform, with formation of a *dibromide*, m. p. 67°, and is reduced by hydrogen in presence of palladium in alcoholic solution to *ethyl 3:6-endomethylene-1:2-piperidazine-1:2-dicarboxylate*, m. p. 42°, b. p. 131°/0.4 mm., which is stable to bromine and permanganate. When heated with hydrochloric acid (37%) in a sealed tube at 100°, the above piperidazine is converted into *ethyl 3-chloro-6-methyl-1:2-piperidazine-1:2-dicarboxylate* (III), m. p. 90°, b. p. 155°/0.5 mm., whilst methyl-alcoholic potassium hydroxide converts it successively into *methyl endomethylenepiperidazine-1-carboxylate*, b. p. 133°/9—10 mm. (*picrate*, m. p. 176—177°), and 3:6-*endomethylene-1:2-piperidazine* (IV), b. p. 65—68°/15 mm., 162°/754



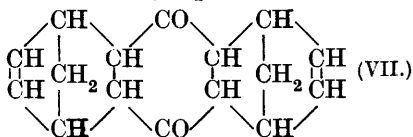
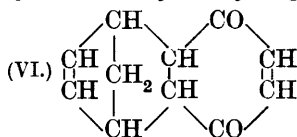
mm., crystallising on cooling. This is very volatile, hygroscopic, strongly basic, and readily oxidised. In aqueous solution, it reacts

with cupric chloride, with formation of an *additive* compound ("cuprochloride," see this vol., i, 989) of endomethylenedehydro-piperidazine and cuprous chloride,  $C_5H_8N_2, CuCl, \frac{1}{2}H_2O$ , dark carmine red, dichroic, insoluble, which is decomposed by alkalis into 3 : 6-endomethylene-3 : 4 : 5 : 6-tetrahydro-1 : 2-pyridazine (V), m. p. 99—99·5°, which is very volatile, with a strong, characteristic odour. The *methiodide*, golden yellow, and *cuprous bromide additive* compound,  $C_5H_8N_2, CuBr$ , are described. Reduction with stannous chloride affords endomethylenepiperidazine stannichloride, m. p. 224—229° (decomp.), whilst the above cuprous chloride compound yields, on reduction with tin and hydrochloric acid, the stannous chloride compound of *cis*-1 : 3-diaminocyclopentane,



m. p. 172° (anhydrous). The free *base* was converted by potassium cyanate into the *carbamide*,  $C_5H_8(NH \cdot CO \cdot NH_2)_2$ , m. p. 217—233° (decomp.). The latter was synthesised by converting dimethyl *cis*-cyclopentane-1 : 3-dicarboxylate (cf. Pospischill, A., 1898, i, 636), b. p. 124—125°/13 mm., successively into the *dihydrazide*, m. p. 205—208°, the *diazide*, the *diurethane*, and finally the above carbamide.

It is suggested that the combination of cyclopentadiene and *p*-benzoquinone (cf. Albrecht, A., 1906, i, 674) takes place by union of the partial valencies of the conjugated system in the former with those of the  $\cdot C:C \cdot$  groups of the latter, to give the structures (VI) and (VII) for the two compounds, the above condensation with the azo ester being explained analogously. This view is supported by the catalytic hydrogenation of the cyclopentadiene-*p*-benzo-



quinone compounds (VI), which yields a *dihydro* derivative, m. p. 190—191° (decomp.) after sintering at 185—188°, whilst (VII) affords a *tetrahydro* compound, m. p. 239—243° (decomp.) after sintering at 220—230°.

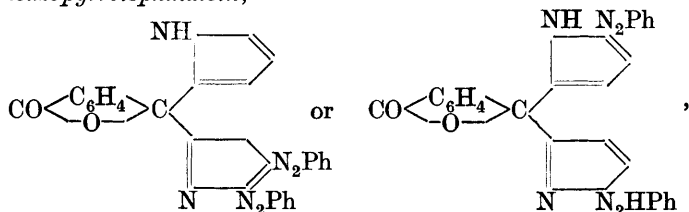
F. G. W.

"Indine," *iso*Indigotin, "Hydrindine" and the Inner Anhydride of  $\alpha\beta$ -Bis-*o*-aminophenylmalic Acid [Hydroxy-dihydroisoindigotin]. L. SANDER (*Ber.*, 1925, 58, [B], 820—824).—According to Laurent (*J. pr. Chem.*, 1842, [i], 25, 430) the action of hydrogen sulphide on a cold, alcoholic solution of isatin yields "sulphisatyd" which is transformed by cold, alcoholic sodium hydroxide solution into "indine." The latter substance is shown to be identical with *iso*indigotin (cf. Friedländer and Sander, A., 1924, i, 662), and the "hydrindine" prepared from it by the action of warm, alcoholic sodium hydroxide solution is identified as hydroxydihydroisoindigotin (*loc. cit.*). Since sulphur is liberated in large amount during the action of hydrogen sulphide on isatin, it is highly probable that "sulphisatyd" is 3-thioxindole formed by reduction from 3-thioisatin.

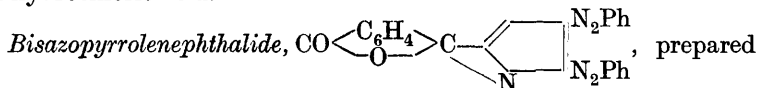
H. W.

**Syntheses by Means of Magnesylpyrrole. V. Pyrrole-phthalides.** B. ODDO and Q. MINGOIA (*Gazzetta*, 1925, 55, 235—241; cf. A., 1923, i, 709).—The action of magnesium pyrrol bromide on phthalic anhydride in ethereal solution does not stop at the formation of the compound  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \begin{smallmatrix} \text{O} \cdot \text{MgBr} \\ \text{O} \end{smallmatrix}$  but yields also the compound  $\text{MgBr} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_4\text{H}_3\text{NH})_2 \cdot \text{OMgBr}$ , which then loses 1 mol. of pyrrole to form pyrrolenephthalide; pyrrolenephthylcarbinol-*o*-carboxylic acid, also formed in this reaction, gives an ammonium salt, m. p. 230°.

*Bisazopyrrolephthalein*,



prepared by the action of phenyldiazonium chloride (2 mols.) on pyrrolephthalein (1 mol.) in alkaline solution, forms reddish-brown crystals, m. p. 126°, and with concentrated sulphuric acid gives an ultramarine coloration changing to purple-red on dilution. It dissolves in boiling concentrated alkali hydroxide solution with opening of the lactonic ring and formation of a raspberry-red liquid, which gives the colourless leuco-compound when reduced with zinc in hydrochloric acid.



from pyrrolenephthalide (1 mol.) and phenyldiazonium chloride (2 mols.), has m. p. 108—110°, and is also reddish-brown and shows reactions similar to those of the preceding compound. T. H. P.

**Syntheses by Means of Magnesylpyrrole. VI. Constitution of the Pyrrolenephthalides.** B. ODDO (*Gazzetta*, 1925, 55, 242—245; cf. preceding abstract).—The formulæ suggested by various authors for the compounds obtained by the action of phthalic anhydride on pyrrole derivatives are discussed, and the conclusion is reached that the pyrrole residue is attached to the tetrolic nucleus at the 2-position, the carbon being most probably connected by a double linking with the 2-pyrrole carbon atom and not by a single linking with the latter and by another single linking with the pyrrole nitrogen atom. T. H. P.

**Reactions of 5-Nitro-2-nitroaminopyridine.** C. RÄTH and G. PRANGE (*Ber.*, 1925, 58, [B], 1208—1210; cf. Tschitschibabin and Menschikov, this vol., i, 437).—Treatment of 5-nitro-2-nitroaminopyridine with warm sodium hydroxide solution gives nitrous oxide and 5-nitro-2-hydroxypyridine, m. p. 191—192°, instead of 184° recorded in the literature (*sodium* salt, decomp. 303°). 5-Nitro-

2-nitroaminopyridine is reduced by zinc dust and sodium hydroxide solution to 5-nitro-2-nitrosoaminopyridine, decomp. about 240°, which is transformed by zinc dust and concentrated hydrochloric acid into 2 : 5-diaminopyridine, m. p. 109—110°. The isomerisation of 5-nitro-2-nitroaminopyridine to 3 : 5-dinitro-2-aminopyridine (Tschitschibabin and Menschikov, *loc. cit.*) under the influence of concentrated sulphuric acid could not be confirmed, 5-nitro-2-hydroxyppyridine being invariably produced. H. W.

**Phenylhydrazino Derivatives of Pyrimidines.** P. A. LEVENE (*J. Biol. Chem.*, 1925, **63**, 653—659).—3-Substituted pyrimidines fail to give the colour reaction with bromine water and barium hydroxide described by Wheeler and Johnson (A., 1909, i, 677); pyrimidines not substituted in the 3-position give, on treatment with bromine and then with phenylhydrazine, a 5-phenylhydrazine derivative; 3-substituted pyridines, under similar conditions, give 4 : 5-diphenylhydrazido derivatives, resembling oxazones. Uridine gives no colour reaction and a diphenylhydrazine derivative; in uridine, therefore, ribose is probably substituted in the 3-position of uracil. 5-Phenylhydrazidouracil yellow, m. p. 252°, and is also obtained by direct action of phenylhydrazine on isobarbituric acid. 1 : 3-Diphenyldimethylhydrazidouracil, orange, m. p. 192°, has the microscopic appearance of glucosazone. Diphenylhydrazidouridine has m. p. 212°. 4-Methyluracil, *s*-methyluracil and cytidine failed to react with phenylhydrazine. C. R. H.

**4 : 5-Diphenyl-2-*m*-nitrophenylglyoxaline, 2 : 4 : 5-Tri(*p*-nitrophenyl)glyoxaline, and Some Derivatives.** J. TRÖGER and H. THOMAS (*J. pr. Chem.*, 1925, [ii], **110**, 42—63).—*m*-Nitrolophine (4 : 5-diphenyl-2-*m*-nitrophenylglyoxaline), m. p. above 300°, prepared by an improved method in 70—90% yield from *m*-nitrobenzaldehyde, benzil, and aqueous ammonia (Tröger, A., 1902, i, 189), is stable to hot concentrated hydrochloric acid or to 50% aqueous potassium hydroxide, but when warmed with 50% alcoholic potassium hydroxide decomposes into ammonia and benzoic and *m*-nitrobenzoic acids.

Nitration of lophine with nitric acid yields 2 : 4 : 5-*tri*(*p*-nitrophenyl)glyoxaline, m. p. 147°, the decomposition of which by alkali gives 90% of the theoretical amount of *p*-nitrobenzoic acid, m. p. 238°. Reduction gave no isolable amine.

4 : 5-Diphenyl-2-*m*-aminophenylglyoxaline (*m*-aminolophine, Tröger, *loc. cit.*), m. p. 295° (darkens, 280°), is best obtained (yield 90%) by reduction of the nitrolophine with zinc and hydrochloric-acetic acid. It may be diazotised by shaking a solution of the hydrochloride and sodium nitrite in a closed flask at 40—50° for 15—30 mins. 4 : 5-Diphenyl-2-*m*-hydroxyphenylglyoxaline (Tröger, *loc. cit.*), m. p. 182° (*O*-benzoate, m. p. 256°), results when the diazo compound is heated at 80—90°. The diazo compound couples with resorcinol,  $\alpha$ -naphthol, and  $\beta$ -naphthol, giving *products* melting at 222°, 194°, and 123°, respectively, with potassium sulphite to form a *diazosulphonic acid* (potassium salt, m. p. 105°, and sodium salt are also described), and by the action of sulphur dioxide is converted

into 2:4:5-*triphenylglyoxaline-m-sulphonic acid* (not obtainable from the diazosulphonic acid).

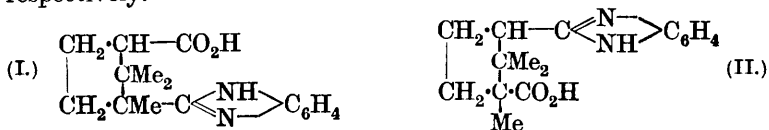
By the action of methyl iodide on *m*-aminolophine there is formed the compound,  $C_{24}H_{25}N_3I_2 \cdot H_2O$  (Tröger, *loc. cit.*), m. p.  $95^\circ$ , which loses  $H_2O$  and HI at  $105^\circ$  or on distilling the aqueous suspension, and loses both iodine atoms when heated with dilute sulphuric acid and ferric chloride. The corresponding *chloride*,  $C_{24}H_{25}N_3Cl_2 \cdot H_2O$ , m. p.  $249^\circ$ , formed by double decomposition with silver chloride, shows similar behaviour. The iodide, heated with moist silver oxide, gives, according to the proportion of the latter used, a *base*,  $C_{10}H_{14}O_2N_2$ , m. p.  $87^\circ$ , or a *base*, m. p.  $152-153^\circ$  (*chloroplatinates* of both described). With 3 mols. of methyl iodide and 3 mols. of potassium hydroxide in methyl alcohol *m*-aminolophine yields the *compound*,  $C_{24}H_{25}N_3I_2 \cdot 3H_2O$ , m. p.  $159-160^\circ$ . Benzoylation of *m*-aminolophine gives a compound,  $C_{43}H_{37}N_3Cl_2$ , m. p.  $172^\circ$ .

C. H.

**Reaction between Aromatic Aldehydes and Phenanthraquinone in presence of Ammonia.** A. C. SIRCAR and N. C. G. RAY (*J. Chem. Soc.*, 1925, 127, 1048—1049; cf. T., 1923, 123, 1559).—When aromatic aldehydes react with phenanthraquinone and ammonia, oxazole formation is favoured by a low temperature and iminazole formation by a higher temperature. Thus phenanthraquinone, benzaldehyde, and aqueous ammonia on heating at  $160-170^\circ$  give 2-*phenylphenanthriminazole* (not melted below  $295^\circ$ ); similarly from *o*-nitrobenzaldehyde is prepared 2-*o-nitrophenylphenanthriminazole*. After phenanthraquinone and salicylaldehyde in amyl alcohol solution have been treated with dry ammonia at  $10-15^\circ$ , concentration yields 2-*o-hydroxyphenylphenanthroxazole*, m. p.  $231-233^\circ$ , and similarly *m*-nitrobenzaldehyde gives 2-*m-nitrophenylphenanthroxazole*, m. p.  $248^\circ$ , whilst *o*-nitrobenzaldehyde gives 2-*o-nitrophenylphenanthroxazole*, m. p.  $166^\circ$ .

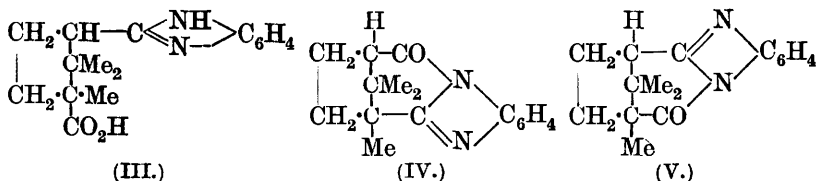
F. M. H.

**Colour of Complex Diazoles [Iminazoles]. II.** G. C. CHAKRAVARTI and I. S. GUPTA (*J. Indian Chem. Soc.*, 1925, 1, 320—328; cf. this vol., i, 162).—Camphoric anhydride condenses with *o*-phenylene-, *o*-tolylene-, and 1:2-naphthylene-diamine to yield compounds which, contrary to expectation, are all colourless. With *o*-phenylenediamine, it yields a mixture of three *benziminazole-2-trimethylcyclopentanecarboxylic acids*, to which the formulæ (I), (II), and (III) are assigned, m. p.  $233^\circ$ ,  $242^\circ$ , and  $203^\circ$ , respectively.



The acid, m. p.  $203^\circ$ , after melting, is converted into the acid, m. p.  $242^\circ$ , the isomerism evidently being similar to that observed in the

case of camphoric and isocamphoric acids. On heating with acetic anhydride, each acid loses 1 mol. of water and is converted into the corresponding *iminazole* (IV) and (V), m. p. 132° and 138°, respectively (mixed m. p. gives a depression). With *o*-tolylene-

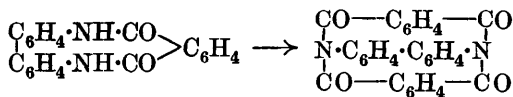


diamine, the corresponding *methylbenziminazole-trimethylcyclopentanecarboxylic acids*, m. p. 239—240° (type I) and 250—252° (type II), are obtained, which, with acetic anhydride, are also converted into the corresponding *iminazoles*, m. p. 93° and 97°, respectively. With 1 : 2-naphthylenediamine, two *naphthiminazole-trimethylcyclopentanecarboxylic acids*, m. p. 180—182° (type I) and 235° (decomp.), are obtained and from the former is obtained the corresponding *iminazole*, m. p. 80—82°. All these compounds contain solvent of crystallisation which is only partially removed by heating.

J. W. B.

**Action of Acid Anhydrides on Benzidine.** A. SHIMOMURA (*Mem. Coll. Sci. Kyōtō*, 1925, 8, 19—33).—Certain dicarboxylic acid anhydrides form with benzidine, in alcohol or benzene solution at the ordinary or a little higher temperature, products of the types :  $\text{CO}_2\text{H} \cdot \text{R} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{R} \cdot \text{CO}_2\text{H}$  and  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{R} \cdot \text{CO}_2\text{H}$ .

Phthalic anhydride yields diphenyl-4 : 4'-diphthalamic acid and 4-aminodiphenyl-4'-phthalamic acid, m. p. 292—295° (decomp.). The former is converted by heat into diphtalylbenzidine (Bandrowski, A., 1884, 1015), which, on heating with sodium hydroxide solution, regenerates the diphthalamic acid. The latter is converted by boiling with water into monophthalylbenzidine (Koller, A., 1904, i, 778), whence the monophthalamic acid is recovered by heating with sodium carbonate solution. Accepting Kaufler's formula for diphenyl and a symmetrical constitution for monophthalylbenzidine, the author postulates the transformation of the latter into diphtalylbenzidine by the action of another molecule of phthalic anhydride as follows :



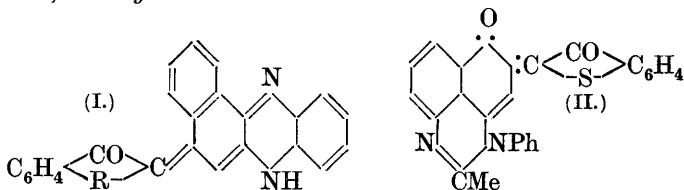
according to the usual formula for diphenyl. He regards as improbable the intramolecular change required to give the alternative formula,  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \\ \text{CO} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \\ \text{CO} \end{array} > \text{C}_6\text{H}_4$ .

*m m\**



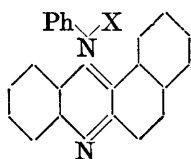
Succinic anhydride yields *diphenyl-4 : 4'-disuccinamic acid*, m. p. above 300°, converted by heat into *disuccinylbenzidine*, m. p. above 300°, obtained by condensation of the base and anhydride at 250° and reconverted into the disuccinamic acid by hot sodium carbonate solution. Diphenic anhydride yields *diphenyl-4 : 4'-di-diphenamic acid*, m. p. about 165° (decomp.), with a little *4-aminodiphenyl-4'-diphenamic acid*, m. p. about 215°. Naphthalic anhydride gives rise only to *dinaphthalylbenzidine*, m. p. above 300°. M. J.

**Indigoid Dyes.** L. SANDER (*Ber.*, 1925, **58**, [B], 824—834; cf. Friedländer and Sander, A., 1924, i, 663).—3-Hydroxy-4-keto-1-indoxenyl-1 : 4-dihydronaphthalene condenses with *o*-phenylenediamine in boiling glacial acetic acid solution, giving the *dye* (I) (R=NH). The analogous *dye* (R=S) is obtained in a similar manner; the *hydrochloride* is described.



Naphthaquinoneanils are readily prepared if the method of Euler (A., 1906, i, 370) is modified by the substitution of ammonia for sodium hydroxide. Thus  $\alpha$ -naphthol and nitrosobenzene in cold ammoniacal alcoholic solution yield 1 : 4-naphthaquinone-monoanil in 92% yield. 5-Acetamido-1 : 4-naphthaquinone-4-anil, m. p. 210° (decomp.), after softening, and 6-acetamido-1 : 4-naphthaquinone-4-anil, m. p. 210—220° (decomp.), are prepared similarly (6-acetamido- $\alpha$ -naphthol, prepared by the action of acetic anhydride and acetic acid on 6-amino- $\alpha$ -naphthol, has m. p. 100°). Anthrone and nitrosobenzene yield *anthraquinonemonoanil*, m. p. 123°. *Acenaphthenquinonemonoanil* has m. p. 189—190°. 5-Acetamido-1 : 4-naphthaquinone-4-anil is reduced by zinc dust and glacial acetic acid or, preferably, by stannous chloride and fuming hydrochloric acid in the presence of alcohol to 7-hydroxy-1-phenyl-2-methylperimidine, m. p. above 300°; the *hydrochloride* is described. Condensation of the quinoneanils with oxythionaphthen or indoxyl is conveniently effected in concentrated alcoholic solution in the presence of glacial acetic acid. Thus 5-acetamido-1 : 4-naphthaquinone-4-anil and oxythionaphthen yield the *dye* (II), the *sulphate* and *hydrochloride* of which are readily hydrolysed. 6-Acetamido-1 : 4-naphthaquinone-4-anil and thionaphthen afford 1-keto-6-acetamido-4-anilino-2-oxythionaphthenylidene-1 : 2-dihydronaphthalene,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown S \end{smallmatrix} C:C \begin{smallmatrix} \diagup CO \\ \diagdown CH:C(NHPh) \end{smallmatrix} C_6H_3 \cdot NHAc$ ; 1-keto-4-anilino-2-oxythionaphthenyl-1 : 2-dihydronaphthalene and 1-keto-4-anilino-2-indoxenyl-1 : 2-dihydronaphthalene are similarly prepared. Anthraquinoneanil and oxythionaphthen yield “2-thionaphthen-9'-anthraceneindolignone,” m. p. 240° (decomp.). H. W.

**Determination of the Constitutional Formulæ of Colouring Matters from their Absorption Spectra. VI.** F. KEHRMANN and M. SANDOZ (*Helv. Chim. Acta*, 1925, 8, 250—259; cf. A., 1924, i, 215).—The absorption spectra of the mono-acid and di-acid



salts of phenyl-“3:4”-benzophenazonium (phenyl-isonaphthophenazonium, annexed formula) and of the mono-, di-, and tri-acid salts of eight of its monoamino derivatives have been measured. The mono-salt of the parent is orange, but unlike the “2:3”-analogue (*loc. cit.*), is not fluorescent. The di-acid salt is reddish-brown and its absorption spectrum is very characteristic, showing well-defined bands at 5950 Å and 5050 Å. This compound must have the orthoquinonoid constitution, and as the tri-acid salts described below show similar spectra, it is concluded that they also are all orthoquinonoid. Except in this respect, however, there are differences which cause the monoamino derivatives to fall into two groups, viz., those in which the amino group is in positions 6, 4, or 2, or in the para position in the *meso*-phenyl radical, and those in which the amino group is in positions 5, 3, 10, or 9. The mono-acid salts of the first group are green or yellow; the di-salts are yellow; the tri-salts are brownish- or reddish-violet. The di- and tri-salts thus resemble the mono- and di-salts of the parent, respectively, and this resemblance is all the more evident in the absorption spectra. The mono-salts of the 5- and 3-amino derivatives, on the other hand, are blue and reddish-violet, respectively, and their di-salts are green. Similarly, the 10- and 9-amino derivatives give red mono-acid salts, and blue or green di-acid salts. All, nevertheless, yield violet-brown tri-acid salts resembling those above. These facts, and a comparison of the absorption spectra, indicate that in the mono- and di-acid salts of this second group the paraquinonoid arrangement prevails, but that the constitution becomes orthoquinonoid in the tri-acid salts. It is evident from the formulæ that the 5-, 10-, and 9-amino derivatives can readily behave in this way, the 3-amino derivative becoming “amphiquinonoid.” It is only when the amino group is in these positions that it has any pronounced auxochromic effect.

The amino derivatives were examined as pure perchlorates and the absorption spectra (curves are given) differ slightly from such as have been described for some of the compounds in earlier papers.

W. A. S.

**Dyes Derived from Phenanthraquinone. VI. Phenanthraquinone-phenyl Azomethines and Phenanthraphenazine Azo Dyes.** A. C. SIRCAR and B. K. S. GUPTA (*J. Indian Chem. Soc.*, 1925, 1, 321—328).—Further attempts to prepare dyes from phenanthraquinone and its derivatives are described. It is not possible to diazotise one only of the amino groups in 2:7-diaminophenanthraphenazine as it is in safranin, and it is therefore concluded that no distinction between the two amino groups can be made, and that this compound does not exist in a tautomeric quinonoid

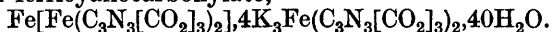
*m m*\* 2

state as suggested by Watson and Dutta (T., 1921, 119, 1211). By condensing aminophenanthraquinones with aromatic aldehydes, a series of azomethines has been prepared. These are crystalline and deeply coloured, but are of little value as dyes, since they are readily decomposed into the original aminoquinone and aldehyde by dilute mineral acids at 100°. By diazotisation of 2 : 7-diaminophenanthraphenazine and coupling with a suitable second component, the following compounds are obtained: *phenanthraphenazine-2 : 7-bis(1'-azo-2'-hydroxy-3'-naphthoic acid*; *phenanthraphenazine-2 : 7-bis(1'-azo-2'-naphthol)*. In solution, only one amino group of 2 : 7-diaminophenanthraquinone reacts with an aldehyde, and thus are obtained: 2-amino-7-p-dimethylaminobenzylideneaminophenanthraquinone, bluish-black needles; 2-amino-7-o : p-dihydroxybenzylideneaminophenanthraquinone, black needles; 2-acetamido-7-o-hydroxybenzylideneaminophenanthraquinone, 2-amino-7-o-hydroxybenzylideneaminophenanthraquinone, 2- and 4-m-nitrobenzylideneaminophenanthraquinone. By heating the aminoquinone directly with excess of the aldehyde both amino groups react, and thus are obtained: 2 : 7-dibenzylideneaminophenanthraquinone, 2 : 7-di-p-tolylideneaminophenanthraquinone, 2 : 7-dicinammylideneaminophenanthraquinone, 2 : 7-di-p-anisylideneaminophenanthraquinone, 2 : 7-di(o-hydroxybenzylideneamino)-phenanthraquinone. These compounds do not melt below 300°. There are also described 4-amino-5-m-nitrobenzylideneamino- and 2-amino-7-m-nitrobenzylideneamino-phenanthraquinone.

J. W. B.

### Complex Iron Derivatives of Triazinetricarboxylic Acid.

P. PASCAL (*Compt. rend.*, 1925, 180, 1850—1851).—Complex iron derivatives of triazinetricarboxylic acid, regarded by the author as analogous to the complex cyanides, are described. These compounds are less stable than the complex cyanides; they are readily transformed into derivatives of cyanoformic acid, and in solution some of the iron is present in the form of ions. By addition of a ferric salt to potassium triazinetricarboxylate, *potassium ferricyanocarboxylate*,  $K_3Fe(C_3N_3[CO_2]_3)_2 \cdot 24H_2O$ , orange, readily depositing the double salt of ferric ferricyanocarboxylate and potassium ferricyanocarboxylate,



Both these salts are photo-sensitive. On adding ferrous salts to potassium triazinetricarboxylate, *potassium ferrocyanocarboxylate*,  $K_4Fe(C_3N_3[CO_2]_3)_2$ , red, depositing from solution violet crystals of a *ferropotassium ferrocyanocarboxylate*,  $FeK_6Fe(C_3N_3[CO_2]_3)_2$ , is obtained.

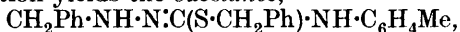
L. F. H.

### Action of Aromatic Amines on Thiosemicarbazide.

H. MAZOUREWITSCH (*Bull. Soc. chim.*, 1925, [iv], 37, 723).—By the action of aniline, o-, m-, and p-toluidines, and benzylamine on thiosemicarbazide (cf. A., 1924, i, 1297) the author has obtained a series of alkali-soluble crystalline substances, probably triazoles, having m. p. 261—262.5° (decomp.), 228—229°, 234—236°, 272—274°, and 161—163°, respectively.

R. B.

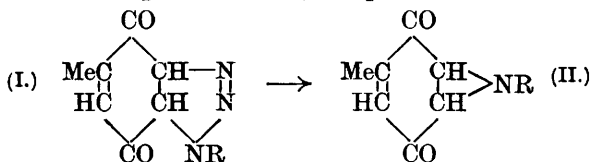
**Derivatives of Di-*o*-tolylhydrazodithiodicarbonamide.** E. FROMM and P. SZENDRÖ (*Ber.*, 1925, 58, [B], 970—975).—The action of a large excess of boiling benzoyl chloride on di-*o*-tolylhydrazodithiodicarbonamide leads to the production of dibenzoyl-2:5-ditoluidino-1:3:4-thiodiazole, m. p. 252° (cf. Fromm, Soffner, and Frey, A., 1924, i, 93), which can also be obtained under similar conditions from 2:5-ditoluidino-1:3:4-thiodiazole or 3-thiol-5-toluidino-4-*o*-tolyl-1:2:4-triazole. 2:5-Di-*o*-toluidino-1:3:4-thiodiazole, m. p. 220°, is prepared from di-*o*-tolylhydrazodithiodicarbonamide by the restricted action of a comparatively slight excess of boiling benzoyl chloride or by boiling with acetic anhydride and subsequent hydrolysis of the compound thus produced (cf. Fromm, Soffner, and Frey, *loc. cit.*). The action of benzoyl chloride and sodium hydroxide on di-*o*-tolylhydrazodithiodicarbonamide or 3-thiol-5-toluidino-4-*o*-tolyl-1:2:4-triazole yields a substance,  $C_{23}H_{24}O_3N_4S$ , m. p. 156°, which is transformed by a small excess of boiling benzoyl chloride into 3-benzoylthiol-5-toluidino-4-*o*-tolyl-1:2:4-triazole, m. p. 188°, obtained previously (*loc. cit.*) by heating 4-*o*-tolylthiosemicarbazide with a slight excess of benzoyl chloride. Alcoholic potassium hydroxide transforms the latter substance into the compound,  $C_{16}H_{20}O_2N_4S$ , m. p. 154°, which on treatment with sodium hydroxide and benzoyl chloride in boiling alcoholic solution yields the substance,



m. p. 112°. 3-Thiol-5-toluidino-4-*o*-tolyl-1:2:4-triazole is converted by iodine in the presence of alcohol or by bromine in aqueous suspension into the corresponding *disulphide*,  $C_{32}H_{30}N_8S_2$ , m. p. 168°, which is reconverted by aqueous alkali hydroxide into the original triazole.

H. W.

**Action of Azides on Toluquinone.** F. D. CHATTAWAY and G. D. PARKES (*J. Chem. Soc.*, 1925, 127, 1307—1311; cf. Wolff and Grau, A., 1912, i, 1034; Wolff, Hercher, and Körbs, A., 1913, i, 1107).—Toluquinone, from the oxidation of *o*-toluidine with chromic-sulphuric acid, is best distilled in steam in small quantities. It reacts with phenylazide in dry benzene at 50° to give 4:7-diketo-1-phenyl-5-methylbenztriazole, (as I) m. p. 206° (darkens 190°), which is converted by a few minutes' heating in aniline into phenylcycloiminotoluquinone (as II), m. p. 130°.

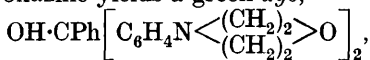


4:7-Diketo-1-*o*-tolyl-5-methylbenztriazole, m. p. 155°, loses nitrogen even during recrystallisation. The following arylcycloiminotoluquinones are described: *o*-tolyl-, m. p. 139°; *p*-chlorophenyl-, m. p. 180°; 2:4-dichlorophenyl-, m. p. 209.5; 2:5-dichlorophenyl-, m. p. 299°; *p*-bromophenyl-, m. p. 185°; 2:4-dibromophenyl-, m. p. 216°;

2 : 4 : 6-tribromophenyl-, m. p. 171°. The arylaziminotoluquinones contain two hydrogen atoms more than the analogous products obtained by Wolff.

C. H.

**1-Phenyltetrahydro-1 : 4-oxazine (4-Phenylmorpholine) and a New Triphenylmethane Dye.** H. ADKINS and R. M. SIMINGTON (*J. Amer. Chem. Soc.*, 1925, **47**, 1687—1689).—When 10% sodium hydroxide solution is used to neutralise the acid produced in the reaction and the dihydroxyethylaniline is dehydrated by heating at 200—250 mm., ethylene chlorohydrin may be converted to the extent of 45% into 4-phenyltetrahydro-1 : 4-oxazine(4-phenylmorpholine) (cf. Knorr, A., 1889, 1218). Kamm and Waldo's method (A., 1922, i, 105) gives a slightly higher yield in terms of aniline used. When heated with benzaldehyde and hydrochloric acid (*d* 1.19), the oxazine yields a green dye,



somewhat lighter in shade than malachite green.

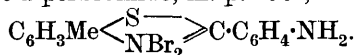
R. B.

**2 : 4 : 5-Triphenyloxazole or Benzilam.** J. TRÖGER and O. PHILIPPSON (*J. pr. Chem.*, 1925, [ii], **110**, 65—85).—When 2 : 4 : 5-triphenyloxazole and imabenzilam, respectively, are treated with nitric acid, they both give benzil, but with the precaution of cooling the nitric acid (*d* 1.5), and gradually adding the substance to be nitrated, a product is obtained which is precipitated by water and after two repetitions of the nitration is considered to be pure trinitro-2 : 4 : 5-triphenyloxazole, m. p. 294°; by heating this at 245° under pressure with concentrated hydrochloric acid, it is partly changed, whilst oxidation of its acetic acid solution with chromic acid yields solely *p*-nitrobenzoic acid and ammonia, showing that its three nitro groups are attached to the three phenyl groups in the *p*-position. By adding benzilam or imabenzilam to nitric acid (*d* 1.46) at 15°, and precipitating with water, a product is obtained from which nitro-2 : 4 : 5-triphenyloxazole, m. p. 194°, may be isolated; its oxazole ring undergoes disruption more easily than that of the trinitro derivative, so that on heating with concentrated hydrochloric acid at 245° under pressure *p*-nitrobenzoic acid is formed and this is also obtained on oxidation with chromic acid, showing that the nitro group is attached in the *p*-position to one of the phenyl groups; by alkali hydroxide nitrobenzilam is converted into azoxy-2 : 4 : 5-triphenyloxazole, m. p. 270°. When a solution of nitrobenzilam in acetic acid and a little hydrochloric acid is treated with zinc, addition of water, and sometimes of sodium acetate, gives amino-2 : 4 : 5-triphenyloxazole, m. p. 214° (*chloroplatinate* and *chloroaurate* described); from the product of heating the amino compound with methyl iodide, methyl alcohol, and ether under pressure at 100°, have been isolated a substance (dimethylaminobenzilam methiodide?) and the *methiodide*, m. p. 171°, which with silver oxide yields a base,  $\text{C}_{19}\text{H}_{14}\text{ON}_2$ , which is characterised as its *chloroplatinate*; aminobenzilam with benzyl chloride gives the *dibenzyl* derivative, m. p. 182°; aminobenzilam may be diazotised and from the diazo compound may be obtained (a) *benzilam-azo-β*-

*naphthol*, (b) *hydroxy-2:4:5-triphenyloxazole*, m. p. 205°, and (c) by treatment with sulphur dioxide a sulphur-free product.  
F. M. H.

**Condensation of Rhodanic Acids with Isatin. 3-Arylrhodanylidene- $\Delta^{5,3}$ -oxindoles.** R. M. HANN (*J. Amer. Chem. Soc.*, 1925, **47**, 1189—1191).—Isatin condenses with arylrhodanic acids in boiling glacial acetic acid in presence of anhydrous sodium acetate, by which reaction the following  $\Delta^{5,3}$ -oxindoles were prepared: 3-phenyl-, 3-o-tolyl-, 3-m-tolyl-, 3-p-tolyl-, 3-o-anisyl-, 3-p-anisyl-, 3(4-m-xylyl)-, 3(2-p-xylyl)-, 3- $\alpha$ -naphthyl-, 3- $\beta$ -naphthyl-, and 3- $\psi$ -cumyl-rhodanylidene- $\Delta^{5,3}$ -oxindoles. The last-named has m. p. 218—219°, the remainder m. p. above 300°. F. G. W.

**Bromination of 4'-Amino-1-phenyl-5-methylbenzthiazole [Dehydrothiotoluidine] and of 1:1-Bisbenzthiazole.** R. F. HUNTER (*J. Chem. Soc.*, 1925, **127**, 1318—1320).—Gattermann's dibromo additive compound from dehydrothiotoluidine (A., 1889, 602) is shown to be a perbromide, m. p. 190°,



1:1-Bisbenzthiazole (Hofmann, A., 1878, 396; Lauth, A., 1896, i, 326) yields a similarly constituted *tetrabromide*. Both lose all their bromine instantly when treated with sulphurous acid.

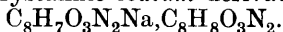
1-Chlorobenzthiazole is unaffected when heated with sodium in dry ether.  
C. H.

**Chlorobenzthiazole Dibromide.** R. F. HUNTER (*J. Chem. Soc.*, 1925, **127**, 1488—1489).—1-Chlorobenzthiazole forms a *dibromide*, m. p. 139°, stable in a vacuum, regenerating chlorobenzthiazole on exposure to air or treatment with sulphurous acid and is therefore assumed to be a *N*-bromo derivative. 1:1-Bisbenzthiazole could not be obtained by the action of sodium on 1-chlorobenzthiazole in boiling ether or boiling xylene. M. J.

**$\alpha$ -Ketoformhydroxamic Acids and their Derivatives. X.** C. GASTALDI [with E. REPOSSI] (*Gazzetta*, 1925, **55**, 201—214; cf. A., 1924, i, 1208).—The two benzoylformhydroxamic acid oximes (cf. A., 1924, i, 733) show the following further differences. (1) The  $\alpha$ -form, m. p. 177°, crystallises in either the monoclinic or triclinic system and the  $\beta$ -isomeride, m. p. 189°, in the rhombic system. (2) With acetic anhydride, the  $\alpha$ -oxime gives, in the cold, a *triacetyl* derivative,  $\text{OAc} \cdot \text{N} : \text{CPh} \cdot \text{C}(\text{OAc}) : \text{N} \cdot \text{OAc}$ , m. p. 85°, and in the hot, a *diacetyl* compound,  $\text{OAc} \cdot \text{N} : \text{CPh} \cdot \text{C}(\text{OH}) : \text{N} \cdot \text{OAc}$ , m. p. 126°, and benzonitrile; hydrolysis of either of these acetyl compounds with sodium hydroxide yields 5-hydroxy-3-phenylfuro(*ab*<sub>1</sub>)diazole, m. p. 202°, phenylhydroxyfurazan, and benzoylformhydroxamic acid  $\alpha$ -oxime. The action of acetic anhydride on the  $\beta$ -oxime gives, in the hot, benzonitrile and in the cold a *triacetyl* compound, m. p. 117°, which, on hydrolysis, yields benzoylformhydroxamic acid  $\beta$ -oxime and, probably, phenylglyoxylic acid  $\beta$ -oxime. (3) When treated with sodium hydroxide, the  $\alpha$ -oxime gives the crystalline *monosodium*

derivative,  $C_8H_7O_3N_2Na$ , whilst with sodium ethoxide it yields the crystalline *disodium* derivative,  $C_8H_6O_3N_2Na_2$ , and this, at  $80-90^\circ$ , is converted into 5-hydroxy-3-phenylfuro(*ab*<sub>1</sub>)diazole and *phenylhydroxyfuran*,  $O \begin{smallmatrix} N:CPh \\ \diagup \\ N \cdot C \cdot OH \end{smallmatrix}$ , m. p.  $176^\circ$ , which has the normal molecular weight in freezing acetic acid and forms a *sodium* derivative,  $C_8H_5O_2N_2Na \cdot 7H_2O$ , and a *silver* derivative,  $C_8H_5O_2N_2Ag \cdot C_8H_6O_2N_2$ .

Benzoylformhydroxamic acid  $\beta$ -oxime, when treated with sodium ethoxide, gives the crystalline *sodium* derivative,



(4) When treated with *o*-phenylenediamine in alcoholic solution, the  $\alpha$ - but not the  $\beta$ -oxime gives the crystalline *compound*,  $NOH:CPh \cdot C(OH):NOH \cdot 2C_6H_4(NH_2)_2$ , m. p.  $151^\circ$ , which reduces silver nitrate and gives coloured precipitates with ferric chloride and cupric acetate.

Ponzo's criticisms (this vol., i, 139) are refuted. T. H. P.

### Cuprohalide Molecular Compounds of Azo Compounds.

O. DIELS and W. KOLL (*Annalen*, 1925, **443**, 262—272).—*endo*-Methylenedehydropiperidazine cuprochloride (cf. this vol., i, 977) dissolves in hot, concentrated aqueous potassium and ammonium chloride to give colourless solutions, which smell of the azo compound owing to dissociation of the additive compound. On cooling, the solutions turn red and deposit the pure additive compound. Additive compounds of the above azo derivative with cuprous iodide (light red), cuprous cyanide (orange), and cuprous thiocyanate (light red) are described.

When hydrazomethane diacetate is warmed in aqueous solution with copper sulphate, a dark red, crystalline precipitate is obtained, apparently not identical with Thiele's product (cf. A., 1909, i, 560). Addition of chlorine ion, either as hydrochloric acid or as sodium or cupric chloride, causes immediate precipitation of *azomethane cuprochloride*,  $NMe \cdot NMe \cdot 2CuCl$ , red, apparently identical with Thiele's product. *Azoisopropane cuprochloride*,  $C_6H_{14}N_2 \cdot CuCl \cdot 2H_2O$ , ruby-red, decomposing in a few hours (cf. Lochte, Noyes, and Bailey, A., 1923, i, 26), and 3:5:5'-*trimethylpyrazolidine cuprochloride*, orange, were obtained similarly.

The additive combination of cuprous halides with azo compounds, which thus appears to be a general reaction, is discussed in relation to the action of cupric chloride on diazonium compounds (cf. Sandmeyer, A., 1884, 1311; Erdmann, A., 1893, i, 150).

F. G. W.

**Azo Derivatives of  $\beta$ -Naphthol Containing *p*-Substituted Auxochromes.** ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 403552; from *Chem. Zentr.*, 1924, **95**, [ii], 2703—2704).—The following compounds are described: 1-*p*-aminobenzeneazo-2:4-dihydroxynaphthalene, m. p.  $226-228^\circ$ ; 1-*p*-aminobenzeneazo-2:4-dihydroxynaphthalene-8-sulphonic acid, red needles, infusible; 1(1'-amino-4'-sulphonaphthaleneazo)-2:4-dihydroxynaphthalene, dyeing orange-red shades on wool; 1(4'-chloro-2'-amino-6'-sulpho-

phenolazo)-2-hydroxynaphthalene-4-sulphonic acid (?); 1(1'-amino-2':4'-dihydroxynaphthaleneazo)-2-hydroxynaphthalene, decomp. 200°; 1-aminobenzeneazo-4-amino- $\beta$ -naphthol, reddish-yellow needles, m. p. 256—257°, and a compound, dark red crystals, m. p. 234°, obtained from aniline and 1-aminoazobenzene- $\beta$ -naphthol-4-sulphonic acid in the presence of sodium acetate. R. B.

**Preparation of Azo Colouring Matters.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (with A. ZITSCHER) (D.R.-P. 393722; from *Chem. Zentr.*, 1924, ii, 2422).—Diazo, tetrazo, or diazoazo compounds which do not contain sulphuric acid or carboxylic acid groups are coupled with acetoacetamidoarylthiazole derivatives of the general formula  $\text{CH}_2\text{Ac}\cdot\text{CO}\cdot\text{NH}\cdot\text{R}\cdot\text{C}\begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix}\text{R}'$ , where R and R' are substituted aromatic radicals. Acetoacetamidoarylbenzthiazole is prepared by heating aminoarylbenzthiazoline with ethyl acetoacetate. *Acetoacetyldehydrothiotoluidide* is a yellow, crystalline powder, m. p. 170—172° (uncorr.). G. W. R.

**Action of Halogens on Phenylhydrazones. II. Action of Chlorine.** J. E. HUMPHRIES, H. HUMBLE, and R. EVANS (*J. Chem. Soc.*, 1925, 127, 1304—1307; cf. T., 1923, 1766).—The action of chlorine on phenylhydrazones in cold carbon tetrachloride solution gives the 2:4-dichloro derivatives. Subsequent action proceeds with difficulty to the 2:4:6-trichlorophenylhydrazone. Under appropriate conditions, the 2:4-dichloro- and 2:4:6-trichlorophenylhydrazones of benzaldehyde undergo further substitution at the carbon of the original carbonyl group to give tri- and tetra-chloro derivatives, respectively. The following compounds are described: *acetophenone-2:4-dichlorophenylhydrazone*, m. p. 85°; *benzophenone-2:4-dichlorophenylhydrazone*, m. p. 105°; *benzophenone-2:4:6-trichlorophenylhydrazone*, m. p. 106°; the *trichloro* derivative,  $\text{CPh}\cdot\text{Cl}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Cl}_3(2:4)$ , m. p. 90°, when reduced gave 2:4-dichlorophenylhydrazine hydrochloride, yielding *m-chlorobenzaldehyde-2:4-dichlorophenylhydrazone*, m. p. 127°, and *p-chlorobenzaldehyde-2:4-dichlorophenylhydrazone*, m. p. 117°; the *tetrachloro* derivative,  $\text{CPh}\cdot\text{Cl}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_2\text{Cl}_4(2:4:6)$ , m. p. 98°, when reduced gave 2:4:6-trichlorophenylhydrazine hydrochloride.

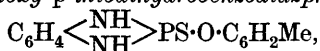
The identity of these products is established by comparison with synthetically prepared specimens and their derivatives. Acetophenylhydrazone gave probably a mixture of the hydrochlorides of phenylhydrazine and 2:4-dichlorophenylhydrazine.

M. J.

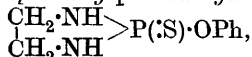
**Compounds Containing Phosphorus and *p*-Thiodiazphospholes.** W. AUTENRIETH and W. MEYER (*Ber.*, 1925, 58, [B], 848—851).—The action of thiophosphoryl dichlorides on *o*-diamines and similar substances leads to the production of cyclic compounds containing two nitrogen and carbon atoms and a phosphorus atom in the ring for which the term “diazphospholes” is suggested.



Thus *p*-tolylxythiophosphoryl dichloride and *o*-phenylenediamine at 180° yield *p*-tolylxy-*p*-thiodihydrobenzodiazphospholium,



m. p. 147°, whereas phenoxythiophosphoryl dichloride and ethylenediamine hydrate afford *phenoxy-p*-thiodihydrodiazphospholium,



m. p. 189°. Phenoxy-*p*-thiodihydrobenzodiazphospholium, m. p. 185° (cf. Autenrieth and Hildebrand, A., 1898, i, 419), has the normal molecular weight in naphthalene. Diphenoxythiophosphoryl chloride and hydrazine hydrate in aqueous solution at 67° yield *diphenylthiophosphorhydrazide*,  $\text{S} \cdot \text{P}(\text{O} \cdot \text{Ph})_2 \cdot \text{NH} \cdot \text{NH}_2$ , m. p. 63° (*benzylidene* derivative, m. p. 129°). Phenoxythiophosphoryl dichloride (1 mol.) and hydrazine hydrate (4 mols.) give phenylthiophosphordihydrazide, m. p. 95° (cf. Strecker and Heuser, A., 1924, i, 1160), which affords a *dibenzylidene* derivative, m. p. 115°, whereas the reagents, if used in the molecular ratio 1 : 2 yield *PP'*-*diphenoxy-PP'*-*dithiotetrazdiphosphinium*,  $\text{O} \cdot \text{Ph} \cdot \text{PS} \begin{smallmatrix} \text{NH} \cdot \text{NH} \\ \text{<} \\ \text{NH} \cdot \text{NH} \end{smallmatrix} \text{PS} \cdot \text{O} \cdot \text{Ph}$ , m. p. 183°.

H. W.

**Oxidations in Turpentine and Olive Oil.** E. WALKER (*J. Chem. Soc.*, 1925, 127, 1491).—The author describes the conversion of either diphenylchloroarsine or diphenylarsenious oxide into diphenylarsinic acid and of  $\beta\beta'$ -dichlorodiethylsulphide into  $\beta\beta'$ -dichlorodiethyl sulphoxide in presence either of turpentine, previously exposed to the air, or of rancid olive oil. This oxidising action, peculiar to the exposed oils, is ascribed to the presence of peroxides.

M. J.

***p*-Dimethylaminomethylphenylarsinic Acid.** ÉTABLISSEMENTS POULENC FRÈRES, E. FOURNEAU, and A. MADINAVEITIA (F.P. 541612; from *Chem. Zentr.*, 1924, 95, [ii], 1511—1512).—*p*-Aminodimethylbenzylamine has been converted by the Bart method into the corresponding *arsinic acid*,  $\text{NMe}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}_3\text{H}_2$ .

R. B.

**Symmetrical Bisarsinoarylbenzamidocarbamides.** C. S. HAMILTON and R. T. MAJOR (*J. Amer. Chem. Soc.*, 1925, 47, 1128—1134).—The following nitrobenzoylaminoarylarsenic acids were prepared by the action of the nitrobenzoyl chloride on the sodium salts of the appropriate aminoarylarsinic acids in boiling toluene or xylene: 4-*o*-, *m*-, and *p*-nitrobenzamidophenylarsinic acids, m. p. above 250°; 2-(*o*-, *m*-, and *p*-nitrobenzamido)-tolyl-5-arsinic acids, m. p. similar; 3-*m*-nitrobenzamido- and 3-*o*-nitrobenzamido-phenylarsinic acids, m. p. above 250° and 249—250° (decomp.), respectively. From these the following amino derivatives were obtained by reduction with ferrous hydroxide in alkaline solution: 4-*o*-, *m*-, and *p*-aminobenzamidophenylarsinic acids, m. p. above 250°; 2(*m*- and *p*-aminobenzamido)-tolyl-5-arsinic acids, m. p. similar; and *m*-amino-

**3-benzamidophenylarsinic acid**, m. p.  $160^{\circ}$  (decomp.). These were converted by the action of carbonyl chloride in alkaline solution into the following carbamides: **4:4'-di-p-arsino-o-methylanilinoformyl-s-diphenylcarbamide** ( $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}$ ) $_2\text{CO}$ , m. p. above  $250^{\circ}$ ; **4:4'-di-p-arsinoanilinoformyl-s-diphenylcarbamide**, m. p. above  $250^{\circ}$ ; **3:3'-di-m-arsinoanilinoformyl-s-diphenylcarbamide**, m. p.  $249\text{--}250^{\circ}$  (decomp.); **3:3'-di-p-arsinoanilinoformyl-s-diphenylcarbamide**, m. p. above  $250^{\circ}$ ; and **2:2'-di-p-arsinoanilinoformyl-s-diphenylcarbamide**, m. p. above  $250^{\circ}$ . The amino derivatives darkened on exposure to air, particularly when moist, whilst the carbamides were stable.

F. G. W.

**Sulphoxyl Compounds. XIV. Aldehydesulphoxylates as Protective Colloids.** A. BINZ and H. BAUSCH (*Ber.*, 1925, **58**, [B], 987—990; cf. A., 1924, i, 1160).—The precipitation of silver salvarsan from aqueous solution by carbon dioxide is inhibited by the presence of formaldehydesulphoxylate or neosalvarsan. The possibility that this effect is attributable to the formation of chemical compounds is rendered improbable by the observation that the components are separable by ultra-filtration. Further, it is found that neosalvarsan has the power of retaining other substances, particularly metals (copper, silver, mercury) in colloidal solution. The solubility of aniline in aqueous solutions of formaldehydesulphoxylate to an extent which is far greater than corresponds with the production of anilinomethylenesulphoxylate appears to be a further instance of a similar phenomenon.

H. W.

**Therapeutic Compound [Sodium *p*-Aminophenylstibinate Glucoside].** THE WELLCOME FOUNDATION and W. H. GRAY (*Brit. Pat.* 234677).—Sodium *p*-aminophenylstibinate condenses in aqueous sodium hydroxide at the ordinary temperature in 3 days with dextrose to form a *glucoside*,  $\text{C}_{38}\text{H}_{49}\text{O}_{22}\text{N}_3\text{Sb}_3\text{Na}$ , a buff-coloured powder. The product forms a clear aqueous solution suitable for the treatment of kala-azar and other tropical diseases.

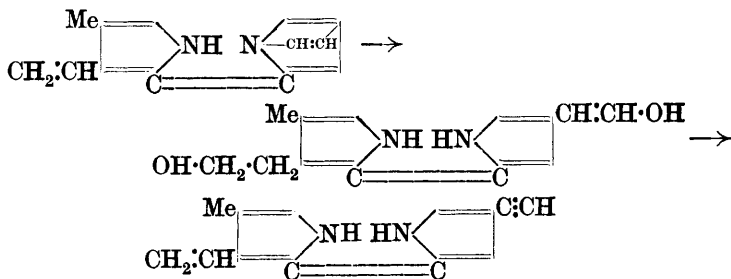
E. H. R.

**Structure of Proteins. Reduction of Dipeptides and Methods of Isolation of Reduction Products given by Proteins.** E. ABDERHALDEN and E. SCHWAB (*Z. physiol. Chem.*, 1925, **143**, 290—296).—The dipeptides and the corresponding diketopiperazines are reduced in different ways by the authors' method (A., 1924, i, 1345). The latter are reduced, not, however, quantitatively, to the corresponding piperazine; the former give amino alcohols with partial deamination. The reduction of *dl*-alanylglycine gives a mixture of  $\beta$ -amino- $\alpha$ -propanol and propionic acid. Glycylglycine on reduction gives aminoethyl alcohol, together with much ammonia. Piperazines are formed during the reduction of proteins, and methods have been sought by which they might be separated and identified. Such a method is condensation with phenylcarbimide. Piperazine itself is precipitated quantitatively by phosphotungstic acid in presence of 4% sulphuric acid.

H. D. K.

**Additive Product of Chlorine and a Monomethyl(chloro)-hæmin.** W. KÜSTER and R. HUTTENLOCHER (*Z. physiol. Chem.*, 1924, **141**, 291—296).—Treatment of monomethyl(chloro)hæmin with chlorine in chloroform solution gives an additive product,  $C_{35}H_{33}O_4N_4Cl_6Fe$ , from which two chlorine atoms may be removed by treatment with aqueous sodium carbonate. When the additive compound is shaken with hydrobromic acid in glacial acetic acid solution and the resulting substance treated with methyl alcoholic potassium hydroxide a product is obtained which contains a small quantity of a porphyrin and gives on acidification a crystalline substance,  $C_{35}H_{35}O_6N_4Cl_3Fe$ . E. S.

**Natural Porphyrins. XIV. Ooporphyrin and its Conversion into Hæmin Ester.** H. FISCHER and F. LINDNER (*Z. physiol. Chem.*, 1925, **142**, 141—154).—Plover's egg-shells contain a greater proportion of ooporphyrin (A., 1924, i, 230, 1130) than gull's egg-shells. The dimethyl ester has now been isolated in an ash-free condition and has the composition  $C_{36}H_{38}O_4N_4$  and not that previously assigned to it. The free ooporphyrin,  $C_{34}H_{34}O_4N_4$ , has also been isolated directly from the shells. The conversion of the ester into hæmatoporphyrin has been confirmed. Conversely, ooporphyrin has been obtained from hæmatoporphyrin by removal of  $2H_2O$  by heating in a vacuum. The identity of oohæmin ester with hæmin ester has been confirmed by crystallographic measurements. When ooporphyrin ester is dissolved in a solution of hydrobromic acid in glacial acetic acid, the product yields, after successive treatment with methyl alcohol and methyl-alcoholic potassium hydroxide, tetramethylhæmatoporphyrin. Ooporphyrin is probably formed in the organism of the bird by autolysis of the blood pigment according to the following scheme, which is based on Willstätter's (incomplete) formula :



Its instability is explained by the presence of the acetylene group. The name protoporphyrin is suggested for the following porphyrins, which have been found to be identical : ooporphyrin, Kammerer's porphyrin,  $H_2S$ -porphyrin,  $HCl$ -porphyrin,  $CO_2$ -porphyrin (A., 1924, i, 441, 1130). E. S.

**Prosthetic Group of Blood Pigments.** W. KÜSTER and W. HEISS (*Ber.*, 1925, **58**, [B], 1022—1027).—Hæmin is converted

successively into chlorohæmin, chlorodimethylhæmin, bromo-dimethylhæmin, and *bromodimethylhæmin bromide*,  $C_{36}H_{34}O_4N_4Br_3Fe$ , in which the bromine is partly displaced by methoxyl by the action of boiling methyl alcohol. Dibromohæmatoporphyrin dimethyl ether is oxidised by chromic acid in dilute sulphuric acid solution to hæmatic acid and *methyl- $\beta$ -bromo- $\alpha$ -methoxyethylmaleinimide*, m. p.  $75^\circ$ , in the approximate molecular ratio, 1 : 2. The presence of four pyrrole nuclei in the prosthetic group of blood pigments is thus established by oxidative methods. The observations are not in agreement with the presence of the pyrroline form (cf. Küster and Oesterlin, A., 1924, i, 1006), and it is suggested that the unsaturated

group,  $C_4H_4$ , has the structure  $\begin{cases} \text{Py} \cdot \text{C} : \text{CH}_2 \\ \text{Py} \cdot \text{CH} : \text{CH} \end{cases}$  H. W.

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## Biochemistry.

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**Relation between Processes of Fission and Respiration in the Cell.** O. MEYERHOF (*Ber.*, 1925, 58, [B], 991—1001).—A lecture delivered before the German Chemical Society. H. W.

**Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen. X. Oxygen Intake during Exercise while Breathing Mixtures Rich in Oxygen.** K. FURUSAWA (*Proc. Roy. Soc.*, 1925, B, 98, 287—289; cf. this vol., i, 92).—Certain errors such as the possible contamination of air in the work already described, are discussed. When all precautions to avoid such errors are observed it is found, as before, that the maximum oxygen intake may be increased by 50% by the breathing of a mixture rich in oxygen. This can be attributed only to an increased circulation of the blood. O. O.

**Oxygen Content of Methæmoglobin.** M. NICLOUX and J. ROCHE (*Compt. rend.*, 1925, 180, 1968—1970).—By studying quantitatively the amount of sodium hyposulphite required to reduce methæmoglobin to hæmoglobin and the amount of carbon monoxide required to convert the hæmoglobin formed into carboxyhæmoglobin, it is concluded that oxyhæmoglobin contains twice as much oxygen as methæmoglobin (cf. Quagliariello, this vol., i, 89). L. F. H.

**Oxidation-Reduction of Hæmoglobin and Methæmoglobin. II. Oxidation and Reduction of Methæmoglobin by Anaërobic Bacteria and by Sterile Plant Tissue. III. Formation of Methæmoglobin during the Oxidation of Auto-oxidisable Substances. IV. Inhibition of "Spontaneous" Formation of Methæmoglobin.** J. M. NEILL (*J. Exp. Med.*, 1925, 41, 535—549, 551—560, 561—570; cf. this vol., i, 868).—II.—Anaërobic

bacteria effect deoxygenation of oxyhæmoglobin, reduction of methæmoglobin to hæmoglobin, and some reversal of the latter process. The action of sterile plant tissue is similar.

III.—Hæmoglobin is oxidised to methæmoglobin by products formed during the oxidation of oleic and linolic acids, turpentine, cod-liver oil, and linseed oil. The same substances which in the presence of air induce the oxidation of hæmoglobin cause the reverse reaction when molecular oxygen is excluded.

IV.—Methæmoglobin is formed in stored sterile blood or hæmoglobin solution. If the hæmoglobin is reduced by biological agents and stored in the absence of air, the formation of methæmoglobin is retarded or prevented.

CHEMICAL ABSTRACTS.

**Hæmoglobin in Relation to Other Metallo-Hæmatoporphyrins.** R. HILL (*Biochem. J.*, 1925, **19**, 341—349).—The absorption spectra of a series of metallic derivatives of hæmatoporphyrin have been examined. It was found that they could be placed in three groups, namely, the acid hæmatoporphyrin, the oxyhæmoglobin, and the hæmochromogen groups. This classification is independent of the valency of the metal. Hæmoglobin is changed by treatment with high concentrations of alkali into a substance having the same spectrum and properties as hæmochromogen. This change is reversible in the cold. Oxyhæmoglobin and carbon monoxide hæmoglobin are unaltered by the alkali treatment in the cold. Hæmochromogen in dry pyridine is not acted on by free oxygen or carbon monoxide. The hæmochromogen ester in organic solvents shows the characteristic reactions of the free substance. Pyridine decomposes the carbon monoxide compound of hæmochromogen setting free hæmochromogen. This solvent forms hæmochromogen from oxyhæmoglobin as well as from hæmoglobin.

S. S. Z.

**Phosphorus Content of the Blood of Ruminants.** H. D. KAY (*Biochem. J.*, 1925, **19**, 447—449).—The main shortage of phosphorus in the blood of the cow, goat, and sheep as compared with the blood of rodents or of man is in the fraction not hydrolysable by bone enzyme. The quantity of phosphoric ester hydrolysed by bone enzyme is low for all three ruminants.

S. S. Z.

**Sugar Content of the Blood in Normal and Under-nourished Children, and the Effect of Fat on the Absorption of Carbohydrate.** M. J. BROWN (*Quart. J. Med.*, 1925, **18**, 175—190).—The sugar content of the blood of normal infants is 0.072—0.096% (up to 2 weeks) or 0.086—0.116% (6 weeks to 1 year); in under-nutrition, there is variation between these limits. Vomiting causes a diminution in blood-sugar. A diet high in fat does not interfere with the absorption of carbohydrate.

CHEMICAL ABSTRACTS.

**Determination of Blood-sugar.** S. R. BENEDICT (*J. Biol. Chem.*, 1925, **64**, 207—213).—The protein-free filtrate of blood obtained by the method of Folin and Wu (*A.*, 1919, ii, 308) is heated with a modification of Benedict's reagent (*A.*, 1911, ii, 340) containing sodium hydrogen sulphite and the amount of cuprous oxide formed

is determined by comparison of the colour developed, on treatment with a mixture of Benedict's uric acid reagent (A., 1922, ii, 405) and formaldehyde, with that obtained from a known solution of dextrose treated in the same way as the blood. The method gives consistently lower results than that of Folin and Wu (A., 1920, ii, 337), and it is considered probable that the lower results approximate more closely to the true concentration of dextrose in the blood.

C. R. H.

**Modification of Bloor's Method for Determination of Cholesterol in Blood.** G. E. SACKETT (*J. Biol. Chem.*, 1925, **64**, 203—205).—A rapid micro-modification of Bloor's method (A., 1917, ii, 275) for determining cholesterol is described in which 0.2 c.c. of blood is employed and the hydrolysis with sodium hydroxide is omitted.

C. R. H.

**Determination of Uric Acid in the Blood.** S. R. BENEDICT (*J. Biol. Chem.*, 1925, **64**, 215—219).—A critical review with special reference to the work of Bulmer, Eagles, and Hunter (this vol., i, 605).

C. R. H.

**Quantitative Determination of the "Primary Ether Extract" of Blood.** H. J. BING and H. HECKSCHER (*Biochem. Z.*, 1925, **158**, 395—402).—The "primary ether extract" of blood, obtained by the authors' technique, contains both free cholesterol and neutral fat. The earlier experiments of the authors determined the sum of these two blood constituents, and not blood-fat alone. The sum varies between 0.06% and 0.12% of the blood in normal, fasting individuals.

Provided certain precautions are taken, the authors' nephelometric method determines triolein, cholesterol, and also naturally occurring vegetable and animal fats quantitatively.

H. D. K.

**Effect of Ultra-violet Irradiation on Calcium of the Blood-serum.** A. R. MORITZ (*J. Biol. Chem.*, 1925, **64**, 81—89).—The diffusible calcium was determined by immersing a collodion bag containing the serum in distilled water exposed to a negative pressure of 150 mm.; under these conditions all the diffusible calcium passed out of the serum in 5 hrs. No changes could be detected in the total calcium or in the proportion of diffusible calcium of rabbits' blood-serum as the result of exposure of the animals or of the serum itself to ultra-violet irradiation.

C. R. H.

**Effect of Hæmolysis on the Calcium and Inorganic Phosphorus Content of Serum and Plasma.** C. C. WANG and A. R. FELSHER (*J. Lab. Clin. Med.*, 1925, **10**, 269—272).—The phosphorus contents of serum and plasma are equal and unchanged by hæmolysis. The calcium content of non-hæmolysed serum is slightly greater than that of the plasma.

CHEMICAL ABSTRACTS.

**Colloidal Characteristics of Muscle Proteins. I. Isoelectric Point and Stability of Myogen. II. Isoelectric Point and Solubility of Myosin.** H. H. WEBER (*Biochem. Z.*, 1925, **158**, 443—472, 473—490).—An investigation of the physical

chemistry of muscle proteins in relation to their function in muscle contraction. I. Myogen. Under the experimental conditions used, the isoelectric point of genuine myogen from rabbit's muscle is about  $p_H$  6.3 and is independent of the nature and concentration of the buffer. The isoelectric point of frog's muscle lies somewhat less certainly at  $p_H$  6.0. Above a definite concentration the presence of salts diminishes the colloidal stability of myogen, and causes a precipitation on the acid side of the isoelectric point ( $p_H$  5 and more acid). The amount of precipitation in the case of the salts of the alkali and alkaline-earth metals is mainly dependent on the nature of the anion. The charge on the precipitate is altered by the nature of the anion. The changes are completely reversible on removal of the anions by washing. Denatured myogen has the same isoelectric point as the original myogen. II. Myosin. The  $p_H$  of the point of maximal precipitation of myosin solutions prepared by Fürth's method, and of myogen solutions of the same salt concentration is about the same—in the neighbourhood of 5. The precipitated protein has in both cases the same isoelectric point. In the case of myogen, the amount of precipitation and the charge on the precipitate depends on the amount and nature of the anions present. In absence of these, the true isoelectric point of myogen fibrin (rabbit's) is 6.3. The residue of rabbit's muscle after removal of the press-juice shows an isoelectric point of 5.1 to 5.2 under the same conditions in which myogen fibrin has an isoelectric point of 6.3. The residue may therefore contain a different protein. A similar protein is also present in frog's muscle. In dilute press-juice there is no evidence of an isoelectric point at any  $p_H$  other than those given by myosin or myogen in the pure state. H. D. K.

**Amount of Cobalt in Organs of Animals.** G. BERTRAND and M. MACHEBŒUF (*Compt. rend.*, 1925, **180**, 1993—1997; cf. this vol., i, 719).—Cobalt occurs in all the tissues examined (except in certain muscles, adipose tissue, and egg-white) of all classes of animals. In general, organs appear to contain more cobalt than nickel (*loc. cit.*). L. F. H.

**Electrolytic Modification of the Gutzeit Method for Determination of Arsenic in Body-tissues.** W. E. LAWSON and W. O. SCOTT (*J. Biol. Chem.*, 1925, **64**, 23—28).—The tissue is incinerated with sulphuric acid, the resulting solution, after dilution, boiled with stannous chloride, and then submitted to electrolysis in a special apparatus; the arsine liberated is determined by the staining of mercuric bromide paper. C. R. H.

**Determination of Nucleic [Acid] Phosphorus in Animal Tissues.** M. JAVILLIER and H. ALLAIRE (*Bull. Soc. Chim. biol.*, 1925, **7**, 486—498).—The fresh tissue is pulped, dried at 0° and 1—2 mm. pressure, and finely powdered. The small quantity of water still present is determined by drying at 105°. About 2.5 g. are extracted twice for 2 hrs. in the cold with a 1:2 ether-96% alcohol mixture. The lipid-free residue is boiled for 10 mins. with 15% sodium chloride solution to remove the nucleic compounds,



and the solution diluted to 50 c.c. with 15% sodium chloride solution. To 25 c.c. are added 10 drops of 1:2 hydrochloric acid, and after 15 mins. the liquid is centrifuged. The precipitate is dissolved in about 10 c.c. of concentrated nitric acid, 2 c.c. of strong sulphuric acid are added, the organic matter is destroyed as usual, and the phosphoric acid determined by the method of Copaux (A., 1921, ii, 707). Values are given of the nucleic phosphorus content of various dried organs, ranging from 1.25% for calf thymus to 0.02% for horse spinal cord. The amount of nucleic acid in tissue as calculated from these phosphorus determinations is always less than that calculated from the determination of purine nitrogen after hydrolysis. This is because the purine nitrogen determined includes the purine nitrogen of nucleic acids, of less complicated substances, and of bases free before hydrolysis. On the other hand, the phosphorus as determined above is only that of nucleic acids, and does not even include the free mononucleotides. B. F.

**Determination of Small Amounts of Protein Nitrogen.** E. R. MAIN and A. P. LOCKE (*J. Biol. Chem.*, 1925, 64, 75—80).—The colorimetric method of Folin and Denis (A., 1916, ii, 573, 574) has been adapted to the determination of amounts of nitrogen of 0.005 mg. by measuring with a spectroscope the absorption of light C. R. H.

**Natural Porphyrins. XVI. Kämmerer's Porphyrin.** H. FISCHER and F. LINDNER (*Z. physiol. Chem.*, 1925, 145, 202—220).—The ester of Kämmerer's porphyrin is prepared and converted by the action of hydrobromic acid in acetic acid solution into hæmatoporphyrin and by the action of hydriodic acid in acetic acid solution into mesoporphyrin. Kämmerer's porphyrin is converted on saturation with hydrogen sulphide and standing at 42—45° into coproporphyrin. The method for preparation of the green colouring matter of egg-shells is improved and attempts made to reduce this substance with amalgam and with hydriodic acid. From these experiments it appeared that this substance was a derivative neither of blood pigments nor of bilirubin. P. W. C.

**Animal Quinoidine.** H. W. KINNERSLEY, R. A. PETERS, and B. T. SQUIRES (*Biochem. J.*, 1925, 19, 404—413).—Quinoidine extracts [extracts which fluoresce blue in ultra-violet light ( $\lambda$ . 3000—4000)] can be obtained from urine, guano, milk, feathers, liver, caseinogen, skin, commercial gelatin, and the lens of the eye. The behaviour of the last three substances to solvents is different from that of the other quinoidine substances. In the plant kingdom, grass leaves, certain oils, yeast extracts, and sawdust also yield quinoidine extracts. When normal urine is fractionated, quinoidine is found in the urochrome fraction. The fluorescence of pure substances such as the porphyrins, chlorophyll, xanthophyll, and bile derivatives is not blue. S. S. Z.

**Preparation of the Glucosamine-containing Phosphatides of Fränkel and Kafka from Brain.** H. THIERFELDER and E. KLENK (*Z. physiol. Chem.*, 1925, 145, 221—226).—The authors

attempted to repeat the isolation of dilignoceryl-*N*-diglucosamine monophosphoric ester from brain, as carried out by Fränkel and Kafka (A., 1920, i, 788; 1923, i, 1257). A substance having the same melting point was obtained, but hydrolysis with concentrated hydrochloric acid did not liberate any free glucosamine. The substance gave the Molisch test (distinction from glucosamine) and cerebrosides are probably present. It cannot have the structure assigned by Fränkel and Kafka.

P. W. C.

**Fractionation of the Proteins of Rattlesnake Venom.** W. H. WELKER (*J. Lab. Clin. Med.*, 1925, 10, 298—302).—Rattlesnake venom was separated into toxic and non-toxic protein fractions, confirming the work of Marshall. The euglobulin, on being dried after the removal of the water-soluble proteins and electrolytes, was no longer soluble in 10% sodium chloride solution. There was an indication that on repeated reprecipitation of the toxic fraction the toxic principle contained in the fraction was removed.

CHEMICAL ABSTRACTS.

**Effect of Heat on Solubility of Calcium and Phosphorus Compounds in Milk.** R. W. BELL (*J. Biol. Chem.*, 1925, 64, 391—400).—Skimmed milk was raised to various temperatures and then filtered through a Pasteur-Chamberland filter or centrifuged at a high speed; the filtrates of those samples which had been heated at 76.5° or higher showed considerably less calcium and phosphorus than the original milk.

C. R. H.

**Phosphorus Compounds of Milk. I. The Presence in Milk of Organic Acid-soluble Phosphorus Compounds.** H. D. KAY (*Biochem. J.*, 1925, 19, 433—446).—There are at least two acid-soluble compounds containing phosphorus in organic combination in cow's, goat's, and human milk. One of these compounds is readily hydrolysable by extracts of various tissues and by dilute acids, the other is less readily hydrolysed. Both compounds diffuse through a collodion membrane which holds back protein and permits the slow passage of methylene-blue. Ptyalin, pepsin, and trypsin do not hydrolyse these phosphorus compounds, whilst pancreas extract, pancreatic juice, intestinal extract, intestinal juice, gastric mucosa and extracts of kidney, mammary gland, and muscle do so. Blood and spleen extract hydrolyse feebly. Milk does not contain a phosphoric esterase. The more readily hydrolysable compound is present to the average extent of 4.4 mg. of phosphorus per 100 c.c. of cow's milk, 13.3 in goat's milk, and 3.3 mg. in human milk. In the last two milks, the acid-soluble organic phosphorus compounds form 10—25% of the total phosphorus of the milk.

S. S. Z.

**Rapid Determination of Small Amounts of Dextrose in the Urine in Diabetes.** J. R. WILLIAMS and G. U. CASEY (*Med. J. and Rev.*, 1924, 119, 237—239).—An adaptation of Joslin's simplification of Benedict's method (A., 1911, ii, 340).

CHEMICAL ABSTRACTS.

**Chemical Analysis of Blood in Asthma, Hay Fever, etc.** M. A. RAMIREZ, A. V. ST. GEORGE, and R. L. MOSES (*J. Lab. Clin. Med.*, 1924, **10**, 199—202).—The chloride in the blood plasma is increased, as also are, to a less extent, the sugar and non-protein nitrogen. CHEMICAL ABSTRACTS.

**Non-protein Sulphur of the Blood.** MAX KAHN and R. S. POSTMONTIER (*J. Lab. Clin. Med.*, 1925, **10**, 317—320).—The non-protein sulphur of the blood is increased by 2—6 times in many diseases, especially in carcinomatosis, tuberculosis, syphilis, diabetes, acute and chronic nephritis, and uræmia. CHEMICAL ABSTRACTS.

**Ultra-filterable Calcium in the Serum of Cancerous Subjects.** A. H. ROFFO and L. M. CORREA (*Bull. Soc. Chim. biol.*, 1925, **7**, 522—525).—Determinations on the plasma of patients suffering from various forms of cancer give values for the ultra-filterable calcium rising to about 62% of the total calcium. The values are fairly constant and approach those found in normal plasma.

B. F.

**Carbohydrate Metabolism of Tumours. I. Free Dextrose-Lactic Acid, and Glycogen Content of Malignant Tumours.**

C. F. CORI and G. T. CORI (*J. Biol. Chem.*, 1925, **64**, 11—22).—A number of spontaneous and transplanted mouse carcinomata and of Jensen rat sarcomata, in fasting animals, contained on the average 0.051% dextrose, 0.034% lactic acid, and 0.196% glycogen. After administration of dextrose the concentration of the latter and of lactic acid in the tumours showed a rise and fall which was parallel to the blood-sugar curve.

C. R. H.

**Fat+Cholesterol Content of the Blood of Cretins.** H. HECKSCHER (*Biochem. Z.*, 1925, **158**, 422—427).—The blood fat+cholesterol in adult cretins is almost invariably markedly greater than that of normal persons. In young cretins the fasting value is about normal, but the increase after a fat meal is considerably greater than with normals of the same age. Individuals showing milder cretinism give intermediate results.

H. D. K.

**Fat+Cholesterol Content of the Blood of Thyroidectomised Horses.** H. HECKSCHER (*Biochem. J.*, 1925, **158**, 417—421).—The removal of the thyroid gland from a healthy horse leads to an increase in the fat+cholesterol content of the blood above that of normal horses on the same diet. If fat is added to the diet, the rise in blood fat+cholesterol is greater in the thyroidectomised horse than in the normal.

H. D. K.

**Fat+Cholesterol Content of the Blood in cases of Basedow's Disease.** H. J. BING and H. HECKSCHER (*Biochem. Z.*, 1925, **158**, 403—416).—The primary ether extract of the blood of patients with Basedow's disease is usually small in quantity, near to the lower normal limit of 0.06%, and not infrequently below this figure. The rise in the value which follows the administration of 1 g. of milk-fat per g. of body weight is of the same order with these patients as with normal controls. As the symptoms of the

disease diminish following treatment, there is an accompanying rise in the fat plus cholesterol content of the blood, and following thyroidectomy this may become greater than the upper normal limit of 0.12%.

H. D. K.

**Lathyrism.** I. L. A. P. ANDERSON, A. HOWARD, and J. L. SIMONSEN. (*Indian J. Med. Res.*, 1925, **12**, 613—643).—Botanically pure seeds of *Lathyrus sativus*, L. ("khesari") have been found to contain no alkaloids and to be non-toxic. Seeds of *Vicia sativa* var. *angustifolia* ("akta"), which are present in ordinary khesari seed, contain the glucosides vicine and vicianine. Vicine is present in amounts up to 0.3%, the immature seeds containing the greatest amount. Seeds of *Lathyrus aphaca*, L., *L. sphaericus*, Retz., and *Vicia hirsuta*, Koch, which are also found in ordinary khesari seed, appear to contain little or no alkaloidal substance. Seeds of akta fed to ducks cause death, whereas pure khesari has no such effect. Divicine, the base obtained on hydrolysis of vicine, injected subcutaneously into young guinea pigs produces a characteristic fatal disease in doses of 0.6 mg. per g. of body-weight. In monkeys, akta produces characteristic nervous and muscular symptoms resembling, in some respects, those of human lathyrism. It cannot yet be definitely stated that akta is the cause of lathyrism in man.

C. P. S.

**Combination of Phenol Red and Proteins.** A. GROLLMAN (*J. Biol. Chem.*, 1925, **64**, 141—160).—Tables are given showing the amount of phenolsulphonephthalein which is adsorbed from its solution by charcoal and by various proteins at different reactions; with charcoal, adsorption increased with increasing acidity (up to  $p_H$  1.2); with the proteins, adsorption was at a maximum at the isoelectric point of the protein, decreasing rapidly on either side of this point. Experiments with various blood-sera showed that the percentage of the dye adsorbed was dependent on the concentration of albumin; it is pointed out that this fact should be considered when the excretion of the dye is used as an index of renal efficiency in patients whose blood-serum may be deficient in albumin.

C. R. H.

**Relation of Blood Phosphates to Carbohydrate Metabolism.** A. BOLLIGER and F. W. HARTMAN (*J. Biol. Chem.*, 1925, **64**, 91—109).—Following administration of dextrose to a patient with mild diabetes, to a partly depancreatized dog, or to a dog suffering from hyperglycæmia as the result of medullary puncture, the concentration of inorganic phosphate in the blood shows a slower and more prolonged fall than in the normal; in the completely depancreatized animal no variation at all is to be observed in the blood phosphates. If insulin be administered simultaneously with the dextrose the fall in the blood phosphates is accentuated; it is also increased on the administration of dextrose to dogs after *pique*. Injection of adrenaline causes a fall in the blood phosphates of the normal dog, but no change in those of the depancreatized animal; pituitrin, on the other hand, causes a rise in the concentration of phosphates

in the normal animal. The results indicate that the fall in the concentration of phosphates in the blood takes place only during active utilisation of carbohydrates in the organism. C. R. H.

**Brain Metabolism. I. Carbohydrate Metabolism.** B. E. HOLMES and E. G. HOLMES (*Biochem. J.*, 1925, **19**, 492—499).—There is no significant difference in the amounts of reducing substance extracted from the brain before and after insulin administration. This reducing substance does not give rise to the formation of lactic acid as does dextrose when added to brain-tissue. It consists partly of a pentose and partly of a substance the reducing power of which is greatly increased by acid hydrolysis. There is a greatly reduced "resting" lactic acid formation in the brains of rabbits treated with insulin. The "resting" lactic acid value of normal or "insulin" brain does not increase after keeping or incubation at body  $p_H$ .  
S. S. Z.

**Cholesterol Synthesis in the Animal Body.** H. J. CHANNON (*Biochem. J.*, 1925, **19**, 424—432).—Rats fed on a cholesterol-free diet from weaning time until they weighed 100 g. show an increase in cholesterol content from 100—220 mg. The increase of cholesterol with increase of body-weight is more marked in early stages of the existence of the rat. The animal body is apparently capable of synthesising cholesterol.  
S. S. Z.

**Calcium Content of the Body in Relation to Age, Growth, and Food.** H. C. SHERMAN and F. L. MACLEOD (*J. Biol. Chem.*, 1925, **64**, 429—459).—The percentage of calcium in the body of the rat at birth is 0.25; it increases rapidly in the first 15 days to 0.6; thence more slowly to 1.0 at 90 days, and thereafter very slowly up to 8 months, when it may be 1.2%. Females which have not raised young have a higher percentage of calcium than males of the same age; during the subsequent life of the female there is a loss of calcium during lactation which is made up in the intervening periods. Animals the growth of which was deficient owing to deprivation of vitamin-A or -B or of cystine showed an abnormally high percentage of calcium. Diets low in calcium resulted in loss of calcium from the body, and this loss could not be prevented by the addition of 1% of cod-liver oil to such a diet. C. R. H.

**Chemistry of Bone Growth. I. Changes in Ash, Organic Matter, and Water during Growth in the Albino Rat.** F. S. HAMMETT (*J. Biol. Chem.*, 1925, **64**, 409—428).—In the white rat at all ages and in both sexes the humerus has a higher percentage of ash (and hence a greater degree of ossification) than the femur; both bones in the female have a greater percentage of ash than in the male. With increasing age, the ash content of the bones increases and the water content falls; the variations in the percentage of organic matter are not strongly marked. Curves obtained by correlating the rates of increment of the various constituents with the age of the animal are of two constant types, according to the sex; the differences can be correlated with the different periods at which the gonads develop, and are apparently due to the influence of these

organs. The relation between the percentage rate of increment and age indicates a marked drop in growth capacity of the bones at the period of weaning, a subsequent increase up to 50 days, and a further fall with final stabilisation at the conclusion of puberty.

C. R. H.

**Conditions for Calcareous Metabolism in Oysters and other Marine Animals.** J. H. ORTON (*Nature*, 1925, **116**, 13).—A summary. There appears to be a minimum temperature below which shell is not laid down, and above which shell-material may be produced automatically. In the good shell-growth of warm and relatively cold, wet seasons in Great Britain the corresponding hydrographical conditions are, respectively, high estuarine salinities, alkalinities, and temperatures, and low fluctuating salinities with medium temperatures and (probably) alkalinities, together with a smaller amount of available food material in the latter case.

A. A. E.

**Influence of Diet on Synthesis of Hippuric Acid.** W. H. GRIFFITH (*J. Biol. Chem.*, 1925, **64**, 401—408).—The low values reported by Abderhalden and Wertheimer (*Pflüger's Archiv*, 1924, **206**, 460) for the excretion of hippuric acid by rabbits on a diet of green vegetables are criticised on the ground that the extraction of hippuric acid from such alkaline urines after the addition of the usual amount of hydrochloric acid is not quantitative.

C. R. H.

**Balanced Diets: Relative Proportions of Mineral Salts and Carbohydrates.** L. RANDOIN, J. ALQUIER, ASSELIN, and CHARLES (*Compt. rend.*, 1925, **180**, 2063—2065; cf. this vol., i, 210).—The ratio of amount of carbohydrate to amount of mineral salts has a marked influence on the growth of rats. In the experiments described a proportion of about 8·7 to 1 proved to be the best.

L. F. H.

**Effect of Iodides on the Human Nitrogen Metabolism.** G. P. GRABFIELD and A. M. PRENTISS (*J. Pharm. Exp. Ther.*, 1925, **25**, 411—421).—Administration of sodium, lithium, strontium, or magnesium iodides, during a 3-day period to subjects placed on a constant protein diet, causes an immediate increase in the urea nitrogen. An increase also occurs in the case of potassium or calcium iodides, but this takes place after the administration period. Changes in the non-protein nitrogen of the blood correspond with urinary changes falling if the rise in urinary output is immediate, and rising if this is delayed.

C. J. S.

**Relation between the Metabolism and the Specific Dynamic Action of Amino-acids.** T. N. SETH and J. M. LUCK (*Biochem. J.*, 1925, **19**, 366—376).—No appreciable increases in the blood urea were found when glycine, alanine, aspartic acid, and glutamic acid were administered orally to rabbits. There was less in the case of cystine, tryptophan, leucine, and histidine. The amino-acid content of the blood attained a very high maximum and persisted at a high

level all through the experimental period after the ingestion of glycine, alanine, or histidine. In the case of the other amino-acids examined, the amino-acid content of the blood comes down to the normal or subnormal level within 3—6 hrs., without ever rising very high. This confirms Bang's observations (A., 1916, i, 579). When dogs were used, the urea formation from glycine and alanine was found to be higher. The change in the amino-acid content in the blood was similar to that observed in rabbits. When glycine, alanine, or aspartic acid was injected into dogs it was found that the amino-acid content of the blood fell very rapidly, reaching almost the normal level within 15 mins. There was no significant increase in the blood urea during the experimental period of 2 hrs. The specific dynamic action of an amino-acid is therefore proportional to its power of increasing the amino-nitrogen content of the blood, following gastro-intestinal absorption of the amino-acid. S. S. Z.

**Metabolism of Glyoxalines.** L. LEITER (*J. Biol. Chem.*, 1925, 64, 125—139).—Intravenous injections of glyoxaline, 4-methylglyoxaline, glyoxaline-4-lactic acid, and histidine were given to dogs and the subsequent concentrations in the blood and urine observed; the highest concentration in the blood was observed after histidine and the lowest after methylglyoxaline, which, alone of the four compounds employed, was toxic; the lowest excretion (signifying the highest degree of retention and metabolism) was observed with histidine and the highest with glyoxaline; in every case the glyoxaline derivative excreted was identical with that injected. C. R. H.

**Relation of Histidine and Arginine to Creatine and Purine Metabolism.** W. C. ROSE and K. G. COOK (*J. Biol. Chem.*, 1925, 64, 325—338).—Growing rats fed on diets of which the sole source of nitrogen was caseinogen or completely hydrolysed caseinogen showed increasing excretion of uric acid, allantoin, and total creatinine, the increase being approximately proportional to the gain in weight; the substitution of a preparation of the hydrolysis products of caseinogen, from which arginine and histidine had been removed, led to a decrease in weight and a decreased excretion of allantoin; the excretion of uric acid was very slightly reduced and that of total creatinine at first raised and then reduced to its former level. The addition of arginine alone to such a deficient diet had no effect, but the addition of histidine alone restored the excretion of allantoin to its former value and the animals gained in weight. The decreased excretion of allantoin was due to deficiency in the diet and not to loss of weight of the animals, as shown by experiments with a diet deficient in tryptophan on which the animals lost weight but the excretion of allantoin was unaltered. Histidine is therefore a precursor of the purines, but is not interchangeable in metabolism with arginine (cf. Ackroyd and Hopkins, A., 1916, i, 237).

C. R. H.

**Function of Creatine in Muscular Contraction.** O. W. TIEGS (*Austral. J. Exp. Biol. Med. Sci.*, 1925, 2, 1—19).—Freshly-excised frog muscles, suspended in Ringer's solution, liberate a small

quantity of a substance which, on boiling with acid, yields creatinine. Much greater amounts are liberated by fatigued muscles, which, however, contain almost the same amount of creatine as fresh muscles. Further, the amount of "creatine" liberated by fatigued muscle is greatly reduced by exposure to a stream of oxygen. Fatigued muscles liberate "creatine" and lactic acid in equivalent amounts. It is suggested that muscle creatine has a cyclic structure similar to that of urea, and that during muscle excitation the ring is opened with production of a strongly basic primary amine which, neutralising the lactic acid simultaneously formed, induces relaxation. During oxidative recovery, the cyclic form of creatine is reproduced.

C. P. S.

**Physiology of Plain Muscle. Comparison of the Reducing Properties of Plain and Striated Muscle.** S. TSUBURA (*Biochem. J.*, 1925, **19**, 397—403).—Plain muscle reduces methylene-blue more slowly but *m*-dinitrobenzene more quickly than striated muscle. Neither reduction is inhibited by cyanide. Washing abolishes the reducing properties in both cases, but these can be partly restored by addition of succinate. The difference in reducing action of the two kinds of muscles is quantitative rather than qualitative. The optimal  $p_H$  for plain muscle reduction of methylene-blue is about 9.0. Plain muscle and its extracts are richer in glutathione than striated muscle or its extracts.

S. S. Z.

**Significance of Ions in Muscular Function. VIII. Action of Different Alkali Salts on the Fermentative Breakdown of Glycogen in Frog's Muscle Pulp.** J. WEBER (*Z. physiol. Chem.*, 1925, **145**, 101—129).—The influence of various anions arranged in order of their activity (Hofmeister) on the breakdown of glycogen of frog's muscle is studied. Thiocyanate, iodide, bromide, and nitrate inhibit the activity diminishing in this order; chloride accelerates; acetate, sulphate, and tartrate accelerate; citrate accelerates, but to a less extent; oxalate and fluoride inhibit, the latter more than the former; phosphate, lactate, and succinate accelerate. The accelerating actions of lactate and phosphate anions are additive. The accelerating action of the chlorine ion is of importance, since  $C_{cr}$  increases during muscular activity, whilst that of the lactate ion is significant, since this ion assists in the synthesis of lactacidogen.

P. W. C.

**Starch-swelling in Living and Dead Cells.** W. W. LEPESCHKIN (*Ber. Deut. bot. Ges.*, 1925, **43**, 16—20).—Starch granules from the same cell of the alga *Spirogyra* behave in the same way when immersed in water, but granules from different cells behave differently. Reaction between starch-polysaccharides and water only starts after the death of the cell.

O. O.

**Permeability of Living and Dead Cells. V. Effects of Sodium Hydrogen Carbonate and Ammonium Chloride on the Penetration of Valonia by Tervalent and Quinquevalent Arsenic at various Hydrogen-ion Concentrations.** M. M. BROOKS (*U.S. Pub. Health Repts.*, 1925, **40**, 139—161).—Differences



in the rate of penetration of arsenic into the marine alga, *Valonia macrophysa*, appear to be due to effects on the protoplasm initiated by changes in both the internal  $p_H$  of the cell and the  $p_H$  of the bath. The difference between the arsenic concentration of the sap and that (greater) of the protoplasm is less marked with tervalent than with quinquevalent arsenic, minimal penetration taking place when the bath is neutral. Accumulation of carbon dioxide in the plant leads to greater absorption of quinquevalent arsenic by both sap and protoplasm, but in the case of tervalent arsenic to greater absorption by the sap and less by the protoplasm. Accumulation of ammonia in the plants leads to greater (tervalent) or less (quinquevalent) absorption of arsenic by the sap and protoplasm. Low external and/or internal  $p_H$  values cause greater penetration of quinquevalent and less of tervalent arsenic, into sap and protoplasm, the converse being the case for alkaline solutions. CHEMICAL ABSTRACTS.

**Blood Chemistry in Acute Histamine Intoxication.** H. HASHIMOTO (*J. Pharm. Exp. Ther.*, 1925, 25, 381—409).—During toxæmia induced in dogs by the repeated intravenous injection of histamine there is an increase in the amount of non-protein nitrogen and urea nitrogen in the blood, accompanied by impaired renal function and increased protein destruction in the body. The symptoms are somewhat similar to those characteristic of high intestinal obstruction. C. J. S.

**Pharmacological Effects of Combined Camphor.** W. LIPSCHITZ and J. OSTERROTH (*Arch. exp. Path. Pharm.*, 1925, 106, 341—368).—The influence of addition of camphor on the pharmacological effects of various drugs on the mechanical functions and respiratory exchange of surviving organs and cells of warm- and cold-blooded animals has been investigated. The non-specific adsorption of the drugs by camphor described by Wieland (*Arch. exp. Path. Pharm.*, 1921, 89, 47) has not been observed. Camphor in low concentration appears to have no influence on the effects on muscle of papaverine, chloral hydrate, amyl nitrite, or adrenaline, and in higher concentration an additive effect alone is observed. The effects of papaverine on heart-beat, on the other hand, are lessened by addition of camphor. Camphor has a powerful inhibiting effect on respiratory exchange of muscle pulp, being approximately 275 times as potent as ethyl alcohol. L. F. H.

**Curative Action of Basic Bismuth 3-Acetamido-4-hydroxyphenylarsinate in Experimental Syphilis.** C. LEVADITI (*Compt. rend.*, 1925, 180, 1971—1972).—Basic bismuth 3-acetamido-4-hydroxyphenylarsinate,  $C_8H_8O_2N \cdot AsO_3HBi(OH)_2$ , obtained by the addition of sodium potassium bismuth tartrate to sodium 3-acetamido-4-hydroxyphenylarsinate in aqueous solution, has a curative action on rabbits infected with syphilis. The salt is injected intramuscularly, a suspension in isotonic salt solution or in oil being employed. The salt is also of value in the treatment of *Trypanosomiasis nagana* in mice, and of fowl spirillosis.

U. F. H.

**Curative Action of Basic Bismuth 3-Acetamido-4-hydroxyphenylarsinate in Syphilis.** L. FOURNIER and A. SCHWARTZ (*Compt. rend.*, 1925, **180**, 1973—1974; cf. preceding abstract).—Basic bismuth 3-acetamido-4-hydroxyphenylarsinate has a curative action on human syphilis. In general, the ill effects of bismuth or arsenic are not observed and in some cases disappearance of the positive Wassermann reaction is recorded. L. F. H.

**Bactericidal Action of Some Organic Compounds of Mercury.** T. A. HENRY, T. M. SHARP, and H. C. BROWN (*Biochem. J.*, 1925, **19**, 513—519).—A number of salts of mercurated hydroxybenzaldehyde, alkylphenols and other related substances were tested for their bactericidal action. The two groups  $-\text{CHO}$  and  $-\text{OH}$  are most effective when present together in the meta-position to each other and least effective when in the para-position. The entrance of a nitro-group when  $\text{CHO} : \text{OH} = 1 : 3$  enhances the effect in position 4, but exerts no influence in positions 2 or 6. The position of the mercuri-group is, however, not the same in all three compounds. In the case of alkylphenols, the introduction of mercury residues markedly increases the bactericidal activity. There is a considerable reduction in the bactericidal action of both organic and inorganic compounds of mercury when they are used in serum in place of water. When the  $-\text{HgOH}$  residue of 2-hydroxymercuri-3-hydroxybenzaldehyde is converted into a radical containing the residue of one of the higher fatty acids and the bactericidal action tested when dissolved in olive oil, the activity is reduced by about half except in the case of the chaulmoogric acid salt, where the activity is doubled. This is undoubtedly due to the chaulmoogric acid residue. S. S. Z.

**Semiselective Antiseptic Effect of the Vapours of Vegetable Oils, Essential Oils, their Constituents, and Similar Compounds.** O. SCHÖBL (*Philippine J. Sci.*, 1925, **26**, 501—506; cf. A., 1924, i, 690).—Experiments on the inhibitory effect of vegetable oils etc. on the growth of bacteria have been extended to include other pathogenic micro-organisms and a larger series of compounds. C. P. S.

**Paramoecial Method for determining the Phenol Coefficient of Disinfectants.** A. SCHNEIDER (*J. Amer. Pharm. Assoc.*, 1924, **13**, 320—321).—The dilution is determined at which an approximately pure culture of *Paramoecium caudatum* is killed within a time between 1 and 3 mins. at the ordinary temperature. This "minimum killing dose" is then compared with that of a 1% aqueous solution of phenol. CHEMICAL ABSTRACTS.

**Influence of  $\text{Rb}$ ,  $\text{SeO}_3$ , and  $\text{SeO}_4$  Ions on the Respiration of Normal and Neoplastic Cells.** A. H. ROFFO and S. M. NEUSCHLOSS (*Bull. Soc. Chim. biol.*, 1925, **7**, 515—521).—The results obtained are based on observations of the reduction of *m*-dinitrobenzene to *m*-nitrophenylhydroxylamine in the presence of various tissues of normal and cancerous white rats. Rubidium and selenium compounds vary in their effects with the tissue used, the difference

between them being only quantitative; they augment the respiration of normal cells of adult animals, and diminish that of normal cells of new-born animals, embryos, and of carriers of neoplasms.

B. F.

**Methods of Fitting the Formula of Michaelis in Relation to the Effect of Hydrogen-ion Concentration on Enzyme Action to the Data, with Some Discussion of the Results.** J. BROWN-LEE (*Biochem. J.*, 1925, 19, 377—384).—Mathematical discussion.

S. S. Z.

**Nature of the Substances which cause the Production of "Protective Enzymes" in the Organism.** G. FRANZEN (*Fermentforsch.*, 1925, 8, 308—325).—In confirmation of Hirsch, the blood of a rabbit, previously injected with emulsion of placenta, is found to contain protective enzymes capable of breaking down the specific proteins of placenta. The activity of these enzymes is estimated by determining, by the interferometer method, the amount of peptone formed in a mixture of the placenta proteins and the serum containing the enzymes. The injection of emulsions of various endocrine glands gives less definite evidence of the production of specific enzymes, since the serum of the untreated animal may already contain such enzymes in varying degree. H. P. M.

**Influence of Tryptophan and other Amino-acids on the Stability and Enzymic Activity of Pancreatic Amylase.** H. C. SHERMAN, M. L. CALDWELL, and N. M. NAYLOR (*J. Amer. Chem. Soc.*, 1925, 47, 1702—1709).—Pancreatic amylase dissolved in pure water rapidly loses its activity even at 10°, the rate of deterioration being about six times that observed in solutions containing optimum concentrations of sodium chloride and sodium phosphate adjusted to optimum hydrogen-ion concentration. At 25°, the inactivation proceeds twelve times as rapidly as at 10° and at 40° nearly twelve times as rapidly as at 25°. Addition of amino-acids, such as glycine and tryptophan, protects the enzyme from inactivation both in the absence and in the presence of its substrate, but the favourable influence of the tryptophan on the amylolytic activity of the enzyme (cf. A., 1922, i, 283; 1923, i, 621) is only apparent in experiments over two hours or more at 40° or in experiments at 50°. These results confirm the views previously expressed (*loc. cit.*) on the protein nature of the enzyme, and support the theory that in aqueous solution the protein compound is slowly hydrolysed to amino-acids.

R. B.

**Specific Action of Plant Ferments. I. The Specific Conditions of Action of Leaf Invertases.** A. V. BLAGOFESCHENSKI and N. I. SOSSIEDOV (*Biochem. J.*, 1925, 19, 350—354A).—The following are the optimum hydrogen-ion concentrations for the action of the invertase of the leaves of the various plants: *Prangos fabularia*,  $p_H$  6·6; *Ungernia Severzovii*, *Vitis vinifera*, and *Gossypium hirsutum*,  $p_H$  5; *Juglans fallax*,  $p_H$  5·9; *Gossypium herbaceum* and *Pyrus malus*,  $p_H$  5·6; *Glycyrrhiza glabra* and *Platanus orientalis*,  $p_H$  4·5; *Quercus pedunculata*,  $p_H$  6·5; *Pyrus communis*, *Syringa*

*vulgaris*, *Fraxinus* sp., and *Salicornia herbacea*,  $p_H$  6.2. There is therefore a definite optimal hydrogen concentration for the action of the enzyme from the various sources. The variation of the ratio of hydrolysis with the change in  $p_H$  is of a very specific character.  
S. S. Z.

**Mutarotation as a Factor in the Kinetics of Invertase Action.** J. M. NELSON and O. BODANSKY (*J. Amer. Chem. Soc.*, 1925, **47**, 1624—1638).—Using the Nelson and Hitchcock empirical equation (A., 1922, i, 184) and the usual experimental methods (cf. Nelson and Bloomfield, A., 1924, i, 800), curves are developed representing (1) the "ideal hydrolysis" of sucrose in which the inverted sugar is regarded as eliminated immediately on formation, (2) actual hydrolysis, in which the invert-sugar is regarded as nascent, and (3) "mutarotated hydrolysis," in which the invert-sugar is regarded as mutarotated immediately on formation. The curves show that invert-sugar freshly formed in the reaction exerts a different effect on the rate of hydrolysis from that produced when it is present in mutarotated form. The course of hydrolysis would thus be different from that ordinarily observed if the invert-sugar underwent mutarotation immediately on formation. If the hydrolysis of the sucrose and mutarotation of the invert-sugar are two simultaneous consecutive reactions, a change in the relative rates of these reactions has no apparent effect on the course of the hydrolysis. With 8, 10, and 12% sucrose solutions, in the first stage of the hydrolysis, where the sucrose concentration exceeds 4—5%, the "nascent" invert-sugar exerts a smaller retarding influence on the hydrolysis than the mutarotated form. When the sucrose concentration is less than 4—5%, the "nascent" invert-sugar exerts the greater retarding influence. R. B.

**Invertase.** H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.* 1925, **145**, 130—143).—Reply to Willstätter and Schneider (this vol., i, 739), summarising the present position in regard to the constitution of invertase (cf. A., 1924, i, 370, 799). P. W. C.

**Distribution of Linamarase Enzymes of *Phaseolus lunatus*.** L. ROSENTHALER (*Fermentforsch.*, 1925, **8**, 279, 281, 282—283).—Many seeds and fruits contain an enzyme, linamarase, which converts linamarin into glucose, acetone, and hydrocyanic acid, although they do not contain the substrate. Linamarin is not hydrolysed by emulsin, invertase, maltase, or diastase.

A preparation containing linamarase (and other enzymes), obtained from the seeds of *Phaseolus lunatus*, hydrolyses starch, maltose, sucrose, amygdalin, and  $\alpha$ -methyl glucoside. H. P. M.

**Specific Nature of Lipases with Respect to Configuration.** R. WILLSTÄTTER (*Sitzungsber. Akad. München*, 1924, 1—2).—Lipase from the pancreas hydrolyses glycerides 10—20 times as rapidly as that from the liver, the explanation may be that the soaps produced in the process cause a large increase in activity of the former enzyme only. The influence of proteins on these two

enzymes is also different. The two enzymes are proved to be definitely distinct by the observation that the enzyme from pig's liver produces *d*-mandelic acid in hydrolysing ethyl *dl*-mandelate, whereas that from the pig's pancreas yields the *laevo* stereoisomeride under the same conditions.

G. M. B.

**Papain Lipase.** M. SANDBERG and E. BRAND (*J. Biol. Chem.*, 1925, **64**, 59—70).—Commercial papain was found to contain a lipolytic enzyme which could be purified to some extent by extraction with water, the lipase remaining in the insoluble portion. The optimum conditions for the enzyme are a temperature of 35—40° and a  $p_H$  of 5.8—6.2. The action was unaffected by egg-albumin, hydrocyanic acid, and bile salts, was inhibited by glycerol in acid and neutral reactions, and was stimulated by glycerol and by calcium chloride at an alkaline reaction; the latter activation was diminished by the presence of egg-albumin. In the absence of an activator, the reaction followed the law of Schütz; the lipase was fairly resistant to the action of the proteolytic enzyme of papain.

C. R. H.

**Specific Action of Plant Ferments. II. Specific Conditions of Action of Leaf Peptases.** A. V. BLAGOVESHCHENSKI and A. N. BIELOZERSKI (*Biochem. J.*, 1925, **19**, 355—356).—The following are the optimum hydrogen-ion concentrations for the action of peptase of the leaves of various plants: *Ungernia Severovii*,  $p_H$  8; *Astrogalus Sieversianus*, *Syringa vulgaris*, *Vitis vinifera*, and *Juglans fallax*,  $p_H$  7.7; *Prangos pabularia*,  $p_H$  6.7; *Glycyrrhiza glabra*,  $p_H$  6.3; *Pyrus communis*, *Fraxinus* sp., *Gossypium herbaceum*, and *Gossypium hirsutum*,  $p_H$  5.8; *Quercus pendunculata*, *Platanus orientalis*, and *Pyrus malus*,  $p_H$  4.5.

S. S. Z.

**Determination of Pepsin in Gastric Juice.** P. ROSTOCK (*Münch. med. Woch.*, 1924, **71**, 1311—1312; from *Chem. Zentr.*, 1924, ii, 2414).—The liquid containing pepsin is allowed to act on coagulated blood fibrin. The course of the digestion due to the action of pepsin is shown by the increase in refractive index of the liquid measured by an immersion refractometer.

G. W. R.

**Enzyme Action. XXIV. Oxydase Effect and the Phenomena of Oxidation in General: Carbon Monoxide.** H. E. ARMSTRONG (*Proc. Roy. Soc.*, 1925, **B**, **98**, 202—206).—Oxidation in general is discussed and attention directed to its importance in vital phenomena. Adrenaline is considered as controlling oxidation at the sympathetic centres and a schematic representation of its possible action is given.

Carbon monoxide is, *per se*, an incombustible gas. Its conversion into carbon dioxide when sparked or fired, in the presence of moisture, may be explained by assuming that some "hydrone" is decomposed and sufficient hydrogen set free by electrolysis of water to act in a "depolarising" circuit together with the oxide.

O. O.

**Oxidising Enzymes. VIII. Oxidation of certain Para-hydroxy Compounds by Plant Enzymes and its Connexion with "Tyrosinase."** M. W. ONSLOW and M. E. ROBINSON (*Biochem. J.*, 1925, **19**, 420—423).—When an enzyme preparation from the potato tuber is added to a *p*-cresol solution, the mixture turns rapidly orange-pink. On addition of guaiacum, a deep blue colour is produced and the production of a pyrocatechol grouping can be demonstrated by the addition of ferrous sulphate or ferrous ammonium sulphate. Tyrosol behaves like *p*-cresol in this respect. This type of oxidation is discussed. The above enzyme preparation when added to a solution of dihydroxyphenylalanine first produces a red colour and eventually the mixture becomes black as in the case of tyrosine. No blue colour is produced when guaiacum is added at the red stage. The authors advance a hypothesis on the action of tyrosinase. S. S. Z.

**Xanthine Oxydase. V. Function of Catalase.** M. DIXON (*Biochem. J.*, 1925, **19**, 507—512).—Xanthine oxydase is gradually destroyed during the course of its action on the purine bases owing to the formation of hydrogen peroxide. Such destruction can be obviated if catalase is introduced in order to remove the hydrogen peroxide. S. S. Z.

**Physiology of Gastric Urease.** J. M. LUCK and T. N. SETH (*Biochem. J.*, 1925, **19**, 357—365).—The action of gastric urease *in vivo* is demonstrated by the fact that in dogs under ether anaesthesia the introduction of urea either by gastric absorption or by intravenous injection is accompanied by an increase in the ammonia content of the gastric venous blood. On the other hand, the gastric absorption of ammonium salts is not accompanied by an increase in the urea content of the gastric venous blood. Shed blood of dogs shows no increase in ammonia content in 24 hrs. at  $-2^{\circ}$  to  $0^{\circ}$ , whilst that of rabbits increases rapidly. S. S. Z.

**Action of Enzyme Accelerators.** M. JACOBY and L. ROSENFELD (*Biochem. J.*, 1925, **158**, 334—336).—The action of urease on urea persists in solutions containing high concentrations of alcohol, but in the higher concentrations the stimulating effect of potassium cyanide on the activity of this enzyme which is shown in absence of alcohol is no longer observed, and in the highest concentrations (from 60% upwards) the addition of potassium cyanide checks the rate of hydrolysis.

In aqueous solution, the presence of potassium cyanide has no qualitative effect on the products of the hydrolysis of urea by urease. H. D. K.

**Fermentation by Dried Yeast Preparations.** A. HARDEN (*Biochem. J.*, 1924, **19**, 477—483).—Air-dried yeast and zymin (yeast dehydrated by acetone) produce fermentation rapidly in a small volume of sugar solution only after considerable delay in a large volume. The addition of yeast extract or solutions of certain salts such as acetates or hydrogen carbonates greatly accelerates the onset of fermentation in presence of a large volume of sugar

solution. Air-dried yeast possesses a definite fermenting power which is not dependent on the presence of living cells. S. S. Z.

**Heat of Combustion of Pyruvic Acid and its Physiological Significance.** H. BLASCHKO (*Biochem. Z.*, 1925, **158**, 428—434).—The heat of combustion of pure pyruvic acid is 3172.4 calories per gram (average of six closely agreeing figures). The heat of solution of the liquid acid is 52.9 calories per gram, and the heat of neutralisation in aqueous solution 129 calories per gram. The heat of solution of acetaldehyde is 101.8 calories per gram. There is a very small but positive heat of decarboxylation of pyruvic acid by yeast juice. H. D. K.

**Effect of Calcium Sulphate on the Growth and Fermentation of Yeast.** O. W. RICHARDS (*J. Amer. Chem. Soc.*, 1925, **47**, 1671—1676).—The optimum concentration of calcium sulphate for maximum growth and fermentation of a pure culture of *Saccharomyces cerevisiae* is about 0.0001*M*. The calcium sulphate content of the water supplies examined was usually a little greater than this optimum concentration for the yeast and may occasionally be fifty times as great. R. B.

**Glycogen. I. Nature of Yeast Glycogen, its Preparation, Determination, and Rôle in Yeast Metabolism.** A. R. LING, D. R. NANJI, and F. J. PATON (*J. Inst. Brewing*, 1925, **31**, 316—321).—Yeast-cells are disintegrated by boiling with dilute sodium hydroxide solution and the crude glycogen is precipitated by alcohol and subsequently mannan is removed by precipitation with Fehling's solution. Determination of glycogen and mannan was carried out by hydrolysis of the precipitate with 8% sulphuric acid before and after the removal of mannan, and the iodometric determination of the dextrose and mannose produced. Determinations made during the course of fermentation showed that the glycogen and mannan contents of yeast decreased during the early stages and then increased again to a maximum. G. S. W.

**Toxicity of Acids towards Yeast.** E. M. TAYLOR (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 115).—The minimum amounts of the various salts needed to ensure the normal rate of reproduction of yeast in various synthetic media consisting of sugar and salts with addition of bios I and bios II, depend on the nature of the bios preparations. The mechanism of the toxic action of acids in aqueous solution is wholly different from that of phenol. On adding yeast-cells to acid solutions, the hydrogen-ion concentration of the latter falls almost immediately. This is ascribed to the action of an exudate from the cells, which "may be said to bleed to death." The later portions of the exudate contain bios I and II. J. S. C.

**Growth of Yeast. I. Influence of Volume of Culture Medium Employed.** G. L. PESKETT (*Biochem. J.*, 1925, **19**, 464—473).—In the absence of "bios," no constant effects on growth were observed as a result of differences in the volume of medium used. In the presence of "bios," growth is not directly

proportional to the volume, but the quickest growth, however, was observed in larger volumes. It is suggested that the differences between the observations of Pasteur and Liebig was not due to differences in the volume of media employed by these workers, but to the presence of different amounts of "bios." These experiments also militate against Robertson's theory of an extracellular autocatalyst for growth, since in such a case the rate of reproduction would be higher in smaller volumes. A method is described for the study of the growth of single cells. S. S. Z.

**Growth of Yeast. II. Allelocatalysis.** G. L. PESKETT (*Biochem. J.*, 1925, **19**, 474—476).—When yeast is washed, allelocatalysis is still not observed (cf. Peskett, A., 1924, i. 1383). S. S. Z.

**Influence of Washing on the Rate of Reproduction of *Colpidium colpoda*.** D. W. CUTLER and L. M. CRUMP (*Biochem. J.*, 1925, **19**, 450—453).—Allelocatalysis has not been observed in cultures from either washed or unwashed individuals. Washing the animals has no deleterious effect on them, nor does it retard the rate of reproduction. Robertson's (*Biochem. J.*, **18**, 1240) explanation that the authors were unable to observe allelocatalysis because they did not wash their organism does not hold. S. S. Z.

**Influence of certain Dyes on the Multiplication of Infusoria (*Enchelys*) with Especial Reference to the Acridine Dyes Acriflavine and Proflavine.** T. B. ROBERTSON (*Austral. J. Exp. Biol. Med. Sci.*, 1925, **2**, 21—44).—Scarlet-red, in concentrations less than 1/45,000 and phenolphthalein in non-lethal concentrations are without effect on the "lag" period (period before multiplication normally commences) and subsequent rate of multiplication of infusoria. Methylene-blue and safranine, in concentrations just below the lethal, slightly prolong the lag. Acriflavine, in concentrations between 1/20,000 and 1/200,000, enormously increases the lag period. Higher concentrations are lethal; lower do not prolong the lag, but reduce the subsequent rate of multiplication. Proflavine has a similar effect, but over a narrower range of concentrations. Janus-green is toxic in concentrations greater than 1/10,000; just below that concentration it produces indefinite prolongation of the lag; still more dilute solutions are without effect. Methylene-blue, safranine, janus-green, acriflavine, and proflavine are more toxic to infusoria in distilled water buffered with sodium hydrogen carbonate than in hay infusion similarly buffered. The lethal dose of acriflavine for mice weighing 20—25 g. is 1 mg.; the lethal dose of proflavine is  $2\frac{1}{2}$  to 3 times as great. C. P. S.

**Hydrogen-ion Concentration and the Oxidation-Reduction Potential of the Cell Interior; A Micro-injection Study.** J. NEEDHAM and D. M. NEEDHAM (*Proc. Roy. Soc.*, 1925, **B**, **98**, 259—286).—Apparatus is described by means of which micro-injections of dyes (neutral red, phenol-red, and bromothymol-blue) into the cell-interior of *Amæba proteus* have been made. The



approximate  $p_H$  value thus obtained was 7.6. No localisation could be found. Although the nucleus of the cell was so obscured by granules that observation was not possible, the cell appeared to react as a whole. From injections of oxidised  $\alpha$ -naphthol-2-sulphonic acid indophenol it is concluded that the oxidation-reduction potential lies between  $r_H$  17 and 19. O. O.

**Pigment Formation by Fungi.** A. N. DANILOV (*Ber. Deut. bot. Ges.*, 1925, 43, 27—33).—The fungus *Isaria virescens*, Elenk. et Danil., growing on suitable media is able to produce a range of pigments. The formation of these pigments depends on light, temperature, and the nature of the medium. For instance, a culture in the dark may be colourless, but on exposure to light rose, orange, and red tints develop; increase in temperature favours the formation of dark brown colours. Magnesium stimulates, whilst lithium suppresses pigment formation; sodium is practically without effect. O. O.

**Chemical Differentiation of Bacteria.** E. W. STEARN and A. E. STEARN (*J. Bact.*, 1925, 10, 13—23).—Certain bacteria are more easily oxidised than others. Any bacterial cell responds to degrees of oxidation. Treatment of an oxidised smear with a reducing agent such as stannous chloride tends to restore the smear to its original state so far as staining reaction is concerned. Gram-positive organisms have a limited isoelectric range of about 2 to 3. Gram-negative organisms have a wider isoelectric range at a higher  $p_H$ , about 5. A few organisms have a range between these extremes. CHEMICAL ABSTRACTS.

**Occurrence of a Red-pigment-producing Organism in Maize Mash of the Acetone Butyl Alcohol Fermentation.** E. B. FRED, W. H. PETERSON, and W. R. CARROLL (*J. Bact.*, 1925, 10, 97—104).—The pigment may be due to a spore former of the mesentericus group, called sometimes *Bacillus mesentericus ruber* and sometimes *B. globigii*. Colour production is most noticeable on potato or on maize mash. In a yeast-water medium plus dextrose or xylose, *B. globigii* grows rapidly and destroys a large part of the sugars, forming ethyl alcohol and acetone. CHEMICAL ABSTRACTS.

**Biochemistry of Acetone Formation from Sugars by *Bacillus acetoethylicum*.** H. B. SPEAKMAN (*J. Biol. Chem.*, 1925, 64, 41—52).—In the fermentation of dextrose and maltose by *Bacillus acetoethylicum* (cf. Northrop and others, A., 1919, i, 507), pyruvic acid is formed in the early stages and later disappears coincidentally with the production of acetone; in the fermentation of glycerol, traces only of both pyruvic acid and acetone are formed, although on adding pyruvic acid to the glycerol medium the acid rapidly disappears and acetone is produced, in about half the theoretical amount, together with volatile acids. From a consideration of these results and those of previous workers, it is suggested that in the fermentation of dextrose by this organism pyruvic acid is first produced, which then gives rise to lactic, acetic, and formic

acids and acetaldehyde; the latter may be reduced to ethyl alcohol, or, if present in excess, may, through the aldol condensation, give rise to  $\beta$ -hydroxybutyric and acetoacetic acids and acetone; in the case of glycerol, the greater amount of hydrogen in relation to the acetaldehyde which can be formed facilitates the reduction of the latter and thus prevents acetone formation. C. R. H.

**Products of Atmospheric Nitrogen Fixation by *Azotobacter agile*.** S. KOSTYTSCHEV and A. RYSKALTCHOUK (*Compt. rend.*, 1925, **180**, 2070—2072; cf. A., 1906, ii, 382; 1910, ii, 988; 1912, ii, 473; 1914, i, 1113).—No nitrous or nitric acid, but only ammonia and amino-compounds have been found to be produced in the fixation of atmospheric nitrogen by *Azotobacter agile*. Ammonia is not produced at the expense of peptone in cultures containing it; no appreciable nitrogen fixation takes place in culture media rich in peptone. L. F. H.

**Carbon of Peptones, Source of Energy for *Bacillus diphtheriae*.** G. ABT (*Ann. Inst. Pasteur*, 1925, **39**, 387—416).—A culture of *Bacillus diphtheriae* in Martin's broth produces about 4 g. of carbon dioxide per 1100 c.c. of culture containing 1.1 g. of bacteria (dried wt.). About 80% of this is produced during the first 10 or 12 days, and 95% in the first 20 days. When the initial reaction is slightly alkaline, the carbon dioxide production is maximal during the first 2 days; with an initial acid reaction, the period of rapid combustion commences at the fourth day, when the reaction has become neutral. More than a third of the carbon dioxide is derived from acetic, lactic, and butyric acids existing in the culture medium at the commencement; the remainder is derived from amino-acids. Acetic and butyric acids appear to be more easily burnt than formic and valeric acids. The ratio of the carbon from amino-acids appearing as carbon dioxide to the nitrogen liberated as ammonia indicates that glutamic acid is principally utilised. Only about 10% of the protein is used by the bacteria, and of the amino-acids produced only 25% are deaminated and combusted. The heat of combustion of the dried bacteria is about 30% of the total heat produced. C. P. S.

**Biochemistry of the Granulated Lactic Acid Bacteria from Cereals.** E. B. FRED, W. H. PETERSON, and H. R. STILES (*J. Bact.* 1925, **10**, 63—78).—The granulated high-acid-forming bacteria of cereal infusions are closely related to *Lactobacillus Delbrücki*. Their cultural characters and fermentations place them in the species described by Henneberg under the name *Lactobacillus Leichmani*. Dextrose, fructose, and mannose are readily fermented. The fermentation of galactose is somewhat slower. Disaccharides are attacked to a lesser degree and trisaccharides scarcely at all. Considerable acid is formed from glucosides and from dextrin. Lævorotatory lactic acid is the major product of fermentation. Only traces of volatile acids, alcohol, and carbon dioxide are found.

CHEMICAL ABSTRACTS.

**Physiology of *Thiobacillus thio-oxidans*, an Autotrophic Bacterium Oxidising Sulphur under Acid Conditions.** R. L. STARKEY (*J. Bact.*, 1925, **10**, 135—163).—Oxidation is most rapid in the early stages of the process following a lag period of 2 days, and decreases as the culture ages, because of the accumulation of sulphuric acid. Growth is vigorous in the presence of 3%, but is inhibited by 10%, of sodium thiosulphate. Sulphur is precipitated during growth. From 50 to 65 parts of sulphur (as thio-sulphate) are oxidised to sulphate per unit of carbon assimilated. In the presence of 1% and 5% sulphuric acid, the quantities of sulphur oxidised per unit of carbon assimilated are 36.6 and 43.0 respectively. The sulphur : carbon ratio is not affected by potassium hydrogen phosphate up to 5.5%. No appreciable stimulation of oxidation was observed in the presence of zinc, caesium, lead, nickel, mercury, or tin, but the first three may stimulate very slightly. Growth ceases in the absence of either oxygen or carbon dioxide.

CHEMICAL ABSTRACTS.

**Carbon and Nitrogen Nutrition of *Thiobacillus thio-oxidans*.** R. L. STARKEY (*J. Bact.*, 1925, **10**, 165—195; cf. preceding abstract).—Dextrose disappears from the sulphur medium during incubation of the organism in amounts proportional to growth and to the sulphuric acid formed. The amount used does not depend on that initially present, and its disappearance is not due to the acid alone. No growth occurs in the presence of dextrose when available sulphur is absent. Citric acid inhibits growth at 5% concentration, but oxidation is active at 2.5%. The reaction is depressed or inhibited by potassium nitrate, the only form of assimilable nitrogen being ammonium salts, but there is some oxidation in media receiving no nitrogen other than that present as impurities or absorbed from the air. In a medium free from nitrogen, 149 parts of sulphur were oxidised per unit of carbon. Urea is not attacked. Oxidation is depressed by 1.25% peptone and inhibited by 2.5%; neither peptone nor amino-acids are available as sources of carbon or nitrogen.

CHEMICAL ABSTRACTS.

**Determination of Indole and Skatole in Bacterial Cultures.** C. R. FELLERS and R. W. CLOUGH (*J. Bact.*, 1925, **10**, 105—133).—Ehrlich's test, performed on the distillate, is accurate to 1 in  $25 \times 10^6$ ; the dimethylaniline test for skatole, when performed on the distillate, is also useful.

CHEMICAL ABSTRACTS.

**Dehydrogenations Produced by Resting Bacteria.** I. J. H. QUASTEL and M. D. WHETHAM (*Biochem. J.*, 1925, **19**, 520—531).—Various fatty acids, saturated dibasic acids, hydroxy-acids, polyhydric alcohols, and monohydric alcohols have been tested as hydrogen donators in the reduction of methylene-blue by resting *Bacillus coli*. The relative reducing powers of the various hydrogen donators are tabulated.

S. S. Z.

**Action *in vitro* of certain Chemical Substances on the Development of *Bacillus tuberculosis*.** L. KARWACKI (*Ann. Inst. Pasteur*, 1925, **39**, 476—483).—The author has studied the

effects of 73 medicinal preparations and 52 dyes and stains on the rate of growth of *Bacillus tuberculosis*. C. P. S.

**Chemical Composition of Residue Antigen.** J. H. MUELLER, M. WAYMAN, and H. ZINSSER (*Proc. Soc. Exp. Biol. Med.*, 1924, **21**, 241—243).—Compounds containing nitrogen (but not proteins) and compounds containing phosphorus (possibly nucleic acid derivatives or carbohydrate phosphate compounds) appear to be present.

CHEMICAL ABSTRACTS.

**Hormonal Action of Choline on Intestinal Movements.** III. Formation of Choline from Phosphatides. IV. Degradation of Phosphatides by Intestinal Juice. V. Synthesis of Choline Esters by an Enzyme of the Duodenum. E. ABDERHALDEN and H. PAFFRATH (*Fermentforsch.*, 1925, **8**, 284—293, 294—298, 299—307).—III. A method for the separate determination of free and combined choline is described, which depends on precipitation of the latter with colloidal iron. The experiments described indicate a conversion of combined into free choline in the surviving intestine of the rabbit which cannot be attributed to bacterial action.

IV. The juice expressed from the duodenum of the pig and the horse is found to liberate choline from lecithin and from acetylcholine.

V. The latter reaction may be reversed, and acetylcholine synthesised, under suitable conditions of concentration. The enzyme is destroyed by heating at 70°, but not at 58°; its activity is greatest in acid solution.

H. P. M.

**Mechanism of Action of Insulin.** G. MANSFELD and E. GEIGER (*Arch. exp. Path. Pharm.*, 1925, **106**, 276—286).—On perfusion of the isolated heart of the depancreatized cat with a solution containing dextrose, less of the dextrose is removed from the solution than in the perfusion of a normal cat's heart. Addition of insulin to the perfusion liquid in the case of the depancreatized cat's heart results in an increase in the amount of dextrose removed.

L. F. H.

**Inorganic Phosphates and Insulin Hypoglycæmia.** A. DESGREZ, H. BIERRY, and F. RATHERY (*Compt. rend.*, 1925, **180**, 1554—1557).—Purified insulin (A., 1923, i, 982) and solutions of disodium hydrogen phosphate and potassium dihydrogen phosphate ( $p_H$  7.4) were injected into fasting dogs. The arterial blood was deproteinised by mercuric nitrate and the dextrose determined by Bertrand's method.

It is concluded that subcutaneous or intravenous injection of phosphates in solutions the  $p_H$  of which is near that of blood, markedly intensifies and prolongs the action of insulin.

R. A. M.

**Presence of Toxic and Insulin-like Substances in Oranges, Grape Fruit, and Lemons.** N. F. FISHER and E. B. MCKINLEY (*Proc. Soc. Exp. Biol. Med.*, 1924, **21**, 248—249).—Substances were found in the juice, pulp, and rind which markedly affected

the blood sugar; one produced a toxic hyperglycæmia; the other acted like insulin.

CHEMICAL ABSTRACTS.

**Physiological Action of Parathyroid Hormone.** J. B. COLLIP and E. P. CLARK (*J. Biol. Chem.*, 1925, **64**, 485—507; cf. this vol., i, 754).—Further experiments with a more purified preparation of the parathyroid hormone indicate that, whilst prolonged overdosage is invariably fatal, a single massive dose is relatively harmless. The rise in the calcium of the blood-serum of dogs after a single dose may be used to estimate the potency of an extract, and a provisional "unit" is suggested which is 1/100 of the amount required to produce an increase of 5 mg. per 100 c.c. of serum calcium in a 20 kg. dog in 15 hrs.; so far as the effect on the blood calcium is concerned, there is no significant difference between normal and thyroparathyroidectomised dogs. Except for the rise in the calcium concentration, the composition of the blood is but little affected by overdosage with the hormone until the terminal stage is reached; there is then a great diminution of the volume of the plasma, an increase in the phosphorus and non-protein nitrogen, and, generally, a decrease in the chlorides.

By the simultaneous injection of the parathyroid hormone and of guanidine it is possible to produce tetany in a dog which nevertheless has a raised serum calcium content; there is therefore no evidence of antagonism between this hormone and guanidine.

C. R. H.

**Preparation and Purification of Bios.** I. H. DES B. SIMS (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 116).—An infusion of tea dust in lead acetate solution is filtered and the bios precipitated by adding ammonia and lead acetate. The bios is brought into solution by treating the washed precipitate with carbon dioxide. After removal of lead by means of hydrogen sulphide, crystalline material with bios activity is thrown down by the addition of methyl alcohol.

J. S. C.

**Formation of Bios in Infusions.** E. V. EASTCOTT (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 117—118).—Comparison of the yeast crops from infusions of ground barley with those from infusions of the same number of barley grains after some days' sprouting shows that the crop depends on the length of time grain and water have been left together in preparing the infusions. The amount of bios I increased to a much greater extent than that of bios II when the infusion was prolonged. If maize be used instead of barley, it is the bios II which increases.

J. S. C.

**Persistence of Vitamin-A in Plant-tissues.** K. H. COWARD (*Biochem. J.*, 1925, **19**, 500—506).—Wheat seeds grown in the dark for 8 days contain no vitamin-A. A small amount of the vitamin is found when the growing plants are exposed for 1 day to daylight after they have grown in the dark for 8 days. The vitamin is not used up by the living plant-tissue in the dark and does not diffuse into water from the cut ends of shoots. It increases

when the leaf loses its green colour and turns yellow, but is completely destroyed when the leaf dries up and dies. S. S. Z.

**Identity of Vitamin-A. Comparative Effects of Human and Cow's Milk.** H. PRINGLE (*Sci. Proc. Roy. Dublin Soc.*, 18, 93—97).—Rats were fed on a vitamin-free diet of dextrose, caseinogen, fat, and salt mixture. During the last four months of one year, a supplement of 12 c.c. of cow's milk, daily, to this ration was not sufficient to promote growth, nor was a further supplement of 1.0 g. of butter; but normal growth was obtained with basal diet +12 c.c. of milk +0.5 g. of yeast. Hence it was concluded that the milk was deficient in vitamin-B.

In the spring months of the next year, 12 c.c. of cow's milk alone added to the vitamin-free diet produced normal growth, but the same animals decreased in weight remarkably when human milk was substituted for cow's milk. Cow's milk again restored them to normal growth and human milk again made them lose weight; this was repeated a third time. Hence human milk contains either a growth-retarding factor for the tissues of a more rapidly growing animal than man, or else vitamin-A is one of a class of catalysts which accelerates growths according to the requirements of the particular species, or else human milk is deficient in vitamin-B. K. H. C.

**Determination of Vitamin-A.** H. C. SHERMAN and H. E. MUNSELL (*J. Amer. Chem. Soc.*, 1925, 47, 1639—1646).—For the quantitative determination of the relative vitamin-A content of foodstuffs, albino rats, the nutritional history of which is known, are used. The rats when 28 or 29 days old are placed on a basal diet (free from vitamin-A) of caseinogen (prepared by a modification of Osborne and Mendel's method, *J. Biol. Chem.*, 1921, 45, 277), starch, dried brewery yeast, Osborne and Mendel salt mixture (*J. Amer. Chem. Soc.*, 1919, 37, 572), and sodium chloride. When growth has ceased the rats are kept in individual cages, and one from each litter is continued on the basal diet until death, as a "negative control." Graded portions of the food under test are fed to the others, daily or at suitable intervals during a period of 8 weeks, and in this way the minimum allowance of food which will induce an average gain in weight of 3 g. per week during the test period is ascertained. The amount of vitamin-A contained in this amount of the food is chosen as the unit for numerical expression of results. By performing autopsies on the animals at the end of the test period any cases of abnormality due to other causes than vitamin-A deficiency can be detected. The possibility of retarded growth through shortage of the antirachitic factor can be excluded by irradiation of the test animal or the food. R. B.

**Quantitative Experiments on the Occurrence and Distribution of Vitamin-A in the Body, and the Influence of the Food.** H. C. SHERMAN and L. C. BOYNTON (*J. Amer. Chem. Soc.*, 1925, 47, 1646—1653).—Using the technique previously developed (cf. preceding abstract), it is shown that in adult rats reared on a

diet of one-third whole milk powder and two-thirds whole wheat, on an average the kidney is at least 40 times as rich in vitamin-A as the muscle, the lung more than 40 times, and the liver 200—400 times. Significant quantities of vitamin-A are also present in the blood. The amount of vitamin-A found in the body and in the separate tissues is influenced by the vitamin-A content of the food. R. B.

**Bodily Store of Vitamin-A as Influenced by Age and other Conditions.** H. C. SHERMAN and L. B. STORMS (*J. Amer. Chem. Soc.*, 1925, **47**, 1653—1657).—Albino rats reared on the same diet (one-third whole milk powder and two-thirds ground whole wheat) showed different survival periods when transferred at different ages to a diet free from vitamin-A. The maximum survival period was found with rats transferred at about 6 months and it is concluded that the maximum body store of vitamin-A (or the maximum store in regard to daily needs) occurs about this period, the beginning of full adult life. The older rats are distinctly less likely to develop the characteristic ophthalmia before death from vitamin-A deficiency, but they are more liable to develop symptoms of the lung infection noted by Steenbock and Nelson (this vol., i, 107). The survival period is markedly affected by a moderate difference in the vitamin-A content of the food previously administered. There is a slight difference in survival period in favour of the female, and this difference becomes more distinct with age and development. R. B.

**Relation of Vitamin-A to Growth, Reproduction, and Longevity.** H. C. SHERMAN and F. L. MACLEOD (*J. Amer. Chem. Soc.*, 1925, **47**, 1658—1662).—Parallel groups of young rats (4 weeks) of identical inheritance and dietary history were placed on two diets, one rather low in vitamin-A (two-thirds wheat and one-third skimmed milk powder) and the other fairly high in vitamin-A (two-thirds wheat and one-third whole milk powder), the relative amounts of vitamin-A in the two diets being approximately seven to one. The smaller amount of vitamin-A was sufficient for normal growth up to nearly average adult size, but not for successful reproduction and rarely for satisfactory longevity. Rats fed on the larger allowance of vitamin-A grew to full average adult size, reproduced normally, and lived on an average rather more than twice as long as those on the diet poorer in this vitamin. Along with the failure in respect of reproduction and lactation, the rats on the latter diet showed an increased susceptibility to infection and a tendency to lung disease at an age corresponding with that at which pulmonary tuberculosis frequently develops in young men and women (cf. Steenbock, Sell, and Buell, *J. Biol. Chem.*, 1923, **56**, 327). R. B.

**Resistance to Reagents of the Antirachitic Substance in Cod-liver Oil.** C. E. BILLS (*J. Biol. Chem.*, 1925, **64**, 1—9).—The antirachitic activity of cod-liver oil is unaffected by treatment of the latter with hydrogen peroxide, hydrogen sulphide, sulphur

dioxide or formaldehyde, but is destroyed by nitrous acid, by prolonged steaming and by boiling with dilute sulphuric acid.

C. R. H.

**Antirachitic Value of Irradiated Cholesterol and Phytosterol. II. Change in Biological Activity. III. Chemical Change shown by Absorption Spectra.** A. F. HESS and M. WEINSTOCK (*J. Biol. Chem.*, 1925, **64**, 181—191, 193—201; cf. this vol. i, 750).—II. Antirachitic properties can be conferred on dried milk, flour, and spinach by irradiation; in the latter case, the activity is retained after boiling for 30 mins. Experiments with light filters indicate that the radiations which activate cholesterol *in vitro* are the same as those which protect animals against rickets by direct irradiation; irradiated cholesterol prevents rickets in animals on diets low in either phosphorus or calcium; oleic acid, the dihydro derivatives of cholesterol and of a phytosterol from wheat, cymene, and citronella oil possessed no antirachitic activity either before or after irradiation.

III. Irradiation by ultra-violet light for periods up to 3 hrs. increases the amount of this light transmitted by cholesterol; prolonged irradiation reverses the effect, the final product being a yellow, waxy substance with m. p. 12° lower, and more opaque than the original cholesterol; the antirachitic activity of the cholesterol runs parallel to its power to transmit ultra-violet light; irradiated cholesterol loses its power of transmission (and its physiological activity) when kept in aqueous suspension or in the dry state, but retains both properties longer when in solution in oil. No change in the absorption spectrum of dihydrocholesterol could be observed after irradiation.

C. R. H.

**Fat-soluble Vitamins. XXIII. Induction of Growth-promoting and Calcifying Properties in Fats by Exposure to Light.** H. STEENBOCK and A. BLACK (*J. Biol. Chem.*, 1925, **64**, 263—298).—Antirachitic properties can be conferred on olive oil and various other vegetable oils (but not mineral oil) and on carefully purified cholesterol by irradiation either with a mercury vapour lamp, an electric arc, or direct sunlight. In all cases, the active substance is present in the unsaponifiable fraction. Irradiation for longer periods than 5 hrs. destroys both the natural activity of cod-liver oil and the acquired activity of the artificially activated vegetable oils. When kept in the dark, irradiated olive oil retained its activity for 10 months. Neither old oils which had become acid in reaction nor the unsaponifiable constituents of such oils could be activated by irradiation.

C. R. H.

**Fat-soluble Vitamins. XXIV. Non-precipitability by Digitonin of the Antiophthalmic and Antirachitic Substances from Cod-liver Oil.** E. M. NELSON and H. STEENBOCK (*J. Biol. Chem.*, 1925, **64**, 299—312).—The antirachitic substance contained in the unsaponifiable fraction of cod-liver oil is not removed therefrom by precipitation with digitonin; the cholesterol which is so precipitated can be activated by exposure to ultra-violet light.



The unsaponifiable fraction of cod-liver oil retained its antirachitic activity when kept in solution in light petroleum for a year and a half.  
C. R. H.

**Biological Action of Light.** D. T. HARRIS (*Proc. Roy. Soc.*, 1925, B, 98, 171—187).—Ultra-violet radiations exert a stimulant action on the gaseous metabolism of small animals and on the movements of the isolated stomach of the frog. This stimulus is completely annulled by the presence of visible radiations. This antagonistic effect is a physiological one rather than one of physical interference. Exposure of an animal to the mixed radiations of a powerful source of light depresses its heat production. This depression is greater in pigmented animals than in albinos. Whilst the pigment appears to be a factor in diminishing heat production, it possesses high absorptive properties, and the heat produced by degradation of the absorbed radiant energy produces appreciable rises of temperature in the dermis. Pigment also appears to protect an animal against the lethal action of certain photo-dynamic substances such as hæmatoporphyrin.  
O. O.

**Effect of Vitamin-B Deficiency on Reproduction.** A. S. PARKES and J. C. DRUMMOND (*Proc. Roy. Soc.*, 1925, B, 98, 147—171).—When a male rat is put on a diet totally deficient in vitamin-B, degeneration of the testes and sterility ensue in a short time. A general correlation exists between the amount of degeneration of the testes and the degree of deficiency and time on the diet. Once severe degeneration of the testes has set in, normal dieting, although restoring vigour and body-weight, does not result in a return to normality in the testes. Whilst there is a definite correlation between the degree of deficiency and fecundating power, there is little variation in the size of the litter as long as fertilisation is possible. The proportion of males among the young decreases with both the degree of deficiency and with the time on diet. To explain the effect on the sex ratio, it is suggested that the deficiency reacts more unfavourably on one type of spermatozoa than it does on the other. The reduction in the number of males with time is probably explained by the fact that, as time goes on, during dieting the animals eat less of the synthetic food and have, therefore, a constantly decreasing supply of vitamin.  
O. O.

**Parasympathetic Stimulants in Vitamin Extracts.** S. MORI (*Arch. exp. Path. Pharm.*, 1925, 106, 320—326; cf. A., 1918, i, 419, 563).—On heating "Orypan" (extracted from rice husks) at 130—175° in an autoclave, the antineuritic vitamin is destroyed, but there is a slight increase in the effect of the extract on the parasympathetic nervous system as measured by the toxicity to pigeons, increase of the secretion of saliva by rabbits, and paralytic action on the isolated frog's heart. The antineuritic vitamin is therefore not identical with the parasympathetic stimulant.  
L. F. H.

**Antiscorbutic Properties of Eggs.** S. M. HAUGE and C. W. CARRICK (*J. Biol. Chem.*, 1925, 64, 111—112).—Neither whites nor

yolks of the eggs of hens fed on a diet rich in vitamin-*C* were able to prevent the onset of scurvy in guinea-pigs when added to a diet otherwise lacking this vitamin.

C. R. H.

**Anti-sterility Vitamin Fat-soluble-*E*.** H. M. EVANS and G. O. BURR (*Proc. Nat. Acad. Sci.*, 1925, **11**, 334—341).—Rats reared on "synthetic" food mixtures together with appropriate amounts of vitamins-*A* and -*B* sooner or later become sterile. This sterility is a dietary deficiency disease and can be cured or prevented by addition of natural foods high in a new food factor, vitamin-*E*, or by addition of much smaller amounts of extracts of such food to the diet. The vitamin exists in the tissues of animals reared on normal foods and is present in the tissues of the normal new-born young.

The vitamin is present in small amounts in various animal tissues and in considerable amounts in the leaves of lettuce, lucerne, pea, and tea plants, as well as in certain cereals, notably the embryo of wheat. 250 Mg. daily of desiccated wheat germ are sufficient to re-establish fertility. Oils efficacious in daily doses of 25 mg. are obtained from the ether extract of wheat germs and lettuce leaves. The vitamin is probably present in most commercial oils.

Vitamin-*E* is stable towards light, heat, air, acids, and alkalis. Wheat germ oil may be hydrogenated in presence of palladium at 75° without injury to the vitamin. It is insoluble in water, but very soluble in a variety of organic solvents. After saponification of wheat germ oil with 20% alcoholic potash in the cold the vitamin is found with the sterols in the unsaponifiable matter. It is washed out of the inactive sterols with pentane, the orange-red oil thus obtained treated with methyl alcohol, and the vitamin removed from the latter solvent by light petroleum. Further purifications are effected by means of digitonin, boiling methyl alcohol, and finally by distillation under reduced pressure. The final yellow oil does not crystallise on long keeping, has a very low ash and contains neither sulphur, nitrogen, phosphorus, nor halogens. It is extremely potent, administration of 5 mg. to a female of proved sterility at the inception of a new gestation being sufficient to ensure normal litters of vigorous young. The daily administration of 0.3 mg. to the male results in complete normality when reared and kept on synthetic foods.

J. S. C.

**Carbonic Acid-Carbonate Equilibrium and other Weak Acids in Sea-water.** L. IRVING (*J. Biol. Chem.*, 1925, **63**, 767—778).—Titration curves were obtained for sea-water under various tensions of carbon dioxide and compared with the theoretical curves for pure carbonate solutions having the same excess base and exposed to the same tension of carbon dioxide, as calculated from the formula of Johnston (A., 1916, ii, 396). Marked differences were observed which are to be ascribed to the buffer effect of various weak non-volatile acids, *e.g.*, boric and silicic acids, which are present in sea-water. It was calculated that the combined effect of these acids is, near the neutral point, equivalent to that of an

acid with a dissociation constant  $n \times 10^{-8}$ , the values of  $n$  determined varying from 2 to 30.

C. R. H.

**Occurrence of Copper, Manganese, Zinc, Nickel, and Cobalt in Soils, Plants, and Animals, and their Possible Functions as Vital Factors.** J. S. McHARGUE (*J. Agric. Res.*, 1925, 30, 193—196).—Several Kentucky soils and a number of plants were found to contain measurable amounts of the above metals, the soils containing arsenic in addition. Animal tissues also contained them, the liver of a week-old calf containing 345 parts of copper per million parts of dried tissue. It is suggested that some or all of these metals are constituents of organic colloidal complexes which exercise catalytic functions in the metabolic processes of plants and animals.

O. O.

**Hydrogen-ion Concentration of Plant Juices. I. Changes in the Hydrogen-ion Concentration of Plants during their Development.** F. G. GUSTAFSON (*Papers Mich. Acad. Sci.*, 1923, 2, 49—52).—Electrometric determinations were made of the hydrogen-ion concentrations of the expressed juice of macerated tops of bean plants of three varieties at different ages. As the plants approached maturity the acidity of the juice decreased.

CHEMICAL ABSTRACTS.

**Descent of Nitrogenous Substances in Leaves towards the Trunk during Autumnal Fading.** R. COMBES (*Compt. rend.*, 1925, 180, 2056—2058).—The leaves of the chestnut and beech lose some 30% of their nitrogen content when they change colour in autumn, the nitrogenous substances proceeding down towards the trunk of the tree. The leaves at the end of the twigs lose least nitrogenous constituents.

L. F. H.

**Action of Photocatalysers on the Bursting of Buds and on Germination of Seeds.** A. NEITHAMMER (*Biochem. Z.*, 1925, 158, 278—305).—The bursting of winter buds of various indigenous trees is accelerated by continuous illumination with light of a high intensity. This stimulating effect of light is increased in the presence of photocatalysers. These may be introduced into the buds by injection, or by placing the latter in a bath containing the photocatalyser at an appropriate concentration.

Seeds the germination of which is normally favoured by light show an increase over the controls in the percentage number which germinate after treatment with photocatalysers in appropriate concentration. The processes of the bursting of buds and the germination of seeds in the normal, untreated plant is probably influenced by photocatalysers already present in the various organs.

H. D. K.

**Action of Sodium Carbonate on Germination and Growth in Plants.** D. FEHÉR and S. VÁGI (*Biochem. Z.*, 1925, 158, 357—365).—This action has been studied mainly with regard to the problem of the utilisation of infertile alkali soils. Sodium carbonate is a plant poison, its toxicity being due to hydroxyl ions. Germin-

ation and plant growth are practically completely checked by a solution of this salt of a concentration of 0.4–0.5%. The salt is scarcely absorbed at all from such a solution by the seedling. In sandy soils poor in humus, a concentration of 1.5% of the salt is necessary to prevent plant growth. In soil which is rich in humus, sodium carbonate is much less toxic, as the hydroxyl ions are taken up by the humus. Trees are less resistant to the alkali than are cereals.

H. D. K.

**Selective Absorption of Chlorine Ions, and the Absorption of Water by the Leaves in the Genus *Atriplex*.** J. G. WOOD (*Austral. J. Exp. Biol. Med. Sci.*, 1925, 2, 45–56).—Water is readily absorbed by the leaves of various species of *Atriplex* and by tomentose microphylls. Plants possessing a cutinised epidermis showed no such absorption. With the water-absorbing power of the leaves of *Atriplex* is associated an abnormally high chlorine content. The chloride content is, within limits, a function of the chloride content of the soil, although the plants die in soil containing sodium chloride in excess of a certain amount. The chloride content also exhibits seasonal variations. *Atriplex* spp. therefore exhibit a high selective absorption of chlorides.

C. P. S.

**Physical and Chemical Properties of Carotin and Preparation of the Pure Pigment.** F. M. SCHERTZ (*J. Agric. Res.*, 1925, 30, 469–474).—The solubility of carotin at 25° in absolute alcohol is 15.5 mg. per l.; in light petroleum (b. p. 30–50°), 626 mg. per l.; and in anhydrous ethyl ether, 1005 mg. per l. In solution in ether, carotin decomposes rapidly even at 0°, whereas alcohol and light petroleum solutions are very stable. Full details are given of the preparation and purification of carotin from carrots. Fifty lb. of fresh carrots yielded 1.13 g. of pure carotin (m. p. 174°). The quantitative determinations were made both by spectrophotometric and colorimetric methods (cf. Schertz, A., 1924, ii, 359).

C. T. G.

**Properties and Preparation of Pure Xanthophyll.** F. M. SCHERTZ (*J. Agric. Res.*, 1925, 30, 575–585).—Full details are given for the preparation of pure xanthophyll from dried green leaves by a method based on that of Willstätter and Stoll. The final purification is carried out by crystallising from methyl alcohol, dissolving the crystals (which contain alcohol) in chloroform, and precipitating by the addition of low-boiling light petroleum. The solubility of pure xanthophyll at 25° in pure dry ether is 952 mg. per l.; in ethyl alcohol, 201.5 mg. per l.; in methyl alcohol, 134.9 mg. per l.; and in light petroleum (b. p. 50–55°) 9.5 mg. per l. Xanthophyll oxidises quite rapidly in solution in ether, but is stable in solution in ethyl alcohol or light petroleum. Exposure to sunlight hastens oxidation. Xanthophyll oxidises more readily than carotin in the dry state and also in solution when kept in the dark; but in sunlight, carotin in solution oxidises more rapidly than xanthophyll. Colorimetric and spectrophotometric methods were used in making determinations of xanthophyll (cf. Schertz, this vol., i, 871).

C. T. G.

**Chemistry of Heterotrophic Phanerogams. V. J. ZELLNER** (*Monatsh.*, 1925, 45, 535—538).—The light petroleum extract (0.89% of the dried material) of *Prosopanche Burmeisteri* de Bary (*Hydnora americana*, R. Br.) contains ceryl alcohol, phytosterol, and palmitic acid. The ethereal extract (0.31%) contains a resin alcohol, obtained as a white powder, together with aliphatic acids. The alcoholic extract (15.81%) contains a tannin of the proto-catechuic acid series, which yields a "tannin red" on hydrolysis with mineral acids, and is converted, when boiled in alcoholic solution, into phlobaphens. These form, together with the tannin, more than half of the dried plant material. The tannin is accompanied by sugars and a base which is precipitated by potassium mercuric iodide. The aqueous extract (26.40%) contains traces of polysaccharides, potassium chloride, and probably potassium hydrogen tartrate, the total dissolved mineral matter being 2.42% of the dried material. The latter contained further: free acid, 1.69% (as KOH); reducing sugars, 1.42%; total nitrogen, 1.49%; raw fibre, 8.86%; and total ash, 10.45%. F. G. W.

**Chemistry of Japanese Plants. VII. Phyto-chemical Study of Yamamomo-Fruit.** S. KOMATSU and R. NODZU (*Mem. Coll. Sci. Kyōtō*, 1925, 8, 223—229).—Myricetin is present as a rhamnoside in the bark of the yamamomo tree (*Myrica rubra*). The fruit contains a red pigment, mainly a mono-*d*-glucoside of anthocyanidin, together with small quantities of diglucoside and free anthocyanidin. Delphinidin is produced when the anthocyanidin is demethylated by Zeisel's method. The sugars in the fruit are dextrose and *d*-fructose in the ratio of 1 : 1.25; the non-volatile free acids are principally citric acid, accompanied by small amounts of malic, oxalic, and inactive lactic acids. C. J. S.

**Plant Cuticles. I. Modern Plant Cuticles. Composition of Coal.** V. H. LEGG and R. V. WHEELER (*J. Chem. Soc.*, 1925, 127, 1412—1421).—By extraction of the cuticle of *Agave americana* with solvents a variety of substances has been obtained. The water-soluble portion, amounting to about 10%, contains glucosides of the saponin type. About 15% is extracted by alcohol and consists of wax, a portion of which is soluble in light petroleum and gives the reaction for phytosterol; another portion dissolves in ether and contains free acids and saponifiable matter. Cuprammonium hydroxide solution extracts approximately 14% of cellulose. About 60% of insoluble material remains after extraction by these solvents, and consists of cutin. By the action of boiling alcoholic potassium hydroxide solution on cutin, several potassium salts, which differ in solubility, are obtained. Those soluble in water give a semi-liquid mixture of two acids, the greater portion of the mixture consisting of *cutic acid*,  $C_{26}H_{50}O_6$ , the *copper* salt of which is soluble in alcohol; the remainder is *cutinic acid*,  $C_{13}H_{22}O_3$ , which gives a *copper* salt, insoluble in alcohol, and also a *silver* salt. The oleocutic acid isolated by Frémy appears to have been a mixture of these two acids.

From the potassium salt sparingly soluble in water there is

obtained an *acid*,  $C_{19}H_{38}O_6$ , m. p. 107—108°, which yields a *silver* salt,  $C_{19}H_{37}O_6Ag$ , and an *ethyl* ester, m. p. 66—67°. The potassium salt insoluble in water gives an *acid*, m. p. 88—90°.

C. J. S.

**Homogeneity of  $\alpha$ -Lignin.** E. HÄGGLUND (*Biochem. Z.*, 1925, **158**, 350—356).— $\alpha$ -Lignosulphonic acid has been precipitated, after boiling the sulphate solution for varying periods, as the  $\beta$ -naphthylamine compound and analysed. Fractional precipitation of one and the same solution of sulphonic acids of lignin has also been undertaken, and the results by both methods indicate that  $\alpha$ -lignin is homogeneous.

H. D. K.

**Chemical Nature of the Membrane of Potato Cork.** E. RHODES (*Biochem. J.*, 1925, **19**, 454—463).—The chloroform-soluble and the unsaponifiable fractions and the normal and the hydroxy-acid contents of the cork layer of potato skin were investigated. It is concluded that the suberin lamella of the cork cell arises by changes taking place in the fatty material resulting in the appearance of bodies no longer soluble in fat solvents. A relatively constant proportion of the soluble fatty substances does not undergo this change and is responsible for the staining properties of the suberin lamella. The main constituents of the suberin lamella consist of relatively insoluble normal and hydroxy fatty acid complexes which can be released on saponification. The non-saponifiable substances of the regenerated cork layers contain considerable amounts of volatile bodies. Traces of glycerol are found in the chloroform extract.

S. S. Z.

**Anthocyanin Formation in *Helianthus annuus*.** C. E. SANDO (*J. Biol. Chem.*, 1925, **64**, 71—74).—From the corollas of an orange-coloured form of the above plant there has been obtained, by extraction with alcohol following removal of the plastid pigments with ether, a *glucoside*,  $C_{21}H_{20}O_{12}$ , which has been identified with quercimeritrin (cf. Perkin, T., 1909, **95**, 2185). It is suggested that this represents the colourless chromogen from which the anthocyanin of the red forms is produced by reduction.

C. R. H.

**Odorous Constituents of the Cotton Plant. Emanation of Ammonia and Trimethylamine from the Living Plant.** F. B. POWER and V. K. CHESNUT (*J. Amer. Chem. Soc.*, 1925, **47**, 1751—1774).—The concentrated distillate obtained by steam-distilling the cotton plant yields on ether extraction 0.003% of an essential oil (cf. Clifford and Fargher, A., 1923, i, 637) (limpid brownish-yellow),  $d_{25}^{25}$  0.9261,  $n_D^{20}$  1.4797,  $[\alpha]_D^{20}$  —3.91°, which gives a strong reaction for furfuraldehyde. The concentrated distillate also contains acetaldehyde with traces of a higher aldehyde yielding a *m*-nitrobenzhydrazide, m. p. 244—245°, possibly identical with that obtained by Curtius and Franzen (A., 1921, i, 644). The  $\alpha\beta$ -hexenaldehyde described by Curtius (*Ber. botan. Ges.*, 1897, **15**, 201) was not detected. Hydrolysis of the esters present in the distillate yielded methyl alcohol and small amounts of amyl alcohol

with traces of higher homologues and of acetone. The acidic products of hydrolysis contained small amounts of vanillin, minute traces of a phenol resembling *m*-cresol, and formic, acetic, and *n*-hexoic acids, the last only in small amount. An optically inactive, dicyclic sesquiterpene,  $C_{15}H_{24}$ , b. p. 250—260°,  $d_{15}^{20}$  0.9109,  $n_D^{20}$  1.4987, resembling one obtained by Power and Tutin (T., 1906, 89, 1090), an optically active *tricyclic sesquiterpene*,  $C_{15}H_{24}$ , b. p. 260—280°,  $d_{15}^{15}$  0.9276,  $[\alpha]_D -12.5^\circ$ ,  $n_D^{20}$  1.4981, a small amount of a paraffin, m. p. 62°, apparently triacontane, and a blue oil which probably contains azulene. Ammonia and trimethylamine are also present with the basic products of hydrolysis, ammonia preponderating. Both bases are detected in the dew on the living cotton plant (cf. Smith, *J. Agric. Res.*, 1923, 26, 192). R. B.

**Physiological Studies on Cereals. III. Polypeptides and Amino-acids in the Ungerminated Maize Kernel.** S. L. JODIDI (*J. Agric. Res.*, 1925, 30, 587—592).—Polypeptides and free amino-acids are present in the ungerminated maize kernel. In three varieties of maize, the figures for total nitrogen were 1.7, 1.59, and 1.46% of the oven-dried grain; for amino nitrogen, 0.045, 0.04, and 0.051%; for peptide nitrogen, 0.069, 0.05, and 0.036%; and for acid amide nitrogen 0.032, 0.019, and 0.021%. Extraction of the maize flour with water at the ordinary temperature for 1 hr. gave substantially the same results as extraction for longer periods or with hot water for  $\frac{1}{2}$  hr. The amount of proteose in the aqueous extract was insignificant. C. T. G.

**Globulins of the Jack Bean (*Canavalia ensiformis*). II. Content of Cystine, Tyrosine, and Tryptophan.** J. B. SUMNER and V. A. GRAHAM (*J. Biol. Chem.*, 1925, 64, 257—261).—Improved methods are described for the preparation from the Jack bean of the proteins canavalline and concanavalline-A and -B. These proteins contain respectively 0.24, 2.2, and 2.3% of tryptophan; 1.0, 0.4, and 3.2% of cystine; 5.5, 5.2, and 9.4% of tyrosine. The figures for tryptophan and cystine are in disagreement with those of Jones and others (this vol., i, 98). C. R. H.

**Proteins of Wheat Bran. II. Comparison of Bran Proteins with those of the Endosperm and Embryo.** D. B. JONES and C. E. F. GERSDORFF (*J. Biol. Chem.*, 1925, 64, 241—251).—Analysis by the method of Van Slyke (A., 1911, ii, 779) of an alcohol-soluble protein, an albumin, and a globulin obtained from wheat bran shows that these proteins differ from those of other parts of the wheat in containing considerably greater amounts of the dibasic amino-acids and of tryptophan; this is especially the case with the albumin, which contains arginine 10.04%, histidine 2.57%, lysine 4.51%, and tryptophan 4.76%, and with the globulin, which has 14.13, 2.76, 11.84, and 2.85% of the same amino-acids. C. R. H.

**Preparation and Properties of Monotropitoideside.** M. BRIDEL and P. PICARD (*Compt. rend.*, 1925, 180, 1864—1866; cf. A., 1923, i, 1275).—Monotropitoideside,  $C_{19}H_{26}O_{12}$ , extracted in 0.3% yield

from the bark of *Betula lenta*, L., gives a red coloration and the odour of methyl salicylate on treatment with concentrated sulphuric acid, is hydrolysed by enzymes yielding equimolecular amounts of methyl salicylate and primeverose, and on acid hydrolysis the disaccharide is hydrolysed yielding dextrose and xylose. The methyl group in the glucoside is split off by the action of alcoholic potassium hydroxide, but no further hydrolysis can be effected by alkalis.

L. F. H.

**Saponins. III. Sapogenin Occurring in *Sapindus saponaria*, L., and *S. Mukorossi utilis*.** W. A. JACOBS (*J. Biol. Chem.*, 1925, **64**, 379—381).—The sapogenins isolated by hydrolysis of extracts of the nut-shells of the above species have proved to be identical with that obtained similarly by the author from commercial soapnuts and identified with hederagenin.

C. R. H.

**Pectin Content of Normal and "Silvered" Apple Leaves.** F. TUTIN (*Biochem. J.*, 1925, **19**, 414—415).—The "silver leaf" disease of apple leaves is associated with a pectin deficiency. Normal apple leaves have a higher pectin content than the peel and pulp of the fresh fruit.

S. S. Z.

**Fruits and their Products. I. Apple Juice as a Source of Sorbitol.** F. TUTIN (*Biochem. J.*, 1925, **19**, 416—417).—The concentrated apple juice is precipitated with basic lead acetate and then fermented. This is repeated and after removing the lead the gum-like residue is acetylated with acetic anhydride in the presence of pyridine. The resulting hexa-acetylsorbitol is recrystallised from ethyl acetate; colourless prisms, m. p. 99°. The sorbitol is regenerated by treating the hexa-acetylsorbitol with sulphuric acid and removing the latter with aqueous baryta.

S. S. Z.

**Fruits and their Products. II. Fate of Sugar during "Cider Sickness."** F. TUTIN (*Biochem. J.*, 1925, **19**, 418—419).—The bacillus producing "cider sickness" reduces a portion of the sugar of the fruit to mannitol. The latter was isolated from diseased fruit as hexa-acetyl- $\alpha$ -mannitol by the method employed in isolating the acetyl compound of sorbitol (see preceding abstract).

S. S. Z.

**Attempted Separation of the Active Constituent of Ragweed Pollen.** L. BAUMAN, M. CHUDNOFF, and G. M. MACKENZIE (*Proc. Soc. Exp. Biol. Med.*, 1924, **21**, 226—227).—The active substance is extracted with 3% ammonia solution and precipitated with acetone; precipitation with ammonium sulphate and dialysis leaves it in the globulin fraction.

CHEMICAL ABSTRACTS.

**Polysaccharides. XXX. isoLichenin.** P. KARRER and B. JOOS (*Z. physiol. Chem.*, 1924, **141**, 311—315).—Contrary to Pringsheim's results (A., 1924, i, 1170), isolichenin is a mixture of carbohydrates. It may be separated into two fractions by precipitation with Fehling's solution from alkaline solution. The precipitated fraction gives no colour reaction with iodine and when hydrolysed



yields mannose, galactose, and dextrose. The authors have also been unable to obtain trihexosan from glycogen according to Pringsheim's method. E. S.

**Lichen Starch.** H. PRINGSHEIM (*Z. physiol. Chem.*, 1925, **144**, 241—245).—A reply to Karrer and Joos (cf. preceding abstract). Details of the preparation of isolichenin are given and the author's original view that this is identical with starch amylose and completely hydrolysable to maltose (A., 1924, i, 1170) is maintained. P. W. C.

**Polysaccharides. XXXII. Kinetics of Enzymic Cleavage of Cellulose.** P. KARRER and H. ILLING (*Helv. Chim. Acta*, 1925, **8**, 245—247).—When cellulose, reprecipitated from "cuprammonium" solutions, is treated with cellulase from *Helix pomatia* (cf. A., 1924, i, 118, 471) at  $p_H$  5.28 it is hydrolysed, although insoluble, at a measurable, regular, rate. When the proportion of enzyme is doubled, 1.45 to 1.65 times as much cellulose is hydrolysed. The reaction is approximately unimolecular. W. A. S.

**"Forcing" (Plants) by Means of Hydrogen Cyanide.** G. GASSNER (*Ber. Deut. bot. Ges.*, 1925, **43**, 132—137).—A number of different species of plants are stimulated by exposure to low concentrations of hydrogen cyanide. Plants which are usually dormant in winter may be "forced" by regular treatment with the gas. Whilst the optimum amount varies for different species a general treatment consists of exposure of the plant for 1 hr. daily to an atmosphere containing one volume of hydrogen cyanide per cent. at the ordinary temperature. O. O.

**Supposed Poisonous Action of Carbon Monoxide on Green Plants.** C. WEHMER (*Ber. Deut. bot. Ges.*, 1925, **43**, 184—188).—Seedlings and young plants of cress and barley showed no injury when kept for 10 days in atmospheres containing up to 50% of carbon monoxide. In pure carbon monoxide, the plants soon die. O. O.

**Action of Soil Solutions on Root Development.** F. TERLI KOWSKI (*Rocz. Nauk Rolnicz.*, 1923, **9**, 544—560; *Exp. Sta. Rec.*, **51**, 517—518).—In general, solutions of calcium sulphate, magnesium sulphate, potassium chloride, or magnesium chloride restrict root growth, calcium sulphate having the least effect when used in saturated solution; magnesium sulphate and chloride have the greatest effect, being completely inhibitory in certain concentrations. Solutions of kainite and Kaluss potash strongly stimulated root growth, as also did sodium nitrate with sodium phosphate, except when used with kainite and in low concentration.

#### CHEMICAL ABSTRACTS.

**From what Depth in the Soil can Plants Usefully Obtain Nutrients?** O. LEMMERMANN, H. WIESSMANN, and K. ECKL (*Z. Pflanz. Düng.*, 1925, **B 4**, 233—241).—Various crops were grown in deep pots, dicalcium phosphate being added to the soil at various

depths down to 75—100 cm. from the surface. In other series different depths of a poor soil were superimposed on different depths of a rich soil and *vice versa*. The crops were weighed and analysed. The general conclusion is reached that plants can take up nutrients in amounts sufficient to affect the yield from a considerable depth; and that the food supply in the subsoil cannot be ignored in plant nutrition studies. C. T. G.

**Fertiliser Nutrients required by Barley, Wheat, and Oats, as shown by both Soil and Water Cultures.** R. L. JONES and F. R. PEMBER (*Soil Sci.*, 1925, **19**, 169—199).—The supplies of nitrogen, phosphorus, and potassium to barley, wheat, and oats, grown both in soil and water cultures, were adjusted so as to give optimum and sub-optimum growth for each nutrient. Full analyses of the plants, excluding roots, showed that for sub-optimum growth the dry matter contained 0.9% nitrogen for barley, 0.9—1.0% for wheat, and 0.6—0.7% for oats. The nitrogen contents were similar in both cultures. With an estimated optimum growth, the phosphorus content of all three cereals in water cultures was only about one-third to one-half of that in soil cultures. The soil cultures gave a higher ratio of grain to straw than the water cultures. E. M. C.

**Effects of Alkali Salts on Bacteriological Activities in Soil. I. Ammonification. II. Nitrification. III. Ammonification, Nitrification, and Crop Yield.** W. M. GIBBS, H. W. BATCHELOR, and H. P. MAGNUSON (*Soil Sci.*, 1925, **19**, 343—356, 357—369, 371—379).—An account of pot experiments in which various amounts and combinations of sodium carbonate, sodium chloride, and sodium sulphate were added to the soil. The yields of two crops of wheat are considered in relation to the total amount of added salts, the amount recoverable in a water extract and the effects on ammonia formation from dried blood and on nitrate formation from ammonium sulphate. The salts used singly in general depressed ammonification; nitrification was stimulated by the carbonate, depressed by the chloride, and unaffected by the sulphate. The crop yields were reduced by the carbonate in most cases, slightly increased by the chloride, and unaffected or increased by the sulphate. Combinations of two or three of the salts depressed ammonification in almost every case, whereas nitrification was in general stimulated; the yield of the first crop was reduced and of the second increased. The inhibiting or stimulating effects were not found to be proportional to the total salt recoverable by extraction with water. [Cf. *B.*, 1925, 561.] C. T. G.

**Toxicity Studies with Dicyanodiamide on Plants.** F. E. ALLISON, J. J. SKINNER, and F. R. REID (*J. Agric. Res.*, 1925, **30**, 419—429).—In pot culture experiments with wheat, dicyanodiamide caused only slight injury and reduction of yield even when given at a rate equivalent to 40 lb. of ammonia per acre. The addition of small quantities of sodium nitrate was sufficient to counteract the injurious effect. On the other hand, cow-peas are very sensitive

to the presence of dicyanodiamide. Small amounts caused a marked decrease in yield; and addition of sodium nitrate in many cases increased this effect. Dicyanodiamide decomposes only slowly in the soil and markedly influenced a crop of cow-peas taken after wheat.

C. T. G.

**Temperature and Moisture Factors in Nitrate Production.** J. C. RUSSEL, E. G. JONES, and G. M. BAHRT (*Soil Sci.*, 1925, **19**, 381—398).—A study of the effect of temperature (5° to 55°) and moisture on nitrate production in two Nebraska soils. One kg. samples of soil were incubated under the desired conditions and determinations of nitrates made at intervals up to 8 weeks. Nitrification was at a maximum at 35°; it was very slight at moisture contents near the hygroscopic coefficient of the soil and increased up to the highest moisture content used. The results confirm those obtained by Schloesing and Müntz in 1879.

C. T. G.

**Action of Calcium Carbonate on the Soil.** A. GEHRING and O. WEHRMANN (*Landw. Versuchs.-Stat.*, 1925, **103**, 279—343).—A long and detailed paper giving the results of experiments on the effect of a number of calcareous materials, including calcium oxide and carbonate and certain commercial products ("Endlaugenkalk" and "Kalikalk") on several different soils. The results are discussed with special reference to the unfavourable effects of some of the treatments on soils which would be expected to respond to liming. Data are given as to the rate of percolation of water through the treated soils, the amounts of carbon dioxide produced under uniform conditions of aëration, and the amounts of nitrates formed; in some cases, the figures are correlated with yields of sugar beet. Some of the results are considered in the light of Hissink's work on the saturation-capacity of soils. General conclusions are not reached; the original should be consulted for details.

C. T. G.

**Formation and Decomposition of Humus in the Soil.** R. BALKS (*Landw. Versuchs.-Stat.*, 1925, **103**, 221—258).—A quantitative study of the changes in composition of the organic matter in soils receiving farmyard manure. Six soils of different types were given heavy dressings of dung and samples were taken for analysis before treatment and at intervals subsequently. The percentages of total nitrogen, of nitrogen compounds soluble in 1% potassium sulphate solution, of pentosans (determined by Tollens' method), and of lignin (calculated from determinations of the methoxyl content) in all the soils reached a maximum after the manuring and then declined, the changes in the amounts of lignin being, however, much smaller than in the case of pentosans. The percentages of methyl pentosans in all cases remained practically constant throughout the experiments. Determinations of total carbon were made by oxidation with silver dichromate (cf. Simon, A., 1923, ii, 506); the use of chromic acid or of mercuric chromate gave unsatisfactory results, as also did Piettre's pyridine extraction method (cf. A., 1923, i, 736). The process of decomposition

of humus is shown in a slow reduction in the total carbon content of the soil after manuring. This reduction was much less marked in a calcareous soil than in the other types of soil studied; probably the acids formed on the breaking down of humus combine with the excess of calcium carbonate and are thus protected from rapid oxidation. [Cf. *B.*, 1925, 605.] C. T. G.

**Inhibition of Bumping in the Determination of Nitrogen in Soil.** F. E. HANCE (*J. Amer. Soc. Agron.*, 1924, 16, 790—792).—Bumping may be prevented by placing an asbestos collar between the flame and the distilling flask. Addition of 2 g. of zinc dust is also used. Only 2.8 g. of soil are used in the determination.

CHEMICAL ABSTRACTS.

**Soil Acidity.** E. KURCKMANN (*Z. Pflanz. Düng.*, 1925, 5A, 1—92).—The nature and occurrence of soil acidity is discussed, and methods for the determination of acidity and lime requirement are examined practically. In the light of the classification of acidity into three forms: "active," "exchange," and hydrolytic (Kappen), variations in soil acidity due to origin, position, moisture, and humus content are examined and recorded. A. G. P.

**Displacement of Aluminium by Potassium Ions in Different Soils.** L. SMOLIK (*Compt. rend.*, 1925, 180, 1773—1776).—The amount of aluminium displaced from combination in the soil on treatment with potassium chloride solution varies from 0 to 229 mg. per 100 g. of dried soil, in different soils and in different depths of sub-soil. L. F. H.

**Soil Colloids as Simple Suspensions.** E. B. POWELL (*Soil Sci.*, 1925, 19, 407—409).—Bouyoucos (*Mich. Agric. Exp. Sta.*, 1915, *Tech. Bull.* 22) found that the rate of percolation of water through heavy soils and sub-soils increased rapidly with the temperature up to 30—40° and then decreased, and suggested that this decrease was due to the swelling of the colloids at higher temperatures, thus causing many of the pore spaces to be closed. The author has measured the viscosity of a solution of the colloidal material separated from a heavy sub-soil over a range of temperature from 0° to 90° at 10-degree intervals and by plotting the absolute viscosities against the temperature obtained a perfectly smooth curve, closely similar to the absolute viscosity curve of water. There was no change of slope or other abnormality in the neighbourhood of 30—40°. The fluidity curve of the colloid was also plotted and found to take the form of a straight line, as in the case of a true suspension. Since the viscosity changes of the colloid may be used as a measure of its swelling, the results do not agree with Bouyoucos' explanation of the variation of rate of percolation with temperature. C. T. G.

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## Organic Chemistry.

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**Liberation of Hydrogen from Carbon Compounds.** J. V. E. DICKSON (*J. Amer. Chem. Soc.*, 1925, **47**, 2061–2062).—Attention is directed to the author's investigations (cf. Boswell and Dickson, A., 1919, ii, 62, 72) in reference to those of Fry, Schulze, and Weitkamp (A., 1924, i, 1277).  
F. G. W.

**Action of Bromine on Hydrocarbons. Bromination of  $\beta$ -Methylbutane.** B. K. MEREJKOWSKY (*Bull. Soc. chim.*, 1925, [iv], **37**, 861–871).—The discrepancies in the results obtained by the author (A., 1923, i, 527) and Kronstein (A., 1921, i, 153) on the bromination of hydrocarbons are attributed to the use of a mixed catalyst by the latter. In the bromination of  $\beta$ -chloro- $\beta$ -methylbutane, Kronstein (*loc. cit.*) obtained a crystalline tribromo compound which he considered to be  $\alpha\beta\gamma$ -tribromo- $\beta$ -methylbutane, whereas logically this should have the structure  $\beta\gamma\gamma$ -tribromo- $\beta$ -methylbutane. In the bromination of  $\beta$ -methylbutane,  $\beta\gamma$ -dibromo-,  $\alpha\beta\gamma$ -tribromo-, and  $\alpha\beta\gamma$ -tribromo- $\beta$ -bromomethylbutane successively are obtained. By the action of bromine on dibromo- $\beta$ -methylbutane in the presence of metallic iron (Ipatiev, A., 1896, i, 401),  $\alpha\beta\gamma$ -tribromo- $\beta$ -methylbutane is obtained as shown by the following evidence. On treatment with potassium acetate the tribromo compound yields  $\gamma$ -bromo- $\beta$ -methyl- $\Delta^2$ -butenyl acetate, b. p. 107–109°/30 mm.,  $d_4^{20}$  1.3552,  $n_D^{20}$  1.4810; this on hydrolysis with sodium hydroxide gives  $\gamma$ -bromo- $\beta$ -methyl- $\Delta^2$ -buten- $\alpha$ -ol, b. p. 103–104°/30 mm.,  $d_4^{20}$  1.4499,  $n_D^{20}$  1.5050, which on oxidation with potassium permanganate gives acetic acid as the only isolable product. The tribromo compound on treatment with bromine in the presence of metallic iron gives  $\alpha\beta\gamma$ -tribromo- $\beta$ -bromomethylbutane, b. p. 160–161°/16 mm.,  $d_4^{20}$  2.3836,  $n_D^{20}$  1.6052, together with a small amount of  $\alpha\beta\gamma\delta$ -tetrabromo- $\beta$ -methylbutane (Mokievsky, A., 1899, i, 726). The former on treatment with potassium acetate yields the *diacetate*,  $\text{CH}_2(\text{OAc})\cdot\text{C}(\text{CH}_2\cdot\text{OAc})\cdot\text{CMeBr}$ , b. p. 144–146°/15 mm.,  $d_4^{20}$  1.5146,  $n_D^{20}$  1.5041, which on hydrolysis yields the corresponding *alcohol*, b. p. 154–156°/15 mm.  $\alpha\beta\gamma$ -Tribromo- $\beta$ -methylbutane, on treatment with potassium hydroxide, gives the unsaturated *dibromide*,  $\text{CH}_2\text{Br}\cdot\text{CMe}\cdot\text{CMeBr}$ , b. p. 179.5°/753 mm. (slight decomp.),  $n_D^{20}$  1.5414,  $d_4^{20}$  1.7461, which when treated with bromine in chloroform solution yields  $\alpha\beta\gamma\gamma$ -tetrabromo- $\beta$ -methylbutane, b. p. 146°/14 mm.,  $d_4^{20}$  2.3291,  $n_D^{20}$  1.6016, converted by potassium acetate into the *acetate*, b. p. 116–117°/13 mm.  
L. F. H.

**Pressure-Temperature Charts for Organic Vapours.** D. S. DAVIS (*Ind. Eng. Chem.*, 1925, **17**, 735–736; cf. *ibid.*, 1923, **15**, 592).—Cox's method for plotting the vapour pressures of the  
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paraffin hydrocarbons has been extended to homologous alcohols of the series  $C_nH_{2n+2}O$ , the organic acid series, and a series of halogen-substituted benzenes. A formula for finding the temperature of the point of convergence is included. D. G. H.

**Exchange of Functional Groups between Two Molecules. Passage of Alcoholic into Ketonic Groups and Inversely.**

A. VERLEY (*Bull. Soc. chim.*, 1925, [iv], 37, 871—874).—By the interaction of ketones and the aluminium derivatives of alcohols interchange of groups takes place as in the case of aldehydes and alcohols (cf. this vol., i, 783). The sodium derivatives of alcohols react more rapidly than the aluminium derivatives. Methyl nonyl ketone and sodium isopropoxide give an almost quantitative yield of undecan- $\beta$ -ol and acetone; acetophenone and sodium  $\beta$ -octoxide yield phenylmethylcarbinol and methyl hexyl ketone. Cyclic ketones (e.g., camphor) do not react in this way. Tischenko's reaction does not proceed in the case of ketones as with aldehydes (*loc. cit.*), but when methyl benzyl ketone reacts to give methylbenzylcarbinol, a yellow oil, b. p.  $215^\circ/6$  mm., probably a pinacone, is formed. Aluminium isopropoxide is prepared by addition of anhydrous aluminium chloride to sodium isopropoxide. L. F. H.

**Preparation of Alkyl Sulphides.** A. E. WOOD (*J. Amer. Chem. Soc.*, 1925, 47, 2062).—Mercaptans are completely removed from alkyl sulphides by distillation, preferably under reduced pressure, over finely-divided copper. Copper mercaptide may remain in the residue, but decomposes at  $125^\circ$  with formation of copper sulphide and alkyl sulphide. F. G. W.

**Coloured Compounds of Mercury Sulphide and Mercaptide.**

G. SACHS and L. BALASSA (*Z. anorg. Chem.*, 1925, 146, 196—199).—When a dilute solution of mercury mercaptide in carbon disulphide is kept for some hours, the yellow compound,  $2HgS.Hg(SET)_2$ , is precipitated according to the reaction  $3Hg(SET)_2 + 2CS_2 = 2HgS.Hg(SET)_2 + 2CS(SET)_2$ . An isomeric red form is produced if a concentrated solution of mercury mercaptide is used. The yellow form is also produced by the action of hydrogen sulphide on an ethereal solution of mercury mercaptide. When ground, both forms decompose to a mixture of mercury mercaptide and black mercury sulphide. The yellow variety has b. p.  $115^\circ/17$  mm. (decomp.  $160$ — $200^\circ$ ). W. H.-R.

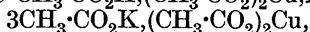
**Reduction of Acetic Acid and some of its Derivatives.**

G. POVARNIN and KALJE (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, 55, 369—374).—Reduction of acetic acid and various derivatives by means of hydrogen in presence of a current of steam and in presence or absence of spongy platinum or platinised asbestos yields very little aldehyde. Reduction in presence of finely-divided nickel at  $330$ — $400^\circ$  gives no more than traces of aldehyde, but leads to intense decomposition of the acid. Direct current electrolysis of a mixture of sodium acetate and oxalate leads mainly to

the formation of formaldehyde. The total quantity of aldehyde formed increases with increase in the pressure. T. H. P.

**Double Acetates of Copper and the Alkali Metals.** E. BÜTTGENBACH (*Z. anorg. Chem.*, 1925, **145**, 141—150).—Solutions of cupric acetate containing amounts of sodium acetate up to Na : Cu = 8 : 1 give on evaporation only the compound  
 $(\text{CH}_3\cdot\text{CO}_2)_2\text{Cu}, \text{H}_2\text{O}$ .

When sodium acetate is replaced by potassium acetate two compound acetates are obtained and these systems are examined in detail by the solubility method. The two *potassium copper acetates* have the compositions  $\text{CH}_3\cdot\text{CO}_2\text{K}, (\text{CH}_3\cdot\text{CO}_2)_2\text{Cu}, \text{H}_2\text{O}$  and



respectively, and the existence of the former compound was confirmed by a break in the specific gravity—potassium acetate concentration curve for the solutions. These double acetates were also prepared and analysed, but no compound of the formula  $4\text{CH}_3\cdot\text{CO}_2\text{K}, (\text{CH}_3\cdot\text{CO}_2)_2\text{Cu}, 12\text{H}_2\text{O}$  (cf. Rammelsberg, *Pogg. Ann.*, 1855, **94**, 519) could be found A. G.

**Anhydrides of Saturated Fatty Acids containing an Even Number of Carbon Atoms ( $\text{C}_8$ — $\text{C}_{18}$ ).** D. HOLDE and R. GENTNER (*Ber.*, 1925, **58**, [B], 1418—1424).—The acids are heated with acetic anhydride, and excess of the reagent and acetic acid are removed under diminished pressure. The residue is dissolved in light petroleum and the solution washed with 5—6% hydrated sodium carbonate solution containing an equal volume of alcohol, whereby any free acid is removed. The following constants are recorded : octoic anhydride, m. p.  $-1^\circ$ ,  $d_4^{17.5}$  0.9065,  $d_4^{20}$  0.8649,  $n_D^{17.5}$  1.4358; *decoic anhydride*, m. p.  $23.9^\circ$ ,  $d_4^{20}$  0.8596,  $n_D^{20}$  1.4234; lauric anhydride, m. p.  $41.4^\circ$ ,  $d_4^{20}$  0.8552,  $n_D^{20}$  1.4292; myristic anhydride, m. p.  $53.4^\circ$ ,  $d_4^{20}$  0.8502,  $n_D^{20}$  1.4335; palmitic anhydride, m. p.  $63$ — $64^\circ$ ,  $d_4^{20}$  0.847,  $n_D^{20}$  1.4364; stearic anhydride, m. p.  $71$ — $71.5^\circ$ ,  $d_4^{20}$  0.8368,  $d_4^{17}$  0.8149,  $n_D^{20}$  1.4368. H. W.

**Stability of the Anhydrides of Saturated Fatty Acids towards Atmospheric Moisture and Sodium Carbonate Solution.** D. HOLDE and R. GENTNER (*Ber.*, 1925, **58**, [B], 1424—1428).—Lauric, myristic, and palmitic anhydrides are converted into the corresponding acids to the extent of 1.5—3% when their solutions in light petroleum are shaken for 10 mins. with 5% hydrated sodium carbonate solution to which an equal volume of alcohol has been added; more protracted agitation causes increased hydration. Anhydrides of saturated fatty acids, in contrast to those derived from unsaturated acids, are very stable towards atmospheric moisture. H. W.

**Correction of the M. P. of Cerotic Acid.** A. KIESEL (*Ber.*, 1925, **58**, [B], 1386—1388).—Cerotic acid, m. p.  $85$ — $85.5^\circ$ , is very readily obtained by extracting the dry spores of *Aspidium filix mas* or *Asplenium filix femina* successively with ether and alcohol.

The acid is identical with that derived from beeswax, from which the homogeneous material is isolated with great difficulty.

H. W.

**Oil Film or "Oxyne."** I. A. EIBNER and E. MUNZING (*Chem. Umschau*, 1925, **32**, 153—162, 166—176).—The non-drying properties of the hydroxyglycerides isolated from castor oil are adduced as proof that the oxygenated compounds, so-called "oxyne," present in a drying oil which has become hardened by exposure are not hydroxyglycerides, but complex and hitherto unidentified oxidation or transformation products of peroxyglycerides.

G. L. R.

**Chemical Equilibrium between Lactic Acid and its Anhydrides in Aqueous Solution.** R. DIETZEL and R. KRUG (*Ber.*, 1925, **58**, [B], 1307—1314).—Concentrated lactic acid solution (90%) is converted when heated for 10 hrs. at 120° into lactyl-lactic acid,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , whereas more prolonged heating affords polylactyl-lactic acids of increasing complexity; these are readily reconverted into lactic acid by treatment with warm sodium hydroxide solution. Dilactic acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , m. p. 106°, is prepared in very small yield by treating barium dilactate (obtained by heating barium lactate during 6 hrs. at 180—200°) with the requisite amount of sulphuric acid; it is produced in better yield (10%) by the union of ethyl lactate and ethyl  $\alpha$ -bromopropionate to ethyl dilactate and hydrolysis of the latter. Lactide,  $\text{O}\langle\begin{smallmatrix} \text{CHMe}\cdot\text{CO} \\ \text{CO}\cdot\text{CHMe} \end{smallmatrix}\rangle\text{O}$ , results

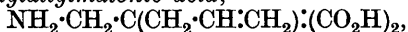
in 90% yield by the distillation of lactic acid at 200°/20 mm. during 15—20 hrs., followed by addition of ignited zinc oxide to the residue and renewed distillation. Formation of the anhydride does not occur directly from lactic acid but by depolymerisation of and loss of water from polylactyl-lactic acids; if the duration of the initial heating in the preparation just described be shortened, *dilactyl-lactic acid* may be isolated from the distillate. The absorption spectra of lactic acid in water and of the anhydrides in chloroform are described. Comparison of them with that of technical lactic acid shows the latter to contain 60% of lactic acid and 30% of the anhydrides, whereas the figures generally adopted (*D.A.B. V.*) are 75% and 15%, respectively. H. W.

**Degradation of *l*- $\beta$ -Hydroxybutyric Acid.** P. KARRER and W. KLARER (*Helv. Chim. Acta*, 1925, **8**, 393—395).—*l*- $\beta$ -Hydroxybutyric acid, obtained from diabetic urine, is converted into *l*- $\beta$ -hydroxybutyramide, m. p. 99—100°,  $[\alpha]_D^{20} - 22.5^\circ$  in methyl alcohol, and thence into *l*- $\alpha$ -amino- $\beta$ -hydroxypropane, isolated as *hydrochloride*,  $[\alpha]_D^{20} - 58^\circ$ , *chloroplatinate*, m. p. 198° (decomp.),  $[\alpha]_D^{20} - 12.2^\circ$  in aqueous solution. The free base has approximate rotation,  $[\alpha]_D^{20} - 25.5^\circ$ . The hydrochloride gives with silver nitrite *l*-propyleneglycol, identical with the compound obtained from the inactive glycol by the action of *Bacterium Termo*. The structural relation of this compound and therefore of *l*- $\beta$ -hydroxybutyric acid to *l*-lactic acid is under investigation. M. J.

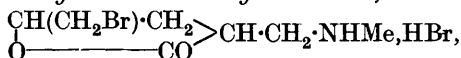


**Lactone Formation and Intramolecular Alkylation with Brominated Aminomethylallylmalonic Acids.** C. MANNICH and K. SUTTER (*Ber.*, 1925, **58**, [B], 1325—1335).—Theoretical considerations lead to the expectation that the products of the action of bromine or hydrogen bromide on aminomethylallylmalonic acids (cf. Mannich and Ganz, A., 1923, i, 19) would be unstable and either pass by intramolecular alkylation into heterocyclic compounds (pyrrolidine- or piperidine-carboxylic acids) or by loss of hydrogen bromide into lactones; the latter reaction is observed.

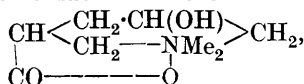
The action of formaldehyde on ammonium hydrogen allylmalonate gives *aminomethylallylmalonic acid*,



m. p. 138° (decomp.). In a similar manner, methylammonium hydrogen allylmalonate affords *methylaminomethylallylmalonic acid*, m. p. 134° (decomp.) [*benzoyl* derivative, m. p. 132° (decomp.)]. An aqueous solution of the acid loses carbon dioxide when shaken with bromine (1 mol.) dissolved in chloroform and yields  $\delta$ -bromo- $\alpha$ -methylaminomethylvalerolactone hydrobromide,

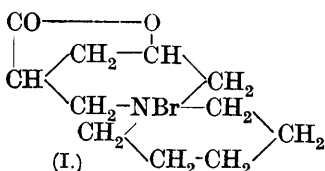


m. p. 135°; the corresponding free base (*benzoyl* derivative, m. p. 82°) is unstable and rapidly passes when dissolved in chloroform into the *hydrobromide* of the lactone of 3-hydroxy-1-methylpiperidine-5-carboxylic acid, decomp. 251°. Similarly, methylamino-methylallylmalonic acid and iodine in chloroform yield  $\delta$ -iodo- $\alpha$ -methylaminomethyl- $\gamma$ -valerolactone hydriodide, m. p. 137° (decomp.). Concentrated hydrobromic acid converts methylaminomethylallylmalonic acid into  $\alpha$ -methylaminomethyl- $\gamma$ -valerolactone- $\alpha$ -carboxylic acid hydrobromide, m. p. 118° (decomp.), which is transformed at 140—150° into  $\alpha$ -methylaminomethyl- $\gamma$ -valerolactone hydrobromide, m. p. 139—140°; the action of sodium hydrogen carbonate on the latter substance gives the corresponding base (*benzoyl* derivative, m. p. 127°).  $\delta$ -Bromo- $\alpha$ -dimethylaminomethyl- $\gamma$ -valerolactone hydrobromide, m. p. 196° (slight decomp.), obtained from dimethylaminomethylallylmalonic acid (Mannich and Ganz, *loc. cit.*) and bromine, is converted by potassium carbonate into the free lactone, which, in chloroform solution, undergoes rapid isomerisation to the lactone of 5-carboxy-3-hydroxydimethylpiperidinium bromide, decomp. 201°; the latter compound is converted by moist silver oxide into the betaine derivative,



decomp. 260—285°. Dimethylaminomethylallylmalonic acid and hydrobromic acid afford  $\alpha$ -dimethylaminomethyl- $\gamma$ -valerolactone hydrobromide, m. p. about 208°, which with potassium carbonate gives the free base. The corresponding *methiodide*, m. p. 224° (decomp.), is readily obtained from it or from  $\alpha$ -methylaminomethyl- $\gamma$ -valerolactone. *Piperidinomethylallylmalonic acid*, decomp. 122°,

obtained from piperidinium hydrogen allylmalonate and formaldehyde, is transformed by bromine into  $\delta$ -bromo- $\alpha$ -piperidinomethyl- $\gamma$ -valerolactone hydrobromide, m. p. 206° (decomp.), from which  $\delta$ -bromo- $\alpha$ -piperidinomethyl- $\gamma$ -valerolactone, m. p. 56°, is obtained by cautious treatment with potassium carbonate. In warm methyl-alcoholic solution the base passes into the lactone of 5-carboxy-3-hydroxy-spiro-di-1:1'-piperidinium bromide, (I), decomp. 218°. Piperidinomethylallylmalonate acid and hydrobromic acid afford  $\alpha$ -piperidinomethyl- $\gamma$ -valerolactone hydrobromide, m. p. 192°; the corresponding base gives a methiodide, m. p. 146°.



H. W.

**Transformation of Maleic Esters into Fumaric Esters.** H. MEERWEIN and J. WEBER (*Ber.*, 1925, **58**, [B], 1266—1267).—The ability of catalysts to cause the transformation of stereoisomeric, ethylenic compounds appears to depend on their power of activating the double bond. In such a condition of the molecule addition may occur or, where this is impossible, other changes such as isomerisation, polymerisation, etc., may take place. It is therefore to be expected that all substances which have the power of addition at the double bond will also catalytically accelerate the transformation of stereoisomeric ethylenic compounds to a greater or less degree. In conformity with this theory, it is found that potassium, which has a known power of addition at the ethylenic linking, effects the transformation of methyl maleate into methyl fumarate in the presence of dry ether; the potassium does not pass into solution and is not visibly affected.

H. W.

**Derivatives of Citraconic Acid. I. Synthesis of Methyltartaric Acid and Decomposition of Dihydroxymaleic Acid.** W. F. GOEBEL (*J. Amer. Chem. Soc.*, 1925, **47**, 1990—1998).—Methyltartaric acid,  $\text{CO}_2\text{H}\cdot\text{CMe}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , m. p. 100° (decomp.) (Carius, *Annalen*, 1863, **126**, 205), is obtained by heating oxycitraconic acid with dilute sulphuric acid at 100°. It is oxidised by hydrogen peroxide in presence of ferrous sulphate in aqueous solution at  $-18^\circ$ , probably to *ketohydroxymethylsuccinic acid*, which, when warmed with water, loses carbon dioxide with formation of lactaldehyde, whilst treatment with barium hydroxide affords  $\alpha$ -keto- $\beta$ -hydroxybutyric acid, identified by its conversion, with phenylhydrazine, into the phenylosazone of *diketobutyric acid*, m. p. 210°. It is suggested that the conversion of dihydroxymaleic acid into glycolaldehyde by loss of carbon dioxide (cf. Fenton, T., 1895, **67**, 774; 1896, **69**, 546) proceeds through its tautomeride,  $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , which decomposes analogously to the above ketohydroxymethylsuccinic acid.

F. G. W.

**New Derivatives of Pentadecaldehyde.** S. LANDA (*Chem. Listy*, 1925, **19**, 264—267).—Pentadecaldehyde gives the following

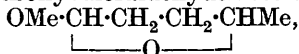
derivatives: *thiosemicarbazone*, m. p. 95—96.5°; *semioxamazone*, m. p. 200—201°; *phenylhydrazone* (very unstable); *p-bromophenylhydrazone*, m. p. 49—50°; *phenylmethylhydrazone*, m. p. 35°; *phenylbenzylhydrazone*, m. p. 51.5°; *p-nitrophenylhydrazone*, m. p. 94—95°; *2:4-dinitrophenylhydrazone*, m. p. 107.5°; *pentadecylidenebenzoylhydrazine*, m. p. 81°; *pentadecylidene-m-nitrobenzoylhydrazine*, m. p. 102°; and (by reaction with methyl phenyldithiocarbazinate) *5-methylthiol-3-phenyl-2-tetradecyl-2:3-dihydro-1:3:4-thiodiazole*, m. p. 70—71°. B. F.

**Hydroxyaldehydes. VIII.** B. HELFERICH and F. A. FRIES (*Ber.*, 1925, 58, [B], 1246—1251; cf. this vol., i, 7).— $\beta$ -Methyl- $\Delta^8$ -hepten- $\zeta$ -ol is converted by benzoyl chloride in the presence of pyridine at 0° into the corresponding *benzoate*, b. p. 159—161°/18 mm.,  $d_4^{79}$  0.9797,  $n_D^{80}$  1.5023, which is transformed by ozone and subsequent decomposition of the ozonide in the usual manner into  $\gamma$ -benzoxylvaleraldehyde, b. p. 133—136°/4 mm.,  $d_4^{81}$  1.0986,  $n_D^{81}$  1.5110, which does not yield a crystalline phenylhydrazone or *p*-bromophenylhydrazone, but is converted by magnesium ethyl bromide into  $\zeta$ -benzoxyl-*n*-heptan- $\gamma$ -ol, b. p. 133—136°/3—4 mm.  $\gamma$ -Benzoxylvaleraldehydedimethylacetal, b. p. 157—163°/8 mm.,  $d_4^{82}$  1.0567,  $n_D^{82}$  1.4900, prepared by the action of methyl-alcoholic hydrogen chloride (1%) on the benzoxyaldehyde, is hydrolysed by potassium hydroxide dissolved in methyl alcohol to  $\gamma$ -hydroxyvaleraldehydedimethylacetal, b. p. 70°/7 mm.,  $d_4^{82}$  0.9760,  $n_D^{83}$  1.4278, which can be distilled unchanged under atmospheric pressure in the presence of barium oxide, but yields the corresponding semi-acetal in the absence of this substance.

To emphasise the relationship of the *cyclo* forms of carbonyl compounds, it is proposed to designate them by a common name, the term "lactoles" being chosen by reason of the similarity to the lactones. Hydroxyaldehydes and hydroxyketones thus give rise to aldo- and keto-lactoles, the suffix lactole being added to the name of the aldehyde or ketone. *o*-Alkyl derivatives of the lactoles are termed lactolides to express their relationship to the glucosides. The following examples are typical:  $\text{OH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}$ ,

$\text{O}$   
 $\text{O} \begin{array}{c} \diagup \quad \diagdown \\ \text{CH} \quad \text{CH} \end{array}$

$\gamma$ -valerolactole ( $\gamma$ -hydroxyvaleraldehydelactole);



$\text{O}$   
 $\text{O} \begin{array}{c} \diagup \quad \diagdown \\ \text{CH} \quad \text{CH} \end{array}$

$\gamma$ -valeromethyl-lactolide ( $\gamma$ -hydroxyvaleraldehydelactole methyl ether);  $\text{AcO}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}$ ,  $\gamma$ -valerolactole acetate. The possibility of extending the nomenclature to the simpler sugars [e.g., dextroselactole ( $\alpha\delta$ )], is discussed. H. W.

**Components of Acetone Oil.** H. PRINGSHEIM and J. BONDI.—(See i, 1072.)

**Simplified Method for the Preparation of Dimethylglyoxime.** W. L. SEMON and V. R. DAMERELL (*J. Amer. Chem. Soc.*, 1925, 47, 2033—2039).—The influence of various factors on

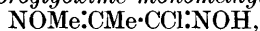
the yields of diacetylmonoxime and dimethylglyoxime in the preparation of these substances from methyl ethyl ketone was investigated, and the following optimum procedures were established. Sodium nitrite (95%, 650 g.) is dissolved in water, 90% alcohol (285 c.c.) added, and the whole diluted with water to 2.5 litres. A mixture of sulphuric acid ( $d$  1.836, 255 c.c.) and 90% alcohol (285 c.c.) is also diluted with water to 2.5 litres. The gaseous ethyl nitrite generated by allowing the latter solution to flow into the former is passed into methyl ethyl ketone (775 c.c.) which has been dried over copper sulphate and freshly distilled, and to which has been added concentrated hydrochloric acid (40 c.c.), the temperature being maintained at 40–55°. The alcohol produced in the reaction is then removed by distilling until the temperature of the liquid reaches 90°. If diacetylmonoxime is required, the residue is then distilled in superheated steam, when the monoxime is completely driven over in the first 5 litres of distillate, from which it is separated by filtration after cooling to 0°. For the preparation of dimethylglyoxime, the distillation with steam is omitted and the filtered residue from the alcohol distillation mixed at 70° with the sodium hydroxylaminesulphonate solution prepared as described below, the mixture being kept warm and occasionally stirred during several hours. The dimethylglyoxime is filtered after cooling and washed free from sulphate. The yield of pure white product, m. p. 235–240°, is 575 g.

The sodium hydroxylaminesulphonate is prepared by stirring a suspension of technical sodium bisulphite (about 1775 g.), containing 1100 g. of available sulphur dioxide, in water (750 c.c.), into a mixture of sodium nitrite (95%, 594 g.) and crushed ice (5 kg.). Glacial acetic acid (150 c.c.) is then added below the surface of the mixture, with stirring, followed by a mixture of concentrated hydrochloric acid (550 c.c.) and ice (400 g.). The mixture is kept below 0° by the addition of ice until reaction is complete, when it is filtered and used as above. F. G. W.

**Dioximes. XXV.** L. AVOGADRO and G. TAVOLA (*Gazzetta*, 1925, **55**, 323–330).—*Methylglyoxime dimethyl ether*,



prepared by the action of methyl sulphate on methylglyoxime in 20% sodium hydroxide solution, has b. p. 145.5–146.5°/738.7 mm. The *monomethyl ether*,  $\text{NOMe}:\text{CMe}:\text{CH}:\text{NOH}$ , m. p. 98–99°, similarly obtained, exhibits normal cryoscopic behaviour in acetic acid, and yields methylglyoxal phenylosazone when heated with phenylhydrazine in presence of acetic acid; its *acetyl* derivative has m. p. 43°. *Methylchloroglyoxime monomethyl ether*,

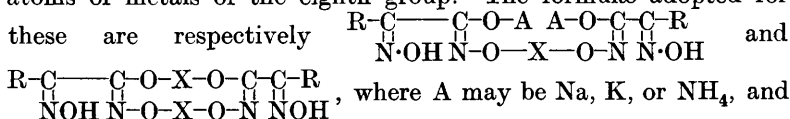


prepared by the action of chlorine on a chloroform solution of methylglyoxime monomethyl ether, has m. p. 49°. Aminomethylglyoxime yields a *monomethyl ether*,  $\text{NOMe}:\text{CMe}:\text{C}(\text{NH}_2):\text{NOH}$ , m. p. 99° (*benzoyl* derivative, m. p. 134–135°), and a *dimethyl ether*, b. p. 192°/738.7 mm.  $\beta$ -*Phenylmethylglyoxime monomethyl ether*,  $\text{NOMe}:\text{CMe}:\text{CPh}:\text{NOH}$ , obtained by the action of phenyl-

diazonium chloride on methylglyoxime monomethyl ether dissolved in 10% sodium hydroxide solution, has m. p. 99°, and forms an *acetyl* compound, m. p. 63°, and a *benzoyl* compound, m. p. 113—114°. The *dimethyl ether*, prepared by the action of methyl sulphate on either the monomethyl ether or  $\beta$ -phenylmethylglyoxime dissolved in 20% sodium hydroxide solution, has m. p. 84°.

*Dimethylglyoxime dimethyl ether*,  $C_6H_{12}O_2N_2$ , m. p. 44°, yields diacetylphenylosazone when heated with alcoholic phenylhydrazine solution. *Diaminoglyoxime dimethyl ether*,  $C_4H_{10}O_2N_2$ , m. p. 144°, yields a *tetra-acetyl* derivative,  $NAc_2 \cdot C(NOMe) \cdot C(NOMe) \cdot NAc_2$ , m. p. 205°. T. H. P.

**Dioximes. XXVI.** G. PONZIO and G. RUGGERI (*Gazzetta*, 1925, 55, 453—462).—Theoretical yields of hydroxyglyoxime derivatives are obtainable by the action of hydroxylamine on esters of the  $\alpha$ -oximino-acids. Thus from the ethyl esters of oximino-acetic, -propionic, -butyric, and -phenylacetic acids, the corresponding monohydroxyglyoxime, and methyl-, ethyl-, and phenyl-hydroxyglyoximes may be obtained. These can form two series of internally complex salts, the one containing an atom each of a metal of the eighth group and an alkali metal, and the other containing two atoms of metals of the eighth group. The formulæ adopted for these are respectively



where A may be Na, K, or  $NH_4$ , and X may be Ni, Cu, or Co. Salts of the first type crystallise well. They are soluble in water, behaving cryoscopically as electrolytes; the heavy metal atom is present in the form of a stable complex anion. Salts of the second type behave as colloids. The nickel salt of methylhydroxyglyoxime gelatinises on boiling with sodium chloride. The gel thus formed redissolves in water, but gelation is irreversible if the gel is formed by boiling with dilute acetic acid. The following compounds are described. *Potassium* salt of *methylhydroxyglyoxime* explodes violently on heating at 115°. *Monohydrate* of the *sodium* salt. *Nickel dimethylhydroxyglyoxime nickelate*,  $[C_6H_8O_6N_4Ni]Ni \cdot 4H_2O$ , loses  $3H_2O$  at 100°. The corresponding *sodium* salt,  $[C_6H_8O_6N_4Ni]Na_2 \cdot 12H_2O$ , separates from dilute solutions as blood-red prisms: from stronger solutions the *tetrahydrate* crystallises in orange-red needles. By heating either to 100° the yellowish-orange *monohydrate* is formed. The *potassium* salt separates from cold water as the trihydrate, and the *ammonium* salt as a tetrahydrate. *Sodium dimethylhydroxyglyoxime cuprate*,  $[C_6H_8O_6N_4Cu]Na_2 \cdot 7H_2O$ . The analogous *ammonium* salt crystallises as tetrahydrate. Both salt and solution evolve ammonia on heating. *Ammonium dimethylhydroxyglyoxime cobaltate*,  $[C_6H_8N_4O_6Co](NH_4)_2 \cdot 4H_2O$ .

F. G. T.

**Induced Oxidation of Carbohydrates.** C. C. PALIT and N. R. DHAR (*J. Physical Chem.*, 1925, 29, 799—807).—The oxidation

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by air of carbohydrates in alkaline solution has been studied in the presence of freshly-precipitated cerous or ferrous hydroxide. Oxidation occurred in the cases of the eight carbohydrates examined, starch being the most and sucrose the least readily oxidised. During the reaction the cerous oxide is almost entirely oxidised to ceric oxide and the carbohydrate oxidation is regarded as induced and not as catalysed. The amount of oxidation increases with the concentration of the alkali and an explanation of the internal use of alkali and alkaline carbonates in diabetes is suggested based on this fact. The oxidation of inorganic salts by this method has also been studied. Oxalates and nitrites were not oxidised.

F. G. S.

### Condensation of Monosaccharides by Dilute Mineral Acid.

P. A. LEVENE and R. ULPTS (*J. Biol. Chem.*, 1925, **64**, 475—483).—In attempting to crystallise chitose the solution obtained after deamination of chitosamine was evaporated in a vacuum and the residue further evaporated repeatedly with alcohol; the product was then found to be not chitose but an insoluble condensation product, which, on boiling with 2% sulphuric acid, readily gave chitose; chondrose behaved similarly, and it was then found that, on evaporating solutions of dextrose, mannose, and lyxose in a vacuum in presence of small amounts of hydrochloric acid, condensation products of a similar nature were obtained. The products appear to be of the nature of polysaccharides (disaccharides in the case of dextrose, mannose, and lyxose). The specific rotations of the condensation products of the simple sugars were higher than those of the equilibrium forms of the parent sugars, whilst the opposite was the case with the  $\beta$ -anhydro-sugars, chitose and chondrose. The condensation products of the simple sugars were more soluble in water and more stable to hydrolysis than those of chitose and chondrose. The product from chitose turned yellow on heating to 150° but was still solid at 222°; it was very insoluble in all solvents; it was completely hydrolysed to chitose on boiling for 90 mins. with 2% sulphuric acid; the product from chondrose had a molecular weight of 351; its reducing power was less than 25% of that of chondrose itself. The product from dextrose has  $[\alpha]_D^{20} +95^\circ$ , molecular weight 309; that from mannose  $[\alpha]_D^{26} +59.5^\circ$ , molecular weight 378; that from lyxose  $[\alpha]_D^{25} +41.5^\circ$ , molecular weight 338; the last three compounds required 7—16 hrs. heating with 2% sulphuric acid for complete hydrolysis.

C. R. H.

**Dextrose and Lævulose in Alkaline and Phosphate-containing Solutions.** H. VON EULER and R. NILSSON (*Z. physiol. Chem.*, 1925, **145**, 184—193).—Polarimetric and freezing-point determinations of solutions of various monosaccharides in acid and alkaline solution with and without addition of phosphate indicate that a reaction occurs between the sugar and phosphate. With lævulose the effect increases from  $p_H$  4.5 upwards and is associated with an increase of the rotation. The effect with lævulose is much greater than with dextrose.

P. W. C.

**Monoacetonegalactose.** [Galactose *iso*Propylidene Ether.] P. A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1925, **64**, 473—474).—From the syrup obtained in the preparation of galactose diisopropylidene ether by the method of Svanberg and Sjöberg (A., 1923, i, 540) there separated, on long keeping, crystals which proved to be *galactose isopropylidene ether*, m. p. 157°,  $[\alpha]_D^{20} -10.9^\circ$ .  
C. R. H.

**Relations between Rotatory Power and Structure in the Sugar Group. X. Chloro-, Bromo-, and Iodo-acetyl Derivatives of Lactose.** C. S. HUDSON and A. KUNZ (*J. Amer. Chem. Soc.*, 1925, **47**, 2052—2055).— $\alpha$ -Chloroacetyl-lactose, obtained by the action of phosphorus pentachloride on lactose octa-acetate in chloroform in presence of aluminium chloride, has m. p. 120—121° (decomp.),  $[\alpha]_D^{20-25} +83.9^\circ$  in chloroform,  $[\alpha]_D^{23} +68.2^\circ$  in benzene (cf. Bodart, A., 1902, i, 347; Fischer and Armstrong, A., 1902, i, 263). Its formation by the above method is accompanied by that of a chloro compound, m. p. 160°,  $[\alpha]_D^{20} +71.7^\circ$  in chloroform.  $\alpha$ -Bromoacetyl-lactose (cf. Fischer, A., 1910, i, 716) has m. p. 145° (decomp.),  $[\alpha]_D^{23} +108.7^\circ$  in chloroform (cf. Ditmar, A., 1903, i, 151).  $\alpha$ -Iodoacetyl-lactose (cf. Mills, A., 1913, i, 707) has m. p. 145° (decomp.),  $[\alpha]_D^{23} +136.9^\circ$  in chloroform. The above observed specific rotations are in satisfactory agreement with those calculated (cf. Hudson, A., 1924, i, 371; Hudson and Phelps, this vol., i, 8). The value  $[\alpha]_D +42^\circ$ , in chloroform, is predicted for  $\alpha$ -fluoroacetyl-lactose.  
F. G. W.

**The  $\gamma$ -Galactan Present in the Seeds of *Cicer arietinum* and its Molecular Constitution.** N. CASTORO (*Annali Chim. Appl.*, 1925, **15**, 146—155).—This galactan (A., 1909, ii, 754), to which the name *cicerose* is now given, is a tetrasaccharide,  $C_{24}H_{42}O_{21}$ , yielding on hydrolysis 2 mols. of *d*-galactose, 1 mol. of dextrose, and 1 mol. of lævulose; when dried at 102° in a current of hydrogen, it has  $[\alpha]_D +146.8^\circ$ , and when kept for some days in a desiccator over sulphuric acid  $[\alpha]_D +132.2^\circ$ .  
T. H. P.

**Starch. XIII.  $\alpha$ - and  $\beta$ -Amylases.** H. PRINGSHEIM and J. LEIBOWITZ (*Ber.*, 1925, **58**, [B], 1262—1265).—Evidence in favour of Kuhn's classification (A., 1924, i, 1170) of the amylolytic ferments into  $\alpha$ - and  $\beta$ -amylases is deduced from the observation that purified amylobiose is hydrolysed by malt extract, but not by animal amylases, whereas dihexosan is quantitatively transformed into maltose by pancreatin. Pringsheim's amylobiase is therefore identical with Kuhn's  $\beta$ -amylase (cf. Oppenheimer, "Die Fermente und ihre Wirkungen," 1925, p. 650). A logical deduction from these relationships is the convertibility of starch into dextrose by the combined action of  $\alpha$ - and  $\beta$ -amylases. Difficulties in the experimental realisation lie in the different optimum conditions of the ferments and the presence in the pancreatin preparations of a feebly active maltase. Nevertheless, an extensive and sometimes quantitative formation of dextrose is observed which cannot be attributed entirely to the feeble pancreas amylase.

Use of a maltase-free pancreatin preparation with a feebly active malt extract gives dextrose in poorer yield.

The hydrolysis of starch by emulsin (Kuhn, A., 1924, i, 692) depends on an amylase present in the mixture of ferments and not on  $\beta$ -glucosidase. The action of malt extract and emulsin on starch leads to a definite but not very extensive production of dextrose even when both ferments are completely free from maltase. The combination of malt and emulsin is therefore analogous to that of malt and pancreatin. The starch-splitting principle of emulsin is therefore probably a very feeble  $\alpha$ -amylase, the presence of which in a plant product is remarkable. The inactivity towards amylobiose of "biolase," a maltase-free, vegetable amylase of unknown origin, indicates that there is no sharp distribution of the  $\alpha$ - and  $\beta$ -amylases between the animal and vegetable kingdoms.

H. W.

**Dehydration of Cellulose Nitrate by Alcohol.** K. ATSUKI (*J. Fac. Eng. Tokyo*, 1925, **16**, 117—133).—After washing, boiling, and pulping, the cellulose nitrate is drained in centrifugals until it contains 26—30% of water, and this water is removed by displacement with 95% alcohol. Generally, 3 parts by weight of moist cellulose nitrate are treated with 2 parts of alcohol and this liquid is forced through the mass by hydraulic pressure of 175 atm. Four consecutive treatments suffice for complete displacement, so that the alcohol comes out at substantially 95% strength. In practice, however, the first two displacements are made with weaker alcohols from previous batches, and the third with fresh 95% alcohol, whereby the final effluent has an alcoholic strength of 90—92%. This is sufficient for celluloid manufacture, and abnormal losses of cellulose nitrate by solubility are avoided. The solubility of cellulose nitrate in alcohol of a given strength is much greater in the case of a pulped and disintegrated fibre and under heavy pressures than in the case of the entire fibre without compression. The soluble cellulose nitrate which is removed during the process of dehydration with alcohol is not less stable than the bulk, and the claim that dehydration improves stability by removal of less stable nitrates cannot be substantiated. The soluble cellulose nitrate, however, contains a slightly lower percentage of nitrogen and possesses a very much lower viscosity than the insoluble bulk. It is therefore to be regarded as a lower nitrate of a chemically degraded cellulose, and its removal may be held to improve the mechanical quality of the celluloid produced.

J. F. B.

**Swelling and Dispersion of Cellulose Nitrate in Ethyl Alcohol.** K. ATSUKI (*J. Fac. Eng. Tokyo*, 1925, **16**, 111—116).—The swelling and gelatinisation of the nitrated fibre in 99.2—99.8% ethyl alcohol is not uniform, but varies according to the different structures of different parts of the fibre. Nitrated cotton fibre swells to 5—10 times its original diameter, presenting a cylinder with spiral markings on its surface. The central canal does not swell, but remains as a thread. The cuticular tissue contributing to the peculiar surface irregularity swells more slowly, but finally disperses if



the solvent is powerful. The nitrated wood fibre swells almost uniformly except at the pitted portions of the tracheids, the pitted pores swelling to a series of spherical enlargements as compared with the smaller diameter of the non-pitted swollen fibre. The bamboo fibre swells and splits up into a number of consecutive separated cylinders strung together by the non-swollen central canal. The solubility of cellulose nitrate in ethyl alcohol increases with lower degrees of nitration within a limited range; it also increases with increase in the degree of chemical modification of the cellulose. Low degrees of nitration and high degrees of chemical modification are both conditioned by more aqueous nitrating mixtures, and it is difficult to differentiate the influence of each factor. Increased solubility is induced by increased strength of alcohol.

J. F. B.

**Cellulose Fibre.** R. O. HERZOG (*Ber.*, 1925, 58, [B], 1254—1262).—It is probable that the orientation of crystallites in the fibre is to be regarded as an effect of growth caused by the influence of tension. In the case of artificial fibres, it is observed that the orientation is well marked in "cuprammonium" silk and becomes increasingly definite as the tension is prolonged. On the other hand, it is but little evident in "viscose" silk, in which the rapidity of the process is governed by ionic reactions. The natural fibres are more complicated in structure, but consist primarily of an isotropic substance in which the crystalline material is formed either by access of the crystallising compound or by chemical transformation of a compound already present. In certain cases (cautious nitration and acetylation of cellulose), topochemical change occurs without alteration of the cellulose mass in the crystallite or micellæ. The processes of deformation caused by tension or pressure can be explained by regarding the fibre as a two-phase system consisting of crystallite and inter-crystallite material.

H. W.

**Hydrolysis of Solutions of Magnesium Chloride.** C. G. SCHWALBE and R. SCHEPP (*Ber.*, 1925, 58, [B], 1354—1355; cf. A., 1924, i, 377, 715).—The hydrolysis of aqueous solutions of magnesium chloride is facilitated by the presence of textile fibres. The adsorptive power of the latter for hydrochloric acid is, however, so great that the production of the acid can be detected only after complete destruction of the fibre by incipient carbonisation.

H. W.

**Constituents of Lignites. III.** R. CIUSA and A. GALIZZI (*Annali Chim. Appl.*, 1925, 15, 209—214).—The ethereal extract from Fognano lignite was found to contain  $C_{15}H_{20}$  (simonellite) and three optically active liquids,  $C_{15}H_{26}$ ,  $C_{15}H_{28}$ , and  $C_{22}H_{34}$ , the two last proving on bromination to be mixtures of a saturated and an unsaturated isomeride. Steam distillation of the same lignite yields a further compound,  $C_{15}H_{24}$ .

G. L. R.

**N-Carboxylic Esters of Asymmetrically Substituted Ethylenediamines.** M. HARTMANN and H. KÄGI (U.S. Pat. 1527868).—N-Carboxylic esters of asymmetrically substituted

ethylenediamines are prepared by interaction of a haloformic ester and the diamine. *Benzyl diethylaminoethylcarbamate*, b. p.  $127^{\circ}/0.015$  mm. (*hydrochloride*, m. p.  $105-106^{\circ}$ ). *Phenyl ethylpiperidinoethylcarbamate*, b. p.  $152^{\circ}/0.015$  mm. (*hydrochloride*). *Benzyl dimethylaminoethylcarbamate (hydrochloride)*, liquids. *Menthyl diethylaminoethylcarbamate*, b. p.  $142^{\circ}/0.015$  mm. (*hydrochloride*). *Hexahydrobenzyl diethylaminoethylcarbamate*, b. p.  $150^{\circ}/0.05$  mm. *Phenetyl diethylaminoethylcarbamate*, b. p.  $147^{\circ}/0.025$  mm. (*hydrochloride*). *Phenylethyl diethylaminoethyliminodicarboxylate*, b. p.  $200-202^{\circ}/0.05$  mm.

CHEMICAL ABSTRACTS.

**Compounds of Formaldehyde with Glycine.** M. BERGMANN and H. ENSSLIN (*Z. physiol. Chem.*, 1925, **145**, 194—201).—By treatment of the copper salt of glycine with 30% formaldehyde at  $50-52^{\circ}$  for 15 hrs., the copper salt of triformalglycine  $[(CH_2)_3O_2N \cdot CH_2 \cdot CO_2]_2Cu$  is obtained. Considerable evidence is brought to show that this is identical with Krause's copper hydroxytrimethyleneglycine (A., 1918, i, 156). Similarly, the barium salts of the so-called hydroxytrimethyleneglycine and of *N*-hydroxymethylglycine are prepared and shown to be identical with the barium salt of methyleneglycine. The formation of hydroxytrimethyleneglycine is discredited.

P. W. C.

**Configuration of Naturally-occurring *l*-Leucine.** P. KARRER, W. JÄGGI, and T. TAKAHASHI (*Helv. Chim. Acta*, 1925, **8**, 360—364).—By the action of magnesium methyl iodide, the ethyl ester of *N*-benzoyl-*l*-leucine is converted into *l*- $\gamma$ -benzamido- $\beta\epsilon$ -dimethylhexan- $\beta$ -ol, m. p.  $113^{\circ}$ ,  $[\alpha]_D^{18} -40.76^{\circ}$  in alcohol, and that of *N*-benzoyl-*l*-aspartic acid into *l*- $\gamma$ -benzamido- $\beta\epsilon$ -dimethylhexan- $\beta\epsilon$ -diol, m. p.  $148^{\circ}$ ,  $[\alpha]_D^{20} -16.4^{\circ}$  (water). The latter loses water on treatment with thionyl chloride or formic acid, giving *l*- $\gamma$ -benzamido- $\beta\epsilon$ -dimethylhexen- $\beta$ -ol, m. p.  $134^{\circ}$ , b. p.  $145-150^{\circ}/1$  mm.,  $[\alpha]_D -36.3^{\circ}$  (alcohol), differing structurally from the *l*-leucine derivative only in having an ethylenic linking. The similarity in rotation is in conformity with the similarity in structure. *l*-Leucine must therefore have the same configuration as *l*-asparagine, *l*-aspartic acid, *l*-cystine, *l*-serine, *d*-alanine, and *l*-histidine (cf. A., 1924, i, 151).

Attempts to bring about catalytic reduction of the hexene to the *l*-leucine derivative were unsuccessful.

M. J.

**Ring Formation from Asparagine. Derivatives of Aminosuccinimide.** E. CHERBULIEZ and I.-F. CHAMBERS (*Helv. Chim. Acta*, 1925, **8**, 395—403).—Piperazine ring formation (Fischer and Königs, A., 1905, i, 31) and pyrimidine ring formation (A., 1922, i, 581) from asparagine are already known. A third type is now described. When asparagine is heated, straight-chain derivatives are formed by successive eliminations of water from the carboxyl group of one molecule and the amino group of the next molecule. This type of condensation is excluded in the acylasparagines, where simple intramolecular dehydration yields aminosuccinimide derivatives. A certain amount of decomposition, probably due to elimination of the amino group, occurs simultaneously and is more

pronounced with low molecular weight of the acyl substituent. With benzoylasparagine, this effect is negligible, with the acetyl compound it is marked, whilst with the formyl derivative it is predominant, and ammonium formate and other decomposition products alone are obtained.

Benzoylasparagine, heated in a vacuum at 170–200° for  $\frac{1}{2}$  hr., yields *benzamidossuccinimide*, m. p. 225–226°, optically inactive, and a small quantity of a *compound*, m. p. 245–250° (*benzoylaspartdiamide?*). *Benzamidossuccinimide* yields an amorphous, very hygroscopic *sodium* derivative, subliming to an acid ammonium benzoate. With formaldehyde, it gives *N-hydroxymethylbenzamidossuccinimide*, m. p. 155–159°, converted by phosphorus pentachloride into *N-chloromethylbenzamidossuccinimide*, m. p. 155–157°. It is hydrolysed by barium hydroxide or by alkaline hypobromite solution in the cold, giving an inactive benzoylasparagine. Distillation in a vacuum of potassium benzoylasparagine yields only benzamide, whereas dihydropyrimidine formation would be unaffected by this replacement. *Acetamidossuccinimide*, m. p. 170–171°, resembles the benzoyl derivative in its reactions. *Formylasparagine*, m. p. 168–169°, is associated with 1H<sub>2</sub>O, which cannot be driven off without decomposition. The authors consider it unlikely that the compound is a simple additive compound of asparagine and formic acid. Attempts to prepare aminopyrroles from the amino-succinimide derivatives are so far unsuccessful. M. J.

**Carbimides. I. Preparation of Aliphatic Carbimides.** K. N. SLOTTA and L. LORENZ (*Ber.*, 1925, 58, [B], 1320–1323).—The low yields of alkylcarbimides obtained by the interaction of potassium alkyl sulphates and potassium cyanate are due to sudden, uncontrollable rises in temperature during the reaction, whereby the alkylcarbimides become polymerised. Much better results are obtained by heating mixtures of alkyl sulphates with potassium cyanate and anhydrous sodium carbonate, the yields of methylcarbimide and ethylcarbimide being 50–55% and 95%, respectively. Alkyl *p*-toluenesulphonates may replace alkyl sulphates if the latter are difficultly accessible, but the yields do not appear to be so good. H. W.

**Investigations on Guanidine.** G. PELLIZZARI (*Mem. R. Accad. Naz. Lincei*, 1924, [v], 14, 707–776).—A summary of the author's investigations on guanidine, published since 1891 in 34 papers. T. H. P.

**Colorimetric Method for the Determination of Guanidine and Methylguanidine. II. Distinction between Guanidine and its Methyl Derivatives.** H. R. MARSTON (*Austral. J. Exp. Biol. Med. Sci.*, 1925, 2, 57–59).—The reagent previously described (this vol., i, 97) gives a reddish-purple colour with methylguanidine and with *as*-dimethylguanidine, whereas guanidine itself gives an orange colour. The reagent can be used for the determination of guanidine or its methyl derivative in tissue fluids provided that uric acid, ammonia, and reducing substances generally are first removed. C. P. S.

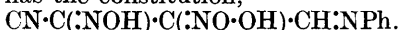
**Some Ammono-carbonic Acids and their Reactions in Liquid Ammonia.** W. L. BURDICK (*J. Amer. Chem. Soc.*, 1925, 47, 1485—1490; cf. Franklin, A., 1922, i, 440; Madelung and Kern, A., 1922, i, 438).—Aqueous solutions of *dicyanoimide* are conveniently prepared by treating aqueous suspensions of the silver salt with hydrogen sulphide. White needles of the *monohydrate*,  $C_2HN_3 \cdot H_2O$ , are deposited on concentration of the filtered solution by evaporation under reduced pressure. Sodium dicyanoimide as prepared by the method of Madelung and Kern (*loc. cit.*) may be purified by recrystallisation from liquid ammonia. *Mercuric dicyanoimide* is precipitated on mixing solutions of mercuric nitrate and sodium dicyanoimide.

*Tricyanomelamine* is prepared by the same general method as dicyanoimide, the *trihydrate*,  $C_6H_3N_9 \cdot 3H_2O$ , separating from the concentrated solution. *Sodium tricyanomelamine* is obtained by fusion of dicyanodiamide and sodium cyanoamide in a gold crucible. The mass is extracted with boiling water, and white needles of  $Na_3C_6N_9 \cdot 3H_2O$  separate out from the cooled solution. *Crystals* of  $Ag_3C_6N_9 \cdot 3NH_3$  (colourless),  $Cu_3(C_6N_9)_2 \cdot 12NH_3$  (blue), and  $Pb_3(C_6N_9)_2 \cdot 6NH_3$  (white) separate on mixing solutions of sodium tricyanomelamine and the corresponding nitrates in liquid ammonia.

Concentration of the clear solution obtained after treatment of an aqueous suspension of silver melonate with hydrogen sulphide gives a white, amorphous powder of hydrated hydromelononic acid,  $C_9H_3N_{13} \cdot 2H_2O$ . *Sodium melonate* is obtained by addition of fused antimony trichloride to fused sodium thiocyanate. The cooled mass is extracted with hot water and the solution freed from sulphides by means of lead hydroxide. On cooling, crystals of  $Na_3C_9N_{13} \cdot 5H_2O$  separate. Colourless crystals of the *silver salt*,  $Ag_3C_9N_{13} \cdot 6NH_3$ , are deposited on mixing solutions of sodium melonate and silver nitrate in liquid ammonia. J. S. C.

**Fulminic Acid. VII. Polymerisation of the Fulminic Acids. *isoCyanilic* and *Erythrocyanic* Acids.** H. WIELAND [with A. BAUMANN, C. REISENEGGER, W. SCHERER, J. THIELE, J. WILL, H. HAUSSMANN, and W. FRANK] (*Annalen*, 1925, 444, 7—40; cf. A., 1912, i, 838).—*isoCyanilic* acid obtained in minute quantities by Scholvien (cf. A., 1886, 137) has now been prepared in considerable amount by treating a strong aqueous solution of sodium fulminate, cooled to  $-18^\circ$ , with concentrated nitric acid, the main reaction product being metafulminuric acid. Contrary to the assumption of Scholvien, analyses of the crystalline *silver salt*,  $C_4H_3O_4N_4Ag$ , and *potassium hydrogen salt* show the acid to be tetrameric. With phenolphthalein as indicator, the titration values are not quite sharp for a monobasic acid. The *dibenzoyl derivative*,  $C_{18}H_{12}O_6N_4$ , has m. p.  $181^\circ$  (decomp.), the *diacetyl* compound has m. p.  $134^\circ$ . The decomposition products formed on treatment with acids, consisting of ammonia, hydroxylamine, hydrogen cyanide, and oxalic acid, appear to give no clue to its constitution. Treatment with excess of cold concentrated ammonia converts *iso-*

cyanilic acid into a yellow salt from which *hydratoisocyanilic acid*,  $C_4H_6O_5N_4$ , m. p.  $187^\circ$  (decomp.), is obtained. This acid is like the parent acid in giving deep red salts with alkalis, but differs in giving a brownish-red coloration with ferric chloride. Warming with hydrochloric acid converts it into *epicyanilic acid*,  $C_4H_4O_4N_4$ , m. p.  $162^\circ$  (decomp.). This isomeride does not give the colour reactions typical of *isocyanilic acid*, but gives a red colour with ferric chloride (presence of *aci*-nitro group). It requires more than one equivalent of alkali on titration. The mother-liquors from the hydrato-acid, on keeping, yield small quantities of *metacyanilic acid*, m. p. about  $147^\circ$  (decomp.), after darkening; the yellow *silver* salt blackens in aqueous suspension. This acid differs from all those previously described by its ready solubility in all organic solvents. Like cyanomethazonic acid (see below), it gives no coloration with ferric chloride, and couples with diazobenzene forming a crystalline substance,  $C_{10}H_8O_4N_6$ , m. p.  $143^\circ$  (decomp.), indicating the presence of a primary nitro group. It appears to be a transformation product of the hydrato-acid and may be obtained direct from *isocyanilic acid* by heating with barium hydroxide (best method). The yellow *ammonium* salt,  $C_4H_4O_4N_4 \cdot NH_3$ , decomposes at about  $150^\circ$ . The constitution of this acid agrees with the formula  $CH(N \cdot OH) \cdot C(N \cdot OH) \cdot CH(NO_2) \cdot CN$ . Aniline hydrochloride reacts with a hot aqueous suspension of *isocyanilic acid* with elimination of hydroxylamine and formation of an *aniloxime*,  $[C_3H_3O_3N_3]C:NPh$ , m. p.  $119^\circ$ . The presence of the anil group exerts a bathochromic effect—no red colour being formed with strong alkalis. The corresponding *phenylhydrazone* has m. p.  $172^\circ$  (decomp.). Warming in absolute alcohol with sodium ethoxide converts the aniloxime into an isomeric *acid*, m. p.  $145^\circ$  (decomp.), which probably has the constitution,



Hot hydrochloric acid causes the loss of aniline and formic acid from the aniloxime and formation of  $\beta$ -nitro- $\alpha$ -oximinopropionitrile (cyanomethazonic acid),  $CN \cdot C(N \cdot OH) \cdot CH_2 \cdot NO_2$ , b. p.  $70^\circ/1 \text{ mm.}$ , in 50—60% yield. Its aqueous solution gives no coloration with ferric chloride, but the *ammonium* salt, decomp.  $124^\circ$ , gives a deep red. It couples with phenyldiazonium chloride, forming a *phenylhydrazone*,  $CN \cdot C(N \cdot OH) \cdot C(N \cdot NPh) \cdot NO_2$ , m. p.  $128^\circ$  (decomp.). The solution of the hydrazone in alkali on acidification yields an isomeric *acid* (obtained also directly from cyanomethazonic acid and phenyldiazonium chloride),  $C_9H_7O_3N_5$ , m. p.  $209^\circ$  (decomp.). Bromine reacts with cyanomethazonic acid (about 2 atoms taken up) to form a compound having the typical odour of bromonitro compounds, the reaction being different from that with bromine and fulminuric acid. Gently heating *isocyanilic acid* with thionyl chloride causes the acid to lose 1 mol. of water and form a neutral substance, *anhydrocyanilic acid*, m. p.  $187^\circ$  (decomp.). By the energetic action of thionyl chloride 2 mols. of water are lost and an extremely volatile substance,  $C_4O_2N_4$ , m. p.  $42^\circ$ , is obtained. This is identical with the "nitroacetonitrile" of Steiner, obtained by the action of concentrated sulphuric acid on fulminuric acid. The "nitro-

acetonitrile" is accompanied by a (supposed) polymerised form, shown to be furoxanedicarbonamide by Ulpiani. Further investigation showed Steiner's nitroacetonitrile (and the above product from isocyanilic acid) to be dicyanofuroxane,  $\begin{array}{c} \text{C}(\text{CN})\text{:N}(\text{:O}) \\ \text{C}(\text{CN})=\text{N} \end{array} > \text{O}$ , and

the course of the reactions to be fulminuric acid  $\rightarrow$  hydroxamic acid  $\rightarrow$  nitrile oxide  $\rightarrow$  furoxane derivative. *iso*Cyanilic acid dissolved in concentrated sulphuric acid is recovered unchanged on the addition of water, but if sodium nitrite is added, nitrous oxide is evolved and a dialdehyde obtained, which, with hydroxylamine, re-forms isocyanilic acid, and with aniline gives a dianil,  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_4$ , m. p.  $166^\circ$  (decomp.). From the foregoing evidence it is concluded that isocyanilic acid is the dioxime of furoxane-dialdehyde,  $\begin{array}{c} \text{C}(\text{CH:N}\cdot\text{OH})\text{:N}(\text{:O}) \\ \text{C}(\text{CH:N}\cdot\text{OH})=\text{N} \end{array} > \text{O}$ , whilst hydratoisocyanilic acid

(formed by cleavage of the ring) is  $\gamma$ -nitro- $\alpha\beta\delta$ -trioximobutane, and anhydroisocyanilic acid is  $\begin{array}{c} \text{C}(\text{CN})\text{:N}(\text{=O}) \\ \text{C}(\text{CO}\cdot\text{NH}_2)\text{:N} \end{array} > \text{O}$  or  $\begin{array}{c} \text{C}(\text{CN})=\text{N} \\ \text{C}(\text{CO}\cdot\text{NH}_2)\text{:N}(\text{:O}) \end{array} > \text{O}$ .

*iso*Cyanilic acid has been synthesised in 50% yields by treating the *syn*-chloroglyoxime in ethereal solution with sodium hydrogen carbonate, the intermediate nitrile oxide,  $\text{CH}(\text{N}\cdot\text{OH})\cdot\text{C}\text{:N}\cdot\text{O}$ , polymerising spontaneously to the ring compound. It has also been found that the  $\alpha$ -methazonic anhydride of Steinkopf (cf. A., 1910, i, 305), m. p.  $168^\circ$ , is identical with isocyanilic acid, and that treatment of methazonic acid with concentrated sulphuric acid and oleum yields isocyanilic acid in 64% yields. It is concluded that in the polymerisation of fulminic acid oximinoacetonitrile oxide is first formed and that the speed of its polymerisation to isocyanilic acid is partly overtaken by that of the reaction with a further mol. of fulminic acid leading to metafulminuric acid.

*Erythrocyanilic acid*,  $\text{C}_4\text{H}_4\text{O}_4\text{N}_4\cdot\text{H}_2\text{O}$ , decomp. about  $125^\circ$  (explosively), is the acid corresponding to the carmine-red salts formed by the action of aqueous potassium hydroxide solution (1:1) on isocyanilic acid. Its water of crystallisation is bound extremely fast and is not removed on warming in a high vacuum. It crystallises from methyl alcohol as  $\text{C}_4\text{H}_4\text{O}_4\text{N}_4\cdot\text{MeOH}$ . These crystals lose about 20% of the alcohol in 8 days under a high vacuum. Metallic salts containing no water have been prepared; the sodium,  $\text{C}_4\text{H}_2\text{O}_4\text{N}_4\cdot\text{Na}_2$ , monohydrated and anhydrous ammonium, silver, copper, and barium salts are described. Heated with an excess of 50% potassium hydroxide solution until of a syrupy consistency, ammonia is evolved whilst the colour gradually disappears; the reaction product consists largely of *N*-hydroxy-triazoledicarboxylic acid, m. p.  $90^\circ$  (the potassium hydrogen salt is described).

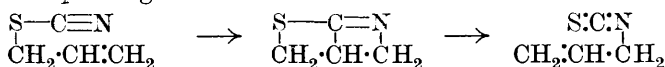
Analogously with the formation of a cyclic nitroso compound from dibenzoylfuroxane (cf. Wieland and Gmelin, A., 1910, i, 784), erythrocyanilic acid is considered to be a *C*-nitroso derivative of *N*-hydroxypyrazole, with which its chemical behaviour fully agrees.

A. C.

**Azido-carbon Disulphide. II. Reaction of Azido-carbon Disulphide and of free Thiocyanogen with Hydrogen Trinitride [Azoimide] in certain Non-aqueous Solvents.**

F. WILCOXON, A. E. MCKINNEY, and A. W. BROWNE (*J. Amer. Chem. Soc.*, 1925, **47**, 1916—1921; cf. A., 1924, ii, 40, 42).—Azido-carbon disulphide reacts with azoimide in ethereal solution according to the equation  $(\text{SCSN}_3)_2 + 8\text{HN}_3 = 2\text{NH}_4\cdot\text{SCN} + 2\text{S} + 13\text{N}_2$ . The reaction occurs in three stages, according to the schemes  $(\text{SCSN}_3)_2 = 2\text{N}_2 + 2\text{S} + (\text{SCN})_2$ ,  $(\text{SCN})_2 + 2\text{HN}_3 = 2\text{HSCN} + 3\text{N}_2$ ,  $\text{HSCN} + 3\text{HN}_3 = \text{NH}_4\cdot\text{SCN} + 4\text{N}_2$ . In support, it is shown that free thiocyanogen reacts with azoimide in ethereal solution in accordance with the equation,  $(\text{SCN})_2 + 8\text{HN}_3 = 2\text{NH}_4\cdot\text{SCN} + 11\text{N}_2$ . Azido-carbon disulphide functions as a source of free thiocyanogen and may be regarded as thiocyanogen loosely combined with nitrogen and sulphur. J. S. C.

**Rearrangement of Thiocyanates into Thiocarbimides.** O. BILLETER (*Helv. Chim. Acta*, 1925, **8**, 337—338).—The following mechanism is suggested for the conversion of allyl thiocyanate into the corresponding thiocarbimide:



A thiocyanate of the general formula  $\text{CNS}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHR}$  would thus yield a thiocarbimide derived from a different and isomeric radical:  $\text{SCN}\cdot\text{CHR}\cdot\text{CH}\cdot\text{CH}_2$  (cf. Claisen and Tietze, this vol., i, 389). The cinnamyl derivative,  $\text{CNS}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHPh}$ , is decomposed by heat without formation of a thiocarbimide, a result difficult to explain if the conversion consists merely in a rearrangement of the CNS atoms, whereas the failure of the nitrogen atom to establish a linking at the opposite end of the C-chain may be an effect of steric hindrance introduced by the phenyl group. Preliminary investigation of the action of nitrous acid on the amine obtained by hydrolysis of the thiocarbimide from crotonyl thiocyanate shows the formation an alcohol different from crotonyl alcohol. M. J.

**Preparation of Neutral Phosphites from the Hydrogen Esters.** (MLLE.) M. JANCZAK (*Rocz. Chem.*, 1924, **4**, 180—181).—The action of dialkyl phosphites on their sodium salts leads to trialkyl phosphites; the sodium salts have therefore the same structure as the latter and contain trivalent phosphorus, e.g.,  $(\text{RO})_2\text{P}^{\text{III}}\cdot\text{ONa}$ , whilst the hydrogen esters themselves have the formula  $(\text{RO})_2\text{P}^{\text{V}}(\text{O})\text{H}$ ; the formation of the sodium salts thus involves tautomeric change. The formation of neutral esters can also be brought about by the action of acetic acid on the above sodium salts; the change is accompanied by partial conversion of the neutral esters into alkylphosphinates,  $(\text{RO})_2\text{P}^{\text{V}}(\text{O})\text{R}$ . The sodium salts are immediately decomposed by water, but not by alcohol. G. A. R. K.

**Tautomerism of Dialkyl Phosphites. III.** T. MIŁOBEDZKI (*Rocz. Chem.*, 1924, **4**, 183—184; cf. preceding abstract).—It has been suggested by Nylén (*Ber.*, 1924, **57**, 1023) that sodium diethyl

phosphite is a derivative of quinquivalent phosphorus from its behaviour towards ethyl chloroacetate; this view is contradicted by the results obtained by Janczak (preceding abstract), which point to the existence of tautomerisms between pseudo-acids of the type  $(\text{RO})_2\text{P}^{\text{V}}(\text{O})\text{H}$  and true acids,  $(\text{RO})_2\text{P}^{\text{III}}(\text{OH})$ , in the process of salt formation. The fact that Nylén could not oxidise the salt by means of iodine in aqueous solution is due to the fact that it is immediately decomposed by water. The corresponding silver salt, which is stable, may be a derivative of quinquivalent phosphorus as suggested by Stelling (A., 1924, ii, 139). G. A. R. K.

**General Method of Synthesis of Allyl Compounds.** L. BERT (*Bull. Soc. chim.*, 1925, [iv], **37**, 879—881).—A further account of some work already described (this vol., i, 803). L. F. H.

**Reducing Action of Organo-magnesium Compounds.** J. STAS (*Bull. Soc. chim. Belg.*, 1925, **34**, 188—190).—Magnesium propyl bromide reacts with dipropyl ketone to yield propylene and dipropylcarbinol in addition to tripropylcarbinol (35%), whilst magnesium isopropyl bromide reacts with diisopropyl ketone to yield only diisopropylcarbinol and propylene, the same two products, in addition to ethyl alcohol, being obtained when ethyl isobutyrate is substituted for the ketone. In the reaction between magnesium isopropyl bromide and acetone, no dimethylcarbinol could be detected, although a small quantity of propylene is produced; phorone is also formed. J. W. B.

**Noble Metals as Catalysts of Hydrogenation and Dehydrogenation.** N. D. ZELINSKY and M. B. TUROWA-POLLAK (*Ber.*, 1925, **58**, [B], 1298—1303).—The activity of rhodium, palladium, iridium, platinum, ruthenium, and nickel towards benzene and cyclohexane has been studied under similar conditions. The noble metal catalysts are prepared by soaking fibrous asbestos in the solution of the metallic chloride and subsequently in 35% formaldehyde, which is followed by treatment with 50% potassium hydroxide. The catalyst is washed successively with water and dilute acetic acid and dried at 120°. The nickel catalysts are obtained (I) from nickel chloride, formaldehyde, and potassium hydroxide, followed by reduction of the product with hydrogen at 300—350°, (II) by reduction of nickel carbonate at 310—320°, (III) by heating nickel powder in hydrogen at 310°, (IV) by impregnating asbestos with nickel nitrate solution, ignition of the product, and subsequent reduction at 310°, (V) by Sabatier's method, (VI) by depositing nickel on clay. Platinum, iridium, rhodium, and ruthenium cause the conversion of benzene into cyclohexane within wide limits of temperature (100—180°). At 200—210°, dehydrogenation occurs to some extent even in the presence of hydrogen, except in the case of iridium. Palladium is a somewhat less effective hydrogenating catalyst, the full activity of which towards benzene is not developed below 155—180°. Nickel black I is a very efficient hydrogenating catalyst at 100—210°, whereas nickel II and III are feeble and useless, respectively. Nickel IV is active



at about  $130^{\circ}$ , nickel V between  $130^{\circ}$  and  $180^{\circ}$ , whereas nickel VI has the optimum temperature  $175$ – $180^{\circ}$ . At  $250$ – $260^{\circ}$ , palladium, platinum, iridium, and rhodium still cause hydrogenation of benzene, whereas ruthenium is almost inactive. At  $300$ – $310^{\circ}$ , hydrogenation is observed with platinum and rhodium, scarcely with palladium, and inappreciably with iridium and ruthenium. Nickel catalysts I, IV, and V cause marked hydrogenation at  $250$ – $260^{\circ}$ , whereas catalysts II and VI are feebly active. All nickel preparations lose their power of causing hydrogenation at  $300$ – $310^{\circ}$ . All the noble metals with the exception of ruthenium are excellent dehydrogenating catalysts at higher temperatures. Nickel black I and nickel II behave similarly, the great activity of nickel II at  $350$ – $360^{\circ}$  being particularly remarkable in view of its feebly hydrogenating power. At  $250$ – $260^{\circ}$ , ruthenium dehydrogenates *cyclohexane*, but also causes decomposition of the benzene thus produced into methane and hydrogen; the latter change is quantitative at  $300$ – $310^{\circ}$ . Nickel catalysts I, II, and VI decompose benzene similarly, but less extensively, at  $350$ – $360^{\circ}$ , whereas with nickel V this action is nearly quantitative at  $300$ – $310^{\circ}$ . Nickel VI is a particularly active dehydrogenating catalyst at  $300$ – $310^{\circ}$ .

It therefore appears that the specific properties as a reducing catalyst towards benzene attributed to nickel by Sabatier and Senderens are not peculiar to this metal, which can frequently be replaced advantageously by platinum or palladium; the noble metals are less liable than nickel to cause secondary decompositions.

H. W.

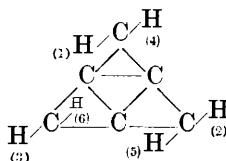
**Isomerisation of Decahydronaphthalene. Transformation of *cis*- into *trans*-Decahydronaphthalene and Dehydrogenation of Decahydronaphthalene.** N. D. ZELINSKI and M. B. TUROVA-POLLAK (*Ber.*, 1925, 58, [B], 1292–1298).—In continuation of the investigation of the problem of the individuality of the different specimens of *trans*-decahydronaphthalene (cf. Zelinsky, this vol., i, 123; Eisenlohr and Polenske, A., 1924, i, 1292; Hückel, this vol., i, 31), the study of a technical decahydro- $\beta$ -naphthol has been undertaken. The latter when preserved deposited *trans*-decahydro- $\beta$ -naphthol, m. p.  $75^{\circ}$ , b. p.  $237^{\circ}/742$  mm. The liquid portion on distillation yielded *cis*-decahydronaphthalene, b. p.  $192$ – $193^{\circ}/741$  mm.,  $d_4^{20.5}$  0.8997,  $n_D^{20.5}$  1.4871, and at a higher temperature, a third *decahydro*- $\beta$ -naphthol, b. p.  $122$ – $123^{\circ}/13$  mm.,  $239$ – $240^{\circ}/742$  mm.,  $d_4^{20}$  0.9889,  $n_D^{20}$  1.4973. The residue remaining after distillation deposited *cis*-decahydro- $\beta$ -naphthol. The liquid decahydro- $\beta$ -naphthol and the *trans*-compound are converted by potassium hydrogen sulphate at  $200^{\circ}$  into the same octahydronaphthalene. Treatment of *trans*-decahydro- $\beta$ -naphthol with fuming hydriodic acid at  $290$ – $340^{\circ}$  yielded methyl- and 1:2-dimethyl-*cyclohexane* together with products of higher b. p. The latter fractions when dehydrogenated by palladised charcoal appeared to give a mixture of the unknown *cyclodecane* and 2:8-dimethyl-*dicyclo*-[0:3:3]-octane. The method of isomerisation is, however, too costly to permit extended application and a more suitable

process is found in the use of aluminium bromide. This causes nuclear isomerisation of decahydronaphthalene and at 100° transforms *cis*- into *trans*-decahydronaphthalene. The latter change can be effected without simultaneous, deep-seated isomerisation if the reaction is effected at the atmospheric temperature.

The presence of the *cis*- and *trans*-isomerides in technical decahydronaphthalene (cf. Hückel, *loc. cit.*) is confirmed by the observation that it is quantitatively dehydrogenated to naphthalene only after four successive treatments with palladised asbestos, whereas a single treatment suffices in the case of *trans*-decahydronaphthalene.

H. W.

**Triangular Benzene Molecule.** C. V. RICHARD (*Sci. Bulleno*, 1925, Mar. Suppl.).—From a consideration of the magnetic double refraction of the liquid compounds of the benzene series, the annexed formula is proposed for benzene.



CHEMICAL ABSTRACTS.

**Isomeric Transformations. II. Isomeration of Rings.** S. S. NAMETKIN (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, 55, 493—513; cf. A., 1916, i, 208).—A theoretical paper in which the mechanism of the conversion of small into larger rings, and *vice versa*, is discussed.

T. H. P.

**Action of Ethyl Hypochlorite on Mixed Organo Magnesium Compounds and on Magnesium-amines.** J. F. DURAND and R. NAVES (*Bull. Soc. chim.*, 1925, [iv], 37, 717—723).—An improved apparatus for the preparation of ethyl hypochlorite by Sandmeyer's method (A., 1885, 1045; 1886, 607) is described. The reaction vessel consists of a series of bulbs separated by constrictions, and rubber connexions etc. are avoided, contact of rubber with ethyl hypochlorite being liable to cause dangerous explosions. The cooling water is kept at 0° (cf. Schäfer, A., 1915, ii, 389) and the escape of excess of chlorine is facilitated by aspiration. The alkaline alcoholic solution is saturated with salt and the operator protected by enclosing the whole apparatus in metal gauze. Ethyl hypochlorite thus prepared is a colourless liquid, b. p. 36°/768 mm.,  $d_4^{20}$  1.013, which turns yellow in the light with liberation of chlorine (cf. Taylor, McMullin, and Gammal, this vol., i, 501). With magnesium phenyl bromide in ethereal solution at 0° it yields magnesium ethoxybromide and chlorobenzene:  $\text{PhMgBr} + \text{ClOEt} \rightarrow \text{PhCl} + \text{MgBr(OEt)}$ . With magnesium anilino-bromide, the reaction appears to follow a similar course, but the phenylchloroamine which is probably first formed:  $\text{NHR} \cdot \text{MgBr} + \text{ClOEt} \rightarrow \text{NHR} \cdot \text{Cl} + \text{MgBr(OEt)}$ , immediately undergoes decomposition, partly into

azobenzene and partly into a mixture of *o*- and *p*-chloroanilines. A blue substance which does not distil without decomposition is also formed.

R. B.

**New Type of Organic Magnesium Compounds.** V. THOMAS (*Compt. rend.*, 1925, **181**, 218—220).—In the reaction between 1 g. atom of magnesium, free from iron, and 1 mol. of *p*-di-iodobenzene in ethereal solution, some of the latter is always unchanged. With 2 g.-atoms of magnesium about 80% of the latter enters into combination and the product, on treatment with water, yields benzene, traces of iodobenzene, and a resinous product from which a substance of the type  $[(C_6H_4)_2H_2O]_n$  was isolated. Of the alternative formulæ for the intermediate *magnesium* compound which is formed,  $C_6H_4(MgI)_2$  and  $(C_6H_4)_2Mg$ , the former is tentatively preferred. The compound forms additive *products* with carbon dioxide and with aldehydes. Similar results were obtained with *o*- and *m*-di-iodobenzenes. *p*-Di-iodothiophen also combines with more than 1 g.-atom of magnesium per mol.

S. K. T.

**Fission of *p*-Iodoxynitrobenzene by Alkali Hydroxide.** D. VORLÄNDER and K. BÜCHNER (*Ber.*, 1925, **58**, [B], 1291).—*p*-Iodoxynitrobenzene is decomposed by aqueous potassium hydroxide solution with formation of nitrobenzene, *p*-iodonitrobenzene, and iodic acid. With silver oxide suspended in water it gives nitrobenzene and silver iodate.

H. W.

**Electrochemical Oxidation of Iodobenzene, *o*-Iodotoluene, and *p*-Iodotoluene.** F. FICHTER and P. LOTTER (*Helv. Chim. Acta*, 1925, **8**, 438—442).—Electrolytic oxidation of iodobenzene in an emulsion with aqueous sulphuric acid, with a lead dioxide anode, gives, without a diaphragm, quinol and iodine, and, with a diaphragm, benzoquinone and iodic acid with partial degradation of the former to fumaric acid and carbon dioxide. When glacial acetic acid solution containing a little concentrated sulphuric acid with a platinum electrode and no diaphragm is used, iodosobenzene acetate is obtained. In acetic acid–perchloric acid solution, increase of time, temperature, and current density give increasing proportions of *p*-di-iodobenzene with the iodosobenzene. Oxidation in acetic acid solution in absence of mineral acid at a low temperature gives a little iodoxybenzene as well as iodosobenzene acetate. *o*-Iodotoluene in an emulsion with aqueous sulphuric acid gives a small yield of *o*-iodobenzaldehyde (*phenylhydrazone*, m. p. 80.5°) and *o*-iodobenzoic acid. In 70% acetic acid solution, *o*-iodosobenzoic acid is produced. It is obtained in better yield by direct oxidation of *o*-iodobenzoic acid in the same solvent. *p*-Iodotoluene in aqueous sulphuric acid solution with a lead dioxide anode and a diaphragm gives at 60° *p*-iodobenzaldehyde (*phenylhydrazone*, m. p. 121°) and *p*-iodobenzoic acid, which breaks down completely into iodic and fumaric acids and carbon dioxide. In 70% acetic acid solution with a platinum anode, the breakdown is checked, and the same products are obtained in better yield with a small quantity of *p*-iodoxybenzoic acid exploding at 227° (cf. Ortoleva, A., 1900, i, 592, 200—202°).

Preparations of the last-named by oxidation of *p*-iodobenzoic acid and *p*-iodotoluene are described. M. J.

**Some Physical Properties of Nitro Compounds.** L. DESVERGNES (*Mon. Sci.*, 1925, [v], 15, 149—158).—Careful measurements were taken of the melting points of various nitro compounds and of their solubilities in water and in twelve common organic solvents. The melting points found were: *m*-dinitrobenzene, 90.0°; *s*-trinitrobenzene, 122.45—122.5°; 2:4-dinitrodiphenylamine, 156—157°; 2:4:5:2'-tetranitrodiphenylamine, 199—199.5°; hexanitrodiphenylamine, 238.5—240.0°; *p*-nitrotoluene, 52.06°; 2:4-dinitrotoluene, 70.15°. These compounds are all very sparingly soluble in water, but most dissolve readily in acetone, chloroform, benzene, and especially in pyridine. With pyridine, however, some form coloured complexes; *s*-trinitrobenzene forms brown crystals, softening at 115—116°, separable into a brown, amorphous substance, m. p. >210°, and the original trinitrobenzene, and 2:4:5:2'-tetranitrodiphenylamine forms orange-red crystals separable into the original substance and a red, amorphous powder, m. p. about 80°. Hexanitrodiphenylamine forms with pyridine deep red crystals with a golden reflection, which, when heated quickly, turn yellow and melt at 244—245°, but when heated in stages melt at about 70°, and resolidify to melt again at 244—245°. This compound is probably  $[C_6H_2(NO_2)_3]_2NH, 5C_6H_5N$ . B. W. A.

**Preparation of Isonuclear Bromonitronaphthalenes from Corresponding Derivatives of Tetrahydronaphthalene [Tetralin].** V. VESELY and L. K. CHUDOZOLOV (*Chem. Listy*, 1925, 19, 260—264; cf. A., 1923, i, 550).—All possible isonuclear bromonitro-, and two isonuclear bromodinitro-naphthalenes have been prepared from the corresponding *ar*-bromonitro- (or -dinitro)-tetrahydronaphthalenes by dehydrogenation, e.g., by introducing 2 atoms of bromine, and subsequently detaching 2 mols. of hydrogen bromide by heating. The following new substances are described: 6-bromo-5-nitrotetrahydronaphthalene, m. p. 101—102°; 5-bromo-6-nitrotetrahydronaphthalene, m. p. 50—51.5°; 1-bromo-2-nitronaphthalene, m. p. 98—99°; 6-bromo-7-nitrotetrahydronaphthalene, m. p. 50—51°; 2-bromo-3-nitronaphthalene, m. p. 82—83°; 5-bromo-7-nitrotetrahydronaphthalene, m. p. 106—106.5°; 1-bromo-3-nitronaphthalene, m. p. 128—129°; 7-bromo-5-nitrotetrahydronaphthalene, m. p. 76—76.5°; 3-bromo-1-nitronaphthalene, m. p. 97—98°; 8-bromo-5-nitrotetrahydronaphthalene, m. p. 68—69°; 5-bromo-6:8-dinitrotetrahydronaphthalene, m. p. 93—94°; 1-bromo-2:4-dinitronaphthalene, m. p. 151—152°; 6-bromo-5:7-dinitrotetrahydronaphthalene, m. p. 135—136°; 2-bromo-1:3-dinitronaphthalene, m. p. 183—184°. B. F.

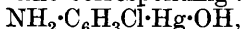
**Derivatives of 2-Methylnaphthalene.** K. DZIEWONSKI, J. SCHOENÓWNA, and E. WALDMANN (*Ber.*, 1925, 58, [B], 1211—1218).—2-Methylnaphthalene-6-sulphonic acid is prepared in about 80% yield by the action of a slight excess of sulphuric acid (*d* 1.84) on 2-methylnaphthalene during 5—6 hrs. at 90—100° and is con-

veniently isolated as the *barium* salt. The *sodium* salt, *ethyl 2-methylnaphthalene-6-sulphonate*, m. p. 79—80°, *2-methylnaphthalene-6-sulphochloride*, m. p. 97—98°, and *2-methylnaphthalene-6-sulphonamide*, m. p. 205—206°, are described. The sodium salt is transformed by molten potassium hydroxide at 280—300° into *6-hydroxy-2-methylnaphthalene*, m. p. 128—129° (*6-methoxy-2-methylnaphthalene*, m. p. 78—79°; *6-benzyloxy-2-methylnaphthalene*, m. p. 128—129°). *6-Hydroxy-2-methylnaphthalene* is converted by sodium nitrite and zinc chloride in aqueous alcoholic solution into *5-nitroso-6-hydroxy-2-methylnaphthalene*, m. p. 119—120° (the zinc and sodium salts are described), which is oxidised by nitric acid (*d* 1.25) to *5-nitro-6-hydroxy-2-methylnaphthalene*, m. p. 81—82°. *5-Amino-6-hydroxy-2-methylnaphthalene*, m. p. 155—157° (decomp.), prepared by the action of hydrogen sulphide and dilute ammonia on the *barium* salt of *5-nitroso-6-hydroxy-2-methylnaphthalene*, is oxidised by potassium dichromate and dilute sulphuric acid to *2-methyl-5:6-naphthaquinone*, m. p. 131—132°. *5-Benzeneazo-6-hydroxy-2-methylnaphthalene*, m. p. 135—136°, *5:4'-nitrobenzeneazo-6-hydroxy-2-methylnaphthalene*, m. p. 244—245°, and *5-benzeneazo-6-hydroxy-2-methylnaphthalene-4'-sulphonic acid* are described. Treatment of *6-hydroxy-2-methylnaphthalene* with ammonia and ammonium sulphite at 150° under pressure yields *6-amino-2-methylnaphthalene*, m. p. 129—130°; the corresponding *acetyl* derivative, m. p. 155—156°, is oxidised by potassium permanganate in the presence of magnesium sulphate to *6-acetamido-2-naphthoic acid*, m. p. 271—272°, which is hydrolysed by hydrochloric acid to *6-amino-2-naphthoic acid*, m. p. 222—223°; the presence of the amino group in position 6 is established by the non-identity of this acid with the other theoretically possible isomeric amino-2-naphthoic acids which have been described previously. H. W.

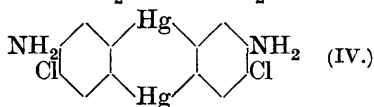
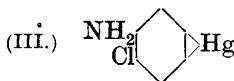
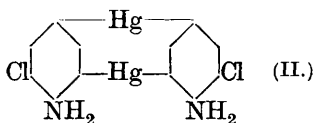
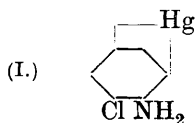
**Reaction between Aryl Sulphonates and Organo-magnesium Halides.** H. GILMAN, N. J. BEABER, and C. H. MYERS (*J. Amer. Chem. Soc.*, 1925, **47**, 2047—2052; cf. this vol., i, 802).—Interaction of aryl sulphonates with organo-magnesium halides takes place according to the general equation  $R \cdot SO_2OAr + R'MgX = R \cdot SO_2R' + ArO \cdot MgX$ , giving a sulphone and a phenol. This is in keeping with the general behaviour of aryl sulphonates, which show a closer resemblance to aryl carboxylates than to alkyl sulphonates. To obtain complete reaction between the Grignard reagent and the aryl sulphonate, it is necessary to reflux the reactants in dry toluene. *4:4'-Diphenyl di-p-toluenesulphonate*, m. p. 189—190°, is described, and the following new sulphones were prepared: *p-anisyl-p-tolylsulphone*, m. p. 159°, and  $\alpha$ -*naphthyl-p-tolylsulphone*, m. p. 119°. Magnesium ethyl iodide and phenyl *p*-toluenesulphonate yielded an oil. Magnesium *n*-butyl bromide afforded phenol and a sulphur compound, m. p. 109°, together with *p*-tolyl *n*-butyl sulphide. Magnesium isoamyl bromide yielded phenol, diisoamyl, *p*-tolyl isoamyl sulphide, b. p. 150—155°/15 mm., and two sulphur compounds, b. p. 190—195°/15 mm., and m. p. 128—128.5°, respectively, the former being probably *p*-tolylisoamylsulphone. Magnesium cyclo-

hexyl chloride and phenyl *p*-toluenesulphonate yielded a small proportion of phenol and an *oil*, whilst magnesium benzyl chloride afforded a sulphur compound, m. p. 166—167°. F. G. W.

**Action of Mercuric Acetate on *o*-Chloroaniline.** L. VECCHIOTTI and A. MICHETTI (*Gazzetta*, 1925, **55**, 372—384; cf. A., 1924, i, 957).—The action of mercuric acetate on *o*-chloroaniline in aqueous or aqueous-alcoholic solution yields four mercury derivatives: (1) *o*-Chloroaniline-*p*-mercuriacetate,  $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{Hg}\cdot\text{OAc}$ , white needles, m. p. 134°, which forms an *acetyl* derivative,  $\text{NHAc}\cdot\text{C}_6\text{H}_4\text{O}_2\text{ClHg}$ , m. p. 238—239°, this giving *o*:*p*-dichloroacetanilide when treated in acetic acid solution with calcium chloride and chlorine. The corresponding *hydroxide*,



and the *chloride* decompose without melting at 205° and 174°, respectively. When digested with excess of sodium thiosulphate solution, the acetate is converted into *mercury di-m-chloro-p-amino-phenyl*,  $\text{Hg}(\text{C}_6\text{H}_3\text{Cl}\cdot\text{NH}_2)_2$ , m. p. 138°. (2) An isomeric *o*-chloroanilinemercuriacetate, yellow needles, m. p. 143°, obtained in small amount and not investigated further. (3) *o*-Chloroaniline-4:6-dimercuriacetate,  $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Cl}(\text{Hg}\cdot\text{OAc})_2$ , decomposing at 220°. The corresponding *hydroxide*,  $\text{NH}_2\cdot\text{C}_6\text{H}_2\text{Cl}(\text{Hg}\cdot\text{OH})_2$ , and *chloride* decompose respectively at 250° and 190°. The *acetyl* derivative of the acetate has m. p. 230° and yields 2:4:6-trichloroacetanilide when mixed in acetic acid solution with alcoholic calcium chloride and subjected to the action of chlorine; the *acetyl* derivative of the chloride decomposes at 276°. Treatment of the dimercuriacetate with sodium thiosulphate solution yields a compound, which decomposes at 200°, and is either 4:6-mercuri-2-chloroaniline (I), or 4:6-dimercuribis-*o*-chloroaniline (II). (4) *o*-Chloroaniline-4:5-di-



*mercuriacetate*, m. p. 232°, which forms an *acetyl* derivative, m. p. 230°; the latter gives 2:4:5-trichloroacetanilide when treated in acetic acid solution with calcium chloride and chlorine. Treatment of this dimercuriacetate with sodium thiosulphate solution yields 4:5-mercuri-2-chloroaniline (III) or 4:5-dimercuribis-*o*-chloroaniline (IV), which decomposes, without melting, at 160°.

T. H. P.

**Influence of Acetyl Chloride on the Nitration of Acetanilide and Dimethylaniline.** A. CHRZASZCZEWSKA and (MLLE.) M. BIATA (*Rocz. Chem.*, 1925, **5**, 77—95; cf. this vol., i, 956 and Menke, *ibid.*, i, 386).—The nitration of acetanilide and of dimethylaniline has

been studied, under various conditions and in various solvents. In particular, the effect of the addition of acetyl chloride as a dehydrating agent to the reaction mixture has been investigated. In general, this increases the yield of nitro derivatives, and, in the case of dimethylaniline, increases the yield of *ortho*- at the expense of the *para*-nitro derivative.

R. T.

**Sodium Arsenite as a Reagent for Loosely Combined Reactive Oxygen, Sulphur, and Nitrogen.** A. GUTMANN (*Z. anal. Chem.*, 1925, **66**, 224—242).—Alkaline solutions of sodium arsenite react readily with organic and inorganic compounds containing loosely combined oxygen, sulphur, or nitrogen with the formation of sodium arsenate and compounds containing less sulphur, oxygen, or nitrogen. Sodium ethyl thiosulphate yields first sodium thioethyl peroxide, then sodium sulphide and sulphite and ethyl mercaptan. Ethyl *p*-toluenethiosulphonate gives sodium toluenesulphonate and ethyl mercaptan, and dimethylaniline-*N*-oxide and quinine oxide are reduced to dimethylaniline and quinine, respectively, but dibenzylsulphoxide, *p*-benzoquinone, and benzaldehyde are not affected by sodium arsenite. Nitric oxide is reduced to nitrous oxide and nitrosobenzene to azoxybenzene, but nitrosomethylurethane yields, owing to side-reactions, a variety of products, among which are nitrogen, methylamine, ammonia, methane, formic acid, and diazomethane; on the other hand, nitrosodimethylaniline and nitrosophenol are unattacked by the reagent. Sodium *p*-diazobenzenesulphonate yields nitrogen and sodium benzenesulphonate, nitrosoacetanilide gives benzene, nitrogen, and sodium acetate, and phenylbenzoylnitrosoamine, benzene, nitrogen, and sodium benzoate. Ethyl and amyl nitrates are reduced to nitrites which are saponified by the alkali, giving the corresponding alcohol; glyceryl trinitrate is, however, not reduced. The reduction of nitrobenzene to azoxybenzene suggests that 2 mols. of nitrobenzene contain three quadrivalent oxygen atoms. Hydroxylamine and its principal organic derivatives are reduced to ammonia or the corresponding primary amine. With alkaline sodium arsenite, diethyl disulphide gives ethyl mercaptan, dithiocyanogen and cyanogen sulphide each give thiocyanic acid, phenyl thiocyanate yields thiophenol, and ethyl thiocyanate sodium cyanide and ethyl mercaptan. Sodium thiosulphate and the polythionates (other than dithionates) are converted by sodium arsenite into sulphide and sulphite, cupric sulphide is reduced to cuprous, and organic polysulphides to monosulphides. Azides are converted by the reagent into primary amines with the evolution of nitrogen.

A. R. P.

**Asymmetric Nitrogen Atom. IV. Function of Solvate Formation in the Decomposition of Asymmetric Amine-Ammonium Salts.** E. WEDEKIND and H. UTHE (*Ber.*, 1925, **58**, [B], 1303—1307; cf. this vol., i, 678).—Further evidence in favour of the view that the acceleration of the decomposition of *d*-phenylbenzylmethyl- $\beta$ -phenylmethylaminoethylammonium nitrate,  $\text{NMePh}(\text{CH}_2\text{Ph})(\text{CH}_2\cdot\text{CH}_2\cdot\text{NMePh})\cdot\text{NO}_3$ , in chloroform

solution by aniline is due to solvate formation is derived from a study of the rate of loss of aniline when a solution of the salt in this solvent is heated under specified conditions and from the observation that the specific rotation of the salt in media of low dielectric constant and pronounced tendency towards the formation of molecular compounds (chloroform, aniline, methylaniline) is much higher than in solvents of high dielectric constant (acetone, methyl alcohol); with chloroform, the salt yields a stable compound ( $+1\text{CHCl}_3$ ). The decomposition appears to depend on initial solvate formation accompanied by exaltation of the specific rotation, followed by racemisation due to irreversible decomposition, yielding phenylmethyl- $\beta$ -phenylmethylaminoethylamine, benzyl nitrate, and aniline; the last two substances react with formation of phenylbenzylamine nitrate, to which the enhanced electrical conductivity of the solution is due. H. W.

**Reduction of Nitrosophenols with Alkali Sulphides.** A. PORAI-KOSCHITZ (*Chem.-Ztg.*, 1925, **49**, 595—596).—The reduction of *p*-nitrosophenol by passing hydrogen sulphide into its strong ammoniacal solution gives 85—88% of the theoretical yield of pure *p*-aminophenol. Using very concentrated sodium sulphide for the reduction and ammonium sulphate to precipitate the aminophenol gave 90% yields of a less pure product. [Cf. *B.*, 1925, 702.]

B. W. A.

**Fluorescence of the Principal Photographic Developers.** A. LUMIÈRE, L. LUMIÈRE, and A. SEYEWETZ (*Bull. Soc. chim.*, 1925, [iv], **37**, 700—704).—A number of diamines, polyhydric phenols, and aminophenols have been examined for fluorescence in the solid state and in aqueous solution, alone and in the presence of sodium sulphite or carbonate. In the solid state, *p*-phenylenediamine, its methyl derivatives, and to a lesser extent its monoacetyl derivative, show a deep violet fluorescence, whilst the isomeric *o*- and *m*-compounds are non-fluorescent, as are the hydrochlorides of all these bases. Of the dihydric phenols, only quinol and chloroquinol show a slight fluorescence in the solid state, and, similarly, of the aminophenols, only the *p*-derivatives are fluorescent. The hydrochloride of *p*-aminophenol is slightly fluorescent, although the free base is not, and, similarly, *p*-methylaminophenol sulphate is strongly fluorescent, whilst the base is only feebly so.

Some substances, such as acetyl-*p*-phenylenediamine and the hydrochlorides of *p*-aminophenol, diaminophenol, triaminophenol, and diaminoresorcinol, which are fluorescent in the solid state, give solutions which are non-fluorescent even in the presence of sodium sulphite or carbonate. In most cases, the substances which give non-fluorescent aqueous solutions give fluorescent solutions on the addition of sodium sulphite or carbonate. Sodium 2:1-aminonaphthol-6-sulphonate (eikonogen), which is feebly fluorescent in the solid state, gives an aqueous solution the intense fluorescence of which is partly destroyed by alkali sulphite or carbonate. On the other hand, the non-fluorescent hydrochlorides of *p*-phenylenediamine and its methyl derivatives, *p*-aminophenol, *p*-dimethyl-



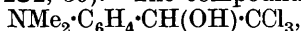
aminophenol and its sulphate, pyrocatechol, and quinolsulphonic acid, yield solutions the fluorescence of which varies according to the presence or absence of alkali sulphite and carbonate. *p*-Methylaminophenol sulphate is readily distinguished from *p*-aminophenol by its intense fluorescence (cf. A., 1924, i, 980; this vol., ii, 604).

R. B.

**Naphthalene Derivatives.** M. TANAKA (*Chem. News*, 1925, **131**, 49—50).—4-Iodo-1-naphthyl ethyl ether, m. p.  $43.5^{\circ}$ , is obtained by means of the diazo reaction from 4-amino-1-naphthyl ethyl ether, or, better, by treatment of  $\alpha$ -naphthyl ethyl ether with iodine and iodic acid in boiling glacial acetic acid solution. Heated with 1-iodo-5-nitronaphthalene and copper powder, it yields a substance, m. p.  $223^{\circ}$ , which is probably an impure specimen of 5-nitro-4'-ethoxy-1 : 1'-dinaphthyl.

G. M. B.

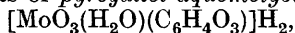
**Fluorescent Derivative of  $\beta$ -Naphthol.** A. SAKOSCHANASKY (*Chem. News*, 1925, **131**, 39).—The compound



formed by the action of chloral hydrate on dimethylaniline, reacts with  $\beta$ -naphthol at  $200^{\circ}$ , giving a substance which shows strong reddish-green fluorescence in concentrated sulphuric acid solution. Chloral hydrate reacts with  $\beta$ -naphthol at high temperatures, giving a non-fluorescent substance.

B. F.

**Complex Compounds of Pyrocatechol and Pyrogallol with Acids of the Molybdenum Group.** L. FERNANDES (*Gazzetta*, 1925, **55**, 424—440; cf. A., 1923, i, 1100; this vol., ii, 71).—Organic compounds containing two hydroxyl groups in the *ortho*-position react to give complex derivatives with salts of molybdic, tungstic, and uranic acids. These compounds are regarded as derived from the hypothetical diaquo acids of the type  $[\text{XO}_4(\text{H}_2\text{O})_2]\text{H}_2$ . Two series are obtained accordingly as one or both water molecules are displaced, giving derivatives of  $[\text{XO}_3(\text{H}_2\text{O})\text{R}]\text{H}_2$ , or  $[\text{XO}_2\text{R}_2]\text{H}_2$ . The intense colour of these derivatives, especially those of the second type, indicates that the organic groups are held by co-ordination valencies, and that the water molecules in the original acid are also to be regarded as water of constitution. Compounds of the first type are easily obtained by evaporating to crystallisation solutions of the phenolic substance and the inorganic salt. The derivatives of the second type must be prepared in alcoholic solution, since in aqueous solution the entrance of the second organic molecule into the co-ordination group is prevented by the active mass of the water present. The pyrogallol derivatives are in general more stable than those of pyrocatechol. The *diguandine*, *monoguanidine*, and *monothallous* salts of *pyrogallol aquomolybdic acid*,

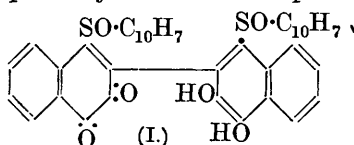


were prepared; the first of these is dark red, the others are chestnut colour. The *diguandine* and *monothallous* salts of *dipyrogallol molybdic acid*,  $[\text{MoO}_2(\text{C}_6\text{H}_4\text{O}_3)_2]\text{H}_2$ , are respectively red, easily soluble in water and alcohol, and chestnut in colour. The *mono-ammonium*, *-potassium*, and *-thallous* salts of *pyrocatechol aquotungstic acid*,

$[\text{WO}_3(\text{H}_2\text{O})(\text{C}_6\text{H}_4\text{O}_2)]\text{H}_2$ , were obtained; the first and last of these are dark brown in colour: the potassium salt varies in colour according to the conditions of preparation. *Ammonium dipyrocatechol tungstate*,  $[\text{WO}_2(\text{C}_6\text{H}_4\text{O}_2)_2]\text{H}\text{NH}_4$ , is almost black and extremely soluble in water. *Mono-ammonium*, *-potassium*, and *-thallous* salts of *pyrogallol aquotungstic acid*,  $[\text{WO}_3(\text{H}_2\text{O})(\text{C}_6\text{H}_4\text{O}_3)]\text{H}_2$ , and *ammonium dipyrogallol tungstate* are all chestnut in colour. *Pyridine pyrocatechol aquouranate*, *pyridine dipyrogallol uranate*, the *mono-ammonium*, *-pyridine*, and *-thallous* salts of *pyrogallol aquouranic acid*,  $[\text{UO}_3(\text{H}_2\text{O})(\text{C}_6\text{H}_4\text{O}_3)]\text{H}_2$ , and *pyridine dipyrogallol uranate* are all chestnut in colour except the *ammonium pyrogallol aquouranate*, which is yellow.

F. G. T.

**Derivatives of *iso*- $\beta$ -Naphthyl-3 : 4-dihydroxy- $\alpha$ -naphthylsulphone.** O. HINSBERG (*Ber.*, 1925, 58, [B], 1335—1339; cf. *A.*, 1919, i, 202).— $\beta$ -Naphthyl-3 : 4-dihydroxy- $\alpha$ -naphthylsulphone, m. p. 172°, is prepared by the action of  $\beta$ -naphthaquinone on 2-naphthalenesulphinic acid in the presence of aqueous acetic acid at the atmospheric temperature. It is converted at 170—180° probably into the corresponding quinone sulfoxide, which partly



during the process and partly during the subsequent purification with acetic acid and water become polymerised to the substance (I), m. p. 75—100°, the position of which in the *iso* series is established by its

low m. p., ready solubility in organic media, and ability to crystallise +  $\text{CHCl}_3$ ; with *o*-phenylenediamine, it yields an *azine*,  $\text{C}_{46}\text{H}_{28}\text{O}_4\text{N}_2\text{S}_2$ , m. p. (+  $\text{CHCl}_3$ ) 120—130°.  $\beta$ -Naphthyl-3 : 4-dihydroxy- $\alpha$ -naphthylsulphone is oxidised by potassium dichromate and acetic acid to  $\beta$ -naphthyl-1- $\beta$ -naphthaquinonylsulphone, m. p. 187°, which with *o*-phenylenediamine affords the *azine*,  $\text{C}_{26}\text{H}_{16}\text{O}_2\text{N}_2\text{S}$ , m. p. 230°. The quinone appears to undergo polymerisation when heated with glacial acetic acid; with *o*-phenylenediamine the product of the change yields an *azine*,  $\text{C}_{46}\text{H}_{28}\text{O}_6\text{N}_2\text{S}_2$ , m. p. 80—125°, apparently related to the compound,  $\text{C}_{46}\text{H}_{28}\text{O}_4\text{N}_2\text{S}_2$ , described above as sulphone to sulfoxide.

H. W.

**Dehydrogenation of Cholesterol.** O. DIELS and W. GÄDKE (*Ber.*, 1925, 58, [B], 1231—1233).—When cholesterol is heated at a gradually increasing temperature with palladised active charcoal in a quartz vessel water is first lost, followed at a somewhat higher temperature by isooctane or isooctylene and possibly methane. The reaction products of highest b. p. contain a crystalline hydrocarbon, m. p. 254—255°, which closely resembles anthracene; elementary analyses and determinations of mol. wt. indicate the formula  $\text{C}_{17}\text{H}_{14}$ . The same product is obtained from cholesterylene.

H. W.

**$\alpha$ -Paltreubyl Alcohol, an Inactive Form of  $\beta$ -Amyrin.** K. A. VESTERBERG (*Pull. Soc. chim.*, 1925, [iv], 37, 742—744).—Crystallographic measurements on the acetates of  $\beta$ -amyrin and of

$\alpha$ -paltreubyl alcohol confirm the view previously expressed (Jungfleisch and Leroux, A., 1906, i, 525) that  $\alpha$ -paltreubyl alcohol is an inactive form of  $\beta$ -amyrin.

R. B.

### Substituted Thiocarbamides. V. Synthesis of Thiocarbamides from Aminoethanols, and of Thiazolidine Derivatives.

F. B. DAINS, R. Q. BREWSTER, I. L. MALM, A. W. MILLER, R. V. MANEVAL, and J. A. SULTZABERGER (*J. Amer. Chem. Soc.*, 1925, **47**, 1981—1989; cf. A., 1923, i, 62).— $\beta$ -p-Xylylaminoethyl alcohol (N-hydroxyethyl-p-xylylidine), m. p. 57°, b. p. 206°/40 mm., was prepared by heating ethylene chlorohydrin with 2 equivalents of p-xylylidine at 135° for 12 hrs.  $\beta$ -p-Bromophenylaminoethyl alcohol (N-hydroxyethyl-p-bromoaniline), m. p. 93°, was obtained by heating ethylene oxide with p-bromoaniline at 75° under pressure. p-Xylylthiocarbimide (cf. Dyson and George, A., 1924, i, 1057), b. p. 249—251°, was obtained by the action of acetyl chloride on di-p-xylylthiocarbamide. The following disubstituted thiocarbamides, obtained by the condensation of appropriate amines and thiocarbimides in alcoholic solution, are described:  $\alpha$ -p-bromophenyl- $\beta$ -p-tolyl-, m. p. 184°;  $\alpha$ -p-bromophenyl- $\beta$ - $\alpha$ -naphthyl-, m. p. 188°;  $\alpha$ -phenyl- $\beta$ -p-xylyl-, m. p. 133°;  $\alpha$ -p-tolyl- $\beta$ -p-xylyl-, m. p. 140°;  $\alpha$ -o-tolyl- $\beta$ -p-xylyl-, m. p. 139°. Disubstituted  $\beta$ -hydroxyethylthiocarbamides,  $\text{NR}(\text{CH}_2\cdot\text{CH}_2\cdot\text{OH})\cdot\text{CS}\cdot\text{NHR}'$ , are obtained smoothly by the condensation of the appropriate arylaminoethyl alcohol with a thiocarbimide. When heated with halogen acids, carbonyl chloride, or other acid chlorides, or, less smoothly, by the action of heat alone, the thiocarbamides are converted into the corresponding thiazolidines,  $\begin{matrix} \text{CH}_2-\text{CH}_2 \\ \text{NR}\cdot\text{CNR}' \end{matrix} > \text{S}$ . The following derivatives

of  $\alpha$ -( $\beta$ -hydroxyethyl)thiocarbamide are described:  $\alpha\beta$ -diphenyl-, m. p. 108°;  $\alpha$ -phenyl- $\beta$ -p-tolyl-, m. p. 101° (thiazolidine, m. p. 113°);  $\beta$ -phenyl- $\alpha$ -p-tolyl-, m. p. 120° (thiazolidine, m. p. 127°);  $\alpha\beta$ -di-p-tolyl-, m. p. 130°;  $\alpha$ -phenyl- $\beta$ -o-tolyl-, m. p. 94°;  $\alpha$ -p-tolyl- $\beta$ -o-tolyl-, oil (thiazolidine, m. p. 110°; cf. Will and Bielschowski, A., 1882, 1090);  $\alpha$ -phenyl- $\beta$ -o-anisyl-, oil (thiazolidine, m. p. 103°);  $\beta$ -phenyl- $\alpha$ -o-anisyl-, m. p. 143° (thiazolidine, m. p. 144°; cf. Foerster, A., 1888, 944);  $\alpha$ -phenyl- $\beta$ -( $\alpha$ -naphthyl-) (thiazolidine, m. p. 130°);  $\alpha$ -p-bromophenyl- $\beta$ -phenyl-, m. p. 98° (thiazolidine, m. p. 113°);  $\alpha$ -phenyl- $\beta$ -p-bromophenyl-, m. p. 131° (thiazolidine, m. p. 112°);  $\alpha$ -p-tolyl- $\beta$ -p-bromophenyl-, m. p. 137° (thiazolidine, m. p. 97°);  $\alpha$ -p-bromophenyl- $\beta$ -p-tolyl-, oil (thiazolidine, m. p. 145°);  $\alpha$ -p-bromophenyl- $\beta$ - $\alpha$ -naphthyl-, m. p. 60° (thiazolidine, m. p. 127°);  $\beta$ -p-bromophenyl- $\alpha$ -( $\alpha$ -naphthyl)-, oil (thiazolidine, m. p. 165°);  $\alpha$ -p-bromophenyl- $\beta$ -allyl-, m. p. 96°;  $\beta$ -p-tolyl- $\alpha$ -p-xylyl-, m. p. 107° (thiazolidine, m. p. 112°);  $\beta$ -o-tolyl- $\alpha$ -p-xylyl-, oil (thiazolidine picrate, m. p. 179°);  $\alpha\beta$ -di-p-xylyl-, oil (thiazolidine, m. p. 86°);  $\alpha$ -phenyl- $\beta$ -methyl-, m. p. 69° (thiazolidine, m. p. 45°);  $\beta$ -phenyl- $\alpha$ -methyl-, m. p. 95° (thiazolidine, m. p. 89°);  $\beta$ -phenyl- $\alpha$ -ethyl-, m. p. 152° (thiazolidine, perchlorate, m. p. 90°);  $\alpha$ -phenyl- $\beta$ -ethyl-, m. p. 97° (thiazolidine, m. p. 42°, perchlorate, m. p. 68°);  $\beta$ -phenyl- $\alpha$ -benzyl-, m. p. 110° (thiazolidine, m. p. 100°); and  $\alpha$ -phenyl- $\beta$ -benzyl-, oil

(thiazolidine perchlorate, m. p. 85°). When the above hydroxyethylthiocarbamides are treated with mercuric oxide in benzene, oxazolidines are produced. The latter are also obtained by the action of lead hydroxide and ammonia or aniline in alcoholic solution, no traces of the expected guanidines being formed. Ethylene chlorohydrin also acts as a desulphurising agent. The thiazolidines are also obtained by the action of ethylene dibromide on  $\alpha$ , $\beta$ -disubstituted thiocarbamides at 110–130°. A small proportion of thiocarbimide is also generally formed. The unsymmetrically substituted thiocarbamides always gave a large preponderance of one of the two possible isomeric thiazolidines, in which the more positive substituent of the thiocarbamide occupies position 2 of the thiazolidine. When the  $\gamma$ -ethylene ether of phenylthiocarbamide (cf. Bertram, A., 1892, 465) is heated with aniline at 125°, diphenylthiazolidine is formed. The following ethylene dithioethers,  $\text{NHR}\cdot\text{C}(\text{NR}')\cdot\text{S}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{C}(\text{NR}')\text{NHR}$ , were obtained by heating the appropriate phenylalkylthiocarbamide with ethylene dibromide at 110°: *phenylmethyl*, m. p. 139° (*hydrobromide*, m. p. 213°); *phenylethyl*, m. p. 130° (*hydrobromide*, m. p. 196°; *perchlorate*, m. p. 160°); *phenyl-n-butyl*, m. p. 92°. Propylene dibromide and phenylmethylthiocarbamide yielded similarly the *propylene ether*, m. p. 120° (*hydrobromide*, m. p. 195°). The following oxazolidines, obtained as above by the action of mercuric oxide, are listed: 2:3-*diphenyl*-, m. p. 124°; 2:3-*di-p-tolyl*-, m. p. 136°; 2-*phenyl*-3-*p-bromophenyl*-, m. p. 149°; 3-*phenyl*-2-*p-bromophenyl*-, m. p. 138°; and 2-*p-bromophenyl*-3-*p-tolyl-oxazolidine*, m. p. 108°.

F. G. W.

**3:3':3''-Trimethylaurin (o-Cresaurin) and 3:3':3''-Trimethyl-N:N':N''-Triphenylpararosaniline (Triphenylrosotoluidine).** M. GOMBERG and L. C. ANDERSON (*J. Amer. Chem. Soc.*, 1925, **47**, 2022–2033).—Condensation of *o*-cresol with carbon tetrachloride in presence of zinc chloride (at 125°), aluminium chloride (at 100°), or stannic chloride (at 130° in a closed vessel), affords di-*o*-tolyl carbonate, 4:4'-*dihydroxy*-3:3'-*dimethylbenzophenone*, m. p. 240° (*diacetate*, m. p. 102°; *dimethyl ether*, m. p. 116°; *oxime*, m. p. 137°), and 3:3':3''-*trimethylaurin* (*o-cresaurin*)

(I), maroon-red (cf. Gomberg and Snow, this vol., i, 660). Fusion of *o*-cresolbenzein with potassium hydroxide yields, not the above dihydroxydimethylbenzophenone (cf. Schroeter, A., 1890, 898), but 4-*hydroxy*-3-*methylbenzophenone*, m. p. 163° (*acetate*, m. p. 68°), which was synthesised by condensing benzoyl chloride with *o*-cresol in presence of aluminium chloride. Synthesis of the above dimethyl ether of 4:4'-*dihydroxy*-3:3'-*dimethylbenzophenone* was effected by the Grignard reaction from 3-methyl-4-methoxybenzaldehyde (cf. Gattermann, A., 1898, i, 476) and 5-bromo-2-methoxytoluene, m. p. 68° (cf. Zincke and Hedenström, A., 1907, i, 124).

*o*-Cresaurin was also obtained by condensing *o*-cresol with oxalic acid in presence of sulphuric acid at 100° (yield, 39–42%); by

the action of carbon tetrachloride on potassium *o*-tolylloxide at 105–110° (cf. Baines and Driver, T., 1923, **123**, 1214) (yield, 7–11%); and by heating 4:4'-diaminodi-*m*-tolylmethane with *o*-toluidine, *o*-toluidine hydrochloride, *o*-nitrotoluene, and iron filings at 150°, and treating the resulting base with nitrous acid (yield, 18%).

Boiling acetic anhydride converts *o*-cresaurin into 4:4':4''-tri-acetoxytri-*m*-tolylcarbinol, m. p. 141°; the trimethyl ether of *o*-cresaurin, m. p. 157°, is obtained both by direct methylation and by Grignard synthesis from 5-bromo-2-methoxytoluene and 4:4'-dimethoxy-3:3'-dimethylbenzophenone. Treatment of this trimethyl ether with hydrogen chloride in benzene, in presence of calcium chloride, affords 4:4':4''-trimethoxytri-*m*-tolylmethyl chloride, m. p. 164°, and this, when treated with molecular silver in bromobenzene, yields the corresponding free radical, from which the peroxide, m. p. 161–162°, is obtained on exposure to air or oxygen. The tribenzyl derivative of the above carbinol, m. p. 182°, is described. Bromination of *o*-cresaurin in glacial acetic acid affords the dibromo derivative (cf. Spiers, A., 1924, i, 385). When air or oxygen is drawn through a solution of *o*-cresaurin in dilute sodium hydroxide, 4:4'-dihydroxy-3:3'-dimethylbenzophenone is obtained.

The *hydrochloride*, light red, with golden lustre, and *hydrobromide*, similar, of *o*-cresaurin are obtained by the action of the appropriate hydrogen halide on *o*-cresaurin in glacial acetic acid. Each crystallises with 1 mol. of this solvent. The *hydrogen sulphate*, light red, obtained similarly, crystallises with 2 mols. of acetic acid. The *normal sulphate*, light orange-red, is obtained by the action of sulphuric acid on *o*-cresaurin in methyl sulphate solution. The *perchlorate*, light red, also crystallises with 1 mol. of acetic acid.

*o*-Cresaurin changes from yellow to red at  $p_H$  6.6–7.6. For use as an indicator, the dye is preferably added to the alkali.

4:4':4''-Trianilinotri-*m*-tolylcarbinol can be obtained by boiling *o*-cresaurin, or its trimethyl ether, or 3:3':3''-trimethyl-*p*-rosaniline (cf. Lambrecht, A., 1907, i, 257), with aniline in presence of benzoic or stearic acid. The *hydrochloride* is precipitated as bronze crystals when dry hydrogen chloride is passed through an ethereal solution of the base. This absorbs 2 further mols. of hydrogen chloride in an atmosphere of hydrogen chloride. Reduction with zinc dust and acetic acid affords 4:4':4''-trianilinotri-*m*-tolylmethane, m. p. 178–180°.

Similar condensation of *o*-cresaurin trimethyl ether with *p*-aminodiphenyl and  $\alpha$ - and  $\beta$ -naphthylamines afforded respectively a greenish-blue, purplish-blue, and pure blue dye. F. G. W.

**Bile Acids. XXII. Some Unexplained Results.** H. WIELAND (Z. *physiol. Chem.*, 1925, **142**, 191–208).—The compound (A., 1917, i, 685) obtained by the rapid distillation of deoxycholic acid has a molecular weight corresponding with the formula  $C_{24}H_{36}O_2$ . It is a lactone and contains one double linking; the *dihydro* compound has m. p. 230–232°.

When sodium cholanate is distilled with soda-lime, two hydrogen atoms are eliminated, in addition to the carboxyl group, with the formation of *dehydrocholan*, b. p. 210—213°. Dehydrocholan is a saturated compound; its formation is apparently due to the closure of a ring.

The ketone,  $C_{22}H_{32}O$  (Borsche, A., 1924, i, 1201), obtained by the distillation of deoxybilanic acid, is also produced when pyrodeoxybilanic acid is similarly distilled and is hence formed from the latter substance by loss of carbon dioxide and water. The oxime contains methyl alcohol of crystallisation and has m. p. 98—99° (cf. Borsche, *loc. cit.*). Hydrogenation of the ketone gives a *dihydro-ketone*, m. p. 136—137° (*oxime*, m. p. 154° after melting at 97° and again solidifying). The *anhydride* of pyrodeoxybilanic acid, m. p. 134°, is also produced during the distillation of deoxybilanic and pyrodeoxybilanic acids. Reduction of the above dihydro-ketone with alcoholic hydrochloric acid and zinc amalgam gives a saturated *hydrocarbon*,  $C_{22}H_{36}$ , m. p. 96°, which evidently contains five rings.

Distillation of choloidanic and pyrocholoidanic acids similarly yields an unsaturated, neutral substance, m. p. 120° (not sharp), which is probably formed from the former acid by loss of 3 mols. each of water and carbon dioxide.

When pyrocholoidanic acid is oxidised with fuming nitric acid, a *keto-tricarboxylic acid*,  $C_{23}H_{30}O_{10}$ , m. p. 278° (*trimethyl ester*, m. p. 132°; *semicarbazone*, m. p. 247°) is formed. This evidently retains the anhydride group, for, on boiling with 15% potassium hydroxide, it yields an *acid*,  $C_{23}H_{32}O_{11}$ , m. p. 298°. The latter acid readily loses water with the re-formation of the former one; hence no derivatives can be prepared.

E. S.

#### Conversion of Cholesterol into 4-Hydroxychoholic Acid.

A. WINDAUS and R. HOSSFELD (*Z. physiol. Chem.*, 1925, **145**, 177—183).—4-Chlorohydrocholic acid, m. p. 175—176°, is obtained by oxidation of 4-chlorocholestan in acetic acid solution with chromic acid for 6 hrs. at 95°; the *methyl ester* has m. p. 128°; *potassium salt*, very sparingly soluble. 4-Hydroxychoholic acid, m. p. 208°, is obtained by heating for 6 hrs. in an autoclave at 160—170° in a silver crucible a mixture of 4-chlorohydrocholic acid, 5% potassium hydroxide solution, and a little copper acetate; *potassium salt* very difficultly soluble; *methyl ester*, m. p. 162°. Oxidation of this acid with chromic acid gave a tribasic acid,  $C_{24}H_{38}O_6$ , identical with that of Staden (A., 1922, i, 541). A lactone *acid*,  $C_{27}H_{44}O_4$ , titrating in the cold as monobasic and in the hot as dibasic, m. p. 195—196°, is obtained by oxidation of the diacetyl derivative of 4:7-dihydroxycholestan in acetic acid with chromic acid at 95°; *methyl ester*, m. p. 99°.

P. W. C.

**Preparation of 3-Nitrophthalic Acid.** E. R. LITTMANN (*J. Amer. Chem. Soc.*, 1925, **47**, 1980—1981).—Phthalic anhydride (185 g.) is mixed with nitric acid, *d* 1.42 (175 c.c.), in a 3-litre flask. Sulphuric acid, *d* 1.84 (175 c.c.), is then added slowly, with constant shaking, and the mixture heated on a steam-bath for 2½—3 hrs.

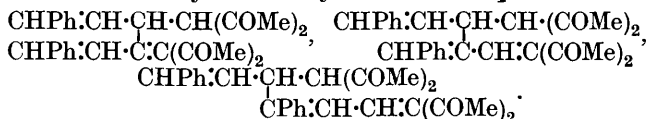
The cooled product is then poured into water (500 c.c.) with vigorous stirring, and the precipitated 3-nitrophthalic acid filtered with suction, washed with water (200—300 c.c.), and drained. Concentration of the combined filtrates yields a further small amount of product. Adherent water and nitric acid are then removed by mixing the crude product with benzene (600 c.c.) and distilling off about one-half of the solvent, or continuing until the distillate is clear, more benzene being added if necessary. The mixture is then cooled, the product filtered off, and air-dried for 12—24 hrs. The yield of crude product is 85—90% of theory, m. p. 198°. It may be purified by recrystallisation from glacial acetic acid, 48 hrs. being necessary for complete deposition from the solvent. The pure acid has m. p. 206°.

F. G. W.

**Halochromism of Fulgides. II.** R. DIETZEL and J. NATON (*Ber.*, 1925, **58**, [B], 1314—1320; cf. Stobbe and Dietzel, A., 1923, i, 39).—Bisdiphenylene fulgide, diphenylpiperonylfulgide, and dipiperonylfulgide give pale yellow or yellow solutions in chloroform or acetic acid, whereas the solutions in mono-, di-, and tri-chloroacetic acid are much darker. Attempts to isolate additive compounds of the fulgides with the halogenated acids were unsuccessful. Measurements of the absorption spectra show that the production of halochromism has an effect optically similar to but quantitatively less marked than that produced by the conversion of a saturated into an unsaturated compound. The production of halochromism in the fulgides depends therefore on the presence of the nucleus,  $\begin{smallmatrix} \text{:C:C:CO} \\ \text{:C:C:CO} \end{smallmatrix} > \text{O}$ . In confirmation of this hypothesis it is observed that halochromism is much more marked in the fulgides than in the corresponding fulgenic acids produced by rupture of the quinonoid nucleus and that halochromism is almost completely absent in the tetrahydrogenated fulgides or fulgenic acids which contain neither a quinonoid nucleus nor an ethylenic chromophore.

H. W.

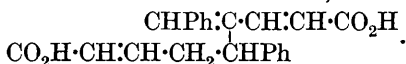
**Polymerisation of Cinnamylidenemalonic Acid, Cinnamylideneacetic Acid, Cinnamylideneacetylacetone, and Cinnamylideneacetone on Exposure to Light.** H. STOBBE, A. HENSEL, and W. SIMON (*J. pr. Chem.*, 1925, [ii], **110**, 129—152).—The authors suggest three possible triene formulæ for the bimolecular compound, m. p. 163° (cf. Ruhemann, T., 1904, **85**, 1453, m. p. 156—159°), obtained from cinnamylideneacetylacetone on exposure to sunlight :



Each of these is enolisable, whereas Ruhemann's *cyclobutane* formula (*loc. cit.*), suggested by analogy with that adopted for the dimeride of cinnamylidenemalonic acid (Rüber, A., 1902, i, 617; Kohler, A., 1902, i, 788), fails to explain the colour reaction with ferric chloride. Moreover, the substance differs from this cyclic dimeride in that its formation is accompanied by autoxidation and

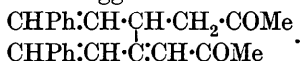
resinification (a *compound*, m. p. 125°, is also formed), that, on oxidation, it yields no truxillic acid, but is broken down into benzoic, acetic, and oxalic acids, and that it is not depolymerised by heat. No distinction is yet possible between the three triene formulæ.

Riiber's *cyclobutane* structure for the dimeride obtained by the action of light on cinnamylideneacetic acid (A., 1913, i, 274) is supported by the depolymerisation of the compound on heating. His second dimeride, obtained by vacuum distillation of bis-cinnamylidenemalonic acid, is not depolymerised by heat and, on oxidation, yields, not truxillic acid, but benzoic and oxalic acids. A triene formula, consequent on intramolecular transformation accompanying elimination of carbon dioxide, is therefore proposed :



Catalytic reduction of the sodium salt gives an *acid*, m. p. 151—152°, regarded as a hexahydro derivative.

Cinnamylideneacetone polymerises in presence of air in the dark, more rapidly on exposure to light, undergoing simultaneous autoxidation to pyruvic acid, benzaldehyde, and cinnamaldehyde or benzoic and cinnamic acids. The *dimeride* is a colourless, non-crystallisable resin, oxidised in acid solution to benzoic acid, in alkaline solution to benzaldehyde, benzoic and pyruvic acids. It is not depolymerised by heat, which induces formation of a resinous *substance*, apparently a trimolecular polymeride. A triene formula is therefore suggested :



The two phenylbutadienecarboxylic acids thus polymerise to *cyclobutane* derivatives, whilst the two ketones give triene derivatives with one isolated ethylenic linking and one conjugated pair. In comparison with these additive reactions, the authors summarise those of the unimolecular compounds with hydrogen and bromine, respectively. A *dibromide* ( $\gamma\delta$ ?), decomp. 106°, and a *bromodibromide*, possibly  $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CBr}\cdot\text{C}(\text{COMe})_2$ , decomp. 116°, of cinnamylideneacetylacetone are described. M. J.

**$\epsilon$ -Phenyl- $\Delta^{86}$ -pentadien- $\alpha$ -al and  $\eta$ -Phenyl- $\Delta^{86\zeta}$ -heptatrien- $\alpha$ -al.** D. VORLÄNDER, E. FISCHER, and K. KUNZE (*Ber.*, 1925, 58, [B], 1284—1290).—The condensation of cinnamaldehyde with acetaldehyde in aqueous-alcoholic solution in the presence of sodium hydroxide leads to the production of  $\epsilon$ -phenyl- $\Delta^{86}$ -pentadien- $\alpha$ -al (*styrylacrolein*),  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CHO}$ , b. p. 160—162°/20 mm.,  $\eta$ -phenyl- $\Delta^{86\zeta}$ -heptatrien- $\alpha$ -al, b. p. 190—195°/16 mm., and higher aldehydes which are separated from one another by rapid fractional distillation during which considerable resinification cannot be avoided.  $\epsilon$ -Phenyl- $\Delta^{86}$ -pentadien- $\alpha$ -al is oxidised by silver oxide to styrylacrylic acid, m. p. 164°. It condenses with malonic acid in the presence of glacial acetic acid to  $\epsilon$ -phenylpentadienylmalonic acid,  $\text{Ph}\cdot[\text{CH}\cdot\text{CH}]_2\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{H})_2$ , m. p. 210—212° (corr., decomp.), the dark yellow, alcoholic solution of which is



decolorised by addition of two equivalents of sodium hydroxide; the *silver* salt is described. *Di-ζ-phenyl-Δ<sup>αγ</sup>-hexatrienyl ketone*, m. p. 189—190° (corr.), prepared by the action of sodium hydroxide on an alcoholic solution of ε-phenyl-Δ<sup>βδ</sup>-pentadien-α-al and acetone, gives with hydrogen chloride a dark blue *hydrochloride*, A, with bromine (2 mols.) in chloroform a green *bromo adduct*, A, and with excess of bromine the colourless *dodecabromide*, C<sub>25</sub>H<sub>22</sub>OBr<sub>12</sub>, m. p. 245° (corr. decomp.) after darkening at 234°. *Di-ε-phenyl-Δ<sup>βδ</sup>-pentadienylcyclohexanone*, m. p. 202° (corr.), gives green and red *adducts* with bromine with elimination of hydrogen bromide and an *adduct*, A, with hydrogen chloride. ε-Phenyl-Δ<sup>βδ</sup>-pentadien-α-al yields condensation *products* with *p*-phenetidine, m. p. 133—134° (corr.), *p*-anisidine, m. p. 143° (corr.), *p*-aminoazobenzene, m. p. I 172° (corr.), II 168° (corr.), phenylhydrazine, m. p. 170—172° (corr.), hydrazine, m. p. 207—209° (corr.), and semicarbazide, m. p. 207—209° (corr., decomp.) after softening at 210°.

η-Phenyl-Δ<sup>βδγ</sup>-heptatrien-α-al is obtained in quantity by the condensation of ε-phenyl-Δ<sup>βδ</sup>-pentadien-α-al with acetaldehyde. It is oxidised by ammoniacal silver oxide to the corresponding acid, which becomes partly resinified during the process. Condensation with acetone or cyclohexanone gives resinous products. With malonic acid, it yields η-phenyl-Δ<sup>βδγ</sup>-heptatrienylmalonic acid, m. p. (indefinite) 195° (decomp.). It yields well-defined *compounds* with *p*-phenetidine, m. p. I 200° (corr.), II 171° (corr.), *p*-anisidine, m. p. I 205—207°, II 165°, and aminoazobenzene, m. p. I about 300°, II 251° (corr.). The products of higher b. p. obtained from cinnamaldehyde and acetaldehyde contain an aldehyde which gives with *p*-phenetidine a *compound*, m. p. I 255°, II 201° (corr.).

H. W.

### Condensation of Aldehydes with Aminomalononitrile.

E. GRISCHKEVITSCH-TROCHIMOVSKI and A. SEMENCOV (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 547).—When aminomalononitrile (1 mol.) isolated from the products of the polymerisation of hydrocyanic acid, is heated with an aldehyde (1 mol.), the condensation,  $R\cdot CHO + NH_2\cdot CH(CN)_2 = CHR\cdot N\cdot CH(CN)_2 + H_2O$ , proceeds readily and with good yield. From benzaldehyde in this way is obtained the *compound* CHPh·N·CH(CN)<sub>2</sub>, cinnamon, prismatic crystals, m. p. 190° (decomp.); from salicylaldehyde, the *compound* OH·C<sub>6</sub>H<sub>4</sub>·CH·N·CH(CN)<sub>2</sub>, yellowish-green needles, m. p. 235° (decomp.); and from anisaldehyde, the *compound*



yellow crystals, m. p. above 280°. The *benzoyl* derivative of aminomalononitrile, NHBz·CH(CN)<sub>2</sub>, forms yellow crystals, m. p. about 220° (decomp.).

These reactions confirm the presence of the amino group in the trimeride of hydrocyanic acid.

T. H. P.

**Oxidations with Ozone. III. Preparation of Methylvanillin, Piperonal, and Anisaldehyde.** E. BRINER, H. VON TSCHARNER, and H. PAILLARD (*Helv. Chim. Acta*, 1925, **8**, 406—412; cf. A., 1924, i, 290, and this vol., i, 274).—Parallel experiments on

the oxidation of *isoeugenol* and *methylisoeugenol* in carbon tetrachloride solution at  $-15^{\circ}$  with ozone of 7—9% strength by volume show that the yield of *methylvanillin* is considerably higher than that of *vanillin*, a result in accordance with the observation of Fichter and Christen (this vol., i, 813) that in electrolytic oxidation of benzene derivatives the resin formation favoured by the presence of a phenolic hydroxyl group is checked by alkylation.

In the preparation of piperonal by ozonation of *isosafole*, the proportion of ozone actually utilised in oxidation reaches 58.3% under the most favourable conditions, viz., at the ordinary temperature with 7% (vol.) ozone conducted through a carbon tetrachloride solution for 30 mins. Thereby 46% of the *isosafole* is converted into piperonal. Variation in temperature between  $-15^{\circ}$  and  $+20^{\circ}$  is without effect. Increase in time of ozonation lowers both efficiency and yield by further oxidation to piperonylic acid. In the preparation of anisaldehyde from anethole, increase of time has a similar effect due to production of anisic acid. Lowering of temperature and raising of ozone concentration, however, exert a favourable influence. The highest oxidation efficiency obtained, in terms of ozone consumed, reaches 57.2% and at the same time 55.7% of the anethole is converted into anisaldehyde, when 9.7% (vol.) ozone is conducted into a carbon tetrachloride solution for 45 mins. at  $-15^{\circ}$ . *p*-Tolyl methyl ether resists attack by ozone. An unsaturated side-chain, lending itself to ozonide formation in the intermediate stage, appears to be an essential for oxidation by this medium.

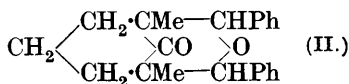
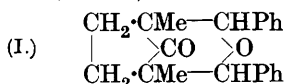
M. J.

**Aldoxime Peroxides. III.** R. CIUSA and E. PARISI (*Gazzetta*, 1925, 55, 416—421; cf. A., 1923, i, 579; 1924, i, 52).—From the behaviour on decomposition of the aldoxime peroxides, which give two sets of products accordingly as the decomposition is uni- or bi-molecular in type (A., 1921, i, 113; 1924, i, 1075), the authors suggest that these "peroxides" are molecular compounds of unchanged oxime with a nitrile oxide,  $[\text{CHR}:\text{NOH}][\text{CR}:\text{N}:\text{O}]$ . The production of  $\alpha$ -dibenzenyloxyazoxime in the oxidation of benzaldoxime peroxide (Robin, A., 1919, i, 592) is simply explained on this hypothesis. In the decomposition of this peroxide in boiling benzene it is now found that 79% of the original oxime is recoverable unchanged. Further evidence for the above constitution was obtained from quantitative measurements of the products of reduction of benzaldoxime peroxide; the amounts of benzaldoxime and benzonitrile formed are in agreement with those expected on the basis of the formula proposed.

F. G. T.

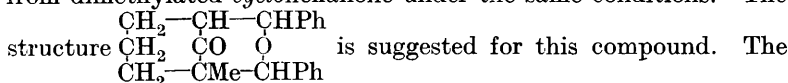
**Constitution of the Dimethylcyclopentanone and Dimethylcyclohexanone Obtained by Methylation in Presence of Sodamide.** A. HALLER and R. CORNUBERT (*Compt. rend.*, 1925, 180, 1988—1993).—The presence of 1 : 4-dimethylcyclopentan-5-one, in the methylation product of 1-methylcyclopentan-5-one is confirmed (cf. A., 1924, i, 1203) by the isolation from the reaction mixture, when treated with benzaldehyde, of the aldehyde condensation product of the symmetrical dimethylcyclopentanone. The

constitution (I) has been assigned to the compound, by analogy with the corresponding compounds prepared by Petrenko-Kritschenko and others (A., 1896, i, 472; 1898, i, 142, 529; 1899, i, 440; 1908, i, 560) and by Vorländer and others (A., 1896, i, 546; 1898, i, 167).



Similar compounds are obtained by the condensation of the dimethylcyclopentanone with *p*-tolualdehyde (m. p. 146°), cumaldehyde (m. p. 192°), and anisaldehyde. By treatment of the reaction mixture from the methylation of 1-methylcyclohexan-6-one with benzaldehyde, the condensation compound (II) of 1:5-dimethylcyclohexan-6-one, m. p. 197—198° (corr.), together with a product, m. p. 119—120°, are obtained. L. F. H.

**Constitution of the Dimethylcyclopentanone and Dimethylcyclohexanone Obtained by Alkylation by the Sodamide Method.** A. HALLER and R. CORNUBERT (*Compt. rend.*, 1925, **181**, 81—85; cf. A., 1920, i, 390, 441; 1924, i, 1203; and preceding abstract).—2-Methylcyclohexanone condenses with benzaldehyde in the presence of sodium ethoxide to give the benzylidene derivative, m. p. 60° (semicarbazone, m. p. 214—215°), and a small amount of a product, m. p. 143—144°. When hydrogen chloride is passed into a mixture of 2-methylcyclohexanone and benzaldehyde at —15°, the products are the benzylidene derivative and a very viscous liquid, b. p. 240—260°/35 mm., from which may be isolated a white compound, C<sub>21</sub>H<sub>22</sub>O<sub>2</sub>, m. p. 120°, or +C<sub>6</sub>H<sub>6</sub>, 91—92° (decomp.; oxime, m. p. 224—226°), identical with the by-product obtained from dimethylated cyclohexanone under the same conditions. The



compound of m. p. 148—150° previously obtained from the ethylation product of 2-methylcyclohexanone (A., 1920, i, 441) is probably similarly derived from 2-methyl-6-ethylcyclohexanone, the compound of m. p. 76—78° being the normal benzylidene derivative of 2-methyl-2-ethylcyclohexanone. In the same way, methyl-*n*-propylcyclohexanone yields 6-benzylidene-2-methyl-2-*n*-propylcyclohexanone, m. p. 25°, and a compound, C<sub>24</sub>H<sub>28</sub>O<sub>2</sub>, m. p. 136—137°, derived from 2-methyl-6-*n*-propylcyclohexanone (Cornubert, unpublished work).

Methylation of 2-methylcyclopentanone by the sodamide method gives 95% of 2:2-dimethyl- and at most 5% of 2:6-dimethylcyclopentanone. 2-Methylcyclohexanone similarly yields 80% of 2:2-dimethyl derivative, a little 2:6-isomeride, and some unchanged 2-methylcyclohexanone. C. H.

**Conversion of Dialkylcyclohexenones into Dialkylbenzenes.** E. E. BLAISE and (MLLE.) M. MONTAGNE (*Compt. rend.*, 1925, **181**, 122—124).—2-Methyl-3-ethyl-Δ<sup>2</sup>-cyclohexenone does not react with

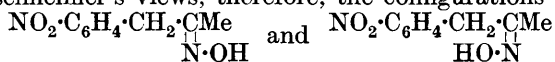
saturated aqueous hydrobromic acid at 0°, but when the mixture is heated in a sealed tube at 100° dehydration occurs, with almost quantitative formation of 1-methyl-2-ethylbenzene (Claus, A., 1887, 240), b. p. 62—63°/20—21 mm.,  $d_{44}^{24.7}$  0.8786,  $n_D$  1.50198, identified further by oxidation to phthalic acid. The only similar reaction recorded is Knoevenagel's conversion of a triphenylcyclohexenone into triphenylbenzene by zinc chloride (A., 1895, i, 49). C. H.

**Components of Acetone Oil.** H. PRINGSHEIM and J. BONDI (*Ber.*, 1925, 58, [B], 1409—1416).—Yellow acetone oil, b. p. 130—250°, obtained after removal of white acetone oil, b. p. 75—130°, and acetone from the product obtained by heating grey acetate, is subjected to preliminary fractional distillation with steam. The first two fractions gave copious and considerable precipitates with sodium hydrogen sulphite, with which the third fraction did not react. The last portion was separated by systematic fractionation under diminished pressure into the following components: 3 : 5 : 5-trimethylcyclohexanone, b. p. 53.5—54°/11 mm.,  $d^{19}$  0.8919,  $n_D^{15}$  1.4454; 2 : 4 : 4-trimethylcyclohexanone, b. p. 61°/11 mm.,  $d^{19}$  0.900,  $n_D^{19}$  1.4545; 3 : 5 : 5-trimethyl- $\Delta^2$ -cyclohexenone, b. p. 74—75°/11 mm.,  $d^{18}$  0.9228,  $n_D^{18}$  1.4766; 3-isopropyl- $\Delta^2$ -cyclopentenone, b. p. 83.5—84.5°/11 mm.,  $d^{20}$  0.9378,  $n_D^{20}$  1.4788; 1 : 3 : 3-trimethyldi-cyclohexenone, b. p. 93.5°/13 mm.,  $d^{19}$  0.9754;  $n_D^{19}$  1.4918 (*semi-carbazone*, m. p. 121°). H. W.

**Stereoisomeric Forms of *o*-Nitrobenzyl Methyl Ketoxime.** P. W. NEBER, K. HARTUNG, and W. RUOPP (*Ber.*, 1925, 58, [B], 1234—1246).—The action of a large excess of fuming nitric acid on benzyl methyl ketone at -5° follows a complicated course, giving a mixture of products which are roughly separated by treatment with alkali hydroxide. The whole of the *o*-nitroketone is present in the insoluble portion, but its isolation therefrom is not directly possible. It is therefore treated with hydroxylamine hydrochloride and sodium acetate in aqueous-alcoholic solution; from the hot solution, *o*-nitrobenzyl methyl  $\alpha$ -ketoxime, m. p. 158°, separates, followed at a lower temperature by *o*-nitrobenzyl methyl  $\beta$ -ketoxime, m. p. 151° after softening at 148°. The mother-liquors from the latter compound contain a mixture of the  $\alpha$ - and  $\beta$ -forms which is worked up for the individual substances by hydrolysis to *o*-nitrobenzyl methyl ketone (m. p. 25—26°) followed by oximation of the latter. The conversion of the labile  $\beta$ -form into the  $\alpha$ -modification is effected by gently heating it above its m. p. or by treating its ethereal solution with gaseous hydrogen chloride and subsequently decomposing the hydrochloride so obtained. Conversely, an indirect transformation of the  $\alpha$ - into the  $\beta$ -form is effected by hydrolysis of the former followed by oximation in the presence of sodium acetate, but not sodium carbonate. The portion of the crude product soluble in alkali hydroxide yields benzaldoxime and *p*-nitrobenzaldoxime (*benzoyl-p-nitrobenzaldoxime*, m. p. 193°, decomposes quantitatively at 140—145° into benzoic acid and *p*-nitrobenzonitrile, m. p. 149°). In addition, 2 : 4-dinitrobenzyl methyl ketone,

m. p.  $75^{\circ}$ , *p*-nitrobenzyl methyl ketone, and *o*- and *p*-nitrobenzoic acids are isolated. The formation of the benzaldoximes in small amount is doubtless due to the presence of nitrous acid in the fuming nitric acid and the consequent formation and subsequent hydrolysis of  $\alpha$ -oximino- $\beta$ -keto- $\alpha$ -*o*-nitrophenylpropane, m. p.  $148^{\circ}$  (conveniently prepared by the action of amyl nitrite and concentrated hydrochloric acid on *o*-nitrobenzyl methyl ketone), but the production of benzaldoxime in 50% yield by the action of sulphuric acid and the quantity of nitric acid required for the introduction of one nitro group on benzyl methyl ketone appears inexplicable.  $\alpha$ -Oximino- $\beta$ -keto- $\alpha$ -*o*-nitrophenylpropane is converted into the corresponding *hydrazone*, m. p.  $217^{\circ}$ , *phenylhydrazone*, m. p.  $160^{\circ}$ , and *phenylmethylhydrazone*, m. p.  $117^{\circ}$  (converted by boiling acetic anhydride into 2-phenyl-4-*o*-nitrophenyl-5-methyl-1 : 2 : 3-triazole, m. p.  $165^{\circ}$ ). *o*-Nitrobenzyl methyl ketone yields a *semicarbazone*, m. p.  $205^{\circ}$ , and an unstable *phenylhydrazone*, m. p. (?)  $76^{\circ}$ . *o*-Nitrobenzyl methyl  $\alpha$ -ketoxime is converted by benzoyl chloride in the presence of pyridine at  $0^{\circ}$  into the corresponding *benzoate*, m. p.  $123^{\circ}$ , which is hydrolysed by alcoholic ammonia at the atmospheric temperature to a mixture of the  $\alpha$ - and (mainly)  $\beta$ -oximes, whereas the *benzoate* of the  $\beta$ -oxime, m. p.  $74^{\circ}$ , is converted under similar conditions into the  $\beta$ -oxime.

Attempts to elucidate the configuration of the oximes by a study of their behaviour towards phosphorus pentachloride in ethereal solution were frustrated by the stability of the substances. Cold concentrated sulphuric acid effects mainly a partial isomerisation of the oximes, whereas either form is converted by the warm acid into acet-*o*-nitrobenzylamide. The  $\alpha$ - and  $\beta$ -oximes are converted by benzenesulphochloride in the presence of pyridine into the corresponding *benzenesulphonates*, m. p.  $91^{\circ}$  and  $115^{\circ}$ , respectively. The  $\alpha$ -ester is transformed by dilute sulphuric acid in the presence of alcohol into acet-*o*-nitrobenzylamide, whereas the  $\beta$ -compound yields *o*-nitrophenylacetomethylamide, m. p.  $145^{\circ}$ . In accordance with Meisenheimer's views, therefore, the configurations



are assigned to the  $\alpha$ - and  $\beta$ -oximes. (The synthesis of *o*-nitrophenylacetmethylamide by the successive action of thionyl chloride and methylamine on *o*-nitrophenylacetic acid is recorded.)

The following derivatives of 2 : 4-dinitrobenzyl methyl ketone are described : *oxime*, m. p.  $140^{\circ}$ ; *hydrazone*, m. p.  $115^{\circ}$ , which is transformed by benzaldehyde, aniline, or *p*-toluidine at  $160^{\circ}$  into 5-di- $\beta$ -2 : 4-dinitrophenylisopropylidenehydrazine;  $\beta$ -chloro- $\alpha$ -2 : 4-dinitrophenyl- $\Delta^{\alpha}$ -propylene, m. p. (indefinite)  $85$ – $96^{\circ}$ , from the ketone and phosphorus pentachloride in the presence of chloroform.

H. W.

**Beckmann Transformation. V. Oximes of *p*-Methoxybenzil.** J. MEISENHEIMER, H. LANGE, and W. LAMPARTER (*Annalen*, 1925, **444**, 94–112).—In continuance of previous work (A., 1924, i, 433) the four mono-oximes and four dioximes of *p p*\*

*p*-methoxybenzil required by the Hantzsch-Werner theory have now all been obtained.

$\alpha$ -Nitro-4-methoxystilbene (A., 1922, i, 177) on heating with methyl-alcoholic potassium hydroxide yields  $\alpha$ -4'-methoxybenzil-7'-oxime-7 : 7-dimethylacetal ( $\alpha_2$ -acetaloxime),  $\text{CPh(OMe)}_2 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ ,  $\text{N} \cdot \text{OH}$ ,

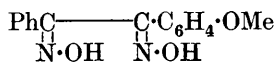
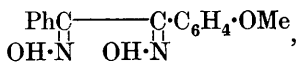
m. p. 205°, which acetic acid converts into  $\alpha$ -4'-methoxybenzil-7'-oxime,  $\text{COPh} \cdot \text{C}(\text{N} \cdot \text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$  ( $\alpha_2$ -monoxime), m. p. 108—110°. No crystalline acyl derivative of this oxime could be obtained with benzoyl chloride or acetic anhydride and on crystallisation from alcohol it is partly converted into the  $\beta$ -form; the transformation is complete on treatment with hydrochloric acid.  $\beta$ -4'-Methoxybenzil-7'-oxime has m. p. 170°; its *acetyl* derivative, m. p. 99—100°, yields the oxime quantitatively on hydrolysis. On further treatment with sodium hydroxide and hydroxylamine, both the  $\alpha$ -4'-methoxybenzil-7'-oxime and  $\alpha$ -4'-methoxybenzil-7'-oxime are converted into  $\alpha$ -*p*-methoxybenzildioxime,  $\text{PhC} \begin{array}{c} \text{---} \\ \text{OH} \cdot \text{N} \end{array} \text{---} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ ,  $\text{N} \cdot \text{OH}$ , m. p.

206—207°, in 75—80% yield. This dioxime is the least soluble of the four isomerides; acetic anhydride converts it quantitatively into a *diacetyl* derivative, m. p. 108°, from which the original dioxime is formed on hydrolysis. Moderately concentrated sodium hydroxide converts this  $\alpha$ -dioxime into a  $\beta$ -isomeride,  $\beta$ -*p*-methoxybenzildioxime,  $\text{PhC} \begin{array}{c} \text{---} \\ \text{N} \cdot \text{OH} \end{array} \text{---} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ ,  $\text{OH} \cdot \text{N}$ , m. p. 176°, the most stable dioxime

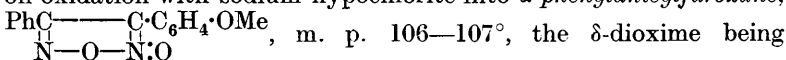
which can be obtained from the other three isomerides, but never formed as the primary product in direct oximation. Its *diacetyl* derivative, m. p. 130°, yields the original dioxime on hydrolysis. A third dioxime,  $\gamma$ -*p*-methoxybenzildioxime, m. p. 89—91°, is obtained on treatment of  $\beta$ -4-methoxybenzil-7-oxime with hydroxylamine and sodium hydroxide, whilst  $\beta$ -4-methoxybenzil-7'-oxime similarly yields the fourth ( $\delta$ ) dioxime,  $\delta$ -*p*-methoxybenzildioxime, m. p. 114—115°. These two dioximes resemble benzil- $\gamma$ -dioxime in their mode of formation and properties. In benzene solution, both  $\gamma$ - and  $\delta$ -dioximes are more or less rapidly converted into the  $\beta$ -dioxime. With the  $\gamma$ -dioxime the transformation is appreciably more rapid, especially in alcohol or ether; in the case of the  $\delta$ -isomeride, the change is quantitative on warming with sodium hydroxide. On heating above its m. p., the  $\gamma$ -dioxime again becomes solid, owing to its conversion into the  $\beta$ -isomeride; the  $\delta$ -dioxime (which crystallises with 0.5 mol. of benzene) behaves similarly. On treatment with aqueous sodium hydroxide the  $\gamma$ -dioxime yields mainly the  $\beta$ -dioxime together with about 5% of phenylanisylfurazane,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} > \text{O}$ . Its *diacetyl* derivative, m. p. 100—102°, on recrystallisation partly undergoes transformation into the  $\beta$ -*diacetyl*-dioxime, whilst hydrolysis with aqueous sodium hydroxide converts it into phenylanisylfurazane, with traces of  $\beta$ -*p*-methoxybenzildioxime. Similarly, the *diacetyl* derivative, m. p. 70—80°, of the  $\delta$ -dioxime on hydrolysis yields a mixture of furazane (67%) and

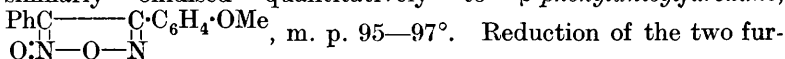
$\alpha$ -dioxime (23%), if the acetylation is performed at  $0^\circ$ ; acetylation at the ordinary temperature yields on hydrolysis 59% of furazane and 34% of dioxime; whilst boiling with acetic anhydride leads to a product yielding on hydrolysis 30–31% of anhydride and 64% of  $\alpha$ -dioxime. These results indicate that transformation to the  $\alpha$ -dioxime occurs in the acetylation stage and not in hydrolysis. Phenylanisylfurazane is produced in 90% yield by heating either the  $\gamma$ - or the  $\delta$ -dioxime at  $200$ – $220^\circ$  in alcoholic solution. The formation of this anhydride establishes the configuration of the  $\gamma$ - and  $\delta$ -oximes as

 $\gamma$ -*p*-Methoxybenzildioxime. $\delta$ -*p*-Methoxybenzildioxime.

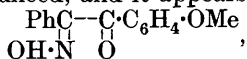
a conclusion which is confirmed by the conversion of the  $\gamma$ -dioxime on oxidation with sodium hypochlorite into  $\alpha$ -phenylanisylfuroxane,



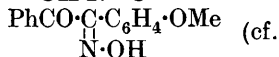
similarly oxidised quantitatively to  $\beta$ -phenylanisylfuroxane,



oxanes by Angeli's method (A., 1892, 1198) at low temperatures yields the corresponding  $\gamma$ - or  $\delta$ -dioxime; at higher temperatures this is admixed with  $\beta$ -dioxime. These results confirm the views previously expressed (A., 1922, i, 152) on the constitution of the oxidation products of oximes. The influence of the methoxy group on the stability of these oximes is very pronounced, and it appears to repel the hydroxyl group, the  $\alpha_1$ -oxime,



being more stable than the  $\alpha_2$ -oxime,



Hantzsch, A., 1891, 439).

$\alpha$ -4'-Methoxybenzil-7-oxime under the conditions used by Atack and Whinyates (T., 1921, 119, 1184), yields a mixture of  $\alpha$ - and a little  $\beta$ -diacetyldioxime, thus confirming earlier results (A., 1924, i, 432). R. B.

#### Dioximes. XXIV. G. PONZIO (*Gazzetta*, 1925, 55, 311–323).

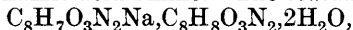
—A preliminary account of this work has been already published (cf. this vol., i, 8). After crystallisation from ether, chlorophenylglyoxime (cf. A., 1923, i, 473) has m. p. (decomp.)  $198^\circ$ .

The *diacetyl* derivative of the dioxime of dibenzoylglyoxime peroxide (cf. A., 1924, i, 56), prepared either from the dioxime or by shaking the ethereal solution of the diacetyl compound of chlorophenylglyoxime with 5% aqueous sodium carbonate solution and heating the benzene solution with silver benzoate, has m. p.  $128^\circ$ .

Benzylidenechloroaldoxime,  $\text{NOH}:\text{CPhCl}$ , has m. p.  $52^\circ$  (cf. Werner and Buss, A., 1894, i, 585).

$\alpha$ -Hydroxy- $\beta$ -phenylglyoxime,  $\text{NOH}:\text{CPh} \cdot \text{C}(\text{OH})\text{:NOH}$ , prepared by the action of sodium acetate on chlorophenylglyoxime in presence

of acetic acid or by the action of hydroxylamine on either benzoylformhydroxamic acid or ethyl  $\alpha$ -oximinophenylacetate, forms white laminæ, m. p.  $191^{\circ}$  (evolving gas), gives a deep red coloration with ferric chloride in aqueous solution, and at  $100^{\circ}$  attacks nickel with liberation of hydrogen and formation of the reddish-brown, amorphous *nickel* salt. Two forms of hydroxyphenylglyoxime were described by Gastaldi (A., 1924, i, 733, 1116) under the name benzoylformhydroxamic acid oxime. The *sodium* salt,



explodes at about  $204^{\circ}$ ; the *potassium* salt and the *ammonium* salt, m. p.  $177$ — $178^{\circ}$  (decomp.), are anhydrous, and the *silver* salt,  $\text{C}_8\text{H}_7\text{O}_3\text{N}_2\text{Ag}$ , is stable towards light, but is blackened by boiling water and explodes when heated.

$\alpha$ -Hydroxy- $\beta$ -*p*-tolylglyoxime, prepared from chloro-*p*-tolylglyoxime, is identical with the  $\alpha$ -oxime of *p*-toluoylformhydroxamic acid (cf. Gastaldi, A., 1924, i, 1208); the author considers that the two supposed oximes of this acid represent one and the same compound.

T. H. P.

**Anthrone Series.** F. MAYER and W. FISCHBACH (*Ber.*, 1925, 58, [B], 1251—1253).—*o*-Bromomethylbenzoyl bromide is converted by aluminium chloride and benzene according to experimental conditions into *phenyl o*-benzylphenyl ketone, m. p.  $152^{\circ}$ , or anthrone, m. p.  $158^{\circ}$ . If chlorobenzene is substituted for benzene, 3-chloroanthrone, m. p.  $142$ — $144^{\circ}$ , is obtained, the constitution of which is established by its conversion into 3-chlorobenzanthrone (cf. Scholl, A., 1922, i, 258). The compound obtained from 2-chloroanthraquinone by Eckert and Tomaschek (A., 1919, i, 163) must therefore be 2-, not 3-chlorobenzanthrone. With *p*-bromotoluene, a compound, m. p.  $135^{\circ}$  after softening, is obtained which is either 4-bromo-1-methyl- or 1-bromo-4-methyl-anthrone. With toluene, *p*-chlorotoluene, *p*-dichlorobenzene, and *p*-dibromobenzene satisfactory results could not be obtained.

H. W.

**Preparation of 2-Aminoanthraquinone from Phthalic Anhydride and Chlorobenzene.** M. PHILLIPS (*Ind. Eng. Chem.*, 1925, 17, 721—725).—The reactions involved in this preparation have been studied in detail and optimum conditions established. Thus the molal ratio of phthalic anhydride to aluminium chloride in the first stage should be 1 : 1; in the second stage (conversion of the chlorobenzoylbenzoic acid into 2-chloroanthraquinone) the ratio of the chlorobenzoylbenzoic acid to the sulphuric acid should be 1 : 6, and the temperature  $150^{\circ}$ . In the third stage of conversion to 2-aminoanthraquinone, the reaction temperature should be  $220^{\circ}$ , the time 6 hrs., and 15—20 parts of ammonia should be used to 1 part of 2-chloroanthraquinone. No catalyst is necessary.

D. G. H.

**Polyhydroxy- and Polyhydroxymethyl-anthraquinones.**  
**VI. Syntheses from Opianic Acid and Phenols or Cresols.**  
 R. A. JACOBSON and R. ADAMS (*J. Amer. Chem. Soc.*, 1925, 47, 2011—2018).—The following phthalides were prepared by the condensation of opianic acid with the appropriate phenol in presence



of sulphuric acid (73—95%) (cf. this vol., i, 272): 5:6-dimethoxy-2-(6'-hydroxy-*m*-tolyl)phthalide, m. p. 181·5—183°; 5:6-dimethoxy-2-(2'-hydroxy-3':5'-xylyl)phthalide, m. p. 170—171°; 5:6-dimethoxy-2-(2'-hydroxy-5'-nitrophenyl)phthalide, m. p. 269—270°; 5:6-dimethoxy-2-(3':4'-dimethoxyphenyl)phthalide, m. p. 122—123°; 5:6-dimethoxy-2-(4'-hydroxy-3'-methoxyphenyl)phthalide, m. p. 171—172°; 5:6-dimethoxy-2-(4'-hydroxy-*m*-tolyl)phthalide, m. p. 185—186°; and 5:6-dimethoxy-2-(3':5'-dibromo-6'-hydroxy-*o*-tolyl)phthalide, m. p. 205—205·5°. *p*-Bromo-*m*-cresol and opianic acid afforded a mixture of 5:6-dimethoxy-2-(5'-bromo-2'-hydroxy-*p*-tolyl)phthalide, m. p. 180—181°, and 5:6-dimethoxy-2-(3'-bromo-6'-hydroxy-*o*-tolyl)phthalide, m. p. 270—271° after sintering at 265°. Reduction of the phthalides with zinc dust in sodium hydroxide solution afforded the following substituted benzylbenzoic acids: 5:6-dimethoxy-2-(2'-hydroxy-5'-methylbenzyl)-, m. p. 125—126°; 5:6-dimethoxy-2-(3':4'-dimethoxybenzyl)-, syrup; 5:6-dimethoxy-2-(2'-hydroxy-6'-methylbenzyl)-, m. p. 173—175°; 5:6-dimethoxy-2-(4'-hydroxy-3'-methylbenzyl)-, syrup; 5:6-dimethoxy-2-(2'-hydroxy-4'-methylbenzyl)-, syrup; and 5:6-dimethoxy-2-(4'-hydroxy-3'-methoxybenzyl)benzoic acid (+H<sub>2</sub>O), m. p. 105—106°. Solution of the benzylbenzoic acids in concentrated sulphuric acid (the latter being diluted to 85% in those cases where sulphonation becomes evident) effects conversion into anthrones, of which the following were prepared: 1:2:6:7-tetramethoxy-9-anthrone, m. p. 153—154°; 7-hydroxy-1:2:6-trimethoxy-9-anthrone, 7-hydroxy-1:2-dimethoxy-6-methyl-9-anthrone, 5-hydroxy-1:2-dimethoxy-7-methyl-9-anthrone, and 5-hydroxy-1:2-dimethoxy-8-methyl-9-anthrone, not purified; the acetyl derivative of the last named, greenish-yellow, has m. p. 188·5—189°. The anthrones are oxidised to the corresponding anthraquinones by chromic acid in acetic acid, the reaction being exothermic. The following anthraquinones, all of which are yellow, are described: 5-hydroxy-1:2-dimethoxy-8-methyl-, m. p. 168—169° (acetyl derivative, m. p. 173—174°); 5-hydroxy-1:2-dimethoxy-7-methyl-, m. p. 231·5—232·5°; 7-hydroxy-1:2:6-trimethoxy-, m. p. 269—270°; 7-hydroxy-1:2-dimethoxy-6-methyl-, m. p. about 310°; and 1:2:6:7-tetramethoxyanthraquinone, m. p. 244—245°. Demethylation was effected by boiling with hydrobromic acid in acetic acid, and acetylation of the resulting hydroxyanthraquinones by boiling with acetic anhydride in presence of sodium acetate. The following are described: 1:2:5-trihydroxy-8-methyl-, red, m. p. 301° after decomposing at 290° (triacetate, yellow, m. p. 204—205°); 1:2:6:7-tetrahydroxy-, m. p. above 330° (tetra-acetate, yellow, m. p. 239—241°); and 1:2:7-trihydroxy-6-methyl-anthraquinone, orange-red, m. p. above 330° (triacetate, yellow, m. p. 232—233°).

F. G. W.

**Hystazarindiquinone (2:3:9:10-Anthradiquinone).** M. TANAKA (*Chem. News*, 1925, **131**, 20—22).—Oxidation of the pyridine salt of hystazarin with lead tetra-acetate in glacial acetic acid gives 2:3:9:10-anthradiquinone, red needles, darkening above 315°.

B. F.

**A New Racemic Menthone and the Two Corresponding Menthols.** P. BEDOS (*Compt. rend.*, 1925, **181**, 117—119; cf. Godchot and Bedos, A., 1922, i, 334; 1924, i, 635).—By the action of magnesium isopropyl bromide on the 2-chloro-5-methylcyclohexanol of b. p. 95—97°/14 mm., there is obtained a *menthol* (allopnanate, m. p. 133°), whilst from the 2-chloro-5-methylcyclohexanol of b. p. 103—105°/14 mm. results a stereoisomeric *menthol* (allopnanate, m. p. 177°), which is also formed by the action of magnesium isopropyl bromide on the oxide of  $\Delta^3$ -methylcyclohexene, and thus prepared has b. p. 92°/14 mm.,  $d_{20}^{20}$  0.901,  $n_D^{20}$  1.45786 (*phenylurethane*, m. p. 109—110°). Attempts to regenerate the alcohols from their allopnanates with boiling aqueous potassium hydroxide yielded in both cases a single *urethane*, m. p. 117—118°. The two menthols are oxidised by chromic acid to a single *menthone*, b. p. 81—82°/13 mm.,  $d_{16}^{16}$  0.891,  $n_D^{16}$  1.4444, from which no crystalline semicarbazone or benzylidene derivative is obtainable. The *oxime*, b. p. 124—125°/10 mm.,  $d_{13}^{13}$  0.9502,  $n_D^{13}$  1.4787, is reduced to a *menthylamine*, b. p. 79—80°/10 mm.,  $d_{25}^{25}$  0.849,  $n_D^{25}$  1.45116, the *phenylcarbimide* derivative of which melts at 122° and is identical with that prepared from either of the two menthols. Reduction of the menthone by various methods gives always the menthol with an allopnanate of m. p. 177°.

The existence of the four racemic menthols and the two corresponding racemic menthones foreseen by theory is thus demonstrated. C. H.

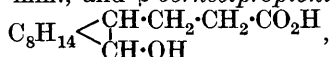
**$\beta$ -Methylcamphenilone.** S. S. NAMETKIN and L. J. BRIUSOVA (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 525—532; cf. A., 1923, i, 1082).—The removal of the elements of water from the molecule of 6-methylisoborneol, which is conveniently effected by heating the compound with twice its weight of sodium hydrogen sulphate in a bath of Wood's metal at 150°, proceeds in two directions, both  $\alpha$ - and  $\beta$ -methylcamphenes being formed.

$\beta$ -Methylcamphenilone (*loc. cit.*) forms an *oxime*,  $C_{10}H_{16}:N:OH$ , m. p. 172°, a *hydrazone*,  $C_{10}H_{16}:N:NH_2$ , m. p. 85—87°, b. p. 245—247°/770 mm., and an *azine*,  $C_{10}H_{16}:N:N:C_{10}H_{16}$ , m. p. 163—164°. Catalytic decomposition of the hydrazone by heating it in a sealed tube with absolute alcohol and sodium (cf. Kijner, A., 1911, i, 678) yields  $\beta$ -methylcamphenilan,  $C_{10}H_{18}$ , which forms a highly volatile, crystalline mass, m. p. 116—117°, with a strong camphor odour. Reduction of  $\beta$ -methylcamphenilone in alcoholic solution by means of sodium gives  $\beta$ -methylcamphenilol,  $C_{10}H_{17}:OH$ , which forms a camphor-like mass with an odour recalling borneol, and yields a *phenylurethane*,  $C_{10}H_{17}:O:CO:NHPh$ , m. p. 104—105°, and a *hydrogen phthalate*,  $C_{10}H_{17}:O:CO:C_6H_4:CO_2H$ , m. p. 174—175°. When dehydrated by means of phosphorus pentachloride,  $\beta$ -methylcamphenilol gives a mixture of hydrocarbons,  $C_{10}H_{16}$ , from which was separated a small proportion of a crystalline compound, m. p. about 110—112°, having the odour of a saturated, dicyclic hydrocarbon. T. H. P.

**Structure of isoCamphenilone.** S. S. NAMETKIN (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 533—538).—It seems probable that Nametkin and Chuchrikova's *isocamphenilone* (A., 1915, i, 701) is identical with Komppa and Hintikka's *fenchocamphorone* (A., 1912, i, 278), the disparity between the physical constants of the two compounds being due to contamination of the fenchocamphorone by camphenilone (cf. Komppa and Roschier, A., 1922, i, 1167). T. H. P.

**$\beta$ -Camphorylpropionic Acid and the Inner Anhydride of  $\gamma$ -Borneolpropyl Alcohol.** H. RUPE and E. TSCHOPP (*Helv. Chim. Acta*, 1925, **8**, 351—357).— $\beta$ -Camphorylidenepropionic acid (A., 1917, i, 141) (hydrobromic acid *additive* compound, m. p. 112° decomp.) and its sodium salt are unattacked by hydrogen in presence of nickel, whilst the ethyl ester is reduced to that of  $\beta$ -camphorylpropionic acid, m. p. 63—64°, b. p. 198—199°/10 mm. (ethyl ester, b. p. 169—170°, chloride, b. p. 142—144°, amide, m. p. 97—98°). Further reduction with sodium in alcohol yields  $\gamma$ -borneolpropyl alcohol,  $C_8H_{14}$   $\begin{smallmatrix} <CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH \\ CH \cdot OH \end{smallmatrix}$ , m. p. 76°,

b. p. 176—177°/10 mm., and  $\beta$ -borneolpropionic acid,



m. p. 82—83°. Direct reduction of the ester of  $\beta$ -camphorylidenepropionic acid in this way yields a mixture of the alcohol and the  $\gamma$ -lactone of  $\beta$ -hydroxycamphorylpropionic acid (A., 1917, i, 141). Distillation of  $\beta$ -borneolpropionic acid with 10% sulphuric acid yields the  $\delta$ -lactone, b. p. 167—168°/12 mm. On a single occasion, treatment of the latter with alkali and subsequent acidification, instead of regenerating the lactone, gave an *isomeride*, m. p. 111—112°, of  $\beta$ -borneolpropionic acid. With phosphorus tribromide,  $\gamma$ -borneolpropyl alcohol yields a *bromohydrin*, b. p. 142—144°/12 mm., converted by alcoholic potassium hydroxide into an inner ether,  $C_8H_{14}$   $\begin{smallmatrix} <CH \cdot CH_2 \cdot CH_2 \\ CH \cdot O - CH_2 \end{smallmatrix}$ , b. p. 108—109°/12 mm.,

$d_4^{20}$  0.9709,  $n_D^{20}$  1.48386,  $[\alpha]_D^{20}$  —0.59°, distilled over metallic sodium without decomposition, better prepared by steam distillation of the glycol with dilute sulphuric acid. Treatment with hydrobromic acid gives a *compound*, b. p. 144—146°, different from the above bromohydrin. M. J.

**Preparation of Active isoBorneol.** G. VAVON and P. PEIGNIER (*Compt. rend.*, 1925, **181**, 183—184).—The mixture of borneol and *isoborneol* obtained by oxidising the magnesium derivative of pinene hydrochloride at low temperatures is converted into a mixture of phthalates from which the greater part of the bornyl ester is removed by a partial hydrolysis, the *isobornyl* ester recrystallised, and the *isoborneol* isolated.

A purer product is obtained when *d*-camphor is hydrogenated with an active platinum catalyst in acetic acid solution, the product being a mixture of *isoborneol* and borneol (9 : 1) with a saturated

hydrocarbon,  $C_{10}H_{18}$ . *iso*Bornyl phthalate is isolated, having  $[\alpha]_{5780} -85^{\circ} 20'$  in ethyl alcohol, and *isoborneol* having  $[\alpha]_{5780} -35^{\circ} 40'$ . The products from pinene had slightly lower rotations attributed to slight racemisation of the latter (cf. A., 1923, i, 1215).

G. M. B.

**Pinane.** P. LIPP (*Ber.*, 1925, 58, [B], 1417).—The differences between the dihydropinenes obtained by hydrogenation of pinene under various conditions have led Zelinski to the supposition that in certain circumstances the tetramethylene ring of the system may become isomerised to the trimethylene ring (cf. this vol., i, 821). According to Lipp, however (A., 1923, i, 1214), it is more probable that these differences are due to stereoisomerism of the pinanes; support of the hypothesis is found in the fact that a new asymmetric centre is developed during the hydrogenation of pinene, thus giving the possibility of formation of diastereoisomerides.

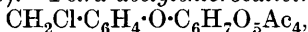
H. W.

**Pinene. I. Action of the Pinenes on certain Compounds Capable of Yielding Hydrogen Halides.** I. L. KONDAKOV and S. ŠAPIRIKIN (*Bull. Soc. chim.*, 1925, [iv], 37, 726—742).—*d*-, *l*-, and *dl*-Pinene when heated with the halogen hydracid salts of various amines, alkaloids, ammonia, or of certain hydrocarbons are converted into the corresponding pinene hydrohalide. The rapidity of the reaction varies with the base or hydrocarbon used and with the temperature. Thus *l*-pinene and camphene hydrochloride at  $160^{\circ}$  in 1 hr. give a 35% yield of *l*-pinene hydrochloride together with some nearly pure camphene and a little viscous product. Similarly, *d*-pinene yields *dl*-camphene, a little *d*-bornyl chloride, pinene hydrochloride, and viscous products. Camphene hydrobromide yields the corresponding products. Camphene hydriodide and *d*-pinene at  $160^{\circ}$  yield *d*-pinene hydriodide, m. p.  $-4^{\circ}$ ,  $d^{175} 1.4630$ ,  $[\alpha]_D +36.3^{\circ}$ . *l*-Pinene hydriodide, m. p.  $-4^{\circ}$ ,  $d^{18} 1.4635$ ,  $[\alpha]_D -33.5^{\circ}$ , and *r*-pinene hydriodide, m. p.  $-5.5^{\circ}$ , b. p.  $108-109/11.5$  mm.,  $d^{175} 1.4630$ , were similarly obtained. Trimethylethylene hydrochloride (amyl chloride) behaves similarly, yielding at  $160^{\circ}$  the pinene hydrochloride and trimethylethylene, together with amylene and sesquiterpenes. With the corresponding hydrobromide, reaction is incomplete at  $130^{\circ}$ , but diamylene, limonene, and sesquiterpenes are formed as secondary products, whilst the reaction with trimethylethylene hydriodide yielded the dihydriodides of dipentene. In the reaction with organic bases, the detection of the primary reaction products is more difficult owing to the increased possibilities of isomerisation. Trimethylamine hydrochloride and French essence of turpentine at  $160^{\circ}$  yield trimethylamine, camphene, dipentene, and *l*-pinene hydrochloride; with the hydrobromide and hydriodide of this base, corresponding products were obtained at  $190^{\circ}$  and  $175^{\circ}$ , respectively. Triethylamine hydrochloride and *l*-pinene at  $160^{\circ}$  yield triethylamine and *l*-pinene hydrochloride, but these two compounds at once react, yielding camphene. Aniline hydrochloride and *l*-pinene at  $160^{\circ}$  yield aniline, camphene, and limonene; with

pyridine hydrochloride, *l*-pinene hydrochloride can be isolated together with camphene and a mixture of hydrocarbons probably containing dipentene. With cocaine hydrochloride or with quinine hydrochloride or hydrobromide the proportion of viscous products is considerable, and the presence of benzoic esters hinders the isolation of pinene hydrochloride. Camphene is formed with dipentene, terpineol, and polyterpenes. The hydrochloride and hydrobromide of morphine similarly yield considerable amounts of polyterpenes and the pinene hydrohalide was only indicated by the isolation of camphene. Hydroxylamine hydrochloride at 160° with *d*- and *l*-pinene yields the corresponding pinene hydrochloride, with dipentene, polyterpenes, and camphene. With ammonium halides at 160—190°, no pinene hydrohalide was produced, but its formation was indicated by yields of camphene together with polyterpenes. R. B.

**Isomeric Transformations. IV. Anomalous Hydration of Pinene Oxide.** S. S. NAMETKIN and A. G. JARCEVA (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 521—524).—The formation of sobrerol by the hydration of pinene oxide (cf. Prile-schaëv, A., 1910, i, 86) appears to be the result of the preliminary rearrangement of the pinene oxide into pinol, which normally yields sobrerol on hydration. It is, indeed, found that if the hydration of pinene oxide is effected in absence of acid, the oxide being merely heated with water at 115—120°, the products contain pinol as well as sobrerol. This isomerisation of  $\alpha$ -oxide (pinene oxide) into  $\gamma$ -oxide (pinol) is doubtless occasioned by the peculiar structure of the former, which includes two internal rings of slight stability and would naturally undergo isomerisation into the simpler and more stable system represented by the pinol molecule. Further, in the autoxidation of pinene in presence of water, giving sobrerol, the fixation of oxygen takes place first at the double linking and yields a compound of peroxidic type, possibly the pinene peroxide formed in absence of moisture (cf. Engler and Weissberg, A., 1899, i, 221). When water is present, this peroxide loses part of its combined oxygen and undergoes rearrangement to pinol, which then forms sobrerol. T. H. P.

**Ethers of Salicin.** G. ZEMPLÉN and G. BRAUN (*Ber.*, 1925, **58**, [B], 1405—1409).—*Tetra-acetylchlorosalicin*,



m. p. 159°,  $[\alpha]_D^{25} + 16.5^\circ$  in chloroform, is prepared in 40% yield by the action of phosphorus pentachloride on salicin tetra-acetate. Tetra-acetylbromosalicin is transformed by silver oxide and methyl alcohol into *tetra-acetylsalicin methyl ether*, m. p. 142°,  $[\alpha]_D^{18} - 21.36^\circ$  in chloroform. *Tetra-acetylsalicin allyl ether*, m. p. 139.5°,  $[\alpha]_D^{25} - 21.36^\circ$  in chloroform, is oxidised by perbenzoic acid in the presence of chloroform to *tetra-acetylsalicin  $\beta\gamma$ -dihydroxypropyl ether*, m. p. 146°,  $[\alpha]_D^{19} - 24.3^\circ$  in chloroform, and is converted by bromine into *tetra-acetylsalicin  $\beta\gamma$ -dibromopropyl ether*, m. p. 124°,  $[\alpha]_D^{25} - 16.07^\circ$  in chloroform. The latter compound is converted by silver acetate into the corresponding, non-crystalline hexa-acetate, which is

probably a mixture of isomerides. *Tetra-acetylsalicin benzyl ether*, m. p. 94.5–95°,  $[\alpha]_D^{20}$  –26.7° in chloroform, and *tetra-acetylsalicin phenyl ether* (from the bromo compound, silver oxide, and phenol in the presence of benzene), m. p. 161°,  $[\alpha]_D^{18}$  –29.33° in chloroform, are also described.

H. W.

### Strophanthin. VII. The Double Bond of Strophanthidin.

W. A. JACOBS and A. M. COLLINS (*J. Biol. Chem.*, 1925, **64**, 383–389; cf. A., 1924, i, 867, 1331).—The acids obtained by hydrolysis of *isostrophanthidin* and its oxidation products, of *dihydrostrophanthidin*, and of the ethylal of *oxidodianhydrodihydrostrophanthidin* readily revert to the corresponding lactones on treatment with mineral acid; the same is not true of corresponding derivatives of *strophanthidin*; further, the ethylal of *oxidodianhydrostrophanthidin* acid forms an oxime, whereas the corresponding *dihydro* derivative does not. It therefore appears that *strophanthidin* and its derivatives are lactones of a  $\gamma$ -keto-acid with the double bond within the lactone ring, and that the change to *isostrophanthidin* probably involves a shifting of the double bond to a position outside the lactone ring. The hydrolysis product of the acid,  $C_{23}H_{30}O_7$ , obtained by the oxidation of *strophanthidin* (A., 1924, i, 65) does not form an oxime; the keto group in the acid formed from this by further oxidation is therefore a true result of oxidation as previously concluded.

*Dianhydrostrophanthidin* acid, obtained either by alkaline hydrolysis of *dianhydrostrophanthidin* or by acid hydrolysis of the ethylal of *oxidodianhydrostrophanthidin* acid, has m. p. 217–219°,  $[\alpha]_D^{24}$  –176° in chloroform and alcohol; it gives an *oxime*, m. p. 170–172° (efferv.). The acid obtained by the hydrolysis of the ethylal of *oxidodianhydrodihydrostrophanthidin* reverted to the lactone even during recrystallisation; precipitated in the cold with acetic acid it formed needles, m. p. 197–202°.

C. R. H.

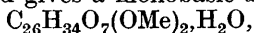
**Digitonin and its Degradation Products.** A. WINDAUS and U. WILLERDING (*Z. physiol. Chem.*, 1925, **143**, 33–47).—No method appears to be available for the preparation of digitonin (cf. A., 1922, i, 848) free from gintonin; digitogenin, however, can be readily purified through its triacetyl derivative.

It is now thought that oxydigitogenic acid is an  $\alpha$ -ketotricarboxylic acid. When it is heated with concentrated sulphuric acid, carbon monoxide is evolved in an amount equal to about 30% of that calculated for 1 mol. Digitoic acid does not undergo an analogous decomposition; this acid is therefore probably a  $\beta$ -keto-acid.

When dimethyl digitogenate is distilled in a vacuum, it is transformed into the isomeric digitoic acid dimethyl ester. Trimethyl oxydigitogenate, on the other hand, when submitted to the same treatment, loses 1 mol. of methyl alcohol and passes into an *enol-lactone*,  $C_{28}H_{40}O_8$ , m. p. 153°, from which oxydigitogenic acid can be again produced by hydrolysis. Apparently the keto group can pass into the enol form and is situated in the  $\gamma$  or  $\delta$  position to a carboxyl group. Digitic acid trimethyl ester distills

without decomposition in a vacuum; the keto group has evidently lost its power of enolisation.

The acid (A) obtained by Kiliani (cf. A., 1919, i, 90) by the energetic oxidation of digitogenic acid with chromic acid is a pentabasic acid and has the formula  $C_{26}H_{38}O_{12}$  and not that ( $C_{16}H_{24}O_7$ ) attributed to it by Kiliani. On heating with acetic and hydrochloric acids it loses carbon dioxide with the formation of a tetrabasic acid,  $C_{25}H_{38}O_{10}$ , m. p. 265—267° (*tetramethyl ester*, m. p. 125°, contains one hydroxyl group). In addition to the acid A, an acid (B),  $C_{26}H_{36}O_9$  (*trimethyl ester*, m. p. 173—174°), is formed during the oxidation of digitogenic acid. Acid hydrolysis of the ester of this acid gives a monobasic acid-ester,



m. p. 125°, and a dibasic acid-ester,  $C_{26}H_{36}O_8(OMe)_2.H_2O$ , m. p. 201°. A third acid (C) produced during the oxidation of digitogenic acid was regarded by Kiliani as ethylsuccinic acid; this has now been identified as  $\alpha$ -methylglutaric acid. The structural formulæ employed in the original to illustrate the above degradation of digitogenin are expressly stated to be of a hypothetical character.

E. S.

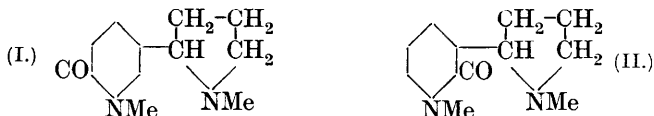
**Dyes from Fungi. II. Dyes from *Dermocybe sanguinea*, Wulf.** F. KÖGL and J. J. POSTOWSKY (*Annalen*, 1925, 444, 1—7).—Treatment of the dried fungus with alcohol gives a solution which on evaporation yields a residue consisting of an orange-yellow dye and a red dye, 3% and 0.2—0.4%, respectively, of the dry material. The mixture is separated by means of aqueous pyridine, in which the yellow dye, 1:6:8-trihydroxy-3-methyl-anthraquinone (emodin) is insoluble (cf. Eder, A., 1924, i, 185; 1925, i, 562). The triacetyl derivative has m. p. 196—197°. The violet-red filtrate on acidification gives brown flakes from which by means of chloroform a compound which has been named *dermocybin*,  $C_{16}H_{12}O_7$ , m. p. 228°, red crystals, is obtained. The spectrum in concentrated sulphuric acid has a broad band at  $\lambda$  596.8—501.8, and on strong dilution at  $\lambda$  587.6—540.0. Wool mordanted with chrome is dyed a violet-red. The *tetra-acetyl* derivative, yellow needles, has m. p. 182°. On reduction with zinc dust dermocybin yields  $\beta$ -methylanthracene. On demethylation by means of concentrated sulphuric acid it gives a compound,  $C_{15}H_{10}O_7$ , m. p. 289°, as a glistening red, crystalline powder, which dyes mordanted wool the same shade as the parent substance. Dissolved in aqueous aluminium sulphate this compound gives a fluorescent solution having a spectrum with 4 bands. Evidence is given to show that dermocybin is a tetrahydroxymethoxy- $\beta$ -methylanthraquinone. It is very similar to, but not identical with, the dyes in the fungus *Dermocybe cinnabarina*. A. C.

**Some Substances Analogous with Graphite.** R. CIUSA (*Gazzetta*, 1925, 55, 385—389; cf. A., 1922, i, 1057).—An amplification of a previous note. Tetraiodothiophen, when heated in a closed tube, decomposes at about 230° with elimination of iodine. The iodine is lost progressively, the ratio of sulphur to iodine in

the product rising from 1.1 to 3.6 as the temperature of heating is increased from 340° to 490°. At incipient red-heat, in an inert atmosphere, the compound  $(C_4S)_n$ , previously reported, is obtained. This substance has a high adsorptive power, and when heated in a sealed tube with water liberates hydrogen sulphide. It has  $d$  2.03—2.77, and a high electrical resistance. The analogous "furan graphite" was prepared by heating tetraiodofuran, prepared from tetra-acetoxymercurifuran. Heating hexaiodobenzene in a sealed tube at 400° gave a black substance still containing 46% of iodine, which was converted at incipient red-heat into a "graphite" with an electrical resistance about six times that of Ceylon graphite.

F. G. T.

**Configuration of Nicotine. Optically Active Hygrinic Acid.** P. KARRER and R. WIDMER (*Helv. Chim. Acta*, 1925, **8**, 364—368).—A method of oxidising nicotine is described whereby the pyridine ring instead of the pyrrolidine ring is destroyed and hygrinic acid is obtained for the first time in an active form. Addition of methyl iodide to the pyridine nitrogen atom is followed by treatment with potassium ferricyanide yielding *N*-methylnicotone (I or II), m. p. 80°, b. p. 143—145°/1 mm.,  $[\alpha]_D -55.87^\circ$ . This



compound is oxidised by chromic acid to *l*-hygrinic acid, which (+H<sub>2</sub>O) has m. p. 116°,  $[\alpha]_D -80.12^\circ$ . Dehydration does not take place except at a temperature involving partial decomposition. Treatment of the acid with methyl iodide and silver oxide yields *l*-stachydrine, identical with the natural product and alternatively prepared by methylation of naturally-occurring *l*-proline. All three natural products, *l*-proline, *l*-stachydrine, and *l*-nicotine, have therefore the same configuration. It becomes increasingly probable that all natural products possessing a single asymmetric carbon atom and containing an amino or hydroxyl group have the same *l*-configuration (cf. A., 1924, i, 1173, and T., 1918, **113**, 526). M. J.

**Amorphous Quinine Iodobismuthate.** M. FRANÇOIS and L. SEGUIN (*J. Pharm. Chim.*, 1925, [viii], **2**, 59—69).—*Quinine iodobismuthate*,  $C_{20}H_{24}O_2N_2 \cdot 2HI \cdot 2BiI_3$ , is a bright red, amorphous precipitate obtained by addition of potassium iodobismuthate to a solution of quinine hydrochloride. Crystallisation from concentrated hydrochloric acid yields garnet-red crystals of the formula  $C_{20}H_{24}O_2N_2 \cdot HI \cdot 3BiI_3$ .

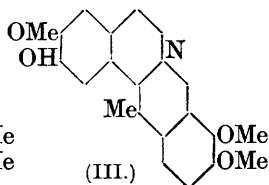
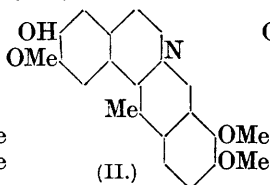
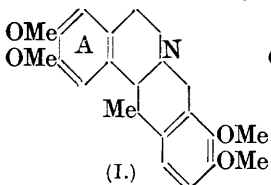
G. M. B.

**Hydrogen-ion Concentration of Some Injection Liquids. Influence of Sterilisation.** L. ROY (*J. Pharm. Chim.*, 1925, [viii], **1**, 525—532).—Cocaine hydrochloride, novocaine, and stovaine in solution show a diminution of  $p_H$  on sterilisation by heating (at 100° and upwards) or tyndallisation (at 60° or 70°). There occurs a slight decomposition (about 1%), apart from the normal hydrolysis into acid and base which may be detected in the unsterilised solution.



As a result of this decomposition, cocaine hydrochloride gives traces of benzoic acid and methyl alcohol, novocaine traces of benzoic acid and ammonia, and stovaine traces of benzoic acid. The diminution of  $p_H$  and the degree of decomposition increase with temperature; in alkaline glass, the diminution of  $p_H$  is less, but the degree of decomposition greater, than in neutral glass. Similar changes in  $p_H$  are found for atropine sulphate. B. F.

**Alkaloids of *Corydalis cava*; Corybulbine and isoCorybulbine.** E. SPÄTH and A. DOBROWSKY (*Ber.*, 1925, 58, [B], 1274—1284).—Since corybulbine and isocorybulbine are converted by nascent diazomethane into corydaline (I), it follows that they differ from the latter only in the replacement of one methoxyl group by hydroxyl. The *ethyl ethers* of corybulbine and isocorybulbine are transformed by drastic oxidation into the methyl ethyl ether of nor-*m*-hemipinic acid, which is characterised as the *ethylimide*, m. p. 205°, so that the two alkaloids differ only in the relative positions of the hydroxyl and methoxyl groups in nucleus A. The synthesis of the acid is effected in the following manner. 3-Methoxy-4-ethoxybenzaldehyde is condensed with nitromethane to  $\omega$ -nitro-3-methoxy-4-ethoxystyrene, m. p. 149°, which is reduced by zinc dust and acetic acid to the corresponding oxime and thence by sodium amalgam and acetic acid to  $\beta$ -amino- $\alpha$ -3-methoxy-4-ethoxyphenylethane, b. p. 153—156°/10 mm. (*picrate*, m. p. 181—182°; *benzoyl* compound, m. p. 99—100°; *m*-nitrobenzoyl derivative, m. p. 114°). The amine is converted by successive treatment with anhydrous formic acid and phosphoric oxide into 6-methoxy-7-ethoxy-3:4-dihydroisoquinoline, m. p. 84—85° (*picrate*, m. p. 206°), which is oxidised to the methyl ethyl ether of nor-*m*-hemipinic acid. Alternatively, 4-methoxy-3-ethoxybenzaldehyde is condensed with nitromethane to  $\omega$ -nitro-4-methoxy-3-ethoxystyrene, m. p. 134°, which is reduced through the corresponding oxime to  $\beta$ -amino- $\alpha$ -4-methoxy-3-ethoxyphenylethane, b. p. 162—165°/13 mm. (*carbonate*; *picrate*, m. p. 184—185°; additive compound with trinitro-*m*-cresol, m. p. 171—172°; *nitrate*, m. p. 136—138°; *benzoyl* derivative, m. p. 117.5—118°). Treatment of the amine with formic acid and phosphoric oxide gives 7-methoxy-6-ethoxy-3:4-dihydroisoquinoline, m. p. 72° (*picrate*, m. p. 195°), which is oxidised to the methyl ethyl ether of nor-*m*-hemipinic acid. The isolation of the same acid from either *isoquinoline* derivative places beyond doubt the structure of the latter and the ring closure of the amine in the para position to an alkoxy group.



Further insight into the constitution of the alkaloids is afforded by the observation that corybulbine ethyl ether is converted by

gentle oxidation into 7-methoxy-6-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydroisoquinoline, whereas under similar conditions isocorybulbine ethyl ether yields 6-methoxy-7-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydroisoquinoline. The constitutions (II) and (III) are therefore assigned to corybulbine and isocorybulbine. The isoquinoline compounds are synthesised in the following manner.  $\beta$ -Amino- $\alpha$ -3-methoxy-4-ethoxyphenylethane is treated with ethyl chloroformate and the product is converted by phosphoryl chloride in the presence of xylene at  $140^\circ$  into 6-methoxy-7-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydroisoquinoline, m. p.  $195.5^\circ$ . Similarly,  $\beta$ -amino- $\alpha$ -4-methoxy-3-ethoxyphenylethane gives successively the carbethoxy derivative, m. p.  $53-54^\circ$ , and 7-methoxy-6-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydroisoquinoline, m. p.  $175^\circ$ . The closure of the ring in the para position to an alkoxy group in each case is established by the oxidation of either isoquinoline derivative to the methyl ethyl ether of nor-m-hempipinic acid.

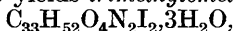
Corydaldine (cf. Dobbie and Lauder, T., 1895, **67**, 20) is prepared synthetically by the successive action of ethyl chloroformate and phosphoryl chloride on homoveratrylamine. Norhydroxyhydrastinine, m. p.  $181-182^\circ$ , identical with the product obtained from berberine (Perkin, T., 1892, **57**, 991), is prepared similarly from homopiperonylamine.

H. W.

**Synthesis of  $\psi$ -Ephedrine.** E. SPÄTH and G. KOLLER (*Ber.*, 1925, **58**, [B], 1268—1271).—Phenylethylcarbinol is conveniently converted by boiling acetic anhydride and phosphoryl chloride into  $\alpha$ -phenyl- $\Delta^a$ -propene, which, with bromine, gives  $\alpha\beta$ -dibromo- $\alpha$ -phenylpropane, m. p.  $66^\circ$ . The latter compound is transformed by methyl alcohol at  $100^\circ$  into  $\beta$ -bromo- $\alpha$ -methoxy- $\alpha$ -phenylpropane, b. p.  $119-121^\circ/10$  mm., which with methyl-alcoholic methylamine at  $100^\circ$  yields  $\beta$ -methylamino- $\alpha$ -methoxy- $\alpha$ -phenylpropane, b. p.  $105-110^\circ/11$  mm. Hydrolysis of the latter compound yields  $\beta$ -methylamino- $\alpha$ -hydroxy- $\alpha$ -phenylpropane, m. p.  $118^\circ$ , the identity of which with  $r$ - $\psi$ -ephedrine is established by direct comparison of the bases, their hydrochlorides and "abnormal" chloroaurates, and by resolution of the synthetic base with *l*-tartaric acid, leading to the isolation of *d*- $\psi$ -ephedrine identical with the natural product.

H. W.

**Alkaloids of Ipecacuanha (*Uragoga ipecacuanha*).** IV. O. KELLER and X. BERNHARD (*Arch. Pharm.*, 1925, **263**, 401—424; cf. A., 1914, i, 428; 1917, i, 409).—Emetine is obtained as a white powder, m. p.  $68^\circ$ , from ether. The hydrobromide,  $C_{30}H_{44}O_4N_2 \cdot 2HBr$ , crystallises  $+3H_2O$ , m. p.  $247^\circ$ , and also  $+4H_2O$ . Exhaustive methylation of emetine yields trimethylemetinedi-iodide,



m. p.  $222^\circ$  (identical with the *N*-methylemetine methiodide of Carr and Pyman, T., 1914, **105**, 1591), whilst methylation of cephaeline gives a different, alkali-soluble substance,  $C_{32}H_{50}O_4N_2I_2 \cdot 3H_2O$  (chloroplatinate described), the free hydroxyl group having remained unmethylated. The results of the zinc dust distillation previously described are confirmed. The "base X," from pure emetine or

from its methylation product and also from cephaeline, resembles trimethylamine closely in its *chloroaurate*, m. p.  $244^{\circ}$ , and *chloroplatinate*, m. p.  $240\text{--}241^{\circ}$ , but differs from it in odour and in solubility in aqueous alkali. The production of guaiacol from both cephaeline and pure emetine is proved conclusively. The paper contains an extensive review of the work of other investigators, and, incidentally, a detailed description of the microchemical appearance and m. p. of the chloroaurates and chloroplatinates of mono-, di-, and tri-methylamine.

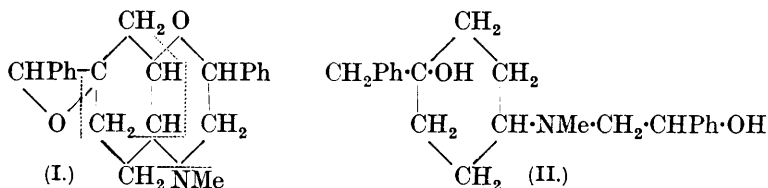
G. M. B.

**Azo Dyes from Alkaloids of Ipecac[uanha] Root and their Identification by Means of the Spectroscope.** S. PALKIN and H. WALES (*J. Amer. Chem. Soc.*, 1925, **47**, 2005—2010).—The phenolic portion of ipecacuanha alkaloids affords, when coupled with *p*-nitrodiazobenzene by the method previously described (A., 1924, ii, 630), a *dye*, the portion of which soluble in amyl alcohol shows maximum absorption at 6100 (blue), 5525 (purple), and 5250 Å. (red), in acetone, alcohol, and water, respectively. The non-phenolic portion affords similarly a *dye* showing maximum absorption at 6275 (bluish-green), 5900 (dark blue), and 5700 Å. (royal purple), in the corresponding solvents. The former is derived from cephaeline, the latter from emetamine. [Cf. B., 1925, 689.]

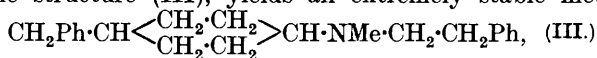
F. G. W.

**Lobelia Alkaloids. II.** H. WIELAND, C. SCHÖPF, and W. HERMSEN (*Annalen*, 1925, **444**, 40—68; cf. A., 1921, i, 802).—Two further alkaloids have now been isolated from the *Lobelia* plant, *lobelanine* and *lobelanidine*, the former being, after lobeline, the most abundant in the leaves. Lobelanine,  $\text{C}_{22}\text{H}_{25}\text{O}_2\text{N}$ , is a tertiary base containing two ether linkings, a conclusion reached from its conversion on reduction with sodium amalgam in acetic acid into lobelanidine,  $\text{C}_{22}\text{H}_{29}\text{O}_2\text{N}$ , which contains two hydroxyl groups, whereas lobelanine contains none. Lobelanine is quantitatively oxidised by permanganate to give 2 mols. of benzoic acid, indicating the presence of two unsubstituted benzene rings. When heated alone or in presence of benzoic or dilute hydrochloric acid, lobelanine affords acetophenone. Fluorene and methylamine are also produced in the last case, and this decomposition may be represented,  $\text{C}_{22}\text{H}_{25}\text{O}_2\text{N} = \text{C}_8\text{H}_8\text{O} + \text{C}_{13}\text{H}_{10} + \text{NH}_2\text{Me} + \text{H}_2\text{O}$ , although only about 50% of the theoretical quantity of methylamine is produced and considerable amounts of basic products. Similarly, if lobelanine is heated with alcoholic potassium hydroxide, 70—80% of the theoretical amount of methylamine is formed, together with benzhydrol (corresponding with the fluorene) and phenylmethylcarbinol. Since the latter substance arises by reduction of the acetophenone first formed under the conditions of the alkali fusion (cf. Montagne, A., 1917, i, 35), this decomposition may be expressed,  $\text{C}_{22}\text{H}_{25}\text{O}_2\text{N} = \text{C}_8\text{H}_8\text{O} + \text{C}_{13}\text{H}_{12}\text{O} + \text{NH}_2\text{Me}$ . The above results suggest that the third benzene ring arises in the decompositions, through the opening of the ether bridge and splitting off of methylamine, a hydroaromatic ring being thus converted into an aromatic ring, as would be the case with

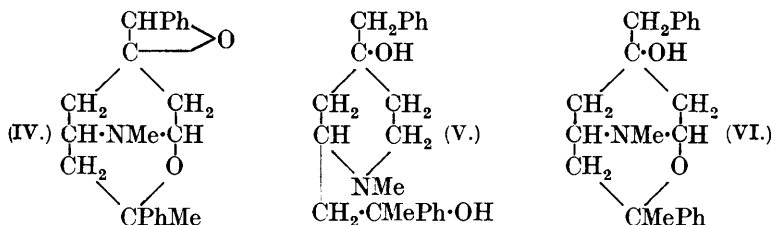
structure (I). Although this structure is in accord with the results of the decomposition of lobelanine with acid and alkali, it involves



the analogous structure (II) for lobelanidine, in which the presence of a secondary hydroxyl group does not agree with the great stability of the base towards oxidising agents, behaviour which points to the presence of two tertiary hydroxyl groups. Moreover, lobelanidine yields a quaternary ammonium base which is very stable and does not undergo the usual Hofmann degradation. Similarly, the parent base, lobelane,  $\text{C}_{22}\text{H}_{29}\text{N}$ , obtained from lobelanidine by reduction of the dichloro derivative,  $\text{C}_{22}\text{H}_{27}\text{NCl}_2$ , which should have the structure (III), yields an extremely stable methiodide



which does not decompose either into benzyl-*N*-dimethylcyclohexylamine and styrene or into benzylcyclohexene and  $\beta$ -phenylethyldimethylamine. Since, however, both  $\alpha$ - and  $\beta$ -phenylethylcyclohexyldimethylammonium hydroxides undergo normal degradation in accordance with von Braun's rule (A., 1924, i, 632) it is improbable that lobelanine and lobelanidine possess the structures (I) and (II) unless the benzyl group exerts a stabilising influence on the molecule in the Hofmann degradation. Accordingly, formulæ (IV) and (V) are proposed for lobelanine and lobelanidine. In these, the portion of the molecule readily split off as acetophenone is linked up through carbon and not through nitrogen as originally suggested.



Lobeline (A., 1921, i, 802) will then be represented by (VI), since, when reduced (2H) with sodium amalgam in acetic acid, it is converted into lobelanidine, a result which leads to the formula  $\text{C}_{22}\text{H}_{27}\text{O}_2\text{N}$  for lobeline in place of that previously given (*loc. cit.*). The presence of the tertiary hydroxyl group is confirmed by the preparation of a benzoate, and of a chloride. The alcoholic mother-liquors from the lobelanidine nitrate contain a fourth alkaloid, *isobelanine*,  $\text{C}_{22}\text{H}_{25}\text{O}_2\text{N}$ .

[With C. SCHÖPF.]—Lobelanine is isolated from the alcoholic mother-liquors after removal of the lobeline by neutralisation with alcoholic hydrochloric or hydrobromic acid and purification of the salt by recrystallisation. Lobelanine, colourless needles or rosettes, m. p.  $99^{\circ}$ , is optically inactive, and yields a colourless chloroplatinate and chloromercurate. With Fröhde's reagent, it gives a brownish-yellow colour. The *hydrochloride* (two forms), m. p.  $188^{\circ}$ , *hydrobromide*, m. p.  $188^{\circ}$ , *hydriodide*, m. p.  $169$ — $172^{\circ}$  (in decreasing order of solubility), *nitrate*, m. p.  $153$ — $154^{\circ}$ , and *perchlorate* are described. Benzoyl chloride, nitrous acid, diazomethane, palladium black and hydrogen, and hydriodic acid are without action. Nitric acid (*d* 1.4) produces partial oxidation to benzoic acid.

[With W. HERMSEN.]—The mother-liquors from the lobelanine hydrochloride are diluted with water, the alcohol and ether distilled off, the lobelanidine is precipitated as nitrate, and recrystallised. Lobelanidine, colourless, prismatic lamina or scales, m. p.  $150^{\circ}$ , is optically inactive and distils unchanged in a high vacuum. It is only slightly attacked by chromic or fuming nitric acids. The *hydrochloride*, m. p.  $135$ — $138^{\circ}$ ; *hydrobromide*, m. p.  $188$ — $190^{\circ}$ ; *diacetyl* derivative (*acetate*, m. p.  $75^{\circ}$ , *hydrochloride*,  $C_{26}H_{33}O_4N, HCl$ , m. p.  $214$ — $215^{\circ}$ ), and *dibenzoyl* derivative, m. p.  $109$ — $110^{\circ}$  [*hydrochloride*,  $C_{36}H_{37}O_4N, HCl$ , m. p.  $239$ — $240^{\circ}$  (decomp.)], are described. Methyl iodide in benzene at  $100^{\circ}$  yields a *methiodide*,  $C_{23}H_{32}O_2NI$ , melting at  $173$ — $175^{\circ}$  to a turbid liquid which becomes clear at  $200^{\circ}$ . The corresponding quaternary hydroxide, m. p.  $152^{\circ}$  (decomp.) on distillation, yields chiefly lobelanidine. Lobelanidine itself when distilled with aluminium oxide yields a small quantity of acetophenone. With phosphorus trichloride, lobelanidine gives *dichlorolobelane*, which was not obtained crystalline. The *hydrochloride*,  $C_{22}H_{27}NCl_2, HCl$ , has m. p.  $158$ — $159^{\circ}$  (decomp.). When reduced with aluminium amalgam in moist ether, with zinc dust and acetic acid, or sodium amalgam, dichlorolobelane is converted into lobelane, b. p.  $175^{\circ}$  in a high vacuum (*hydrochloride*, m. p.  $194$ — $195^{\circ}$ ; *methiodide*, m. p.  $234$ — $235^{\circ}$ ). Lobeline,  $C_{22}H_{27}O_2N$ , with benzoyl chloride in pyridine, yields the *benzoate hydrochloride*,  $C_{29}H_{31}O_3N, HCl (+ H_2O)$ , m. p.  $155$ — $157^{\circ}$  (decomp.), and with phosphorus trichloride *chlorolobelide* [*hydrochloride*,  $C_{22}H_{26}ONCl, HCl$ , m. p.  $172$ — $174^{\circ}$  (decomp.)].

*iso*Lobelanine,  $C_{22}H_{25}O_2N$ , has m. p.  $120$ — $121^{\circ}$  and is optically inactive. The *nitrate*, m. p.  $193^{\circ}$  (decomp.), *hydrochloride*, m. p.  $201$ — $202^{\circ}$ , and *methiodide*, m. p.  $183$ — $184^{\circ}$ , are described. The base does not react with benzoyl chloride. On heating, it yields some acetophenone; reduction with sodium amalgam gives a base, *isobobelanidine*, m. p.  $217$ — $218^{\circ}$  (sinters) (*hydrochloride*, m. p.  $247$ — $248^{\circ}$ ).

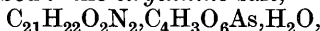
[With O. DRAGENDORFF.]— $\alpha$ -Phenylethyl bromide and cyclohexylamine on warming not above  $50^{\circ}$  yield  $\alpha$ -phenylethylcyclohexylamine, b. p.  $135^{\circ}/10$  mm. (*hydrobromide*, m. p.  $251$ — $252^{\circ}$ ); at higher temperatures, appreciable quantities of styrene are formed. Attempts to prepare the amine from cyclohexyl bromide

and phenylethylamine failed. Methyl iodide and alkali convert the amine into its *methiodide*, m. p. 149°, which with silver oxide yields styrene and cyclohexyldimethylamine (*hydrobromide*, m. p. 197°).  $\beta$ -Phenylethylcyclohexylamine, b. p. 152°/13 mm. (*hydrobromide*, m. p. 232—233°), is similarly prepared, a small quantity of the tertiary base,  $(\text{CH}_2\text{Ph}\cdot\text{CH}_2)_2\text{N}\cdot\text{C}_6\text{H}_{11}$  (*hydrobromide*, m. p. 168°), being also formed. Methyl iodide and methyl-alcoholic potassium hydroxide convert the secondary base into its *methiodide*, m. p. 133°, which on distillation with thallium hydroxide similarly yields styrene and cyclohexyldimethylamine. Di- $\beta$ -phenylethylmethylamine, b. p. 188°/13 mm. (*picrate*, m. p. 101°), is obtained as a by-product in the action of 30% alcoholic methylamine on  $\beta$ -phenylethyl bromide.

An unstable form of benzophenone *p*-nitrophenylhydrazone, red crystals, m. p. 144°, which on repeated crystallisation change into the stable yellow form, m. p. 154°, is described. Benzophenone is quantitatively converted by alcoholic potassium hydroxide into benzhydrol. The latter substance with 0.5*N*-hydrochloric acid at 120—130° yields benzhydrol ether, m. p. 108—109°, but no fluorene.

R. B.

**Arsenical Emetics. Emetics of Pyridine, Quinoline, and Some Alkaloids.** L. DEBUCQUET (*J. Pharm. Chim.*, 1925, [viii], 2, 5—13).—By treating various alkaloids with a solution of arsenious oxide in tartaric acid, substances are obtained which are described as salts of the acid,  $\text{C}_4\text{H}_3\text{O}_6\text{As}$  (in which arsenic replaces the hydrogens of one carboxyl and of two hydroxyl groups). The following are described: the *strychnine* salt,

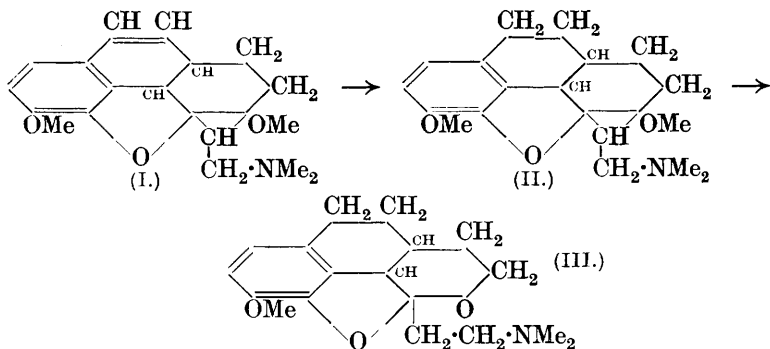


$[\alpha]_{\text{D}}^{20}$  —6.69° (anhydrous salt in aqueous acetone); the *codeine* salt,  $\text{C}_{18}\text{H}_{21}\text{O}_3\text{N}, \text{C}_4\text{H}_3\text{O}_6\text{As}$ ,  $[\alpha]_{\text{D}}$  —67.38° (saturated solution); the *morphine* salt,  $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}, \text{C}_4\text{H}_3\text{O}_6\text{As}, 2\text{H}_2\text{O}$ ,  $[\alpha]_{\text{D}}^{15}$  —66.39°; the *cocaine* salt,  $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}, \text{C}_4\text{H}_3\text{O}_6\text{As}$ ,  $[\alpha]_{\text{D}}$  —35.55° (2% solution); and the *quinine* salt,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2, 2\text{C}_4\text{H}_3\text{O}_6\text{As}, 2\text{H}_2\text{O}$ ,  $[\alpha]_{\text{D}}$  —98.75°.

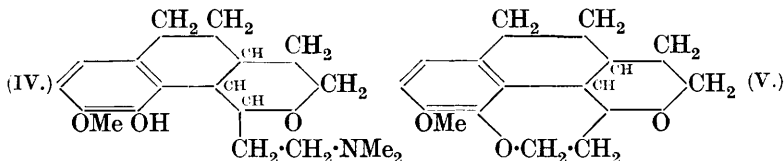
B. F.

**Constitution of the Morphine Alkaloids.** H. WIELAND and M. KOTAKE (*Annalen*, 1925, 444, 69—93).—In continuation of earlier work (A., 1923, i, 1222) the behaviour of morphine derivatives in which the third ring of the molecule has been saturated by reduction in order to limit the possibilities of complicated reactions has been studied with a view to determine the point of attachment of the carbon atom 15. The dihydrode-*N*-methyl dihydrocodeine previously described (*loc. cit.*) is converted by oxidation into a ketone, dihydrode-*N*-methyl dihydrocodeinone (III), which still contains ring III and in which the carbon atom,  $\text{C}_{15}$ , will be attached to  $\text{C}_5$ , according to Knorr's formula (A., 1907, i, 789), to  $\text{C}_5$  or  $\text{C}_8$  according to Freund (A., 1921, i, 125), and to  $\text{C}_8$  or  $\text{C}_{13}$  according to Robinson. The same ketone is more easily obtained from thebaine, by decomposing the methiodide of dihydrothebaine with potassium hydroxide. The resultant tertiary base (I), after catalytic reduction and treatment with hydrochloric acid, affords methyl

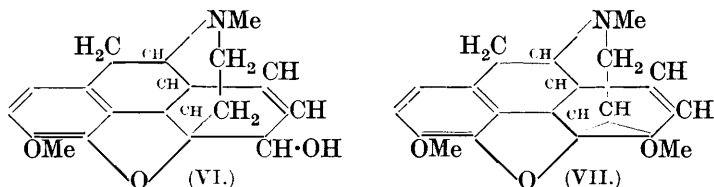
alcohol and the ketone (III). When reduced with aluminium amalgam, the oxygen bridge in this ketone is ruptured, yielding a tertiary base (IV) with weak phenolic properties, which yields only one *isonitroso* derivative and only one monobenzylidene or piperonylidene derivative, and accordingly contains only one reactive methylene group. The structure (IV) is therefore assigned to this ketone, and is further supported by the decomposition of its



methiodide into trimethylamine, water, and a cyclic ketone, thebenone (V), corresponding in its properties with the thebenol similarly obtained by Freund from thebenine, which on oxidation yields a

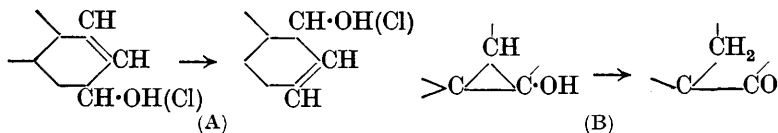


crystalline diketone. In view of the above relations, the authors propose the structures (VI) and (VII) for codeine and thebaine respectively, the presence of a double bond in ring III being indicated

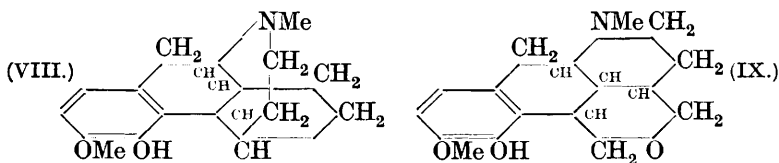


by the permanganate test in dilute sulphuric or acetic acid. These structures admit of readier interpretations of the isomeric relations of the methylmorphimethines, and of the relations between codeine and  $\psi$ -codeine, the conversion of codeine into the chloride or bromide of the isomeric series involving displacement of a double bond according to the scheme (A). The conversion of dihydrothebaine into dihydrocodeinone under the influence of acid is attributed, on the above formula for thebaine, to isomerisation of the *cyclopropyl*

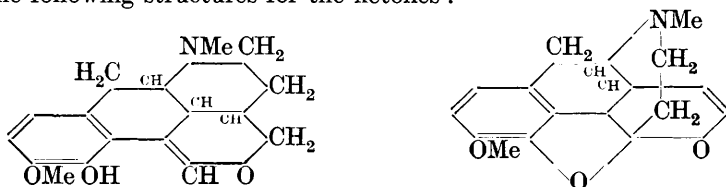
alcohol system (B). The change into the *isoquinoline* series (*apomorphine*, *morphothebaine*) similarly involves saturation of the



double bond and formation of a new carbon linking between  $C_{15}$  and  $C_8$ . The character of ring III in thebaine and its derivatives depends on the nature of the substituent attached to the  $C_5$  carbon atom, the breaking of the O-bridge by catalytic reduction involving also rupture of the  $C_{5-6-15}$  system of linkings, as seen in the conversion of dihydrothebaine into dihydrothebainone (VIII). The latter formula involves a structure (IX) for Gulland and Robinson's thebainol (T., 1923, 123, 980), and the relations of thebaine and



codeine to thebainone and codeinone are interpreted by assuming the following structures for the ketones:—



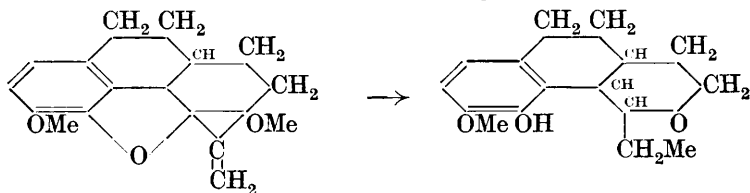
von Braun's formula for the morphine alkaloids (A., 1914, i, 1138) being rejected on account of the unsaturated character of the bases and its failure to explain the oxidation of codeine to codeinone.

Dihydrothebaine is obtained in 50–60% yield by reduction of thebaine hydrochloride with hydrogen in the presence of palladous chloride and gum arabic. De-*N*-methyl dihydrocodeinone is obtained by hydrolysis of de-*N*-methyl dihydrothebaine with hydrochloric acid (cf. Freund and Speyer, A., 1921, i, 125). The *oxime* has m. p. 191–192.5°. The de-*N*-methyl dihydrothebaine (I), m. p. 131–134°, of Freund and Speyer (*loc. cit.*) on reduction with hydrogen in acid palladous chloride yields *dihydrode-N-methyl dihydrothebaine* (II), a colourless oil (*methiodide*, m. p. 217–222°), which on heating with 2*N*-hydrochloric acid gives (yield 80%) *dihydrode-N-methyl dihydrocodeinone* (III), colourless needles, softening at 95°, m. p. 110° (*methiodide*, m. p. 295°; *oxime hydrochloride*, m. p. 271–272°; *oxime*, m. p. 183–185°), identical with the ketone obtained from dihydrode-*N*-methyl dihydrocodeine (tetrahydro-methylmorphimethine) by oxidation with chromic acid in acetic



acid. The following salts of dihydrode-*N*-methylhydrocodeine are described: *perchlorate*, m. p. 218—219°; *chloroplatinate*, m. p. 202°; *nitrate*, m. p. 174—175°. Nitrodihydro-*N*-demethylhydrocodeine nitrate has m. p. 220—221°. Dihydrode-*N*-methylhydrocodeinone on reduction with aluminium amalgam yields *dihydrode-N-methylhydrothebainone* (IV), m. p. 154—156° [*picrate*, m. p. 185—188°; *picrate* of acetyl derivative, m. p. 188—192; *methiodide*, m. p. 226—229°; *piperonylidene* derivative,  $C_{27}H_{31}O_5N$ , m. p. 179—181° (which with excess of piperonal and sodium ethoxide yields an alcohol additive compound,  $C_{29}H_{37}O_6N$ , m. p. 179—181°)]. The same ketone is also obtained by a similar reduction of de-*N*-methylhydrothebainone, m. p. 180—182° (*piperonylidene* derivative, m. p. 174—175°), prepared by reduction of the tertiary methine base of dihydrocodeinone, but it is best obtained by hydrogenation of de-*N*-methylhydrothebaine in acetic acid by Skita's method. The methiodide of dihydrode-*N*-methylhydrothebainone on heating with aqueous sodium hydroxide gives trimethylamine and *thebenone* (V), m. p. 134—136° (yield 80%). The *oxime*, m. p. 201—204°, *isonitroso* compound,  $C_{17}H_{19}O_2N$ , m. p. 165° (decomp.), *benzylidene* derivative, m. p. 162°, and *piperonylidene* derivative, m. p. 185—186°, are described. Chromic and acetic acids convert thebenone into a *diketone*,  $C_{17}H_{18}O_4$ , m. p. 185—187°; the *dioxime* (m. p. 155—160°, with effervescence, solidifying and melting again at 260°) of this diketone is isomeric with the *oxime*, m. p. 236—239°, obtained by the action of hydroxylamine on *isonitrosothebenone*.

The methiodide of dihydrode-*N*-methylhydrothebaine on treatment with silver oxide and distillation yields a strongly unsaturated substance,  $C_{18}H_{20}O_3$ , m. p. 119°, which on hydrogenation in alcohol in the presence of palladium-black yields a *phenol*,  $C_{17}H_{22}O_3$ , m. p. 148—150°. These two substances are assigned the structures:



Piperonylidenedihydrothebainone has m. p. 174—175° (cf. Guland and Robinson, *loc. cit.*). R. B.

**Constitution of Tritopine.** E. SPÄTH and R. SEKA (*Ber.*, 1925, **58**, [B], 1272—1273).—Tritopine, isolated by Kauder (*A.*, 1891, 227) in very small amount from the minor alkaloids of opium, has m. p. 184°; it is identical with laudanidine. Since the latter substance is related closely to laudanine, it is suggested that the name be retained and the term "tritopine" be deleted from the literature. H. W.

**Optical Properties of Coniine Hydrochloride.** G. L. KEENAN and R. M. HANN (*J. Amer. Chem. Soc.*, 1925, **47**, 2063—2064; cf. this vol., ii, 94).—Coniine forms a double compound with mercuric

chloride,  $C_8H_{17}N_2HgCl_2$ ,  $n_D$  1.535,  $n_\gamma$  1.540. It shows parallel extinction and negative sign of elongation, with biaxial interference figures in convergent polarised light, the optic axial angle being  $30-35^\circ$ . The convenience of optical examination for the identification of crystalline compounds, even in mixtures, is pointed out.

F. G. W.

**Synthesis of 4-(3' : 4' : 5'-Tri-iodophenyl)-2-pyrrolidone-5-carboxylic Acid.** C. R. HARINGTON (*J. Biol. Chem.*, 1925, **64**, 29—39).—In an attempt to elucidate the constitution of thyroxin (cf. Kendall, A., 1920, i, 180), 4-(3' : 4' : 5'-tri-iodophenyl)-2-pyrrolidone-5-carboxylic acid, a substance of the same empirical formula as thyroxin and likely to possess similar chemical properties to those described by Kendall, has been synthesised. The synthetic substance has been found to be without effect on the basal metabolic rate and is therefore not identical with thyroxin. The tribasic ester obtained by condensing ethyl malonate and ethyl cinnamate in presence of sodium (cf. Vorländer, A., 1902, i, 309) on treatment with ethyl nitrite and sodium ethoxide gave *ethyl  $\alpha$ -isonitroso- $\beta$ -phenylglutarate*, an oil which could not be crystallised; on hydrolysis with potassium hydroxide in concentrated aqueous solution, this gave  *$\alpha$ -isonitroso- $\beta$ -phenylglutaric acid*, blunt needles, m. p.  $129-130^\circ$  (decomp.); from this, by reduction with sodium amalgam in aqueous solution, was obtained  *$\beta$ -phenylglutamic acid*, rhombic plates which become pasty at  $170^\circ$  and melt with loss of water at  $179^\circ$ ;  *$\alpha$ -benzamido- $\beta$ -phenylglutaric acid*, prepared from the above by benzylation in an alkaline sodium acetate solution, formed needles, m. p.  $171-172^\circ$ . On boiling in 10% aqueous solution for 6 hrs.,  *$\beta$ -phenylglutamic acid* lost the elements of water to give *phenylpyrrolidonecarboxylic acid*, narrow prisms, m. p.  $196.5-197.5^\circ$ , which could be quantitatively reconverted into the amino-acid by boiling for 4 hrs. with 50% hydrochloric acid. Phenylpyrrolidonecarboxylic acid on nitration with fuming nitric acid at  $0^\circ$  gave chiefly the *p-nitro* derivative, rectangular plates, darkening at  $229^\circ$ , m. p.  $252^\circ$  (decomp.); this was reduced with ferrous sulphate and barium hydroxide to *p-aminophenylpyrrolidonecarboxylic acid*, sheaves of needles, m. p.  $254^\circ$  (decomp.), which from an alkaline solution of iodine took up 2 atoms of the latter to give *3 : 5-di-iodo-4-aminophenylpyrrolidonecarboxylic acid*, needles, m. p.  $234^\circ$  (decomp.); diazotisation of the last compound in strong sulphuric acid and treatment with potassium iodide gave the desired *3 : 4 : 5-tri-iodophenylpyrrolidonecarboxylic acid*, needles, m. p.  $247^\circ$  (decomp.).

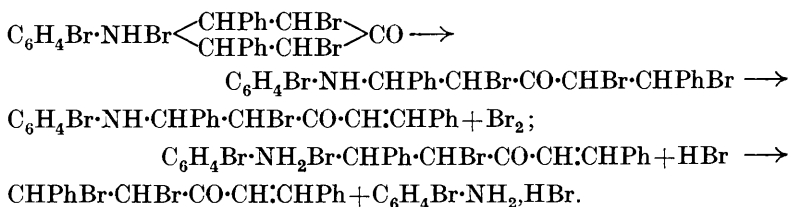
C. R. H.

**Modification of Hofmann's Decomposition Reaction of Heterocyclic Compounds.** P. PETRENKO-KRITSCHENKO and V. BUTMI DE KAZMAN (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 397—402).—The action of bromine (6 atoms) on 1 : 2 : 6-triphenyl-4-piperidone (cf. A., 1923, i, 480) (1 mol.) in benzene solution results in the formation of *3 : 5-dibromo-2 : 6-diphenyl-1-bromophenyl-4-piperidone*, m. p.  $148^\circ$ , which, when boiled in

chloroform, yields *p*-bromoaniline and *dibenzylideneacetone dibromide*, m. p. 145—151°. Treatment of the latter with bromine in chloroform solution gives a quantitative yield of *dibenzylideneacetone tetrabromide*, m. p. 210°.

Similar treatment with bromine of the isomeride of 1 : 2 : 6-triphenyl-4-piperidone (cf. A., 1909, i, 961) yields a *tetrabromo* compound,  $C_{23}H_{19}ONBr_4$ .

The decomposition of 3 : 5-dibromo-2 : 6-diphenyl-1-bromophenyl-4-piperidone, which occurs with spontaneous liberation of bromine, is evidently a modification of Hofmann's reaction and appears to follow the scheme :



The hydrogen bromide necessary for the reaction is probably supplied by decomposition of part of the tribromo compound.

The above scheme differs from that usually accepted in that it assumes a passage into the unsaturated form and decomposition of the isomerised product or, more accurately, transference of the negative groups. The literature contains indications, but no convincing proof, that Hofmann's reaction proceeds by means of such isomerisation. This proof is now supplied by the formation of the unsaturated bromide, which is explainable only on the hypothesis of preliminary isomerisation.

T. H. P.

**Catalytic Reduction of Cyano Compounds.** H. RUPE and F. GISIGER (*Helv. Chim. Acta*, 1925, **8**, 338—351; cf. A., 1923, i, 1199).—Purely aliphatic nitriles and compounds of the phenylacetonitrile type, on reduction with hydrogen in presence of nickel, yield almost exclusively the corresponding secondary bases. When a second and a third phenyl group are introduced, the primary base becomes the main product and reduction is slow and incomplete. Diphenylacetonitrile gives  $\beta$ -diphenylethylamine (cf. A., 1890, 357), m. p. 38°, b. p. 170°/11 mm. (*phenylthiocarbamide*, m. p. 171°, *acetyl* derivative, m. p. 86°, *benzoyl* derivative, m. p. 123°), and a very small quantity of secondary *di-( $\beta$ -diphenylethyl)amine (hydrochloride*, m. p. 159°, *nitrosoamine*, m. p. 179°), together with a small, unexplained yield of benzophenone. Triphenylacetonitrile gives only the primary base,  $\beta$ -triphenylethylamine (*hydrochloride*, m. p. 214°). Reduction of cyanomethylanthranilic acid is very complicated, giving only a trace of acid of uncertain constitution, isolated as barium salt. Reduction of hydrocyanodiphenylcarbodiimine,  $NHPh \cdot C(CN) : NPh$ , is also complex, aniline being the chief product.

Two cyanoketones were investigated.  $\alpha$ -Phenyl- $\beta$ -benzoyl-

propionitrile yields the primary base, at once eliminating water to give *diphenylpyrroline*, m. p.  $50^{\circ}$  (N-acetyl derivative, m. p.  $105^{\circ}$ , N-benzoyl derivative, m. p.  $180^{\circ}$ , *picrate*, m. p.  $156^{\circ}$ , *hydrogen oxalate*, m. p.  $157$ — $158^{\circ}$ ), and a small quantity of an *isomeride* (?), m. p.  $176^{\circ}$ . Reduction at a higher temperature gives both *diphenylpyrroline* and *diphenylpyrrolidine*, b. p.  $193$ — $195^{\circ}/12$  mm. (normal *oxalate*, m. p.  $230^{\circ}$ , *hydrochloride*, m. p.  $154^{\circ}$ , *phenylthiocarbamide*, m. p.  $188^{\circ}$ ), easily separated through the oxalates. The  $\alpha$ -cyanoketone, cyanodeoxybenzoin, behaves differently, giving the *aldimine*,  $\text{CHPhBz}\cdot\text{CH}\cdot\text{NH}$ , m. p.  $173^{\circ}$ , and benzoylphenylacetaldehyde, instantly converted into the enolic form, hydroxymethylenedeoxybenzoin,  $\text{CPhBz}\cdot\text{CH}\cdot\text{OH}$ , yielding with phenylhydrazine 1 : 4 : 5-triphenylpyrazole, m. p.  $207^{\circ}$ . A *substance*, m. p.  $91$ — $92^{\circ}$ , apparently an *isomeride* of cyanodeoxybenzoin, obtained as the main product in the preparation of the latter by Bodroux's method (A., 1911, i, 545), is described.

M. J.

**Organic Chloro-stannites and -stannates. VII. Some Miscellaneous Compounds.** J. G. F. DRUCE (*Chem. News*, 1925, 130, 385—386).—*Piperidine chlorostannate* ( $\text{C}_5\text{H}_{10}\text{N}$ ) $_2$ ,  $\text{H}_2\text{SnCl}_6$ , has m. p.  $230^{\circ}$ . *Quinine chlorostannite*,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$ ,  $\text{H}_2\text{SnCl}_4$ , m. p.  $120^{\circ}$ , is converted by chlorine water into *quinine chlorostannate*,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$ ,  $\text{H}_2\text{SnCl}_6$ .  $\gamma$ -*Picoline chlorostannate* is  $(\text{NC}_5\text{H}_4\cdot\text{Me})_2$ ,  $\text{H}_2\text{SnCl}_4$ .

C. J. S.

**Iodo Derivatives of Pyrrole and their Behaviour towards Nitric Acid.** A. PIERONI and D. NOCENTINI (*Gazzetta*, 1925, 55, 348—361; cf. A., 1923, i, 613).—A number of iodo and iodo-carboxy derivatives of pyrrole, now described, were obtained by the following general method. The starting product, usually the dicarboxylic acid corresponding with the iodo compound desired, was dissolved in a large excess of concentrated sodium carbonate solution and the clear liquid treated, when cold, dropwise with the requisite amount of a normal solution of iodine in potassium iodide. The monoiodo-acids formed remained in solution and, after separation by filtration from small proportions of the di-iodo compounds, were precipitated by means of acetic or dilute sulphuric acid. The monoiodo-acids undergo change, with lowering of m. p., when crystallised from solvents, and are best purified by precipitation from solution in potassium hydroxide by addition of sulphuric acid. Treatment of some of these iodo compounds of pyrrole with nitric acid results in replacement of the halogen by the nitro group.

3 : 5-Di-iodo-2 : 4-dimethylpyrrole, prepared from the corresponding 3 : 5-dicarboxylic acid, decomposes at  $65^{\circ}$ .

Ethyl 5-iodo-2 : 4-dimethylpyrrole-3-carboxylate, prepared from the ester of the 3 : 5-dicarboxylic acid, forms pink needles, m. p.  $148^{\circ}$ .

3 : 4-Di-iodo-2 : 5-dimethylpyrrole forms red crystals, m. p.  $134^{\circ}$ .

4-Iodo-2 : 5-dimethylpyrrole-3-carboxylic acid, prepared from the corresponding dimethyl-3 : 4-dicarboxylic acid, has m. p.  $162^{\circ}$ .

(decomp.), and, when treated with concentrated nitric acid, yields a *compound* forming silky needles, m. p. 125°. The action of nitric acid on ethyl 2:5-dimethylpyrrole-3:4-dicarboxylate gives a *compound* crystallising in needles, m. p. 167—168°.

3:4-Di-iodo-1-phenyl-2:5-dimethylpyrrole, prepared from the corresponding 3:4-dicarboxylic acid, has m. p. 115°, and does not react when heated in a reflux apparatus with magnesia in presence of ether or benzene; when treated with nitric acid it gives a reddish-yellow *compound*.

4-Iodo-1-phenyl-2:5-dimethylpyrrole-3-carboxylic acid, prepared from the 3:4-dicarboxylic acid, has m. p. 190° (decomp.); its silver salt decomposes at 192° and is soluble in excess of ammonia.

The action of iodine on 2-acetylpyrrole in aqueous solution containing sodium carbonate yields di-iodo-2-acetylpyrrole, m. p. 168°, and 3:4:5-tri-iodo-2-acetylpyrrole, m. p. 202°. Neither of these products reacts with *p*-bromophenylazoxycarbonamide, but the action of concentrated nitric acid on the tri-iodo compound gives a crystalline iodo compound, decomposing, without melting, at 225°. Another iodo compound, m. p. 172° (decomp.), is obtained by treating the tri-iodo derivative with hydroxylamine.

3:4-Dinitro-1-phenyl-2:5-dimethylpyrrole, obtained by the action of nitric acid on either the corresponding 3:4-dicarboxylic acid or 4-iodo-1-phenyl-2:5-dimethylpyrrole-3-carboxylic acid, forms golden-yellow needles, m. p. 205°.

The action of concentrated nitric acid on 2:5-dimethylpyrrole-3:4-dicarboxylic acid gives a crystalline *compound*, m. p. 115°.

T. H. P.

### Catalysts for the Synthesis of Indoles by Fischer's Method.

A. KORCZYŃSKI and L. KIERZEK (*Gazzetta*, 1925, 55, 361—369). —When heated at about 150° in presence of 1% of anhydrous nickel, cobalt, or zinc chlorides, or of powdered copper, iron, nickel, cobalt, zinc, aluminium, tungsten, titanium, uranium, or molybdenum, phenylhydrazine undergoes decomposition with formation of ammonia, benzene, aniline, and resinous substances. Decomposition of phenylhydrazones with formation of indoles also takes place in presence of powdered metals or various salts, and several indoles have been prepared in this way. In cases where isolation of the indoles by means of their picrates is not possible owing to the instability or non-formation of these salts, use may be made of the picryl compounds for this purpose.

Picryl-2-methylindole,  $C_{15}H_{10}O_6N_4$ , prepared by boiling 2-methylindole (1 mol.) and picryl chloride (1 mol.) in alcoholic solution with the calculated amount of sodium carbonate in a reflux apparatus, occurs in two isomeric modifications, forming red needles and an orange powder, m. p. 110° and 225°, respectively. Picryl-2:3-dimethylindole, similarly prepared, forms red needles and a cherry-red powder, m. p. 133—134°.

*p*-Methoxyacetophenonephenylhydrazone, pale yellow leaflets, m. p. 142°, is turned brown by the action of light and decomposes immediately, with resinification, on exposure to the air. When

heated at 230—240° with nickel chloride, it yields 2-*p*-methoxyphenylindole, which forms needles with silvery lustre, m. p. 228—229°, and imparts a violet colour to a splinter of pine moistened with hydrochloric acid. *p*-Methoxyacetophenone-*p*-bromophenylhydrazone, pink lamellæ, m. p. 154°, undergoes profound decomposition, with generation of heat, when heated with nickel chloride. Acetophenone-*p*-methoxyphenylhydrazone, m. p. 63—64°, yields 5-methoxy-2-phenylindole when heated with nickel chloride. *p*-Methoxyacetophenone-*p*-methoxyphenylhydrazone forms lustrous, yellow lamellæ, m. p. 162—163°, is highly sensitive to the action of light and air, and, when heated with nickel chloride, yields 2-*p*-methoxyphenyl-5-methoxyindole, yellow, lamellar crystals, turning brown at 204°, m. p. 213—214°.

2-*p*-Hydroxyphenylindole, yellow lamellæ, m. p. 70°, imparts an intense coloration to pine wood, and with diphenylcarbonyl chloride gives an amorphous, yellow condensation product,  $C_{22}H_{20}O_2N_2$ , m. p. 65°.

2-Pentylindole, prepared as above from cenanthaldehydephenylhydrazone, has m. p. 54° and gives a picrate, m. p. 91—92°, but is not accompanied by heptonitrile, so that the action of nickel chloride on phenylhydrazones differs from that of cuprous chloride (cf. Arbusov, A., 1910, i, 721).

Dibromo-*p*-hydroxyacetophenone-*p*-bromophenylhydrazone, m. p. 180°, is apparently stable towards the air and light, but undergoes profound decomposition when heated in presence of nickel.

T. H. P.

**Quinoline and the Centroid Structure.** R. C. FUSON (*J. Amer. Chem. Soc.*, 1925, **47**, 2018—2021; cf. this vol., i, 253).—Whilst the centroid structure suggested for quinoline by Huggins (A., 1922, i, 928, 997) demands a *peri* bridge formation between positions 4 and 8, the only quinoline derivative known to possess such a linking is the lactam of 5-aminocinchoninic acid (Koenigs and Lossow, A., 1899, i, 456). To test the possibility of obtaining a similar linking between positions 4 and 8, 8-hydroxycinchoninic acid was prepared by a modification of Weidel and Cobenzl's method (*Monatsh.*, 1880, **1**, 844, and A., 1881, 742) and submitted to various methods of dehydration. No indication of lactone formation was obtained, and it is concluded that the centroid structure for quinoline is untenable, and also probably untenable for aromatic nuclei in general. 8-Sulphocinchoninic acid decomposes to a black mass, without melting, above 400°, and pure 8-hydroxycinchoninic acid has m. p. 258—259°.

F. G. W.

**Carbazole.** H. LINDEMANN and W. WESSEL (*Ber.*, 1925, **58**, [B], 1221—1230).—The preparation of 1-aminocarbazole from chloro-2 : 6-dinitrobenzene suffers from the disadvantage that the latter substance is somewhat difficult to obtain; attempts are therefore described to prepare this compound or one of the intermediates of the previous synthesis (A., 1924, i, 1234) in better yield. Elimination of carbon dioxide from 4-chloro-3 : 5-dinitrobenzoic acid could not be effected satisfactorily. 4-Chloro-3 : 5-

*dinitrobenzenesulphonic acid*, m. p.  $293^{\circ}$ , prepared conveniently by the simultaneous nitration and sulphonation of chlorobenzene, and *4-bromo-3:5-dinitrobenzenesulphonic acid*, m. p. above  $300^{\circ}$ , do not suffer loss of the sulphonic group when treated with superheated steam or with hydrochloric acid at  $200^{\circ}$ . *4-Chloro-3:5-dinitrobenzoyl chloride*, m. p.  $58^{\circ}$ , is converted by cold ammonia into *4-chloro-3:5-dinitrobenzamide*, m. p.  $186^{\circ}$ , and by the warm reagent into *3:5-dinitro-4-aminobenzamide*, m. p.  $252^{\circ}$ . Attempts to apply Hofmann's method for the conversion of 4-chloro-3:5-dinitrobenzamide into the corresponding amine gave *3:5-dinitro-4-methoxybenzamide*, m. p.  $165^{\circ}$ , which is readily prepared from ammonia and *3:5-dinitro-4-methoxybenzoyl chloride*, m. p.  $42^{\circ}$ . The degradation of *4-chloro-3:5-dinitrobenzazide*, m. p.  $86^{\circ}$ , by Curtius' method proceeds smoothly, but the preparation of this substance through the hydrazide is not possible, since the halogen atom of the esters of 4-chloro-3:5-dinitrobenzoic acid reacts more rapidly than the ester group with hydrazine hydrate (*ethyl 3:5-dinitro-4-hydrazinobenzoate*, m. p.  $138^{\circ}$ , is described). It is, however, readily prepared by the action of sodium azide on 4-chloro-3:5-dinitrobenzoyl chloride in cold acetic acid solution. It reacts explosively with concentrated sulphuric acid, but is transformed by somewhat diluted acid into *4-chloro-3:5-dinitroaniline*, m. p.  $187-188^{\circ}$ , which is more smoothly produced from the corresponding acetyl derivative, m. p.  $228^{\circ}$  (decomp.), prepared by heating the azide with acetic anhydride and a few drops of concentrated sulphuric acid. The azide is converted by boiling water or dilute acetic acid into *s-di-4-chloro-3:5-dinitrophenylcarbamide*, m. p.  $295^{\circ}$  (decomp.), which, somewhat unexpectedly, is also produced in neutral media such as toluene or nitrobenzene. Attempts to replace the amino group of 4-chloro-3:5-dinitroaniline by hydrogen in the customary manner were unsuccessful. The halogen atom is firmly retained in the free amine, whereas it is mobile in the corresponding acetyl derivative, which is transformed by aniline into *3:5-dinitro-4-anilinoacetanilide*, m. p.  $216^{\circ}$ . The latter substance is hydrolysed to *2:6-dinitro-4-aminodiphenylamine*, m. p.  $154^{\circ}$ , which is smoothly diazotised (the corresponding *diazonium nitrate*, decomp.  $148^{\circ}$ , *chloride*, decomp.  $175^{\circ}$ , and *sulphate*, decomp.  $180^{\circ}$ , are described); the solid diazonium salts when heated with alcohol give in good yield *2:6-dinitrodiphenylamine*, m. p.  $107-108^{\circ}$ , identical with the substance employed by Kehrman and Kaiser (A., 1906, i, 12) and Lindemann and Werther (A., 1924, i, 1234) in the synthesis of 1-aminocarbazole.

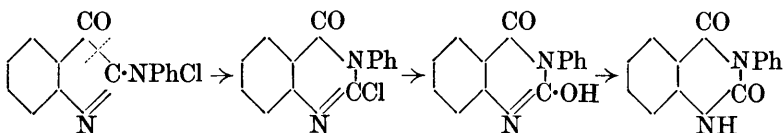
*3:5-Dinitro-4-anilinobenzoic acid* is converted by phosphorus pentachloride into *3:5-dinitro-4-anilinobenzoyl chloride*, m. p.  $123^{\circ}$ , which is transformed by sodium azide into *3:5-dinitro-4-anilino-benzazide*, m. p.  $135^{\circ}$ . The smooth transformation of the latter substance into the corresponding amine or its acetyl derivative could not be effected. It is converted by glacial acetic acid into *s-di-3:5-dinitro-4-anilino-carbamide*, m. p.  $252^{\circ}$  (decomp.).

*3:5-Dinitro-4-anilinobenzoic acid* is smoothly reduced by ammonium sulphide to *5-nitro-3-amino-4-anilinobenzoic acid*, which is

converted by acetic anhydride and sodium acetate into 7-nitro-1-phenyl-2-methylbenziminazole-5-carboxylic acid, m. p. 289°, and transformed by sodium nitrite and dilute sulphuric acid into 7-nitro-1-phenylbenztriazole-5-carboxylic acid (I), m. p. 279°. The nitro-acid shows little tendency to pass into a carbazole derivative. The corresponding amino-acid, m. p. 248° (acetyl compound, m. p. 281—282°), readily loses carbon dioxide and nitrogen when heated with an excess of barium oxide and gives 1-aminocarbazole in satisfactory yield. H. W.

**Oxidation of Thymine. 4:5-Dihydroxythymine.** O. BAUDISCH and D. DAVIDSON (*J. Biol. Chem.*, 1925, **64**, 233—239).—On shaking 5-bromo-4-hydroxyhydrothymine with moist silver oxide there was obtained 4:5-dihydroxythymine, m. p. 220° (decomp.); this substance, on hydrolysis either with sodium hydrogen carbonate or barium hydroxide, yielded carbon dioxide, carbamide, and acetylcarbinol; on reduction with hydriodic acid thymine was obtained and among the products of oxidation pyruvic acid was detected. C. R. H.

**Conversion of Isatin into a Tetrahydroquinazoline Derivative.** H. RUPE and G. A. GUGGENBUHL (*Helv. Chim. Acta*, 1925, **8**, 358—359).—Repeated experiments on the action of thionyl chloride on isatinphenylhydroxylamine fail to give again the isatin-*N*-chloroanilide, described in a previous communication (cf. A., 1924, i, 764), and yield instead 3-phenyldiketotetrahydroquinazoline and a small quantity of isatin. The authors suggest that the *N*-chloroanilide primarily formed is decomposed thus:



They defend their formula for isatinphenylhydroxylamine (cf. Heller, *Z. angew. Chem.*, 1924, **37**, 1017). M. J.

**Tenacity of Organic Radicals with Respect to Nitrogen.** K. VON AUWERS and W. PFUHL (*Ber.*, 1925, **58**, [B], 1360—1369).—The comparative firmness of the union between alkyl groups and the nitrogen atom is examined by a study of the thermal decomposition of quaternary indazolium salts,  $\left[ \text{C}_6\text{H}_4 \left\langle \begin{smallmatrix} \text{CH} \\ \text{NR}' \end{smallmatrix} \right\rangle \text{NR} \right] \text{X}$ , and measurement of the relative proportions of 1- and 2-alkylindazoles thereby produced, the latter being determined as the picrates. Comparative experiments with salts containing the methyl group in position 1 and various alkyl groups in position 2 show that the tenaciousness of saturated alkyl groups increases with increasing weight from methyl through ethyl to propyl; thereafter a diminution is observed. The allyl and various benzyl radicals are less



firmly united than methyl. The same order is generally maintained in a series of observations with alkylindazolium salts containing various alkyl groups in position 1. In general, the sequence of radicals agrees with that observed by von Braun except as regards the position of the *n*-butyl group and the relative tenaciousness of the propyl and *isopropyl* groups, which in these experiments appear almost equal. The latter observation suggests that valency demand is possibly not the sole factor governing tenacity, but that steric influences also have an effect.

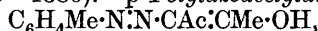
The following new or revised data are recorded : 2-ethylindazole, m. p. 37—39°; 2-propylindazole, b. p. 143·5—144·5°/14 mm., m. p. 28—29°; 2-*isobutyl*indazole, b. p. 139·5—140·5°/13 mm., m. p. 52—56°; 2-*o*-chlorobenzylindazole, m. p. 57—58° (*picrate*, m. p. 141—142°); 2-*p*-chlorobenzylindazole, m. p. 115° (*picrate*, m. p. 152°); 1 : 2-dimethylindazolium chloride, m. p. 137—138°, bromide, m. p. 111—113°; 1-methyl-2-ethylindazolium chloride, m. p. 186—187°, bromide, m. p. 197°, iodide, m. p. 173°; 1-methyl-2-propylindazolium chloride, m. p. 145°, bromide, m. p. 201—202°, iodide, m. p. 199°; 1-methyl-2-butylindazolium iodide, m. p. 175°; (?) 1-methyl-2-*isobutyl*indazolium iodide, m. p. 161—163°; 1-methyl-2-allylindazolium iodide, m. p. 140·5°; (?) 1-methyl-2-*o*-chlorobenzylindazolium iodide, m. p. 148—150°; 1-methyl-2-*p*-chlorobenzylindazolium iodide, m. p. 183—183·5°; 1-methyl-2-*o*-nitrobenzylindazolium iodide, m. p. 164°; 1-methyl-2-*p*-nitrobenzylindazolium iodide, m. p. 188°; 1-ethyl-2-propylindazolium iodide, m. p. 150°; 1-ethyl-2-allylindazolium iodide, m. p. 152°; 2-methyl-1-propylindazolium iodide, m. p. 131—132°; 2-ethyl-1-propylindazolium iodide, m. p. (*indef.*) 81—86°; 1 : 2-di-propylindazolium iodide, m. p. 120—121°; 2-methyl-1-allylindazolium iodide, m. p. 137°; 2-ethyl-1-allylindazolium iodide, m. p. 131—132°; 2-propyl-1-allylindazolium iodide, m. p. 126—127°; 1 : 2-dibenzylindazolium iodide, m. p. 150°; 1-*o*-chlorobenzyl-2-methylindazolium iodide, m. p. 167°; 1-*p*-chlorobenzyl-2-methylindazolium iodide, m. p. 164°; 1-*o*-nitrobenzyl-2-methylindazolium iodide, m. p. 202°; 1-*p*-nitrobenzyl-2-methylindazolium iodide, m. p. 179·5°. H. W.

**Formation of Indazoles from the Hydrazones of 2 : 6-Dinitrobenzaldehyde.** K. VON AUWERS and E. FRESE (*Ber.*, 1925, 58, [B], 1369—1375).—The production of 1-substituted indazoles and sodium nitrite by the action of sodium hydroxide on certain substituted hydrazones of 2 : 6-dinitrobenzaldehyde has been established by Reich and Gaigailian (*A.*, 1913, i, 995). Attempts to extend the method to the synthesis of 1-acylindazoles have not been successful. Observations with a large number of hydrazones show that the success or failure of the synthesis depends on unknown factors.

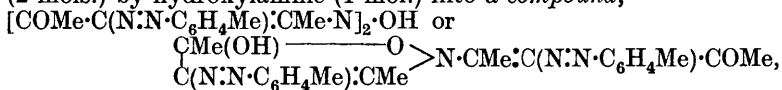
2 : 6-Dinitrobenzaldehyde is conveniently prepared from 2 : 6-dinitrotoluene through the corresponding bromide, anilino derivative, and anil. 2 : 6-Dinitrobenzaldehyde-semicarbazone and -*p*-nitrophenylhydrazone have m. p. 217° and 223—225° (instead of 207—208° and 207—208° recorded by Reich and Gaigailian); 4-nitro-1-*p*-nitrophenylindazole has m. p. 264° (instead of 261°). The following

hydrazones of 2:6-dinitrobenzaldehyde are described: 2':4'-*di*nitrophenylhydrazone, m. p. 233—235°; picrylhydrazone, m. p. 219—220° (decomp.); *o*-tolylhydrazone, m. p. 193° (decomp.); *p*-tolylhydrazone, m. p. 157·5—158·5°; *as*-*m*-xylylhydrazone, m. p. 174°; benzoylhydrazone, m. p. 234—236°; carbethoxyhydrazone, m. p. 219—220° (decomp.); methylhydrazone, m. p. 120—121°. From the appropriate hydrazone the following indazoles are prepared: 4-nitro-1-*o*-tolylindazole, m. p. 92—94°; 4-nitro-1-*p*-tolylindazole, m. p. 155—156°; 4-nitro-1-*as*-*m*-xylylindazole, m. p. 112—113°; 4-nitro-1-methylindazole, m. p. 138—139°. 4-Nitroindazole is converted by methyl iodide or methyl sulphate into a mixture of 4-nitro-1-methylindazole and 4-nitro-2-methylindazole, m. p. 101—103°, which can be separated from one another by taking advantage of the greater basicity of the latter. Similarly, 4-nitroindazole and benzyl chloride give a mixture of 4-nitro-1-benzylindazole, m. p. 97°, and 4-nitro-2-benzylindazole, m. p. 123—124°. H. W.

**Arylazoacetylacetones and the Products of their Condensation and Fission.** C. BÜLOW and W. SPENGLER (*Ber.*, 1925, 58, [B], 1375—1386).—*p*-Tolylazoacetylacetone,



m. p. 97°, is converted by nitric acid in glacial acetic acid solution into 3-nitro-*p*-tolylazoacetylacetone, m. p. 171°, the constitution of which is established by its formation from acetylacetone and diazotised *m*-nitro-*p*-toluidine. The compounds are converted by hydrazine into 4-*p*-tolylazo-3:5-dimethylpyrazole, m. p. 149°, by phenylhydrazine into 4-*p*-tolylazo-1-phenyl-3:5-dimethylpyrazole, m. p. 78°, and 4-*m*-nitro-*p*-tolylazo-1-phenyl-3:5-dimethylpyrazole, m. p. 162°, and by hydroxylamine into 4-*p*-tolylazo-3:5-dimethylisooxazole, m. p. 81·5°, and 4-*m*-nitro-*p*-tolylazo-3:5-dimethylisooxazole, m. p. 140°. The isolation of intermediate products appears impossible in the case of hydrazine, but with phenylhydrazine and hydroxylamine the primary *p*-tolylazoacetylacetonephenylhydrazone, m. p. 70°, and *p*-tolylazoacetylacetoneoxime, m. p. 124·5°, can be obtained. The conversion of *p*-tolylazoacetylacetone (2 mols.) by hydroxylamine (1 mol.) into a compound,



m. p. 62°, is remarkable. *m*-Nitro-*p*-tolylazoacetylacetone is converted by aniline into the unstable *anilide*, m. p. 138°.

Pyrazoles which contain an imino hydrogen atom are capable of yielding relatively stable salts with mineral acids, whereas this property is not exhibited by pyrazoles in which the atom is replaced by an aryl group; the *nitrate*, m. p. 150—151° (decomp.) after darkening at 138°, *hydrochloride*, m. p. 230°, and *perchlorate*, m. p. 224—225°, of 4-*p*-tolylazo-3:5-dimethylpyrazole are described. The latter substance is converted by nitric and acetic acids into 4-*m*-nitro-*p*-tolylazo-3:5-dimethylpyrazole and 4-nitro-3:5-dimethylpyrazole. *p*-Tolylazo-3:5-dimethylisooxazole and concentrated nitric acid yield *m*-nitro-*p*-tolylazoacetylacetone.

Oxidative fission by chlorine proceeds smoothly in the case of *m*-nitro-*p*-tolylazoacetylacetone in acetic acid solution and leads to the production of the *m*-nitro-*p*-tolylhydrazone of pyruvyl chloride,  $\text{CAcCl} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2$ , m. p.  $144^\circ$ , which is also prepared by coupling  $\gamma$ -chloroacetylacetone with *m*-nitro-*p*-tolyl diazonium chloride in acetic acid solution; the presence of the ketonic group is established by the preparation of the corresponding phenylhydrazone,  $\text{C}_{16}\text{H}_{16}\text{O}_2\text{N}_5\text{Cl}$ , m. p.  $214.5^\circ$ . Pyruvyl chloride *p*-tolylhydrazone, m. p.  $142^\circ$ , is formed by similar methods. *p*-Tolylazoacetylacetone is converted by cautious treatment with bromine in the presence of acetic acid into pyruvyl bromide *p*-tolylhydrazone, m. p.  $135^\circ$ , and by a larger proportion of the halogen into pyruvyl bromide *m*-bromo-*p*-tolylhydrazone, m. p.  $108-109^\circ$ ; pyruvyl bromide *m*-nitro-*p*-tolylhydrazone has m. p.  $160-162^\circ$ . The latter substance is converted by hydrazine and phenylhydrazine in acetic acid solution into 4-*m*-nitro-*p*-tolylazo-3 : 5-dimethylpyrazole, m. p.  $192^\circ$ , and 4-*p*-tolylazo-3 : 5-dimethylpyrazole, m. p.  $162^\circ$ , respectively. Pyruvyl bromide *m*-nitro-*p*-tolylhydrazone is converted by relatively short treatment with hydroxylamine hydrochloride into the corresponding oxime, m. p.  $235^\circ$ , and by protracted treatment into 4-*m*-nitro-*p*-tolylazo-3 : 5-dimethylisooxazole. The reactivity of the halogen atoms in the compounds just described is established by the isolation of pyruvamide-*p*-tolylhydrazone, m. p.  $164^\circ$ , and pyruvamide-*m*-nitro-*p*-tolylhydrazone, m. p.  $174^\circ$  (corresponding phenylhydrazone, m. p.  $204^\circ$ ), by the action of ammonia on the corresponding chloride or bromide.

Attempts to obtain tetrazole derivatives by the action of sodium nitrite and hydrochloric acid on pyruvamide-*m*-nitro-*p*-tolylhydrazone led to the production of *m*-nitro-*p*-tolylazoacetylacetone, the effect being due to the mineral acid.

The presence of the enolic group in *p*-tolylazoacetylacetone is established by the isolation of the corresponding sodium salt, m. p.  $228^\circ$ , and copper salt, m. p.  $191^\circ$ . H. W.

**Formation of Salts from Glyoxaline-4 : 5-dicarboxylic Acid.** K. LEHMSTEDT (*Ber.*, 1925, 58, [B], 1219-1220).—A solution of glyoxaline-4 : 5-dicarboxylic acid is neutral towards phenolphthalein after addition of sodium hydroxide sufficient to saturate the first and 74% of the second carboxyl group; concentration of such a neutral solution leads to the separation of the sodium hydrogen salt, whereas the normal salt is precipitated by addition of alcohol to the concentrated mother-liquor. The normal ammonium salt, obtained by precipitation of a solution of the acid in concentrated ammonia by alcohol, loses ammonia when preserved at the atmospheric temperature and passes quantitatively into the ammonium hydrogen salt. Thermal decomposition of the barium or calcium hydrogen salt gives glyoxaline and hydrocyanic acid, but no ketone. The incomplete existence of the normal sodium salt in aqueous solution shows that the determinations of the first and second dissociation constants of the acid (cf. Pauly and Ludwig, A., 1922, i, 953) are inaccurate. H. W.

**Behaviour of the Sulphides of Sodium in Aqueous and Alcoholic Media. A Contribution towards Elucidating the Structure of Sulphide Dyes.** H. H. HODGSON (*J. Soc. Dyers and Col.*, 1925, **41**, 241—244).—A more detailed account of work already published (this vol., i, 532; see also *B.*, 1925, 665).

W. A. S.

**Action of Nitrous Acid on the Nitrile of Aminomalonic Acid.** E. GRISCHKEVITSCH-TROCHIMOVSKI (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 548—550).—Diazotisation of aminomalononitrile yields 4:5-dicyano-1:2:3-triazole, which forms orange-yellow crystals, m. p. 145—150° (decomp.):  $\text{NH}_2\cdot\text{CH}(\text{CN})_2 + \text{HNO}_2 = \text{H}_2\text{O} + \text{OH}\cdot\text{N}\cdot\text{N}\cdot\text{CH}(\text{CN})_2$ ; the latter  $+ \text{NH}_2\cdot\text{CH}(\text{CN})_2 = \text{H}_2\text{O} + \text{CH}(\text{CN})_2\cdot\text{N}\cdot\text{N}\cdot\text{NH}\cdot\text{CH}(\text{CN})_2 = 2\text{HCN} + \text{N} \begin{smallmatrix} \text{N} \text{---} \text{C} \text{---} \text{CN} \\ | \\ \text{NH} \text{---} \text{C} \text{---} \text{CN} \end{smallmatrix}$ . The

dicyanotriazole forms: a *silver* compound,  $\text{C}_4\text{N}_5\text{Ag}$ , stable towards light, but inflammable when heated; analogous *ammonium* and *potassium* compounds; a blue *copper* compound,  $(\text{C}_4\text{N}_5)_2\text{Cu}$ ; a *calcium* compound ( $+3\text{H}_2\text{O}$ ); and a *methyl* derivative, m. p. 57.5—58.5°. When hydrolysed by means of hydrochloric acid, it yields 1:2:3-triazole-4:5-dicarboxylic acid monoamide,



infusible at 275°, whilst hydrolysis by sulphuric acid gives 1:2:3-triazole-4:5-dicarboxylic acid. When treated with hydrochloric acid in absolute alcoholic solution it gives an unstable salt of an imino-ether which, on decomposition by water, yields *ethyl cyano-1:2:3-triazolecarboxylate*,  $\text{CN}\cdot\text{C}_2\text{HN}_3\cdot\text{CO}_2\text{Et}$ , m. p. 114—115°. When heated at about its melting point, the triazole undergoes partial sublimation, with formation of a white isomeride (cf. following abstract).

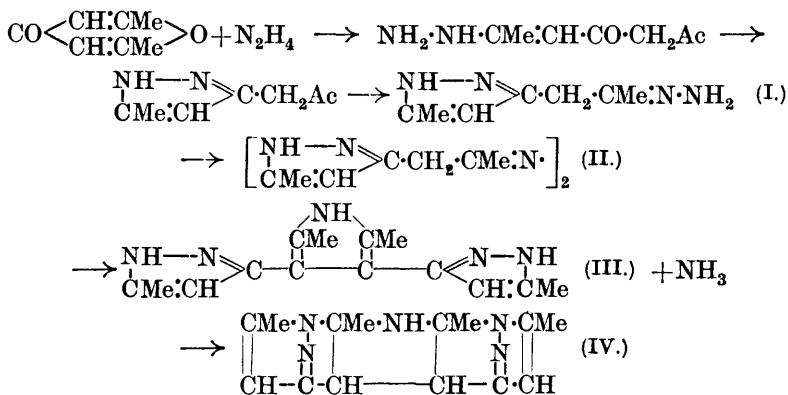
T. H. P.

**Structure of Dicyanotriazole.** E. GRISCHKEVITSCH-TROCHIMOVSKI and L. KOTKO (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 551—553).—Both forms of dicyano-1:2:3-triazole (see preceding abstract) have m. p. 145—150°. The action of alkali hydroxide on the yellow variety results, according to the concentration of the alkali and the temperature, in either the formation of a salt, which reverts to the original yellow compound on acidification, or hydrolysis of one cyano group and formation of *cyano-1:2:3-triazolecarboxylic acid*, m. p. 215—216° (decomp.), or hydrolysis of one and partial hydrolysis of the other cyano group with formation of the monoamide of the dicarboxylic acid.

When hydrolysed by means of concentrated sulphuric acid, the methyl derivative of the dicyanotriazole yields, not 1:2:3-triazole-4:5-dicarboxylic acid, but 1-methyl-1:2:3-triazole-4:5-dicarboxylic acid, m. p. 202.5—203.5° (decomp.), which gives a *methyl* ester, m. p. 83.5—84°; it is, therefore, 1-methyl-4:5-dicyano-1:2:3-triazole,  $\text{NMe} \begin{smallmatrix} \text{C}(\text{CN})\text{:C}\text{---}\text{CN} \\ | \\ \text{N} \text{---} \text{N} \end{smallmatrix}$ , and not  $\text{NMe}\text{:C}\text{---}\text{C} \begin{smallmatrix} \text{C}(\text{CN})\text{:N} \\ | \\ \text{N} \text{---} \text{N} \end{smallmatrix}$ , as would be indicated by the yellow colour. Both forms of dicyano-1:2:3-triazole yield the same methyl derivative when treated with

diazomethane, and the nature of their isomerism remains unexplained.  
T. H. P.

**Action of Hydrazine on Dimethylpyrone.** N. KIJNER (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 539—545).—Dimethylpyrone reacts energetically with hydrazine hydrate, the final product being a compound of the formula  $C_{14}H_{17}N_5$ . The pyrone first unites with the hydrazine with rupture of the pyrone ring, the resulting compound undergoing transformation into pyrazole, the hydrazone of which (I) yields the azine (II). The latter is then converted, by a reaction analogous to the formation of pyrroles from ketazines (cf. Piloty, A., 1910, i, 277), into the compound III. Since, however, the final product does not give the reactions of pyrroles, it is probable that compound III undergoes condensation into the isomeric form IV :



The compound IV has m. p.  $254^\circ$ , and yields an unstable compound with alcohol; a compound,  $C_{14}H_{17}N_5 + \text{MeOH}$ , stable at the ordinary temperature; a compound,  $C_{14}H_{17}N_5 + 4C_2H_4O_2$ , m. p.  $73^\circ$ ; a compound,  $C_{14}H_{17}N_5 + 4\text{HCl}$ ; and a colourless methiodide,  $C_{14}H_{17}N_5 \cdot \text{MeI}$ .  
T. H. P.

**Condensation of Isomeric Tolylyl-2-thio-4-ketothiazolidines (Rhodanic Acids) with Substituted Vanillins.** R. M. HANN (*J. Amer. Chem. Soc.*, 1925, **47**, 1998—2002).—5-Chlorovanillin (5-chloro-4-hydroxy-3-methoxybenzaldehyde), m. p.  $165^\circ$ , is obtained by the action of chlorine on vanillin in glacial acetic acid in presence of sodium acetate. The following substituted vanillylidene-thiothiazolidines were prepared by condensation of the substituted vanillins with the thiothiazolidines in boiling glacial acetic acid in presence of sodium acetate: 5(5-bromovanillylidene)-, yellowish-brown, iridescent, m. p.  $207^\circ$  (decomp.); 5(5-chlorovanillylidene)-, yellow, m. p.  $196^\circ$ ; 5(5-iodovanillylidene)-, orange-red, m. p.  $213^\circ$ ; and 5(5-nitrovanillylidene)-2-thio-3-o-tolyl-4-ketothiazolidine, golden-brown, m. p.  $205^\circ$  (decomp.); 5-vanillylidene-, deep yellow, m. p.  $210^\circ$ ; 5(5-bromovanillylidene)-, light yellow, m. p.  $201^\circ$ , subse-

quently re-solidifying and re-melting at 223—224°; 5(5-chlorovanillylidene)-, yellow, m. p. 210°; 5(5-iodovanillylidene)-, yellowish-brown, m. p. 190—191°; and 5(5-nitrovanillylidene)-2-thio-3-m-tolyl-4-ketothiazolidine, brown, m. p. 220° (decomp.); 5(5-bromovanillylidene)-, light yellow, m. p. 223°; 5(5-chlorovanillylidene)-, yellow, m. p. 224°; 5(5-iodovanillylidene)-, deep yellow, m. p. 243°; and 5(5-nitrovanillylidene)-2-thio-3-p-tolyl-4-ketothiazolidine, golden-brown, m. p. 214—215° (decomp.). F. G. W.

**Green Modification of *pp'*-Dihydroxyazobenzene.** D. VORLÄNDER and K. KUNZE (*Ber.*, 1925, **58**, [B], 1403—1404).—The action of water at 0° or, preferably, of sodium chloride or sodium acetate solution at -10° to -15° on the bluish-black *hydrochloride* of *pp'*-dihydroxyazobenzene (preferably prepared by passing hydrogen chloride into the alcoholic solution of the parent substance) leads to the separation of a very unstable, dark-grey or olive-green *modification* of *pp'*-dihydroxyazobenzene. The *disodium* and *diammonium* salts of *pp'*-dihydroxyazobenzene are described. H. W.

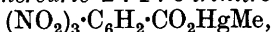
**Quinone Diazides of the Anthraquinone Series.** M. TANAKA (*Compt. rend.*, 1925, **181**, 180—182).—3-Nitro-2-aminoanthraquinone (m. p. 316°) is diazotised in concentrated sulphuric acid solution, and the *diazo* compound (yellow needles exploding at 133°) is converted by boiling with acetic anhydride into 9:10-anthraquinone-2:3-quinonediazide (annexed formula), crystals (+ $\frac{3}{4}$ Ac<sub>2</sub>O) with a metallic reflex, decomp. 227°, which couples slowly with R-salt to give a blue coloration. It is reduced by sodium thio-sulphate in alkaline solution to 3-hydroxy-2-hydrazinoanthraquinone, reddish-brown needles, decomp. 335°. Boiling acetic anhydride converts this into 2-methyl-5:6-anthraquinono-1-oxa-3:4-diazine, C<sub>14</sub>H<sub>6</sub>O<sub>2</sub>  $\begin{matrix} \text{NH}\cdot\text{N} \\ \diagup \quad \diagdown \\ \text{O}-\text{CMe} \end{matrix}$ , m. p. 314°.

1-Nitro-2-aminoanthraquinone (m. p. 310°) is converted in the same way into anthraquinone-1:2-quinonediazide. G. M. B.

**Reaction between Phenylhydrazine and Mercuric Acetate.** L. VECCHIOTTI and A. CAPODACQUA (*Gazzetta*, 1925, **55**, 369—371).—Gradual addition of phenylhydrazine, with agitation, to mercuric acetate solution results in the formation of the mercuric salt of diazoaminobenzene, Hg(NPh·N·NPh)<sub>2</sub> (cf. Ciusa and Pestalozza, A., 1911, i, 678). Apparently the phenylhydrazine undergoes oxidation to aniline and diazobenzene, these then condensing to diazoaminobenzene. T. H. P.

**Salvarsan. I. Determination of an Isoelectric Point.** A. S. HUNTER and W. A. PATRICK (*J. Lab. Clin. Med.*, 1925, **10**, 343—359).—The *p<sub>H</sub>* value of salvarsan is 7.60; of the dihydrochloride, 2.41; monohydrochloride, 3.00; monosodium salt, 10.88; disodium salt, 11.43. The presence of an isoelectric point at *p<sub>H</sub>* about 3.4 was indicated. CHEMICAL ABSTRACTS.

**Preparation and Decomposition of Unsymmetrical Mercuri-organic Compounds. A Method of Establishing the Relative Degree of Negativity of Organic Radicals.** M. S. KHARASCH and M. W. GRAFFLIN (*J. Amer. Chem. Soc.*, 1925, **47**, 1948—1954).—*Methylmercuric 2:4:6-trinitrobenzoate*,



m. p. 165° (decomp.), was prepared by shaking together silver trinitrobenzoate and mercuric methyl chloride in benzene. When heated at 160—162° in a vacuum, this affords mercury 2:4:6:2':4':6'-hexanitrodiphenyl (cf. Kharasch, A., 1922, i, 189) and probably mercury dimethyl.

*Phenylmercuric trinitrobenzoate*, m. p. 228°, obtained similarly, affords *phenylmercury 2:4:6-trinitrophenyl*, m. p. 227.5°, when heated in a vacuum at 222°. When boiled with mercuric chloride in alcohol, the latter yielded mercuric phenyl chloride and mercuric trinitrophenyl chloride. *p*-Tolylmercuric trinitrobenzoate, m. p. 234—237° (decomp.), and *p*-tolylmercury 2:4:6-trinitrophenyl, m. p. 203° (cf. Koten and Adams, this vol., i, 236) were obtained similarly. Decomposition of phenylmercury and *p*-tolylmercury trinitrophenyls with hydrogen chloride yielded benzene and toluene, respectively, and mercuric 2:4:6-trinitrophenyl chloride. This is taken to indicate that both tolyl and phenyl groups are more electronegative than 2:4:6-trinitrophenyl, as the more electronegative radical should break off more readily. The method may be extended to establish the relative negativity of all types of organic radicals.

F. G. W.

**Constitution of Hydrargyrum Salicylicum and Related Substances.** F. BOEDECKER and O. WUNSTORF (*Arch. Pharm.*, 1925, **263**, 430—435).—"Hydrargyrum salicylicum" is readily converted by an aqueous solution of potassium cyanide into a mixture of the salts of 3- and 5-cyanomercurisalicylic acids, which form respectively a sandy powder (*potassium salt* + 2.5H<sub>2</sub>O soluble in 25 parts of water at 15°, *strontium*, *zinc*, and *silver* salts described), and felted needles (*potassium salt* + 2H<sub>2</sub>O soluble in 10 parts of water at 15°, and *silver* salt described). The potassium salts react with a solution of iodine in potassium iodide to give iodosalicylic acids, which were identified with synthetic specimens, the orientation of the cyanomercuri derivatives being thus established. When the iodo-acid from the 3-cyanomercuri acid was fused with potassium hydroxide, and the resulting acid distilled, resorcinol was obtained, but this is no proof of constitution. All specimens of "hydrargyrum salicylicum" are mixtures except that prepared according to Dimroth (A., 1902, i, 849), which contains only the 1:2:5-isomeride. Dimroth's conclusion that it had the orientation 1:2:3 was probably due to a change of constitution during a potassium hydroxide fusion.

G. M. B.

**Mercury Derivatives of Azo Dyes.** A. PROSKOURIAKOFF and G. W. RAIZISS (*J. Amer. Chem. Soc.*, 1925, **47**, 1974—1979).—*Dihydroxymercuridihydroxyazobenzenesulphonic acid* was obtained as the orange-brown, amorphous *potassium salt*, by the action

of mercuric acetate on the monopotassium salt of chrysoine in hot aqueous or alcoholic solution in presence of a trace of acetic acid. *Dihydroxymercuri-β-naphtholazobenzenesulphonic acid* was obtained similarly from the sodium salt of "orange II." *Mercuribis(hydroxymercuri-β-naphtholazobenzenesulphonic acid*, red, amorphous, was obtained by the action of 2 equivalents of mercuric acetate on "orange II" in methyl alcoholic solution in presence of acetic acid. *Dihydroxymercurihydroxyazobenzenesulphonic acid*, brownish-red, was obtained similarly in aqueous solution. It yields a *disodium* salt. *Mercuribis(nitrobenzeneazosalicylic acid)*, light brown, was prepared similarly from the sodium salt of the azo compound and mercuric acetate in aqueous solution, or from the free acid in alcoholic solution. The toxicity of the above mercury compounds is less than that of mercuric chloride, but is not proportional to the mercury content. The compounds are weaker bactericides than mercuric chloride, but stronger than "mercurochrome" (hydroxymercuridibromofluorescein). F. G. W.

**Mercurisation of Methylene-blue.** L. CHALKLEY, jun. (*J. Amer. Chem. Soc.*, 1925, **47**, 2055—2061).—When benzoyl-leucomethylene-blue is boiled in aqueous alcoholic solution with 3 molecular equivalents of mercuric acetate in presence of acetic acid, it yields an *acetoxymmercuri* derivative, a white powder, m. p. indefinite, which affords a yellow *sulphide* when its solutions are treated with hydrogen sulphide. When methylene-blue acetate is heated with 15 mols. of mercuric acetate in aqueous solution in presence of acetic acid, combination of the dye with mercury takes place. A small quantity of the *chloride* of the *mercury* derivative,  $C_{32}H_{34}N_6S_2Cl_2Hg$ , was isolated, together with a trace of a *compound*,  $C_{16}H_{16}N_3SClHg \cdot 2H_2O$ . The former readily passes into colloidal solution on treatment with water, the 4% solution forming a semi-solid gel, more dilute solutions forming syrupy liquids.

Benzoyl-leucomethylene-blue has m. p. 196—198° (cf. Cohn, A., 1900, i, 455). F. G. W.

**Germanium. XII. Tetra-alkyl and Tetra-aryl Compounds of Germanium. Germanium Tetraethoxide.** D. L. TABERN, W. R. ORNDORFF, and L. M. DENNIS (*J. Amer. Chem. Soc.*, 1925, **47**, 2039—2044).—Germanium tetrachloride was prepared by passing hydrogen chloride into a suspension of germanium dioxide in concentrated hydrochloric acid at about 70°, the product distilling over with small amounts of hydrochloric acid. The latter is removed by several distillations of the crude material in a current of dry air, followed by treatment with solid sodium carbonate. *Germanium tetraphenyl*, m. p. 226°, was obtained both by the action of magnesium phenyl bromide, and bromobenzene and sodium, on the tetrachloride. The latter reaction was also applied successfully to the preparation of tin tetraphenyl from stannic chloride (cf. Polis, A., 1890, 166). *Germanium tetra-p-tolyl*, m. p. 224°, obtained similarly, is described. *Germanium tetrapropyl*, m. p. —73°, b. p. 225°/746 mm.,  $d_{20}^{20}$  0.9539,  $n_D^{17.5}$  1.451,  $n_D^{30}$  1.443,  $n_D^{40}$  1.440,  $n_D^{51}$  1.453, and *germanium tetraisoamyl*, b. p.



163—164°/10 mm.,  $d_{20}^{30}$  0.9147,  $n_D^{17.5}$  1.457,  $n_D^{30}$  1.451,  $n_D^{45}$  1.444,  $n_D^{61}$  1.438, were obtained from the tetrachloride and magnesium propyl bromide and magnesium *isoamyl* bromide, respectively. Germanium tetraethyl (cf. Dennis and Hance, A., 1922, ii, 302), obtained similarly from magnesium ethyl bromide, has b. p. 162.5—163°,  $n_D^{17.5}$  1.443,  $n_D^{30}$  1.439,  $n_D^{45}$  1.430,  $n_D^{61}$  1.422. *Germanium tetraethoxide*, m. p. —81°, b. p. 185—187°, was obtained by the action of sodium ethoxide on germanium tetrachloride. It hydrolyses on exposure to air.

F. G. W.

**Degradation of Proteins by Hypobromite.** S. GOLDSCHMIDT and C. STEIGERWALD (*Ber.*, 1925, 58, [B], 1346—1353).—Gelatin, casein, and egg-albumin show characteristic differences in the rates at which they react with alkaline hypobromite solution at 0°, so that it appears probable that each protein may be analytically distinguished by a "hypobromite number" which expresses the equivalent weight of the protein which has reacted with 1 mol. of hypobromite after a definite interval of time. In the case of gelatin, the rate of reaction depends on the age of the solution. Hydrolysis due to the excess of alkali hydroxide present does not influence the change. The action is probably due to the attack of the hypobromite on the imino group of diketopiperazines and other ring systems in accordance with the scheme:  $\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}\cdot \xrightarrow{+\text{HOBr}} \cdot\text{CO}\cdot\text{NBr}\cdot\text{CH}\cdot \xrightarrow{\text{NaOH}} \cdot\text{CO}\cdot\text{N}\cdot\text{C}\cdot \xrightarrow{\text{H}_2\text{O}} \cdot\text{CO}\cdot\text{NH}_2 + \cdot\text{CO}$ . The inability of the  $\cdot\text{NH}\cdot\text{CO}\cdot$  group in polypeptides to react with hypobromite in this sense is established by the observations that whereas glycine is rapidly converted into nitrogen and carbon dioxide, glycylglycine consumes rapidly only 2 mols. of the reagent without evolution of nitrogen, thus:  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \xrightarrow{2\text{HOBr}} \text{CN}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \xrightarrow{\text{NaOH}} \text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{NH}_3 + \text{H}_2\text{C}_2\text{O}_4$ ; the intermediate product has not been isolated, but its formation is deduced from the identification of ammonia and oxalic acid. Benzoylglycine and benzoylalanylglycine are only very slowly attacked by hypobromite. On the other hand, diketopiperazine is rapidly converted by hypobromite (2 mols.) into a compound,  $\text{C}_4\text{H}_4\text{O}_3\text{N}_2$ , m. p. 113° (decomp.) after softening at 110°, which, since it contains a carboxyl and an activated methylene group, is regarded as 4-glyoxalone-2-carboxylic acid. Alanine anhydride is readily attacked in a similar manner.

*Benzoylalanylglycine*, m. p. 161° after softening at 159°, is incidentally described.

H. W.

**Depolymerisation of Proteins and Re-synthesis of Protein-like Substances from the Fission Products.** K. SHIBATA (*Acta Phytochim.*, 1925, 2, 39—47).—Carefully dried casein, serum-albumin, fibroin, gelatin, or Witte's peptone when heated with glycerol at 180—190° passes into a mixture of anhydrides of the simple amino-acids. Human hair, wool, feathers, tortoise-shell, and horn are similarly depolymerised, but they require more glycerol and longer heating. The conversion of amino-acid

anhydrides into protein-like substances is accomplished by heating with glycerol, *e.g.*, glycyityrosine anhydride gives a product showing the Millon and xanthoproteic acid reactions. Free amino-acids behave similarly, since they are converted into anhydrides under the conditions of the experiment. Asparagine yields an amorphous powder giving a colloidal solution which shows the carbonyl and biuret reactions. Asparagine with tyrosine gives a product showing the Millon test and with cystine a product showing the lead sulphide test. The action of proteolytic enzymes is discussed.

P. W. C.

#### **Interfering Effect of Glycerol on the Biuret Reaction.**

F. B. SEIBERT and E. R. LONG (*J. Biol. Chem.*, 1925, **64**, 229—231).—The presence of 0.33% of glycerol in a protein solution reduces the intensity of the biuret reaction by 50%; 16.66% of glycerol reduces it four-fold; the test has therefore to be used with caution on bacterial media containing glycerol. C. R. H.

#### **Proteins. VIII. Solubility of the Serum-globulins.**

S. P. L. SØRENSEN (*Compt. rend. Trav. Lab. Carlsberg*, 1925, **15**, No. 11, 1—29; cf. this vol., i, 602).—From experiments on the solubility and fractional precipitation of the serum-globulins, it is concluded that after repeated fractionation, even the best purified preparations still consisted of easily dissociable complexes containing both euglobulin and pseudoglobulin having the general formula  $E_pP_q$ . The solubility of these substances in water and salt solutions is less the greater  $p$  may be supposed to be in proportion to  $q$ .

C. P. S.

**Heat Denaturation of Proteins.** H. WU and D. Y. WU (*J. Biol. Chem.*, 1925, **64**, 369—378).—After heating egg-albumin in faintly acid or alkaline solution (to prevent coagulation following denaturation), it gives a deeper colour with Folin's phenol reagent (A., 1912, ii, 1011) than before this treatment; further, the filtrate obtained by treating with tungstic acid the filtrate from heat-coagulated albumin gave a deeper colour than that obtained similarly from untreated albumin. The results indicate that denaturation, whether brought about by heat or by acid or alkali, is essentially a hydrolytic process, the increased colour obtained being probably due to tyrosine split off the protein molecule. Anomalous behaviour was observed with horse-serum-albumin, which was not denatured on heating in 0.05*N*-hydrochloric acid, and with pigeon's-egg-albumin, which becomes insoluble on heating in presence of small amounts of acid or alkali.

C. R. H.

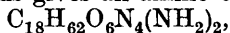
#### **Specific Nature of Animal Proteases. I. Importance of Diketopiperazines in the Synthesis of Proteins.**

E. WALDSCHMIDT-LEITZ and A. SCHÄFFNER (*Ber.*, 1925, **58**, [B], 1356—1360).—Glycine anhydride is not hydrolysed to an appreciable extent by pepsin, trypsin, erepsin, papain, or the proteases of yeast under physiological conditions. The stability of the anhydride ring towards acid and alkali of such concentrations as are encountered

in biochemical work is much greater than has been assumed hitherto. It is suggested therefore that there are probably two types of proteins, one of which is readily hydrolysed by enzymes and is poor in anhydrides, whereas the other is resistant towards enzymes (*e.g.*, fibroin, keratin) and is characterised by the presence of diketopiperazines as fundamental structural units. H. W.

**Preparation of Crystalline Oxyhæmoglobin by Ultra-filtration.** L. THIVOLLE and J. ROCHE (*Bull. Soc. Chim. biol.*, 1925, 7, 753—754).—Defibrinated blood is centrifuged and the corpuscles, after being freed from protein by repeated washing with isotonic saline, are laked with the minimum amount of water. The stromata are removed by centrifuging, and after reduction of the oxyhæmoglobin to hæmoglobin, the liquid is ultra-filtered by means of a collodion membrane (10% collodion in acetic acid). The solution is then treated by the method of Dudley and Evans (*A.*, 1921, i, 749). H. J. C.

**Biochemical Study of Phycoerythrin and Phycocyanine.** Z. KITASATO (*Acta Phytochim.*, 1925, 2, 75—97).—Phycoerythrin and phycocyanine are obtained crystalline by salting out the aqueous extract of a Bangiaceae, *Porphyra tenera* Kjellm., with ammonium sulphate and are purified by repeated solution and salting out followed by dialysis to remove adhering salts. Analysis then gives the following results, for phycoerythrin, C 50.87, H 7.04, N 15.34, S 1.76, O 24.99%, and for phycocyanine, C 50.60, H 6.90, N 15.76, S 1.69, O 24.97%. These substances are decomposed by acids, alkalis, and proteolytic enzymes into a protein and a coloured substance. The protein from phycoerythrin resembles a globulin in its general properties and that from phycocyanine is very similar. Phycoerythrin on digestion with pepsin gives a reddish-violet, water-soluble pigment,  $C_{48}H_{120}O_{18}N_{12}$ , which on warming with acids gives an amino complex,



and a blue pigment soluble in organic solvents, insoluble in water and acidic in character,  $C_{30}H_{54}O_{12}N_6 \cdot 1\frac{1}{2}H_2O$ . Phycocyanine on peptic digestion gives directly a protein constituent and the blue pigment, the reddish-violet intermediate substance not being formed. It appears therefore that the amino compound determines the difference between phycoerythrin and phycocyanine and in the case of the former gives the more basic character and the resistance to alkali and acids. Spectrographic investigation of phycoerythrin, phycocyanine, and their decomposition products confirms these views. P. W. C.

## Biochemistry.

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**Cytochrome, a Respiratory Pigment common to Animals, Yeast, and Higher Plants.** D. KEILIN (*Proc. Roy. Soc.*, 1925, **98**, **B.**, 312—339).—The myohæmatin or histohæmatin of MacMunn has been renamed cytochrome. It is an intracellular respiratory catalyst common to animals, bacteria, yeast, and higher plants. The highest concentrations are found in the thoracic wing-muscles of flying insects, the striated muscles of mammals and birds, and baker's yeast. In the reduced form it shows four characteristic absorption bands, the positions of which are approximately the same in all organisms: *a* 6046, *b* 5665, *c* 5502, *d* 5210 Å. (bees). Band *d* is composed of three secondary bands, *x*, *y*, *z*. In the oxidised form there are no clear absorption bands, but only faint shading extending 520—540/550—570 $\mu$ . Cytochrome is easily oxidised by air and reduced by the normal cell or by chemical agents. In the living animal it exists in the oxidised or only partly reduced form. Sodium pyrophosphate and *N*/10,000 potassium cyanide stop the oxidation of cytochrome, but do not prevent the cell from reducing the already oxidised pigment. On the other hand, ethyl-urethane, alcohol, and formaldehyde do not interfere with the oxidation of the pigment, but inhibit the reduction of the oxidised form. Evidence is advanced to show that cytochrome contains three components, *a'*, *b'*, *c'*, of which two, *b'* and *c'*, have an iron-pyrrole nucleus similar to that of hæmoglobin. The hæmochromogen nature of *a'* has not yet been definitely proved. The three components give oxygen and carbon monoxide compounds. Cytochrome and its derivatives are responsible, at least partly, for the peroxydase reactions in organisms. Cytochrome is distinct from muscle-hæmoglobin (myochrome) which differs from blood-hæmoglobin only in having the absorption bands slightly shifted towards the red; both pigments can be seen in the same muscle of a bird or mammal. The non-coloured portions of plants show a hæmochromogen-like complex (modified cytochrome) as well as cytochrome.

C. P. S.

**Use of Acetylene for the Determination of Hæmoglobin.** H. R. MILLER (*J. Lab. Clin. Med.*, 1924, **10**, 248—250).—Acetylene can be used with a special apparatus described or can be substituted for carbon monoxide in the Palmer and the Sahli methods.

CHEMICAL ABSTRACTS.

**Modification of the Kramer-Tisdall Method for the Determination of Sodium in Blood.** R. L. HADEN (*J. Lab. Clin. Med.*, 1924, **10**, 236—237).—The blood-serum or plasma is mixed in a crucible with the potassium pyroantimonate reagent and centrifuged after the addition of alcohol. The precipitate, after decantation of the supernatant liquid, is twice washed with aqueous alcohol and centrifuged and weighed after drying at 110°.

CHEMICAL ABSTRACTS.

**Determination of Urea and Sugar in Blood.** B. GRUSKIN (*J. Lab. Clin. Med.*, 1924, **10**, 233—236).—The blood, after incubation with urease, is treated with sulphuric acid and sodium tungstate. One portion of the filtrate is used for the determination of sugar by the Folin-Wu method, whilst another is treated with Nessler's reagent and the colour developed is compared with a standard simultaneously prepared. Detailed directions for the preparation of the special urease solution are given.

CHEMICAL ABSTRACTS.

**Determination of Urea in Blood and Urine.** T. ADDIS (*J. Lab. Clin. Med.*, 1925, **10**, 402—409).—A special apparatus is described for collecting the ammonia from the action of urease on the urea of blood and urine.

CHEMICAL ABSTRACTS.

**Determination of Urea in the Blood of a Normal Dog.** E. VARTEJEANU (*Bul. Soc. Chim. România*, 1925, **7**, 36—37).—The sample treated with a small quantity of potassium oxalate to prevent coagulation is mixed with a 20% solution of trichloroacetic acid and the solution is filtered. The filtrate is rendered exactly neutral to phenolphthalein with sodium hydroxide, treated with sodium hypobromite, and the evolved nitrogen measured as usual. The quantity of urea in the blood of a normal dog varies considerably during the day, rising to a maximum and falling to a minimum in an oscillatory manner irrespective of the nature or quantity of the food consumed.

A. R. P.

**Application of Electrical Conductivity to Quantitative Analysis in Biochemical Practice. I. Titration of certain Inorganic Salts with Sodium Hydroxide.** S. DEMJANOVSKI (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 327—333).—The use of electrical conductivity as an indicator is applicable, not only to acidimetry and alkalimetry, but also to the titration of salts with alkali hydroxide, and no complicated apparatus or special care is necessary. The results obtained when metals are determined by this method are usually of sufficient accuracy for industrial purposes. When compounds giving basic or complex salts are titrated with sodium hydroxide, they usually give either a curve with no sharp minimum of conductivity or a curve diverging in one or the other direction; in such cases, satisfactory results are obtained by adding the salt to the sodium hydroxide solution, instead of *vice versa*. Preliminary tests indicate that the above method is applicable also to biochemical practice.

T. H. P.

**Determination of Chloride in Animal Tissue.** R. VLĂDESCU (*Bul. Soc. Chim. România*, 1925, **7**, 29—31).—Distillation of the tissue with nitric and sulphuric acids sometimes produces hydrocyanic acid, whilst fusion with sodium carbonate and nitrate leads to loss of chlorine by volatilisation. The most rapid and accurate procedure consists in heating the substance with concentrated nitric acid and silver nitrate in a Kjeldahl flask until the organic matter is dissolved. After dilution, the silver chloride is filtered off and

the excess of silver in the filtrate determined by titration with thiocyanate. A. R. P.

**Presence of Lecithin in Fats.** E. BOEDTKER (*J. Pharm. Chim.*, 1925, [viii], 2, 107—113).—A positive qualitative test for the presence of phosphorus in a number of animal and vegetable oils has been obtained. Castor oil alone gave a negative result. The lecithin content of linseed oil calculated from the value obtained for phosphorus is 0.58%, whilst the nitrogen percentage corresponds with 4.5% lecithin, the disagreement in the two values being ascribed to the presence of a lecithin-albumin complex. H. J. C.

**Comparative Physiological Importance of Iron and Zinc.** G. BERTRAND and H. NAKAMURA (*Ann. Inst. Pasteur*, 1925, 39, 698—707).—A repetition of results already published (A, 1924, i, 1151). H. J. C.

**Inorganic Phosphates in Milk.** R. VLĂDESCU (*Bul. Soc. Chim. România*, 1925, 7, 31—32).—The phosphoric acid content of the milk of healthy cows is constant within narrow limits, but is much below the normal when the animal is tuberculous; thus a low content of phosphoric acid in milk indicates either dilution or the presence of tubercle. A rapid determination of the phosphoric acid present in milk as inorganic phosphates and as lipoids may be made by heating the milk with nitric acid until a clear solution is obtained and precipitating the phosphoric acid directly with ammonium molybdate. A. R. P.

**Organic Phosphorus Compounds in Milk-serum.** B. PFYL and W. SAMTER (*Z. Unters. Nahr. Genussm.*, 1925, 49, 253—262).—Milk-serum contains organically combined phosphorus in proportions varying from 90 to 140 mg. per litre. Analytical processes for the determination of inorganic phosphates by titration with calcium chloride solution are described. The organic phosphorus compound examined is compared with that described by Siegfried (A., 1897, ii, 220). A. G. P.

**Abnormal Crystal-formation and its Relation to Oxalate Precipitation and to Red Blood-corpuscles.** B. BARDACH (*Chem.-Ztg.*, 1925, 49, 662).—The different forms assumed by calcium oxalate, separating from urine, are due to the presence of traces of calcium salts of other acids which influence the crystallisation either by actual inclusion in the solid crystal or by affecting the surface forces. A strong resemblance exists between some of the forms of calcium oxalate and of the stromata of laked red blood-corpuscles. W. H.-R.

**Micro-determination of Ammonia in Urine.** A. YOVANOVITCH (*Bull. Soc. Chim. biol.*, 1925, 7, 665—672).—A slight excess of saturated lithium carbonate solution is added to 1—2 c.c. of urine through which air saturated with water vapour at 40—50° and under reduced pressure is then drawn. The ammonia is received into standard acid, which is then titrated with *N*/70-sodium hydroxide solution. Urea and amino-acids are not affected by the

lithium carbonate solution; the maximum error of the method does not exceed 3%.  
H. J. C.

**Effect of Sodium Carbonate Concentration in the Determination of Sugar by Benedict's Method.** A. J. QUICK (*Ind. Eng. Chem.*, 1925, **17**, 729—730).—The error due to the alteration of the final concentration of sodium carbonate, which is marked when dealing with solutions containing less than 0.2% of dextrose, may be overcome by keeping a sufficient concentration of sodium carbonate throughout, *i.e.*, more than 25 g. in 100 c.c. of solution. [Cf. *B.*, 1925, 684.]  
D. G. H.

**Effect of High Concentrations of Alkali on the Colour of Phenolsulphonaphthalein.** R. S. HUBBARD and D. O. MEEKER (*J. Lab. Clin. Med.*, 1924, **10**, 229—232).—Alkali in concentration of 0.1N or more destroys the colour of the dye. 0.001—0.002N-Alkali is recommended for permanent standards.

CHEMICAL ABSTRACTS.

**Excretion of Lactic Acid in the Urine after Muscular Exercise.** S. H. LILJESTRAND and D. W. WILSON (*Proc. Soc. Exp. Biol. Med.*, 1924, **21**, 426).—After 1—2 mins. of strenuous exercise, the lactic acid content of the urine, as determined by Clausen's method, rose from 2 to 150 mg. in 10 mins., reaching a maximum in 20 mins., and returning to the normal value in 1 hr.

CHEMICAL ABSTRACTS.

**Changes in the Composition of the Urine after Muscular Exercise.** D. W. WILSON, W. L. LONG, H. C. THOMPSON, and S. THURLOW (*Proc. Soc. Exp. Biol. Med.*, 1924, **21**, 425—426).—Strenuous exercise was accompanied by a fall in the volume of urine, an increased excretion of acids and inorganic phosphates, a conservation of bases, and a decreased excretion of chlorides and of total nitrogen.

CHEMICAL ABSTRACTS.

**Influence of Asparagine and Ammonium Nitrate on the Nitrogen Metabolism of Ruminants.** M. STARZEWSKA (*Rocz. Nauk. Rolnicz.*, 1923, **10**, 527—544).—The addition of asparagine or ammonium nitrate to rations poor in protein had a favourable influence on the nitrogen metabolism; the unretained portion was eliminated in the urine as urea. It is probable that the two substances are converted into the same or similar compounds.

CHEMICAL ABSTRACTS.

**Concentration in the Blood and Excretion of Alcohol at High Altitudes.** W. BIEHLER (*Arch. Exp. Path. Pharm.*, 1925, **107**, 20—37).—Groups of rabbits at sea-level, at 1500 m. and at 2500 m. were treated with similar amounts of alcohol administered by stomach tube; both the rate of rise of concentration of alcohol in the blood and the absolute maximum concentration reached were less the lower the atmospheric pressure. Similar results were obtained at sea-level with animals kept in vessels in which the pressure was artificially reduced. The differences were accounted for by increased excretion of alcohol by the lungs at the lower

pressures; at 635 mm., the rate of excretion by the lungs was four times as great and the total amount so excreted 3.3 times as great as at 760 mm. C. R. H.

**Distilled Water in Biological Work.** E. CANALS and R. GENEVET.—(See ii, 847.)

**Progress in Chemical Toxicology.** KOHN-ABREST (*Bull. Soc. chim.*, 1925, [iv], 37, 773—812).—An address. L. F. H.

**Absorption of Potassium Iodide by the Skin.** E. CANALS and M. GIDON (*J. Pharm. Chim.*, 1925, [viii], 2, 102—107).—Potassium iodide solution is not absorbed by the skin even when soap is present, but when applied as an emulsion in such substances as vaseline, lanoline, and stearic acid, iodine can be detected in the urine within 12 hrs. H. J. C.

**Variations in Physiological Action of Morphine Derivatives with Diverse Substituent Groups.** A. ZAMPARO (*Boll. Chim. Farm.*, 1925, 64, 385—390).—A critical review of our knowledge of the physiological action of morphine and its methyl, ethyl, benzyl, and acetyl derivatives. Substitution in a group (such as hydroxyl) modifies or suppresses its contribution to the general properties of the substance. The group in question functions either by attaching the molecule to the tissue, or else by producing a specific effect after such attachment has been brought about by another group. G. M. B.

**Protoplasmic Action of Copper and Gold.** C. VOEGTLIN, J. M. JOHNSON, and H. A. DYER (*Proc. Nat. Acad. Sci.*, 1925, 11, 344—345).—The toxic action of copper and gold salts in very dilute solution on protoplasm is essentially a chemical process, the metal ions exerting their action on some vital constituent which is present in very small amounts. The relatively large surface of such organisms as *Spirogyra* and bacteria allows the adsorption of the metal with subsequent storage in the cells. Cysteine and glutathione in its reduced (R·SH) form react with copper and gold salts, part of the ·SH group being oxidised with conversion of the metal ion into the cuprous and aurous states, respectively. It is suggested that the toxic action is due to a disturbance of the glutathione equilibrium,  $2\text{R}\cdot\text{SH} \rightleftharpoons (\text{R}\cdot\text{S})_2 + \text{H}_2$ . In support, it is found that whereas amino-acids, dextrose, lecithin, and other protoplasmic constituents have no protective action, the presence of an excess of cysteine or glutathione protects the protoplasm against the toxic action of these metal ions. J. S. C.

**Electrolysis of Enzymes and their Phosphoric Acid and Silica Content.** F. MAIGNON (*Compt. rend.*, 1925, 181, 51—54; cf. A., 1924, i, 350, 464).—Prolonged electrolysis of aqueous solutions of enzymes results in the loss of all activity. This is not due to the secondary formation of some harmful substance such as hypochlorous or persulphuric acid etc., but to the decomposition of the organo-mineral grouping in the enzyme itself. The ash of



enzymes from animal tissues contains considerable amounts of phosphate, but only traces of silica. J. S. C.

**Effect of Hydrogen-ion Concentration on the Extracellular Pectinase of *Fusarium cromyophthoron*.** C. P. SIDERIS (*Phytopathology*, 1924, **14**, 481—489).—When grown in onion extracts, the fungus tends to bring the  $p_H$  value to about 5.5, irrespective of its original value, by the formation of carbonate or hydrogen carbonate ions. Pectinase is not formed in, or is not excreted by, young cultures; it is rapidly excreted at  $p_H$  7, and that from the culture kept at 5.0 was more active than that from other cultures.

CHEMICAL ABSTRACTS.

**Energy Balance during Growth of Micro-organisms and its Dependence on Composition of the Nutrient Medium.** E. F. TERROINE, S. TRAUTMANN, and R. BONNET (*Compt. rend.*, 1925, **180**, 2060—2063; cf. A., 1923, i, 413; 1924, i, 804; this vol., i, 709, 755).—The energy losses during the growth of *Bacillus St. nigra* and *B. Phlei* reach 42% and 40%, respectively, of the energy content of the nutrient materials utilised by the organisms. The energy balance is in each case independent of the concentration of nutriment in the culture medium. L. F. H.

**Hydrogen Peroxide and Bacterial Growth.** F. M. BURNET (*Austral. J. Exp. Biol.*, 1925, **2**, 65—76).—Traces of hydrogen peroxide sufficient to inhibit the growth of isolated staphylococci are produced by exposure to light of nutrient agar plates. *Staphylococcus* cultures produce diffusible substances, some of which are thermostable, which reduce hydrogen peroxide and allow growth to take place. These substances also neutralise the inhibitory action of potassium cyanide (cf. McLeod and Gordon, A., 1924, i, 125; Avery and Morgan, *ibid.*, 808). E. C. S.

**Effect of Dyes on Bacterial Growth.** F. M. BURNET (*Austral. J. Exp. Biol.*, 1925, **2**, 77—82).—Gram-positive bacteria are more sensitive to inhibition of growth by acid-magenta and by hydrogen peroxide than gram-negative ones. The inhibitory action of the dye is due to diminution in the power of the organism to reduce hydrogen peroxide. E. C. S.

**Trypanocidal Action of Gold and Platinum.** C. LEVADITI, A. GIRARD, and S. NICOLAU (*Compt. rend.*, 1925, **181**, 163—165).—The double thiosulphate of gold and sodium ("sanocrysine"), which contains 37.4% of gold, is tolerated by rabbits in doses up to 0.05 g. per kg. of body-weight intravenously or subcutaneously. In rabbits infected with *virus Truffi* and *Spirochaeta cuniculi*, the curative dose per kg. is 0.05 g. intravenously or 0.02 g. subcutaneously, whilst *per os* 0.20—0.50 g. per kg. is effective, showing that gold in this form is absorbed by the digestive tract. Potassium chloraurate is quite ineffective, as is colloidal gold. The double thiosulphate of platinum and sodium is less active than the gold compound; both are inferior to bismuth. C. H.

**Respiration of Lactic Bacteria.** S. KOSTYTSHEV and M. AFANASIEVA (*Compt. rend.*, 1925, **181**, 61—62).—Fermentation is the only source of energy of *Bacillus lactis acidi*, Leichm., and *B. caucasicus* and cannot be replaced by normal respiration, however efficient the aëration. J. S. C.

**Factors Influencing the Destruction of Uric Acid by *Aerobacter aerogenes*.** E. E. ECKER and J. L. MORRIS (*J. Infect. Dis.*, 1924, **35**, 479—488).—The utilisation of uric acid by *Aerobacter aerogenes* (*Bacillus lactis aerogenes*) is stimulated at optimal concentrations by sodium citrate, oxalate, tartrate, or lactate; amino-acids, ammonium salts, and dextrose inhibit uric acid destruction, whilst sodium hydrogen carbonate, besides decreasing the growth of the bacillus, decreases uric acid utilisation.

#### CHEMICAL ABSTRACTS.

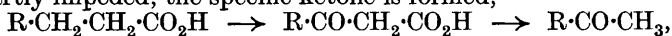
**Radioactivity, Nitrogen-fixing Bacteria, and Alcoholic Yeasts.** E. KAYSER and H. DELAVAL (*Compt. rend.*, 1925, **181**, 151—153; cf. A., 1924, i, 1016).—Addition of a radioactive mineral (60% uranium oxide) stimulates the action of *Azotobacter*, the optimum effect being with 40 mg. of mineral per litre of culture for *A. agile*, 30 mg. for *Azotobacter* from Comoro. As the proportion of the mineral is increased, the soluble and total nitrogen both increase; the fermenting power is greatest at 30 mg., but the nitrogen fixed per g. of sugar is greatest at 45 mg. Bacteria grown under radioactive influence are superior in nitrogen-fixing power to normal bacteria, but continued exposure to the rays eventually diminishes this superiority (which can be restored by removing the radioactive influence for a time). The maximum effect is obtained in white light, the minimum in the dark; yellow, green, and blue light are intermediate.

Alcoholic fermentation of sugar is similarly stimulated by the addition of 20 mg. of radioactive mineral per litre. C. H.

**Conditions Influencing Production of Colouring Matter of *Monascus purpureus*, Went.** S. HIBINO (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 182—190).—The colouring matter of *Monascus purpureus*, Went., consists of a yellow and a carmine component, both water-soluble, and a yellow and a carmine component, both insoluble in water but dissolved by organic solvents; by drying the fungus, production of the water-soluble portion may be prevented. By growing the fungus on a medium of potassium nitrate, potassium dihydrogen phosphate, magnesium sulphate, and soluble starch, and by omitting in turn each one of the five ions, or adding only a trace, it is concluded, from a comparison of the various intensities in colour of the water-soluble factor, that the mineral constituents influence the colour tone, but that the relation of the essential elements towards growth and towards colour-production respectively is not similar. Magnesium, especially at a concentration of 0.00001N, acts as a stimulant in the production of colouring matter. Lactose is valueless and inulin little better, whilst dextrose, sucrose, starch, glycogen, maltose, lævulose, and

galactose are good nutrients, but of varying influence on colour production. For the production of colouring matter, oxygen is essential and the optimum temperature is 27—30°; colour production is independent of light but influenced by the water-content of the solid medium; it is correlated with spore formation. F. M. H.

**Oxidative Cleavage of Fats by Fungi.** H. G. DEX (Proc. K. Akad. Wetensch. Amsterdam, 1925, 28, 96—107).—The growth of *Penicillium cyclopium* on a nutrient medium is hindered by addition of one of the fatty acids from butyric acid to lauric acid, but is favoured by adding higher fatty acids; when the potassium salt is used, the octoate, nonoate, decoate, laurate, and myristate tend to inhibit growth. In every case where growth is partly impeded, the specific ketone is formed,



but is no longer produced when growth becomes normal. The formation of ketones, corresponding with decrease in the rate of growth, due to addition of fat, may be caused when coconut oil (but not butter fat) is added to the nutrient medium. [Cf. B., 1925, 640.] F. M. H.

**Influence of Cholesterol and Oxysterol on the Multiplication of Infusoria (*Enchelys*).** T. B. ROBERTSON (Austral. J. Exp. Biol., 1925, 2, 83—90).—Oxysterol prepared by the Lifschütz method (A., 1908, ii, 233) has no influence on the rate of multiplication of infusoria. Oxysterol is not a chemical individual, but a mixture of varying composition. A product similar to that of Lifschütz is produced by aëration of a warm, stable emulsion of cholesterol in water, in presence of traces of acetone-soluble substances from brain tissue. Emulsions of pure cholesterol are not oxidised. E. C. S.

**Pharmacological Assay of Preparations of Thyroid Gland.** F. HAFFNER and T. KOMIYAMA (Arch. Exp. Path. Pharm., 1925, 107, 69—127).—The loss of weight following administration of thyroid to normal mice kept on a standard diet may be used as a qualitative or very approximate quantitative test of the activity of the preparation; a difference of 400% in dosage is the least which can be detected with certainty by this method. Thyroidectomy in mice is followed by loss of weight and subsequent administration of thyroid by restoration of the original weight; attempts to utilise this phenomenon as a test met with no greater success, and the same applies to the effect of thyroid administration on the gaseous exchange of normal or thyroidectomised mice. Better results were obtained by studying the protective effect of administration by stomach tube of aqueous suspensions of desiccated thyroid against the toxic effect of an intravenous or subcutaneous injection of acetonitrile given 24 hrs. later (cf. Reid Hunt, A., 1905, ii, 847); by this means, either varying the dosage of thyroid and keeping that of acetonitrile constant or *vice versa*, it was possible to detect differences of 30% in the dosage of thyroid. C. R. H.

**Cod-liver Oil. I. Effect of Hydrogenation on the Vitamin Content. II. Concentrate Manifesting both Antirachitic and Antiophthalmic Properties.** H. E. DUBIN and C. FUNK (*Proc. Soc. Exp. Biol. Med.*, 1923, **21**, 139—141, 458—460).—I.—Hydrogenated cod-liver oil, and its alcoholic extract, in amounts equal to 0.1 g. of cod-liver oil daily, prevented and cured rickets in rats.

II.—Extraction and saponification of cod-liver oil yielded a yellowish-brown, crystalline substance containing carbon, hydrogen, oxygen, and sulphur, which retained all the antirachitic and antiophthalmic properties in concentrations of 1 in 15,000.

CHEMICAL ABSTRACTS.

**Equilibrium of Cell Constituents and Mode of Oxidation in the Cell. Imbibition and Respiratory Types in Reviviscent Plants.** A. MAYER and L. PLANTEFOL (*Compt. rend.*, 1925, **181**, 131—132).—The respiratory quotient for mosses saturated with water is about 1. It is less than 1 for mosses in which the imbibition exceeds unity, and increases considerably when the imbibition is less than 0.6, becoming as high as 13.7 for an imbibition of 0.25. In the case of dry mosses, the very high respiratory quotient is shown to be due, not to evolution of oxygen or of dissolved carbon dioxide, but to an anaërobic process induced by the anhydrobiosis. It decreases to about unity in the course of some weeks. C. H.

**Does Light Directly Effect the Decomposition of Chlorophyll in Leaves in Autumn?** R. COMBES (*Compt. rend.*, 1925, **181**, 129—130).—Leaves covered partly or completely with tin-foil, or protected by blackened glass, become brown at the same rate and at the same time as neighbouring unprotected leaves. Light has therefore no direct effect on the disappearance of chlorophyll from leaves in autumn, and differences previously observed between trees of thick and of thin habit are indirect effects due to different rates of nutrition and maturation. C. H.

**Respiration Apparatus for Plant and Soil Studies.** J. M. GINSBURG (*Soil Sci.*, 1925, **19**, 411—415).—A modification of the Pettenkofer type of respiration apparatus consists of two bell-jars connected edge to edge by a heavy rubber band. The lower (inverted) bell-jar contains the soil in which the plants are grown and the upper one is connected with an air pump and absorbing reagents in the usual way. The risk of leaks, such as are apt to occur with the older form of apparatus, is avoided. C. T. G.

**Influence of Water and Salt Solution on Absorption and Germination of Seeds.** W. RUDOLFS (*Soil Sci.*, 1925, **20**, 15—37).—A study of the effect on germination and absorption of water by seeds of preliminary soaking in various salt solutions for 15 hrs. and of continuous contact with the solutions for 6 days. Previous soaking in distilled water was harmful to the germination of all the seeds studied, maize being least affected. Many seeds absorbed more and made longer roots and shoots in weak salt solutions than in water. Potassium carbonate was invariably, and

magnesium sulphate in many cases, injurious; calcium nitrate was also harmful, except to maize. Constant contact with salt solutions was in general harmful. Absorption, germination, and root-growth decreased with increase in concentration of the salt solutions, except for some of the weaker solutions. [Cf. *B.*, 1925, 731.]

C. T. G.

**Carbohydrates in Foliage Leaves in Relation to Water Content.** T. HORN (*Bot. Archiv*, 1923, 3, 137—172).—In withering leaves of *Tropaeolum majus* starch is broken down into sugar. Sucrose steadily increases with decreasing water content. The hexoses increase only after prolonged wilting. With increasing water content the quantity of sucrose decreases, and *vice versa*.

CHEMICAL ABSTRACTS.

**Composition and Appearance of Soya-bean Plants Grown in Culture Solutions Each Lacking a Different Essential Element.** J. M. GINSBURG (*Soil Sci.*, 1925, 20, 1—13).—The total ash content of soya-bean plants grown in culture solutions lacking magnesium, sulphur, or iron was considerably higher, and of plants lacking calcium, phosphorus, potassium, or nitrogen much lower, than that of the control plants, the lowest ash content being shown in absence of calcium. There was no definite relationship between ash content and yield of dry matter. The plants from all the incomplete solutions, except those without calcium and without sulphur, absorbed more calcium than the control plants, variations in the amount of calcium taken up being very marked. Where calcium absorption was high, magnesium and nitrogen absorption was low and *vice versa*, relative to the absorption by the control plants. Pathological conditions were most pronounced in absence of calcium, followed in order by absence of nitrogen, potassium, magnesium, sulphur, iron, and phosphorus.

C. T. G.

**Economical Use of Nitrogen, Phosphorus, and Potassium by Barley, Oats, and Wheat in Solution Cultures.** F. R. PEMBER and F. T. McLEAN (*R. I. State College Agric. Exp. Sta. Bull.*, 1925, No. 199, 53 pp.).—Solution cultures of barley, oats, and wheat were grown to maturity with limited amounts of nitrogen, phosphorus, and potassium. Growth was not significantly modified by increasing the total osmotic pressure of the solutions from 0.25 to 1.5 atm. The minimum nitrogen requirement for high yield over a 4 yr. period was for oats 0.7%, for wheat or barley 1.0% of the total dry matter. When the phosphorus content was low, the stalks had a purple tint. The minimum requirement for high yields was 0.1%  $P_2O_5$  in total dry matter for oats, and 0.2% for wheat or barley. The nitrogen and potassium contents of culture plants were similar to the values for these elements in field-grown plants, but the culture plants contained about 33% as much phosphorus as field plants.

CHEMICAL ABSTRACTS.

**Nitrogen and Carbohydrate Composition of the Developing Flowers and Young Fruits of the Apple.** F. S. HOWLETT (*Proc. Amer. Soc. Hort. Sci.*, 1923, 20, 31—37).—Determinations

were made of the moisture content of the flowers and young fruits of the Roxbury Russet apple; the nitrogen content was high when the flowers were expanding and then fell slightly to about 4%, maintaining that value until the petals had fallen. There was practically no change in the nitrogen content of setting fruits, but in those about to drop the value declined to 3%. The free reducing substances gave high values with enlargement of the apples, but declined in those fruits which survived the first drop. The free reducing substances made up the greater part of the total sugars.

## CHEMICAL ABSTRACTS.

**Nitrogen in Algæ.** E. B. FRED and W. H. PETERSON (*Bot. Gaz.*, 1925, **79**, 324—328).—The nitrogen in pure cultures of *Chlorella vulgaris* and *Scenedesmus quadricauda* (7.4% of the ash-free plant) is largely in an insoluble form. The water-soluble portion (25%) consists chiefly of protein, amino, and peptide nitrogen.

## CHEMICAL ABSTRACTS.

**[Metabolism of the Tomato.]** H. R. KRAYBILL and T. O. SMITH (*New Hampshire Agric. Exp. Sta. Bull.*, 1924, No. 212, 7—9).—Tomato plants grown in nutrient solution lacking in phosphorus were lower in insoluble nitrogen, but higher in soluble and lipid nitrogen than plants grown in a complete nutrient solution. Plants made poor growth in a solution free from nitrogen or phosphorus.

## CHEMICAL ABSTRACTS.

**Detection of Plant Phenols by the Use of Nitrites or Nitric Acid.** A. H. WARE (*Analyst*, 1925, **50**, 384—389).—Specific colour reactions involving the use of sodium nitrite and nitrous or nitric acid are described for Curacao aloes and commercial aloin, phloridzin, ellagitannins in aqueous extractives, catechins, tobacco tannin, and commercial chrysarobin (purified Goa powder). [Cf. *B.*, Oct. 2nd.] D. G. H.

**Determination of Pentosans in Wood.** W. GIERISCH (*Cellulosechem.*, 1925, **6**, 61—74, 81—93).—Of the various colour reagents for furfuraldehyde derivatives, resorcinol does not distinguish clearly between methyl- and hydroxymethyl-furfuraldehyde, nor orcinol between furfuraldehyde and hydroxymethylfurfuraldehyde. The protein reaction is improved by substituting peptone for egg-albumin, and the  $\beta$ -naphthylamine reaction, in a modified form, can be used to test simultaneously for furfuraldehyde and for methyl- or hydroxymethyl-furfuraldehyde. Phloroglucinol gives quantitative results only for the sum of the three furfuraldehyde compounds, the hydroxymethylfurfuraldehyde precipitate being only partly soluble in alcohol. Barbituric acid gives better results, precipitating furfuraldehyde and methylfurfuraldehyde with only a little hydroxymethylfurfuraldehyde. When distilled with hydrochloric acid by Tollens' method, beech wood gives at first a considerable amount of hydroxymethylfurfuraldehyde, which, however, is not formed from cellulose, but from lower carbohydrates; the rate of production reaches a minimum and then again increases. The production of furfuraldehyde and methylfurfuraldehyde is complete when 150 c.c. of distillate have been collected. The

yield of furfuraldehyde substances depends on the weight and fineness of the sample and on the rate of distillation. A simple method of distilling with 200 c.c. of 12% hydrochloric acid, without further additions of acid, is recommended. The volume (200—400 c.c.) and the concentration (6—12%) of acid have little influence and the results agree with those obtained by Tollens' method. [Cf. *B.*, 1925, 704.] A. G.

**Absorption of Mineral Elements by Plants.** R. B. DUSTMAN (*Bot. Gaz.*, 1925, 79, 233—264).—Limitation of the supply of calcium does not increase the hydrogen-ion concentration of the sap. CHEMICAL ABSTRACTS.

**Mineral Matter in Green and in Chlorotic Leaves.** H. COLIN and A. GRANDSIRE (*Compt. rend.*, 1925, 181, 133—135).—Albinism (congenital chlorosis) in leaves leads to a higher ash content, although the percentage of dry matter is smaller than in normal green leaves. The ash of chlorotic leaves contains less calcium and more potassium. These differences are not found in etiolated or autumnal leaves, and thus do not always accompany an absence of chlorophyll (cf. Church, T., 1879, 35, 33). C. H.

**Formation of Essential Oils.** H. POPOVICI (*Compt. rend.*, 1925, 181, 126—128).—Observations made on plants of widely different families, using neutral-red and indophenol-blue as stains, show the essential oil (violet) very distinctly in the cytoplasm, the vacuole being filled with (red) particles in Brownian movement. The centre of the cell is occupied by a large vacuole, completely void of tannoid compounds, showing that the latter play no part in the elaboration of the essential oil. The vacuole system in secretory hairs contains tannin, but this bears no relation to the oil and is of epidermal origin. C. H.

**Essential Oils obtained by Extracting Fresh Flowers with Volatile Solvents (Essential Flower-extract Oils).** II. H. VON SODEN (*J. pr. Chem.*, 1925, [ii], 110, 273—278; cf. A., 1904, i, 515).—The method of extraction is described in the earlier paper. Fresh violet leaves yield 0.002% of purified green oil with a narcotic odour,  $d^{15}_4$  0.909,  $\alpha + 20^\circ 20'$ , acid number 20, ester number 75, containing small quantities of free acid (higher fatty acids?), of phenolic and lactonic compounds, and of an aldehyde resembling decaldehyde in odour. Indole is absent. The oil is markedly different from the flower-extract. Its characteristic perfume is associated only with the green calyx and the leaves. The strongly optically active oil obtained by extraction of the flowers is almost, if not entirely, absent. Mimosa flowers yield 0.018% of greenish-yellow oil with characteristic odour, m. p.  $9^\circ$ ,  $d^{15}_4$  0.816, rotation zero or slightly lævo, acid number 12, ester number 20.5, without fluorescence in alcoholic solution. Saponification yields acid products, partly solid. Jonquil flowers yield 0.158% of a nearly colourless oil, discolouring on exposure to air (contains indole), showing strong bluish-violet fluorescence in alcoholic solution,  $d^{15}_4$  1.064,  $\alpha - 2^\circ 45'$ , ester number 250. The oil contains considerable quantities of methyl and benzyl

benzoates, methyl anthranilate, methyl and ethyl cinnamates, and linalool. Yellow narcissus flowers yield 0.0068% of nearly colourless oil with narcotic odour, darkening in air to reddish-yellow, solidifying at 20—22°,  $d^{15}$  0.985, rotation zero or slightly dextro, acid number 7, saponification number 202. M. J.

**Oil from *Pistacia terebintus*.** V. TIMOSUFF (*Chem. Umschau*, 1925, **32**, 162).—The fruit of the *Pistacia terebintus* of Asia Minor, Syria, and Palestine contains about 37% of a pleasant-tasting edible oil, which, however, becomes rancid within two or three months. The characteristics of the oil are given. G. L. R.

**American Palm Tree Fats. Murumuru Butter.** E. ANDRÉ and F. GUICHARD (*Compt. rend.*, 1925, **181**, 228—230).—Light petroleum extraction of the seed of *Astrocaryum Murumuru* yielded a fat, m. p. 34—35°, in which the following fatty acids were detected by the technique of Haller (A., 1907, i, 9): lauric, myristic, palmitic, stearic, oleic, and probably arachidic, acids. [Cf. B., 1925, 728.] S. K. T.

**Presence of Calcium Oxalate Crystals on the Surface of Certain *Caryophyllaceæ*.** P. R. BOHN (*Compt. rend.*, 1925, **181**, 135—137).—Octahedral crystals of calcium oxalate (up to 4 mm. in diameter) are found loose on the epidermis of *Lychnis dioica*, L., *L. coronaria*, L., *Flos Jovis*, Lam., and *Spergula arvensis*, L., the amount being very small before and during inflorescence, but becoming considerable in old plants. The epidermis evidently plays an important part in the excretion of calcium oxalate by the plant. C. H.

**Non-volatile Organic Acids of Alfalfa [Lucerne].** W. A. TURNER and A. M. HARTMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 2044—2047).—Examination of the non-volatile acids of green lucerne plants by the ester-hydrazide method indicated the presence in the plant of citric, malic, and malonic acids, in the approximate relative proportions of 12 : 8 : 3.

Citric trihydrazide forms a monohydrate, m. p. 103—104°, the water of crystallisation of which is retained in a vacuum at the ordinary temperature, but lost at 70°, the anhydrous substance having m. p. 149—150° (cf. Nelson, A., 1924, i, 1390).

F. G. W.

**Tannin of *Rhus glabra*.** J. C. PEACOCK and B. L. DEG. PEACOCK (*Amer. J. Pharm.*, 1925, **97**, 463—471).—The fruit of *Rhus glabra* was extracted with water, and the crude tannin removed by shaking the extract with ethyl acetate. Repeated solution of the substance in water, extraction with ether after sufficient dilution to prevent the formation of an ether-tannin-water layer, and subsequent removal of the tannin from the water layer by ethyl acetate, gave a tannin which corresponds in properties with gallotannic acid, and yields gallic acid on treatment with dilute sulphuric acid. Freshly-prepared decoctions of the fruit of *R. glabra* contained inappreciable amounts of gallic acid, which, however, was slowly formed on keeping with parallel disappearance of the tannin. C. P. S.



## Organic Chemistry.

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**Decomposition of Paraffin Wax at 450° in Presence and in Absence of Hydrogen under High Pressure.** H. I. WATERMAN and J. N. J. PERQUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 286—296).—The presence of hydrogen causes the molecules to break down more regularly, and prevents the polymerisation and consequent formation of coke which occurs in its absence; it does not combine with the unsaturated hydrocarbons normally formed. Whilst the proportions of gas and volatile compounds formed are less in the early stages if hydrogen is present, they increase with the time of reaction, and after 4 hrs. are greater than they would be in the absence of hydrogen. Practically no non-volatile residue is obtained in presence of hydrogen after 4 hrs. S. I. L.

**Action of Aluminium Chloride on Heptanaphthene.** N. D. ZELINSKI and W. A. SMIRNOV (*Brennstoff-Chem.*, 1925, **6**, 249—255).—Heptanaphthene is decomposed by aluminium chloride in the presence of hydrogen chloride, with the formation of a gas of the paraffin series, whilst the boiling point of the residual hydrocarbon is raised and a layer containing a complex compound,  $C_4H_8 \cdot AlCl_3$ , remains. The reaction proceeds even at the ordinary temperature and is accelerated by warming; relatively small amounts of aluminium chloride are sufficient to bring about considerable decomposition. The gas evolved is found to be *isobutane* by its behaviour on bromination, and it is produced by the decomposition of the aluminium chloride complex, which exists as an intermediate product breaking down into dicyclic paraffins. This decomposition is not complete at 140°, although the original hydrocarbon is all decomposed by prolonged treatment at this temperature. B. W. C.

**Dehydration of Rectified Spirit by Means of Anhydrous Calcium Chloride.** J. J. SUDBOROUGH and P. R. AYYAR (*J. Indian Inst. Sci.*, 1925, **8A**, 49—54; cf. Noyes, A., 1923, i, 433).—On distillation with one-sixth of its weight of anhydrous calcium chloride a 95% yield of 95% ethyl alcohol is obtained from 88% "rectified spirit." On further distillation of this 95% solution with 5/12th of its weight of anhydrous calcium chloride an 86% yield of 98% ethyl alcohol is obtained. A further quantity of alcohol is obtained on treating the residue with water and subjecting to further distillation. For the concentration of alcohol above 98%, distillation over metallic calcium is advisable. L. F. H.

**Rapid Preparation of Cetyl Alcohol.** M. A. YOUTZ (*J. Amer. Chem. Soc.*, 1925, **47**, 2252—2254).—Cetyl alcohol in a nearly pure state may be rapidly prepared in good yield by the hydrolysis of

spermaceti with aqueous-alcoholic potassium hydroxide followed by extraction of the product with light petroleum. The method given must be followed exactly to prevent the formation of emulsions and gels difficult to separate. The cetyl alcohol is best purified by conversion into its acetate, which is distilled under reduced pressure. [Cf. *B.*, 1925, 769.] J. W. B.

**Method of Diagnosing Potential Optical Activity. I. Optical Activity of Chlorobromomethanesulphonic Acid.** J. READ and A. M. McMATH (*J. Chem. Soc.*, 1925, 127, 1572—1599).—The failure of Pope and Read (*T.*, 1914, 105, 811) to resolve chlorobromomethanesulphonic acid is now shown to be due to the very rapid racemisation of this compound. *l*-Hydroxyhydrindamine chlorobromomethanesulphonate has been separated by crystallisation from acetone into two substances having the form of needles and plates, respectively. These forms are interconvertible, the form obtained depending chiefly on the solvent employed. A study of the mutarotation of these two forms in various solvents shows that they are the diastereoisomeric forms *l**B**l**A* and *l**B**d**l**A* (*A* and *B* represent acid and base, respectively). In acetone, the salt *l**B**l**A* shows downward mutarotation from  $[M]_D = -256^\circ$  to  $-187^\circ$ , and the salt *l**B**d**l**A* upward mutarotation from  $-71^\circ$  to  $-187^\circ$ . It is calculated that the equilibrium mixture contains 81% of *l**B**l**A* and 19% of *l**B**d**l**A*. The brucine salts also show mutarotation. The principle is enunciated that facile racemisation involves the complementary possibility of facile "deracemisation" under appropriate conditions. Thus in the case of a stable *dl*-acid combined with a stable *l*-base no resolution of the acid takes place in solution. If, however, the acid is optically labile, an equilibrium mixture may be formed containing a preponderating proportion of one of the diastereoisomerides. The bearing of this work on the resolution of labile asymmetric compounds and the diagnosis of potential optical activity is discussed fully. E. E. W.

**$\beta\beta'$ -Dichloro- and  $\beta\beta'$ -Dibromo-diethyl Selenides and their Simple Halogen Derivatives.** H. C. BELL and C. S. GIBSON (*J. Chem. Soc.*, 1925, 127, 1877—1884; cf. Boord and Cope, *A.*, 1922, i, 421).—An almost quantitative yield of  $\beta\beta'$ -dichlorodiethyl selenide dichloride is obtained by the action of ethylene on selenium tetrachloride; in aqueous solution, the dichloride decomposes at  $35^\circ$  with evolution of ethylene.  $\beta\beta'$ -Dibromodiethyl selenide dibromide, m. p.  $118^\circ$ , is prepared in an analogous manner, and this, when reduced with potassium metabisulphite, yields  $\beta\beta'$ -dibromodiethyl selenide; m. p.  $44.2^\circ$ . Similarly,  $\beta\beta'$ -dichlorodiethyl selenide, m. p.  $24.2^\circ$ , is formed by reduction of the corresponding dichloride; bromine reacts with this compound to form  $\beta\beta'$ -dichlorodiethyl selenide dibromide, m. p.  $117^\circ$  (decomp.). By the action of chlorine on  $\beta\beta'$ -dibromodiethyl selenide,  $\beta\beta'$ -dibromodiethyl selenide dichloride, m. p.  $98-99^\circ$ , is formed. A quantitative yield of  $\beta\beta'$ -dichlorodipropyl selenide dichloride, m. p.  $76.5^\circ$ , results from the

reaction between selenium tetrachloride and propylene, and this compound on reduction yields  $\beta\beta'$ -dichlorodipropyl selenide.

B. W. A.

**Esterification.** B. V. BHIDE and J. J. SUDBOROUGH (*J. Indian Inst. Sci.*, 1925, **8A**, 89—127; cf. A., 1923, i, 1009).—Esterifications have been carried out by means of ethyl alcohol in the presence of hydrogen chloride and the following velocity constants have been obtained, using the equation of Goldschmidt and Udby (A., 1907, ii, 852): *n*-valeric acid, 0.268; *n*-hexoic acid, 0.267; *n*-nonoic acid, 0.270; *n*-decoic acid, 0.269; lauric acid, 0.272; myristic acid, 0.269; palmitic acid, 0.276; stearic acid, 0.276; erucic acid, 0.279; brassidic acid, 0.273;  $\Delta^7$ -pentenoic acid, 0.274;  $\beta$ -phenylpropionic acid, 0.321;  $\beta$ -methyl-*n*-butyric acid, 0.0518;  $\beta$ -methyl-*n*-valeric acid, 0.247;  $\beta$ -methyl-*n*-hexoic acid, 0.267;  $\alpha$ -methyl-*n*-valeric acid, 0.393;  $\alpha$ -methyl- $\Delta^7$ -pentenoic acid, 0.0421;  $\alpha$ -methyl-*n*-hexoic acid, 0.0345;  $\beta$ -phenyl- $\alpha$ -methylpropionic acid, 0.0553;  $\alpha$ -methyl-*n*-valeric acid, 0.0110;  $\alpha\gamma$ -dimethyl-*n*-valeric acid, 0.0318;  $\alpha$ -ethyl-*n*-hexoic acid, 0.00283;  $\alpha$ -*n*-propyl-*n*-valeric acid, 0.00285; cycloheptanecarboxylic acid, 0.0499; dicycloheptanecarboxylic acid, 0.0137; cyclohexylacetic acid, 0.0809;  $\Delta^1$ -cyclohexeneacetic acid, 0.108; cyclohexylideneacetic acid, 0.00228; *p*-methylcyclohexylacetic acid, 0.0999; *p*-methyl- $\Delta^1$ -cyclohexeneacetic acid, 0.118; *p*-methylcyclohexylideneacetic acid, 0.00234;  $\Delta^1$ -tetrahydrobenzoic acid, 0.00220;  $\Delta^2$ -tetrahydrobenzoic acid, 0.0829;  $\Delta^{1:3:5}$ -cycloheptatrienecarboxylic acid, 0.00184; *o*-toluic acid, 0.000718; *m*-toluic acid, 0.00261; *p*-toluic acid, 0.00197; hexahydro-*p*-toluic acid, 0.0850; hexahydro-*m*-toluic acid, 0.0827;  $\beta$ -cyclohexylpropionic acid, 0.141;  $\Delta^2$ -cyclohexeneacetic acid, 0.0731; adipic acid, 0.301; pimelic acid, 0.282; suberic acid, 0.264;  $\alpha$ -cyclogeranic acid, 0.0;  $\beta$ -cyclogeranic acid, 0.0.  $\Delta^{\alpha}$ -Unsaturated monobasic acids have lower velocity constants, whilst  $\Delta^{\beta}$ -unsaturated acids have slightly higher velocity constants than the corresponding saturated compounds. When substitution occurs at a considerable distance from the acidic grouping, practically no effect on the velocity constant is observed; thus the series of saturated monobasic acids from butyric acid up to stearic acid, also  $\Delta^7$ -pentenoic acid, erucic acid, brassidic acid,  $\delta$ -methyl-*n*-hexoic acid, and suberic acid, all have velocity constants lying between 0.264 and 0.279. The introduction of a methyl group into the saturated monobasic fatty acids has most effect when introduced into *n*-butyric acid, decreasing the constant five-fold. The benzyl group has less inhibiting effect on esterification than the ethyl group. In most cases, the cyclic acids are esterified more readily than the open-chain analogues. When adjacent to the carboxylic group, reduction of the benzene ring accelerates the rate of esterification, but the reverse is the case when the phenyl group is further removed from the acidic group. In general, the introduction of a methyl group in the 4-position into a cyclic acid increases the esterification constant. On introduction of 1:6-disubstituents into reduced benzoic acids esterification is markedly inhibited.

$\Delta^7$ -Pentenoic acid was obtained by distillation of allylmalonic acid.  $\alpha$ -Methyl- $\Delta^7$ -pentenoic acid was prepared by addition of methyl iodide to the sodium derivative of ethyl allylmalonate, and hydrolysis of the ester formed, giving *methylallylmalonic acid*, m. p. 98—99°, which when heated yielded  $\alpha$ -methyl- $\Delta^7$ -pentenoic acid, b. p. 188—189°/683 mm.

L. F. H.

**Argemone Oil.** S. N. IYER, J. J. SUDBOROUGH, and P. R. AYYAR (*J. Indian Inst. Sci.*, 1925, **8A**, 29—38).—Extraction of the seeds of *Argemone mexicana* with light petroleum yields a pale yellow oil (29.4%). The refractive indices and iodine values of hardened samples of the oil are similar to those for the rape-oils, but this is not due to the presence of acids such as behenic, lignoceric, or erucic, but to some hydroxy-acids. The completely hardened oil retains an acetyl value, whilst the acids or methyl esters from it have no acetyl value, so that the acetyl value of the oil (39) may be attributed to the presence of glycerides of hydroxyoleic acid and to diglycerides. The acids from the completely hardened oil are palmitic and stearic, whilst in the original oil are found in addition palmito-oleic, oleic, linoleic, linolenic, and ricinoleic acids.

G. M. B.

**Walden Inversion. IX. Influence of the Solvent on the Sign of the Product in the Conversion of  $\beta$ -Bromo- $\beta$ -phenylpropionic Acids into  $\beta$ -Hydroxy- $\beta$ -phenylpropionamides.** G. SENTER and A. M. WARD (*J. Chem. Soc.*, 1925, **127**, 1847—1851).—By reaction with ammonia in dry ether,  $\beta$ -bromo- $\beta$ -phenylpropionic acid yields *ammonium  $\beta$ -bromo- $\beta$ -phenylpropionate*, decomp. 60°. Similarly, with diethylamine, *diethylammonium  $\beta$ -bromo- $\beta$ -phenylpropionate* (decomp. 44—45°) is formed. Solutions of *r*- $\beta$ -bromo- $\beta$ -phenylpropionic acid in liquid ammonia, acetonitrile ammonia, aqueous or alcoholic ammonia, all yield  $\beta$ -hydroxy- $\beta$ -phenylpropionamide (probably through intermediate lactone formation) together with styrene and ammonium bromide. In the same solvents, optically active forms of the bromo-acid yield the hydroxyamide of opposite sign, *i.e.*, of the same sign as the parent hydroxy-acid. Thus there is no Walden inversion detected here by variation of the solvent.

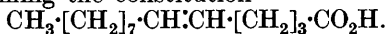
B. W. A.

**Butyrin.** L. S. WEATHERBY, L. McILVAINE, and D. MATLIN (*J. Amer. Chem. Soc.*, 1925, **47**, 2249—2252).—The rates of esterification of glycerol with various quantities of butyric acid are determined, an excess of acid (6 mols. to 1 mol. of glycerol) forcing the esterification more nearly to completion and increasing the yield of the triglyceride. The pure ester is colourless, and has b. p. 190°/15 mm., 305—310°/760 mm.,  $d^{21}_4$  1.027. It thickens to a viscous mass, but does not solidify at -75°.

J. W. B.

**Constitution of the Tetradecenoic Acid Derived from Sperm Oil.** M. TSUJIMOTO (*Chem. Umschau*, 1925, **32**, 202—204).—On disruption by Harries' oxonide method, the tetradecenoic acid derived from sperm oil (cf. A., 1923, i, 297) yields

nonaldehyde, with the corresponding *n*-nonoic acid, and glutaric acid, thus confirming the constitution



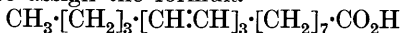
G. L. R.

**Oxidation Products of Oleic Acid. I. Conversion of Oleic Acid into Dihydroxystearic Acid and the Determination of Higher Saturated Acids in Mixed Acids from Natural Sources.** A. LAPWORTH and E. N. MOTTRAM (*J. Chem. Soc.*, 1925, 127, 1628—1631).—The nearly quantitative conversion of oleic acid into dihydroxystearic acid is conditioned by (i) a temperature of 0—10° during oxidation, (ii) a concentration of oleic acid not greater than 0.1%, (iii) a concentration of permanganate not higher than 1%, (iv) a very short reaction time (about 5 mins.), and (v) the presence of slight excess of alkali from the beginning. For the determination of oleic acid and higher saturated acids by this method, 5 g. of the sample are dissolved in 500 c.c. of hot water containing 5 g. of sodium hydroxide, cooled and diluted with 4 litres of ice-water. To this, well agitated at 10°, 400 c.c. of 1% permanganate are quickly added. After 5 mins. the colour is discharged with sulphur dioxide, 150 c.c. of concentrated hydrochloric acid are added, and the precipitated crude dihydroxystearic acid, after being washed with 50 c.c. of light petroleum (b. p. 70—80°), is dried to constant weight in a vacuum desiccator. On extraction of this product with 100—150 c.c. of warm light petroleum, nearly pure dihydroxystearic acid remains; it is washed several times with cold light petroleum, dried, and weighed. It represents 96% of the pure oleic acid actually present in the sample. From the combined petroleum extracts and washings the higher saturated fatty acids are recovered by evaporation, lower acids are removed by steam distillation, and the residue is extracted by light petroleum. The solution on evaporation and drying on the water-bath gives the higher saturated acids present in the original sample. C. H.

**Separation of the Highly Unsaturated Fatty Acids in Train Oil.** Y. TOYAMA and T. TSUCHIYA (*Chem. Umschau*, 1925, 32, 204—207).—The method consists in neutralising a solution of the acids in acetone with aqueous or alcoholic sodium hydroxide, preferably the latter, with subsequent addition of water. After cooling, the relatively insoluble salts of the saturated and slightly unsaturated fatty acids are separated by filtration from the soluble salts of the highly unsaturated acids. A very incomplete fractionation only is obtained, but the method is recommended on account of the cheapness of the reagent. [Cf. *B.*, Oct. 30th.] G. L. R.

**Constitution of  $\alpha$ -Elæostearic Acid from Chinese Wood Oil and from its Isomeride  $\beta$ -Elæostearic Acid.** J. BÖSEKEN and (Miss) H. J. RAVENSWAAY (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, 28, 386—389).—The values for the molecular refraction of  $\alpha$ -elæostearic acid from Chinese wood oil, its ethyl ester,  $\beta$ -elæostearic acid, and its glyceryl ester (obtained by the intense illumination of the  $\alpha$ -ester with a mercury vapour lamp) show an exaltation of

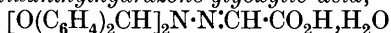
5—7 units on the value calculated by the Lorentz formula, assuming two conjugated double bonds, and therefore correspond with compounds containing a system of three conjugated double bonds. On catalytic reduction of the wood oil and the products derived from it, the quantity of hydrogen absorbed is always largely in excess of that calculated for two double bonds, but slightly less than that for three double bonds in each molecule of the fatty acid. The authors therefore assign the formula



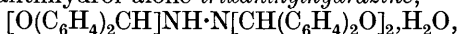
to elæostearic acid, which is in good agreement with the products of oxidation by ozone (cf. Vercruysse, A., 1923, i, 533), its high refractivity, and its rapid drying and polymerisation. The following values for  $n_D$  are obtained:  $\alpha$ -elæostearic acid, 1.5080 (56°); ethyl ester, 1.5038 (15°);  $\beta$ -acid, 1.4970 (80°); glyceryl ester, 1.5051 (80°); the corresponding values for  $d$  being 0.8980, 0.8968 and 0.9074, 0.8839, and 0.8991, respectively.

J. W. B.

**Identification of Glyoxylic Acid by Reaction with Hydrazine and Xanthhydrol to form Dixanthylhydrazone-glyoxylic Acid.** R. FOSSE and A. HIEULLE (*Compt. rend.*, 1925, **181**, 286—288).—Xanthhydrol and hydrazine hydrate in presence of acetic acid precipitate from even dilute solutions of glyoxylic acid the compound *dixanthylhydrazone-glyoxylic acid*,



(silver salt). The reaction probably proceeds through the intermediate formation of the hydrazone,  $\text{NH}_2 \cdot \text{N}:\text{CH}:\text{CO}_2\text{H}$ . Hydrazine forms with xanthhydrol alone *trixanthylhydrazone*,



m. p. 159—162° (decomp.), and m. p. 167—175° after resolidification. The two compounds are separable by alcoholic alkali, which dissolves only the acid.

B. W. A.

**Potassium Antimonoxalate.** L. H. A. HOLMES and E. E. TURNER (*J. Chem. Soc.*, 1925, **127**, 1753—1754).—Preliminary examination of the antimonoxalates has shown that they are too unstable to give any hope of their being resolvable into optically active forms. Potassium antimonoxalate has been prepared and is found to have the formula  $\text{K}_3\text{Sb}(\text{C}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$ .

E. E. W.

**Lead Salts of some Fruit Acids.** F. AUERBACH and H. WEBER (*Z. anorg. Chem.*, 1925, **147**, 68—80).—Precipitation of solutions of the alkali salts of citric, succinic, malic, tartaric, and benzoic acids made faintly acid with acetic acid by means of lead acetate solution results in the precipitation of the neutral lead salt, independent of the relative concentrations of lead acetate or alkali salt. The solubilities of the lead salts at 18° in water, dilute hydrochloric acid, 50% alcohol, and solutions of sodium and ammonium acetates have been determined. Lead citrate and, under certain conditions, lead malate slowly pass into modifications which are sparingly soluble. The solubility data for dilute hydrochloric acid indicate the existence of complex salts in solution. Lead tartrate is practically insoluble in 50% alcohol. Measurements of the  $p_H$  values of the saturated aqueous solutions at 18° indicate only slight hydrolysis.

J. S. C.

**Synthesis of Aldehydes.** H. STEPHEN (*J. Chem. Soc.*, 1925, 127, 1874—1877).—When a nitrile is added with shaking to anhydrous stannous chloride in dry ether saturated with hydrogen chloride, a white, crystalline aldimine stannichloride separates, due to reduction of the imino-chloride first formed:  $R\cdot CN + HCl \rightarrow R\cdot CCl:NH$ ;  $R\cdot CCl:NH + SnCl_2 + 2HCl \rightarrow R\cdot CH:NH, HCl + SnCl_4$ . This salt is readily hydrolysed by warm water, and the aldehyde removed by distillation or extraction. From both aliphatic and aromatic nitriles the yields of aldehyde are usually almost quantitative. By this method have been prepared: *n*-octaldehyde (*p*-nitrophenylhydrazone, m. p.  $80^\circ$ ); myristaldehyde (*p*-nitrophenylhydrazone, m. p.  $95^\circ$ ); palmitaldehyde (*p*-nitrophenylhydrazone, m. p.  $96\cdot5^\circ$ ); stearaldehyde, m. p.  $38^\circ$  (*p*-nitrophenylhydrazone, m. p.  $101^\circ$ ); *o*-tolualdehyde (*p*-nitrophenylhydrazone, m. p.  $222^\circ$ ); *p*-tolualdehyde (*p*-nitrophenylhydrazone, m. p.  $200\cdot5^\circ$ ); *p*-tolylacetaldehyde (*p*-nitrophenylhydrazone, m. p.  $144\cdot5^\circ$ );  $\alpha$ -naphthaldehyde (*p*-nitrophenylhydrazone, m. p.  $234^\circ$ ), and others. A notable application is the formation of indole by reduction of *o*-nitrophenylacetonitrile.

B. W. A.

**Oxidation of Acetic Acid, Acetone, and Toluene.** F. KNOOP and M. GEHRKE (*Z. physiol. Chem.*, 1925, 146, 63—71).—The oxidation over a period of 2—4 weeks at the ordinary temperature with varying amounts of hydrogen peroxide of freshly-distilled acetic acid and acetone was carried out with or without addition of ferrous sulphate, in acid, alkaline, or neutral solution. Very little oxidation of acetic acid occurs and succinic acid could not be detected in the product. With acetone, however, much more oxidation occurs and tartaric, malic, and succinic acids are obtained. This does not support the hypothesis that acetic acid can act as an intermediate compound giving rise directly to succinic acid. The oxidation of toluene, stilbene, deoxybenzoin, and the corresponding alcohol in the animal body has been carried out. Since toluene is recovered as benzoic acid (76% yield), whereas feeding the hydrocarbon, ketone, or alcohol does not give rise to any increased excretion of benzoic acid, these substances cannot be intermediate compounds in the metabolism of toluene. A little stilbene is obtained after feeding dibenzyl.

P. W. C.

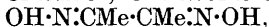
**Reactions of Nitrosyl Chloride. I. "Nitrosochlorination" with Nitrosyl Chloride.** H. RHEINBOLDT and O. SCHMITZ-DUMONT (*Annalen*, 1925, 444, 113—135).—Whilst the action of nascent nitrosyl chloride (for example, from amyl nitrite and hydrochloric acid) on methyl ketones affords oximinoketones (cf. Claisen, A., 1887, 463; 1889, 584; 1893, i, 464), free nitrosyl chloride affords similarly chloro-oximinoketones, according to the general equation  $R\cdot COMe + 3NOCl = R\cdot CO\cdot CCl:NOH + 2NO + 2HCl$ . Chloro-oximinoacetone was prepared by the addition of acetone (1 mol.) to nitrosyl chloride (2·2 mols.) dissolved in carbon tetrachloride, and cooling the reaction mixture in ice (cf. Behrend and Tryller, A., 1895, i, 201). Separation of the crystalline product is complete in 27 hrs. The pure material gives no immediate color-

ation with ferric chloride (cf. Henry, A., 1903, i, 725). *Benzoyl-chloro-oximinoacetone*, m. p. 113—114°, is described. Methyl propyl ketone affords similarly *chloro-oximinomethyl propyl ketone*, [oxime, m. p. 154° (decomp.)]. *Chloro-oximinomethyl isopropyl ketone*, m. p. 87°, is described. *Chloro-oximinopinacolin*, m. p. 133—134° (*benzoyl* derivative, m. p. 63—64°), affords, on treatment with aniline in ether, *anilino-oximinopinacolin*, m. p. 103—104°, which, when treated in ethereal solution with dilute sulphuric acid and sodium nitrite, yields 7-nitro-3- $\alpha$ -dimethylpropionyl-1:2:4-benzoxadiazine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \cdot \begin{array}{c} \text{NH} \cdot \text{C} \cdot \text{CO} \cdot \text{CMe}_3 \\ | \\ \text{O} - \text{N} \end{array}$ , m. p. 154—155° (decomp.) (cf. Semper and Lichtenstadt, A., 1913, i, 1242). *p-Toluidino-oximinopinacolin*, m. p. 123—124° (decomp.), was prepared. *Chloro-oximinolævulic acid*, m. p. 145—146° [*ethyl* ester, m. p. about 145° (decomp.)], is described.

Acetophenone reacts much less readily than the above aliphatic ketones with nitrosyl chloride (cf. Claisen, A., 1889, 584). *Chloro-oximinoacetophenone*, m. p. 132—133° (Ponzio and Charrier, A., 1907, i, 828), is obtained when acetophenone is distilled into nitrosyl chloride vapour at 50°. The *oxime*, m. p. 193—194° (decomp.), *benzoyl* derivative, m. p. 91° after softening, and *anilino* derivative, m. p. 147°, are described. *Chloro-oximinomethyl p-tolyl ketone*, m. p. 128—129°, obtained similarly, yields *p*-toluic acid when boiled with alkalis. The action of nitrosyl chloride on *p*-chloroacetophenone under similar conditions yields only *p*-chloro-oximinoacetophenone, m. p. 127°, whilst phenylacetone affords similarly oximinophenylacetone (cf. Kolb, A., 1896, i, 576; Borsche, A., 1907, i, 326). *Chloro-oximinomethyl styryl ketone*, m. p. 121—122° (decomp.) after blackening at 110—115°, obtained by adding methyl styryl ketone to nitrosyl chloride in carbon tetrachloride at -12°, affords cinnamic acid on treatment with alkali. The *dibromide*, m. p. 156—157° (decomp.) after blackening at 140°, and the *anilino* derivative, m. p. 176—177° after turning brown, are described. *Chloro-oximinomethyl p-methoxystyryl ketone*, m. p. 143—144° (decomp.), is obtained similarly, together with *oximinomethyl p-methoxystyryl ketone*, m. p. 173°.

The intermediate formation of oximino compounds in the production of the above chloro-oximino derivatives is indicated by the formation of chloro-oximinoacetone and chloro-oximinoacetophenone by the action of nitrosyl chloride on the respective oximino derivatives. F. G. W.

**Compounds of Nickel and Copper with Diacetyldioxime.** F. PANETH and E. THILO (*Z. anorg. Chem.*, 1925, 147, 196—216).—The compound,  $(\text{DH}_2\text{NiH}_2\text{D})\text{Cl}_2$ , where *D*, *DH*, *DH*<sub>2</sub> represent the structures,  $\cdot\text{NO}:\text{CMe}:\text{CMe}:\text{NO}\cdot$ ,  $\text{OH}\cdot\text{N}:\text{CMe}:\text{CMe}:\text{NO}\cdot$ , and



respectively, is obtained as a bluish-grey amorphous powder on passing dry gaseous hydrogen chloride over dry nickel diacetyldioxime. It may be obtained as dark blue crystals from acetone solutions. The substance is stable in dry air. Acids, bases, and



water cause decomposition. When boiled, acetone solutions yield bright green crystals of the *compound*,  $(DH_2NiH_2O)Cl_2$ , which is also unstable except in dry air. When heated in a vacuum over phosphorus pentoxide the bright green crystals lose water to form a yellow to brown mass of the *substance*,  $(DH_2Ni)Cl_2$ , unstable in moist air and decomposed by acids, bases, and alcohol.

On passing dry gaseous ammonia over the salt,  $(DH_2NiH_2D)Cl_2$ , nickel diacetyldioxime and ammonium chloride are formed. The other two salts under similar treatment yield ammonium chloride and a deep carmine-red mass of the *compound*  $DNi(NH_3)_2$ .

Of the corresponding copper compounds only  $(DH_2Cu)Cl_2$  and copper diacetyldioxime,  $Cu(HD)_2$ , are known. The former is obtained as a dark bluish-green substance on passing dry hydrogen chloride gas over dry copper diacetyldioxime or into an ethereal suspension, an equivalent amount of diacetyldioxime being formed:  $Cu(HD)_2 + 2HCl = DH_2CuCl_2 + DH_2$ . The substance is stable in air, but is decomposed by water, acids, and ammonia. J. S. C.

#### Revision of the Structural Formula of Dextrose. W. N.

HAWORTH (*Nature*, 1925, 116, 430).—Normal tetramethylglucose yields on oxidation a  $\delta$ -lactone, whilst the corresponding  $\gamma$ -lactone is derived from the  $\gamma$ -sugar. The annexed formula is therefore proposed for dextrose; thus all aldoses exist normally in the amylenoxide form.

A. A. E.

**Clerget's Method (Inversion Coefficient of Sucrose).** E. SAILLARD (*Compt. rend.*, 1925, 181, 139—140).—The rotatory power of invert sugar diminishes appreciably with decreasing initial concentration of the sucrose, and Clerget's formula for the inversion coefficient is exact only for a (French) normal sucrose solution (*i.e.*, about 16 g. per 100 c.c. of solution, giving a rotation of  $21.66^\circ$  in the polarimeter, or  $100^\circ$  in the saccharimeter). For 4% sucrose the coefficient is 142.86, and for 12% 143.60, instead of the normal 144.

C. H.

#### Preparation of Asymmetrically Acylated Derivatives of Ethylenediamine and their N- and C-Substituted Compounds.

SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pats. 107776 to 107782; from *Chem. Zentr.*, 1925, i, 2409—2410; cf. Swiss Pat. 107202; *Chem. Zentr.*, 1925, i, 1129).—N-Diethylaminoethyl-linoleamide, a viscous oil; N-piperidinoethyloleamide; N-dimethylaminoethylstearamide, m. p.  $71^\circ$ ; N-aminoethylstearamide, m. p.  $103^\circ$ ; N-aminoethyloleamide; N-stearylpropylenediamine; N-palmitylpropylenediamine; and N-oleylpropylenediamine have been prepared.

G. W. R.

**Preparation of Sarcosine Ester.** W. STAUDT (*Z. physiol. Chem.*, 1925, 146, 286—289).—A mixture of methylamine sulphate and formaldehyde solution is treated with potassium cyanide and the resulting nitrile hydrolysed with alcoholic hydrogen chloride;

r r\*

sarcosine ester hydrochloride, m. p. 121—122°, is obtained in a yield of 40% (reckoned on the original methylamine sulphate).

C. R. H.

**Transformations of Peptide Substances. V. Conversion of Serine into Pyruvic Acid and Alanine.** M. BERGMANN, A. MIEKELEY, and E. KANN (*Z. physiol. Chem.*, 1925, **146**, 247—266).—By treating *dl*-alanyl-*dl*-serine in the manner previously described (this vol., i, 235, 795) for glycylserine, an *anhydride*,  $C_6H_8O_2N_2$ , is obtained which darkens at 280° and decomposes at 340°; this substance on boiling for 30 mins. with 5*N*-hydrochloric acid yields a mixture of ammonium chloride, alanine, pyruvic acid, and *pyruvylalanine*,  $C_6H_9O_4N$ , m. p. 143·5°, which on further hydrolysis with hydrochloric acid, gives pyruvic acid and alanine. The anhydride, on oxidation with ozone, gives a *compound*,  $C_5H_6O_3N_2$ , m. p. 212—213°, which, on hydrolysis, gives oxalic acid and alanine; since, further, it is hydrogenated to alanine anhydride, it is to be regarded as 3-methylene-6-methyl-2 : 5-diketopiperazine, and the substance  $C_5H_6O_3N_2$  formed from it by oxidation as 6-methyl-2 : 3 : 5-triketopiperazine. The anhydride from glycylserine behaves similarly, giving among the products of hydrolysis *pyruvylglycine*, on oxidation with ozone 2 : 3 : 5-triketopiperazine, darkening at 220° and decomposing at 240°, and, on hydrogenation, glycyl-alanine anhydride; it is therefore 3-methylene-2 : 5-diketopiperazine. The 3-methylene-6-methyl-2 : 5-diketopiperazine, on keeping in solution in *N*-sodium hydroxide, polymerises to an insoluble product which darkens on heating, but does not melt. On treatment of 2 : 5-diketopiperazine with trioxymethylene and acetic anhydride there was obtained the *diacetate* of 1 : 4-dihydroxymethyl-2 : 5-diketopiperazine, m. p. 111—112°.

C. R. H.

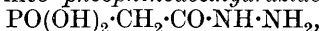
**Hydrolysis of Amides of  $\Delta^{\alpha}$ -Unsaturated Acids and of their Saturated Analogues.** A. R. YATHIRAJA and J. J. SUDBOROUGH (*J. Indian Inst. Sci.*, 1925, **8A**, 55—69).—As in the case of the esterification of the acids (T., 1905, **87**, 1840; 1907, **91**, 1033; 1909, **95**, 313; 1911, **99**, 2307) and the hydrolysis of the ethyl and methyl esters (T., 1912, **101**, 412; Bürki, A., 1918, ii, 434), the amides of the  $\Delta^{\alpha}$ -unsaturated monobasic acids react less readily than the corresponding saturated compounds. The velocity constants of the hydrolysis of *n*-butyramide, crotonamide,  $\beta$ -phenylpropionamide, and cinnamamide by sodium hydroxide at 100°, and by sulphuric acid at 100°, have been determined. The ratio of the velocity constants for *n*-butyramide and crotonamide is 1·6 : 1·0 for alkaline hydrolysis, and 9 : 1 for acid hydrolysis. In the case of  $\beta$ -phenylpropionamide and cinnamamide the corresponding ratios are 3·4 : 1·0 and 11 : 1. The two methods used for determining the amount of hydrolysis, *i.e.*, heating with magnesium hydroxide and treating with sodium hypobromite, give concordant results.

L. F. H.

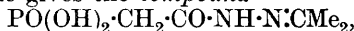
**Organic Compounds of Phosphorus.** P. NYLÉN (*Ber.*, 1924, **57**, [B], 1023—1038).—Although arsinoacetic acid is readily

produced from chloroacetic acid and an excess of sodium arsenite (cf. Palmer, A., 1924, i, 152), an analogous reaction does not appear to occur with sodium phosphite. The interaction of the sodium salts of phosphorous and chloroacetic acids involves the partial conversion of phosphorus into the quinquevalent state, and, apparently, the production of an unstable ester-like compound of glycollic and phosphorous acids which could not be isolated. Somewhat similarly, methyl iodide and sodium phosphite yield the very readily hydrolysed methyl phosphite unaccompanied by methylphosphinic acid.

Diethyl phosphite, b. p. 71—71.5°/10 mm. (corr.), conveniently prepared by the action of phosphorus trichloride on ethyl alcohol, is converted by sodium in the presence of ether into *sodium diethyl phosphite*, which reacts with ethyl chloroacetate to give ethyl phosphinoacetate,  $\text{PO}(\text{OEt})_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , b. p. 140—141°/9—10 mm. The corresponding *amide*,  $\text{PO}(\text{OEt})_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2$ , has m. p. 78—80° (corr.). The ester is hydrolysed with considerable difficulty, being converted by boiling acid or alkali solutions at the atmospheric pressure into the *mono ester*,  $\text{PO}(\text{OH})(\text{OEt}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , which is identified as the *sodium* and *silver* salts. The attachment of the ethoxy group to the phosphorus atom is established by the preparation of the same compound from *methyl diethyl phosphinoacetate*,  $\text{PO}(\text{OEt})_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , b. p. 131.5—132°(corr.)/9 mm. Ethyl phosphinoacetate is converted by hydrochloric acid (1%) at 140—160° into *phosphinoacetic acid*, m. p. 142—143° (corr.), which behaves towards thymolphthalein as a tribasic acid. When esterified with ethyl alcohol and hydrogen chloride it gives the *C-ethyl ester*,  $\text{PO}(\text{OH})_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ , of which the *sodium*, *zinc*, *manganese*, *lead*, *silver*, and *copper* salts are described. The acid is converted by phosphorus pentachloride into the corresponding *trichloride*, b. p. 79—80°/1—2 mm., from which the *trianilide*, m. p. 191.5°—192.5° (corr.), and *tri-p-toluidide*, m. p. 190—192° (corr.), are derived. Ethyl phosphinoacetate is transformed by boiling hydrazine hydrate into *phosphinoacethydrazide*,



which with acetone gives the *compound*



m. p. 185—186° (decomp.). The following salts of phosphinoacetic acid are described: *disodium hydrogen*, *diammonium hydrogen*, *potassium dihydrogen*, normal *calcium* (+H<sub>2</sub>O), normal *barium* (+H<sub>2</sub>O), *copper hydrogen* (+2H<sub>2</sub>O), normal *copper* (+8H<sub>2</sub>O), normal *manganese* (+6H<sub>2</sub>O), normal *zinc* (+H<sub>2</sub>O), normal *lead*, normal *silver*, *disilver hydrogen*. Ethyl phosphinoformate, b. p. 122.5—123°(corr.)/8 mm., is conveniently prepared from ethyl chloroformate and sodium diethyl phosphite; the corresponding *amide*,  $\text{PO}(\text{OEt})_2 \cdot \text{CO} \cdot \text{NH}_2$ , has m. p. 134—135° (corr.). The ester is hydrolysed by boiling water or acids to carbonic and phosphorous acids, whereas with sodium hydroxide the main product is *sodium phosphinoformate*; the phosphinoformates of *zinc* (+12H<sub>2</sub>O), *manganese* (+12H<sub>2</sub>O), *copper* (+8H<sub>2</sub>O), *lead*, and *silver* are described.

Ethyl  $\alpha$ -phosphinopropionate undergoes partial decomposition

into phosphorous acid during hydrolysis. *α-Phosphinopropionic acid*, m. p. (indef.) 75—95°, can, however, be isolated from the product through the *lead* salt; the normal *silver* and *manganese* salts are described. H. W.

**Tetrachloronitrobenzenes, Tetrachlorodinitrobenzenes, and their Reaction with Sodium Methoxide.** V. S. F. BERCKMANS and A. F. HOLLEMAN (*Rec. trav. chim.*, 1925, **44**, 851—860; cf. A., 1921, i, 549).—The three tetrachloronitrobenzenes and the three tetrachlorodinitrobenzenes have been prepared as follows. 2 : 3 : 5 : 6-Tetrachloronitrobenzene was obtained by nitration of *s*-tetrachlorobenzene with fuming nitric acid alone, whilst a mixture with fuming sulphuric acid yielded 2 : 3 : 5 : 6-tetrachloro-*p*-dinitrobenzene, m. p. 227—228°. 2 : 3 : 4 : 6-Tetrachloronitrobenzene, m. p. 41—42°, has been prepared by four methods: 2 : 4 : 6-trichloroacetanilide was nitrated, the product hydrolysed to 2 : 4 : 6-trichloro-*m*-nitroaniline, and the amino group replaced by chlorine; chlorination of *p*-nitroaniline and replacement of the amino group by chlorine yielded 3 : 4 : 5-trichloronitrobenzene, which was converted into 3 : 4 : 5-trichloroacetanilide and the latter nitrated; the product was hydrolysed to 3 : 4 : 5-trichloro-*o*-nitroaniline and the amino group finally replaced by chlorine; nitration of *s*-trichlorobenzene gave 2 : 4 : 6-trichloro-*m*-dinitrobenzene, which was reduced by titanous chloride to 2 : 4 : 6-trichloro-*m*-nitroaniline and the preparation completed as before; lastly, it was found that under carefully regulated conditions the substance was obtained by nitration of 1 : 2 : 3 : 5-tetrachlorobenzene. More vigorous nitration of 1 : 2 : 3 : 5-tetrachlorobenzene, the preparation of which has been improved, yielded 2 : 4 : 5 : 6-tetrachloro-*m*-dinitrobenzene. 2 : 3 : 4 : 5-Tetrachloronitrobenzene was prepared from 2 : 5-dichloroacetanilide, which was nitrated, the product hydrolysed and chlorinated by means of potassium chlorate to give 2 : 3 : 6-trichloro-*p*-nitroaniline, and the amino group finally replaced by chlorine. Nitration of the resulting tetrachloronitrobenzene gave 3 : 4 : 5 : 6-tetrachloro-*o*-dinitrobenzene, m. p. 151°. Pentachloronitrobenzene was prepared by nitration of pentachlorobenzene.

The action of a dilute solution of sodium methoxide on these tetrachloro-nitro- and -dinitro-benzenes has been examined. In 2 : 3 : 5 : 6-tetrachloronitrobenzene and the corresponding *p*-dinitrobenzene one nitro group is mobile, the products being 2 : 3 : 5 : 6-tetrachloroanisole and 2 : 3 : 5 : 6-tetrachloro-*p*-nitroanisole, m. p. 105—106°, respectively, and sodium nitrite. Pentachloronitrobenzene gives as the chief product pentachloroanisole. In the remaining cases, no definite products were isolated. G. M. B.

**Photochemical Oxidation of Aromatic Hydrocarbons. I.** J. J. SUDBOROUGH, H. E. WATSON, and B. T. NARAYANAN (*J. Indian Inst. Sci.*, 1925, **8A**, 1—7; cf. Weger, A., 1903, i, 239).—Toluene, when mixed with water and anthraquinone and exposed for a long period to ultra-violet light or to tropical sunlight, is oxidised (cf. Eckert, *Ind. Pat.* 8425, 1922) to the extent of 30% to benzoic acid and a small amount of an acid of lower mol. wt. (cf.

Ciamician and Silber, A., 1912, i, 174, 645). The quantity of water present influences the amount of oxidation. L. F. H.

**Sulphuryl Chloride. III. Influence of Catalysts on the Chlorination of Toluene.** O. SILBERRAD, C. A. SILBERRAD, and B. PARKE (*J. Chem. Soc.*, 1925, **127**, 1724—1731).—The influence of sixteen catalysts (metallic and non-metallic elements or their chlorides) on the chlorination of toluene by sulphuryl chloride has been investigated. Action takes place well below 115° without catalysts with the formation of chlorotoluene and benzyl chloride. Phosphorus pentachloride inhibits substitution in the ring without hindering the formation of benzyl chloride. Manganese chloride and arsenic behave similarly, almost entirely inhibiting ring substitution. All the other catalysts examined accelerate substitution in the ring and retard it in the side chain, the latter action being entirely inhibited by aluminium chloride, antimony, bismuth, and iron. E. E. W.

**Syntheses of Disulphoxides.** D. T. GIBSON, C. J. MILLER, and S. SMILES (*J. Chem. Soc.*, 1925, **127**, 1821—1824).—The failure of previous workers to effect the synthesis of a disulphoxide from a mercaptan and a sulphochloride is due to the fact that the reaction between these substances proceeds in two stages, giving a sulphinic acid and a disulphide as final products:— $R\cdot SO_2Cl + R'SH = HCl + R\cdot SO_2\cdot SR'$ ;  $R\cdot SO_2\cdot SR' + R'SH = R\cdot SO_2H + R'S\cdot SR'$ . The destruction by the excess of mercaptan of the sulphoxide formed in the first stage can be avoided either by adding the mercaptan slowly to an excess of boiling sulphochloride, or preferably by the interaction of a sulphioidide and a silver mercaptide. By the first method di-*p*-tolyl disulphoxide was obtained in 25% yield from 2 mols. of the mercaptan and 5 mols. of *p*-toluenesulphochloride. 2 : 5 : 2' : 5'-Tetrachlorodiphenyl disulphoxide was obtained (5% yield) from 2 : 5-dichlorothiophenol and 2 : 5-dichlorobenzenesulphochloride, whilst *p*-tolyl *m*-nitrobenzenethiolsulphonate,  $C_6H_4Me\cdot S\cdot SO_2\cdot C_6H_4\cdot NO_2$ , m. p. 109°, was isolated (30% yield) from the reaction between *m*-nitrobenzenesulphochloride and *p*-tolyl mercaptan.

For the second method of preparation, the sulphioidides were obtained by the action of iodine on the sodium sulphinate. 2 : 5-Dichlorobenzenesulphioidide, m. p. 100°, and naphthalene-2-sulphioidide, m. p. 96—97°, were prepared by this method. By the addition of dry silver mercaptide to a dry solution of the sulphioidide in ether or benzene the following thiosulphonates were obtained : 2 : 5-dibromophenyl 2 : 5-dichlorobenzenethiolsulphonate; *p*-tolyl 2 : 5-dichlorobenzenethiolsulphonate, m. p. 74°; 6-methoxy-*m*-tolyl 2-naphthalenethiolsulphonate, m. p. 113—114°; 2 : 4-xylyl 2-naphthalenethiolsulphonate, m. p. 80—81°. F. R.

**Aromatic Hydrocarbons in Low-temperature Tar.** O. KRUBER (*Ber.*, 1924, **56**, [B], 1008—1015).—The following compounds have been identified : 4-ethyl-*o*-xylene, b. p. 189°,  $d_4^{20}$  0.8704 [*trinitro* derivative, m. p. 121°; *tribromo* compound, m. p. 93°;

sodium 4-ethyl-o-xylenesulphonate (+1.5H<sub>2</sub>O); 4-ethyl-o-xylenesulphonamide, m. p. 126—127°; 4-methylhydrindene, b. p. 203°,  $d_4^{20}$  0.9350 [tribromo-4-methylhydrindene, m. p. 183°; 4-methylhydrindenesulphonic acid and its sodium (+H<sub>2</sub>O) and calcium salts; 4-methylhydrindenesulphonamide, m. p. 175°: the hydrocarbon is oxidised to hemimellitic acid and dehydrogenated by passage through a tinned iron tube at 650°, mainly to a mixture of methylindenes and indene]; 1:2:4-trimethylbenzene (sulphonic acid; sulphonamide, m. p. 179—180°); 1:2:3-trimethylbenzene (sulphonic acid and its sodium salt; sulphonamide, m. p. 194°); hydrindene; 4-isopropyl-o-xylene, b. p. 199°,  $d_4^{20}$  0.8710 (4-isopropyl-o-xylenesulphonic acid and its hydrated sodium salt; 4-isopropyl-o-xylenesulphonamide, m. p. 160—161°; trinitro-4-isopropyl-o-xylene, m. p. 119°: the hydrocarbon is converted by bromine in the presence of aluminium into tetrabromo-o-xylene, m. p. 260°, and is oxidised by boiling dilute nitric acid to o-xylene-4-carboxylic acid, m. p. 164—165°); durene. The presence of 4-ethyl-o-xylene, 4-isopropyl-o-xylene, and methylhydrindenes in low-temperature tar is noteworthy, since these compounds do not appear to be contained in the hydrocarbons of coke-oven tar. H. W.

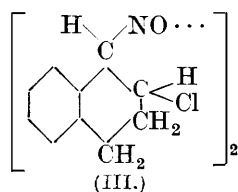
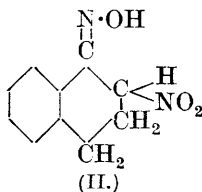
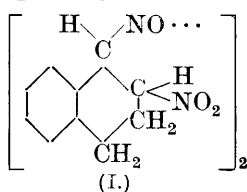
**$\alpha$ -Chlorostyrene.** C. DUFRASSE and J. E. VIEL (*Bull. Soc. chim.*, 1925, [iv], **37**, 874—879; cf. Auwers, A., 1912, ii, 1015; Ley and Rinke, A., 1923, ii, 201; Bourguet, A., 1924, i, 701).—Pure  $\alpha$ -chlorostyrene is conveniently prepared by adding acetophenone in light petroleum to phosphorus pentachloride mixed with fragments of glass in boiling light petroleum solution. It has b. p. 64°/9 mm., m. p. —24 to —23°,  $d_4^{20}$  1.1224,  $n_D^{20.5}$  1.5584.

L. F. H.

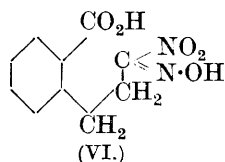
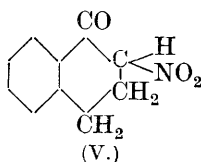
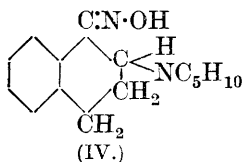
**$\Delta^1$ -Dihydronaphthalene. V. Addition of Nitrogen Oxides and of Nitrosyl Chloride to  $\Delta^1$ -Dihydronaphthalene.** F. STRAUS and W. EKHARD (*Annalen*, 1925, **444**, 146—164; cf. A., 1921, i, 170).— $\Delta^1$ -Dihydronaphthalene is obtained in 85% yield by adding coppered zinc dust (100 g.) to a solution of  $\alpha\beta$ -dibromotetrahydronaphthalene (60 g.) in a mixture of ether (200 c.c.) and alcohol (30 c.c.), with external cooling, and then boiling the reaction mixture for  $\frac{3}{4}$  hr. (cf. von Braun and Kirschbaum, A., 1921, i, 407). When a solution of the hydrocarbon in light petroleum is placed above dilute sulphuric acid, and sodium nitrite (4 mols.) added below the surface of the latter, the nitrogen oxides are completely absorbed, and a pure, bimolecular  $\psi$ -nitrosite (I), pale yellow, m. p. 95—96° (decomp.), separates from the solvent. This decomposes on keeping or on boiling in alcoholic solution into ac-2-nitro-1-oximinotetrahydronaphthalene (II), m. p. 136.5°, decomposing at 138°, which is also obtained by the action of sodium nitrite on a solution of the dihydronaphthalene in glacial acetic acid, together with dihydronaphthalene, 2-nitro- $\Delta^1$ -dihydronaphthalene, and a compound, m. p. 171—172°. Treatment of the  $\psi$ -nitrosite with aniline in alcohol affords the above ac-2-nitro-1-oximinotetralin, whilst piperidine or potassium hydroxide yields similarly the ac-2-nitro- $\Delta^1$ -dihydronaphthalene, yellow, with an intense odour

of cinnamon, m. p. 52°. This yields, on reduction with zinc dust and acetic acid,  $\beta$ -tetraloneoxime and a *substance*, m. p. 206° (decomp.).

When the above 2-nitro-1-oximinotetralin is boiled with 25% sulphuric acid, it yields *o*-carboxyhydrocinnamic acid, m. p. 165—166°, and hydroxylamine, the free nitro-ketone not being obtained. 2-Nitro-1-oximinohydrindene (cf. Dennstedt and Ahrens, A., 1895, i, 475) affords under similar conditions the *aci* form of the corresponding nitro-ketone.



When fuming hydrochloric acid is added to a cooled mixture of  $\Delta^1$ -dihydronaphthalene and amyl nitrite, a *bisnitrosochloride* (III), m. p. 128—129° (varies with the rate of heating), is obtained, together with an emerald-green oil which decomposes on keeping. When treated with piperidine in alcohol, the former yields 1-oximino-2-piperidinotetrahydronaphthalene (IV), m. p. 171—172°. Indene yields similarly an analogous *bisnitrosochloride*, blackening at 180°, from which the corresponding 1-oximino-2-piperidinohydroindene, m. p. 155—156°, was prepared. Treatment of  $\Delta^1$ -dihydronaphthalene in acetone with nitrogen peroxide afforded a *compound*, m. p. 172—173° (decomp.), which yielded 2-nitro- $\Delta^1$ -dihydronaphthalene when treated with piperidine or methyl-alcoholic potassium hydroxide.



2-Oximino-1-ketotetrahydronaphthalene, m. p. about 135° (decomp.), was obtained by adding a solution of  $\alpha$ -tetralone and amyl nitrite to alcoholic potassium ethoxide, as the reddish-brown *potassium salt*. Attempts to hydrolyse the oxime to the  $\alpha\beta$ -diketone failed. The action of potassium ethoxide on  $\alpha$ -tetralone and ethyl nitrate yielded similarly the *potassium salt* of *aci*-2-nitro-1-ketotetrahydronaphthalene, brownish-red (V). The latter couples, in alkaline solution, with diazobenzenesulphonic acid with formation of an intense bluish-red *dye*, and is decomposed by dilute sulphuric acid with formation of  $\gamma$ -(*o*-carboxyphenyl)propylnitric acid (VI), m. p. 104—106° (decomp.), depending on the rate of heating. Careful neutralisation of the above potassium salt yielded a small quantity of the free *aci*-2-nitro-1-ketotetrahydronaphthalene, m. p. 71° (decomp.), decomposing when kept, which was converted into (VI) when boiled with methyl alcohol.

F. G. W.

**Mechanism of Substitution Reactions in the Aromatic Nucleus. IV.** E. DE B. BARNETT, J. W. COOK, and M. A. MATTHEWS (*Rec. trav. chim.*, 1925, **44**, 818—826; cf. this vol., i, 648).—The behaviour of 1:5-dichloroanthracene dichloride and dibromide with a number of bases is described. The reactions which occur are of four types: (i) the simple removal of the halogen to give 1:5-dichloroanthracene and (ii) the complete replacement of the two *meso* halogen atoms with production of a substituted dihydroanthracene derivative; (i) and (ii) are regarded as reactions arising from a *cis* configuration of the original dihalide, whereas (iii) the removal of hydrogen halide to yield a 1:5:9-trihalogenated anthracene and (iv) the production of the corresponding 1:5-dichloro-9-amino derivative are regarded as involving a preliminary change to the *trans* configuration.

1:5-Dichloroanthracene dibromide is converted by methylamine into the parent 1:5-dichloroanthracene, by dimethylamine in benzene solution into 1:5-dichloro-9:10-tetramethyldiamino-9:10-dihydroanthracene, m. p. 175°, by diethylamine into the corresponding tetraethyl derivative, m. p. 130°, and by piperidine into 1:5-dichloro-9:10-dipiperidino-9:10-dihydroanthracene, m. p. 195°. When the dichloride is used in place of the dibromide in this last reaction the same substance is formed together with a large proportion of 1:5:9-trichloroanthracene.

The action of aniline on 1:5-dichloroanthracene dichloride or dibromide yields 1:5-dichloro-9:10-dianilino-9:10-dihydroanthracene, m. p. 211°, which is also produced when 1:5-dichloro-9:10-dihydroanthraquinyl-9:10-dipyridinium dibromide is boiled in alcoholic solution with aniline. This last reaction involves an unexpected change from the *trans* to the *cis* configuration. If the aniline acts at its boiling point without a solvent, 1:5-dichloroanthranylaniline, m. p. 177°, results, and *o*- and *p*-toluidines yield the corresponding dichloroanthranyl-*o*-toluidine, m. p. 189°, and -*p*-toluidine, m. p. 190°, respectively. *m*-Nitroaniline reacts with 1:5-dichloroanthracene dibromide in boiling toluene or on the corresponding dipyridinium dibromide in alcohol to give 1:5-dichloroanthranyl-*m*-nitroaniline, m. p. 268°, together with 1:5-dichloroanthracene and 1:5-dichloroanthranylpyridinium bromide, respectively. 1:5-Dichloroanthracene dichloride or dibromide or the corresponding dipyridinium dibromide is converted by methyl-aniline into 1:5-dichloro-9:10-di(methylanilino)-9:10-dihydroanthracene, m. p. 245° after darkening at 230°. Dimethylaniline reacts with the dichloride to produce 1:5-dichloro-9:10-tetramethyldiaminodiphenyl-9:10-dihydroanthracene, not melted at 300°, whereas with the dibromide 1:5-dichloroanthracene is the sole product.

1:5-Dichloroanthracene dichloride combines with pyridine to give 1:5-dichloro-9:10-dihydroanthraquinyl-9:10-dipyridinium dichloride, (decomp.), converted by aqueous ammonia into 1:5-dichloroanthranylpyridinium chloride, m. p. 330° after blackening.

$\alpha$ -Picoline and quinoline regenerate 1:5-dichloroanthracene from its dibromide, whilst quinoline converts its dichloride into 1:5:9-



trichloroanthracene. The dichloroanthracene is regenerated from its dibromide under the influence of sulphur dioxide, hydrogen sulphide, sodium sulphide, ethyl sodioacetoacetate or sodiomalonate and magnesium phenyl bromide, but by the action of alcoholic potassium cyanide there results 1:5-dichloroanthronitrile, m. p. 230—242°. G. M. B.

**Directive Influence of Substituents in the Benzene Ring.**  
**II. Relative Rates of Bromination of certain *o*-, *m*-, and *p*-Isomerides.** A. W. FRANCIS, A. J. HILL, and J. JOHNSTON (*J. Amer. Chem. Soc.*, 1925, **47**, 2211—2232).—The relative rate in the several successive steps in the bromination of certain aromatic amino and phenolic compounds by a bromide-bromate mixture in aqueous acid solution is measured, either by a determination of the weight of the highest brominated product precipitated by varying proportions of bromine insufficient for complete bromination and a mathematical analysis, based on the kinetics of the reactions, of the curves obtained, or by allowing two compounds to compete for insufficient amounts of bromine (cf. Michael's partition method, A., 1906, i, 550) and determining the weight of precipitate formed. From the results of such competitions combined with the results of the partial bromination of each compound singly, the relative velocity of each step of bromination of the series of compounds is determined. In this way about 100 velocity constants of bromination are evaluated. The general conclusions from the results are as follows: in aniline and *m*-amino compounds two of the bromine substitutions (never three except in the case of *m*-phenylenediamine) are simultaneous, suggesting that two bromine atoms are first substituted in the amino group, whilst this is never the case with monohydric phenols, which can only substitute one bromine atom in the directing group. The rate of substitution of the first bromine atom is greater in the *o*- than in the *p*-isomeride, the substituent entering in the *p*-position in the former and the *o*-position in the latter, whilst the rate for the second bromine atom may be greater than for the first in the *p*-, but never in the *o*-isomeride. The rate of bromination of the *m*-compound exceeds that of the *o*- and *p*-isomerides when each group already present is *o*- or *p*-directing, and conversely is least when one of the groups is *m*-directing. The effect is most marked when both groups are amino or hydroxyl, *p*-aminophenol and quinol being oxidised to the quinonoid form rather than brominated under the conditions used, whilst phloroglucinol has a very high velocity constant. The arrangement of the *o*:*p*-directing groups in order of their directive influence is  $\text{OH} > \text{NH}_2 > \text{Cl} > \text{CH}_3$ , in agreement with Holleman and Obermiller, and for *m*-directing groups,  $\text{NO}_2 > \text{CHO} > \text{CO}_2\text{H} > \text{SO}_3\text{H}$ , in agreement with Obermiller rather than with Holleman if only the first velocity constants are considered, but if the second constant is taken into account the  $\text{NO}_2$  group comes last, in agreement with Holleman. The results indicate that the directive influence of a particular group is less easy to specify than has been supposed, for in the case of an equimolecular solution of aniline and phenol, for example,

the bromine first converts the whole of the phenol into monobromophenol, then the aniline completely into tribromoaniline, and finally the mono- into the tri-bromophenol.

J. W. B.

**Alternating Effect in Carbon Chains. III. Directive Efficiencies of Oxygen and Nitrogen Atoms in Aromatic Substitution.** E. L. HOLMES and C. K. INGOLD (*J. Chem. Soc.*, 1925, 127, 1800—1821).—To compare the merits of the alternating polarity and affinity theories, a comparative study has been made of the nitration of benzyl alcohol, benzylamines, and their respective *O*- and *N*-substitution derivatives. According to the affinity theory, derivatives of benzylamine should show a greater tendency towards *m*-substitution and a smaller tendency towards *o*:*p*-substitution than the benzyl alcohols, and *m*-directive action should never prevail amongst the latter. According to the polarity theory, since nitrogen is more feebly negative than oxygen, it follows, whether "onium" action occurs or not (cf. Robinson, *Chem. and Ind.*, 1925, 44, 260), that benzylamine should show a greater tendency towards *o*:*p*-substitution and a smaller tendency to *m*-substitution than the benzyl alcohols. With derivatives of benzyl alcohol, substitution occurs mainly or exclusively in the *p*-position, and no instance of *m*-substitution has been observed. *s*-Tribromophenyl benzyl ether nitrated at  $-5^{\circ}$  gave *s*-tribromophenyl *p*-nitrobenzyl ether (m. p.  $145^{\circ}$ ), identified by synthesis from *p*-nitrobenzyl chloride and sodium *s*-tribromophenoxide. *o*:*p*-Dinitrophenyl benzyl ether gave *o*:*p*-dinitrophenyl *p*-nitrobenzyl ether. Benzyl nitrate gave *p*-nitrobenzyl nitrate. Benzyl ethyl ether and benzyl alcohol could not be nitrated owing to the occurrence of considerable oxidation.

Aniline nitrate is *m*-orienting, but under ordinary nitrating conditions loses water, giving the nitroamine  $\text{NHPH}\cdot\text{NO}_2$ , which, being only weakly basic, substitutes in *o*:*p*-positions. According to the affinity theory, benzylamine should react oppositely and on nitration in the cold should give predominantly *m*-substitution. Benzylamine was prepared from potassium phthalimide and benzyl chloride, and the phthalobenzimide converted by boiling with 10% potassium hydroxide into *phthalobenzylamic acid* (m. p.  $155^{\circ}$ ), from which by hydrolysis benzylamine was obtained. Nitrated at  $-10^{\circ}$ , this gave mainly (80%) *m*-nitrobenzylamine, together with some *p*-nitrobenzylamine, and possibly a trace of the *o*-compound. Nitration at  $100^{\circ}$  gave a quantitative yield of the *m*-nitro compound. The three nitrobenzylamines were synthesised for comparison from the respective nitrobenzyl chlorides by treatment with ammonia: *o*-nitrobenzylamine, colourless oil (*hydrochloride*, m. p.  $248^{\circ}$ ; *nitrate*, m. p.  $173$ — $174^{\circ}$ ); *m*-nitrobenzylamine, colourless oil (*hydrochloride*, m. p.  $250^{\circ}$ ; *nitrate*, m. p.  $214^{\circ}$ ); *p*-nitrobenzylamine, oil (*hydrochloride*, m. p.  $224^{\circ}$ ; *nitrate*, m. p.  $180$ — $181^{\circ}$ ).

The phenomena observed with benzylamine should be reproduced in secondary benzylamines, but should disappear in tertiary derivatives, as these lack the amino-hydrogen necessary for dehydr-

ation to the nitro-amine. This was observed as predicted. Benzylmethylamine was synthesised by a modification of Hinsberg's process and also by the regulated action of methylamine on benzyl chloride. By the first method, benzylamine by treatment in dry pyridine solution with *p*-toluenesulphochloride gave *p*-toluenesulphobenzylamide, m. p. 114°, from which by treatment with methyl iodide, alcohol, and aqueous sodium hydroxide, *p*-toluenesulphobenzylmethylamide, m. p. 95°, was obtained. By hydrolysis with hydrochloric acid at 165–170°, basification, and extraction with ether, the pure benzylmethylamine was obtained, b. p. 184–186°; *hydrochloride*, m. p. 195°. When nitrated at a low temperature, *m*-nitrobenzylmethylamine was obtained in 80% yield, together with 10% of the *p*-isomeride. Nitration at 100° gave only the *m*-nitro compound. The three nitrobenzylmethyamines were prepared for identification by the action of methylamine on the corresponding nitrobenzyl chlorides and were characterised by their hydrochlorides (*o*-hydrochloride, m. p. 175°; *m*-hydrochloride, m. p. 182°; *m*-nitrate, m. p. 150°; *p*-hydrochloride, m. p. 226°). Dibenzylamine nitrated at –5° to 0° gave the *pp'*- and *mm'*-dinitro products in the proportion of 5% and 80%, respectively. A third isomeride appeared to be present, but could not be purified. Nitration at 70–90° yielded the *mm'*-dinitro derivative exclusively. The three dinitro isomerides were prepared pure for comparison: *oo'*-dinitrobenzylamine, m. p. 101° [*hydrochloride*, m. p. 238° (decomp.)]; *mm'*-dinitrobenzylamine, m. p. 83.5° [*hydrochloride*, m. p. 253°; *nitrate*, m. p. 235° (decomp.)]; *pp'*-dinitrobenzylamine, m. p. 93° (*hydrochloride*, m. p. 217–218°; *nitrate*, m. p. 210–211°). Dibenzylmethylamine nitrated with cold or warm nitric acid gave chiefly the *pp'*-dinitrodibenzylmethylamine, together with a small amount of the *oo'*-isomeride. *oo'*-Dinitrodibenzylmethylamine has m. p. 63° (*hydrochloride*, m. p. 216°; *nitrate*, m. p. 125°); *mm'*-dinitrodibenzylmethylamine, m. p. 83–84° [*hydrochloride*, m. p. 223–224°; *nitrate*, m. p. 163° (decomp.)]; *pp'*-dinitrodibenzylmethylamine *hydrochloride*, m. p. 204–205°; *nitrate*, m. p. 146°.

The introduction of an acyl group into a benzylamine should prevent the formation of a nitroamine, except, possibly, at high temperatures, so that substitution in these compounds should be mainly in the *o*:*p*-positions. Further, since acetodibenzylamide is a weaker base than dibenzylmethylamine, larger quantities of the *m*-by-products should be obtained in the former case. Also acetobenzylamide and acetobenzylmethylamide should give less *m*-compound than the weaker base acetodibenzylamide, and the addition of different quantities of water to the nitric acid in the nitration of the last substance should change the proportion of by-products, the more dilute acid giving more of the *m*-product. All these predictions have been verified. Diacetylbenzylamine, being non-basic, must nitrate as such and cannot form a nitroamine. In this case, mainly *m*-substitution was predicted and obtained. It is concluded, therefore, that not only is *m*-substitution a frequent experience with benzylamine derivatives, but prevails in every case

in which substitution through a salt is precluded. *Acetobenzylmethylamide* has m. p. 41—43°; b. p. 155°/16 mm.; *aceto-m-nitrobenzylmethylamide*, m. p. 56—57°; *aceto-p-nitrobenzylmethylamide*, m. p. 80—81°; *acetodibenzylamide*, b. p. 194—195°/3 mm.; *aceto-oo'-dinitrodibenzylamide*, m. p. 154°; *aceto-mm'-dinitrodibenzylamide*, m. p. 146°; *aceto-pp'-dinitrodibenzylamide*, m. p. 183—184°; *diacetylbenzylamine*, viscous liquid, b. p. 176—178°/30 mm.

F. R.

**Acenaphthene Series. II. 1-Aminoacenaphthene.** G. T. MORGAN and A. D. SHEASBY (*J. Soc. Chem. Ind.*, 1925, **44**, 408—410T; cf. this vol., i, 133).—Substitution in the acenaphthene series occurs predominantly in the 3-position but the first product is probably the 1-isomeride and in the presence of water or mineral acid the substituent changes over to the 3-position (cf. Dziewonski and Stolyhwo, A., 1924, i, 1178). Nitration of acenaphthene by the usual methods leads to the exclusive formation of 3-nitro-acenaphthene (Quincke, A., 1888, 843; Graebe, A., 1903, i, 408), but when treated with benzoyl nitrate in light petroleum solution at -15° acenaphthene yields 1-nitroacenaphthene, yellow, m. p. 68°. Nitration of acenaphthene with diacetylorthonitric acid (Pictet and Genequand, A., 1902, i, 584) gives 70% of 1-nitro- and 30% of 3-nitro-acenaphthene. On treatment with a mixture of acetic and nitric acids 1-nitro- yields pure 3-nitro-acenaphthene. Reduction of the 1-nitro compound by means of sodium hyposulphite gave 1-aminoacenaphthene, m. p. 92°, *picrate*, m. p. 180—200°, *hydrochloride*, m. p. 250—260°, *acetyl* compound, m. p. 168°, *benzoyl* compound, m. p. 208°. 1-Aminoacenaphthene when diazotised gives a green solution; it gives a green coloration with ferric chloride, and with *p*-nitrobenzenediazonium acetate yields 2-*p*-nitrobenzeneazo-1-aminoacenaphthene, purple, in these respects resembling 3-amino- and differing from 2-amino-acenaphthene.

L. F. H.

**Nitration of *m*-Chlorophenol.** H. H. HODGSON and F. H. MOORE (*J. Chem. Soc.*, 1925, **127**, 1599—1604).—Mononitration of *m*-chlorophenol (liquefied by 6% of its weight of alcohol) by sodium nitrate and sulphuric acid below 25° gives 22% of 3-chloro-6-nitrophenol (Auwers and Deines, *Chem. Zentr.*, 1924, ii, 2268), m. p. 41°, volatile in steam, and 60% of 3-chloro-4-nitrophenol (*ibid.*), m. p. 121—122°, not volatile in steam, also obtained by oxidation of 3-chloro-4-nitrosophenol with ferri cyanide. Uhlemann's anomalous m. p. for the 6-nitro compound, becoming normal after several days (A., 1878, 978), is not confirmed. 3-Chloro-2-nitrophenol, m. p. 37.5° (*silver salt*, *benzoate*, m. p. 123°, and *methyl ether*, m. p. 55°, are described) is obtained by adding *m*-chlorophenol to fuming sulphuric acid, nitrating the disulphonic acid with a mixture of nitric acid and fuming sulphuric acid, diluting, and hydrolysing in a current of steam; the nitrophenol passes over in the steam (yield 66%).

3-Chloro-4 : 6-dinitrophenol (Fries and Roth, A., 1912, i, 659), m. p. 92—93°, is prepared by nitration of *m*-chlorophenol or 3-chloro-

4-nitrophenol or by hydrolysis of 1 : 3-dichloro-4 : 6-dinitrobenzene. 3-*Chloro-2 : 6-dinitrophenol*, m. p. 114.5°, results from 3-chloro-2-nitrophenol by direct nitration or by nitration after sulphonation (with subsequent hydrolysis in steam), or from *m*-chlorophenol by monosulphonation, dinitration, and hydrolysis. 3-*Chloro-2 : 4-dinitrophenol*, m. p. 138—140° (*silver salt* described), is prepared, together with the 2 : 6-dinitro compound, from 3-chloro-2-nitrophenol by sulphonation, nitration, and hydrolysis in steam, the steam distillate being extracted with ether after removal of the crystallised 2 : 6-compound. Direct dinitration of disulphonated *m*-chlorophenol gives 2-nitro-, 2 : 4- and 2 : 6-dinitro, but no 4 : 6-dinitro derivative. The 2- and 6-mononitro compounds are stable towards fuming sulphuric acid, but the 4-nitro compound is destroyed; so that nitration of 3-chloro-4-nitrophenol in fuming sulphuric acid gives the 4 : 6-dinitro compound only when the solution is kept cool and not kept before nitration. No 4 : 6-dinitro compound is formed from 3-chloro-4-nitrophenol. All three dinitrated *m*-chlorophenols are volatile in steam.

3-*Chloro-2 : 4 : 6-trinitrophenol*, m. p. 114°, is formed by direct nitration of *m*-chlorophenol in fuming sulphuric acid. If the *m*-chlorophenol is first sulphonated, then nitrated, and hydrolysed in steam, the product is 3-*chloro-2 : 5 : 6-trinitrophenol*, m. p. 112.5—113.5°, volatile in steam. The dipotassium salt of 3-*chloro-2 : 5 : 6-trinitrophenol-4-sulphonic acid* is described. C. H.

**Alkyl Ethers of Monohydric Phenols and their Halogen Substitution Products.** AKT.-GES. FÜR ANILIN-FABRIKATION (D.R.-P. 411052; from *Chem. Zentr.*, 1925, i, 2411; cf. A., 1922, i, 1145).—The preparation of the following new compounds is described: 2 : 4 : 5-*trichloroanisole*, m. p. 75°; 2 : 4 : 5-*trichlorophenetole*, m. p. 95°; a mixture of *isobutylcarbinol* and *sec.-butylcarbinol ethers* of 2 : 4 : 5-*trichlorophenol*, a liquid, b. p. 174°/18 mm.,  $d_4^{21}$  1.244. G. W. R.

**Additive Products of Lead Oxide with Lead Compounds of Acidic Polynitro Compounds.** AKT.-GES. LIGNOSE, F. THOMAS, and J. DYCKERHOFF (D.R.-P. 407416; from *Chem. Zentr.*, 1925, i, 2484).—Additive products of lead oxide with lead picrate, the lead salt of hexanitrodiphenylamine, lead trinitrobenzoate, the lead salt of trinitroresorcinol, and lead nitroanilate are described. G. W. R.

**Mechanism of Oxidation of Unsaturated Compounds by Permanganate.** S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1924, 55, 70—74).—It has been suggested by Lvov (*J. Russ. Phys. Chem. Soc.*, 1889, 21, 350) that the first step in the oxidation of unsaturated compounds by potassium permanganate consists in the addition of the reagent in the form of permanganic acid at the double bond; the additive compound then breaks up with the formation of a glycol. Wagner has modified the original scheme by assuming that an unstable heterocyclic compound is first formed. It is now pointed out that neither of these schemes explains the

G. A. R. K.

G. A. R. K.

$$\text{C}_6\text{H}_4 \begin{array}{c} \text{CPh(OH)} \cdot \text{CH} \\ | \\ \text{CPh(OH)} \cdot \text{CH} \end{array} \rightarrow \text{C}_6\text{H}_4 \begin{array}{c} \text{C(OH)} \cdot \text{CPh} \\ | \\ \text{CPh}=\text{CH} \end{array} \rightarrow \text{C}_6\text{H}_4 \begin{array}{c} \text{C(OAc)} \cdot \text{CPh} \\ | \\ \text{CPh}=\text{CH} \end{array}$$

(I.)
(II.)
(III.)

Acetylation of (I) yields an acetyl compound, m. p. 163°, to which the constitution 2 : 4-diphenyl-1-naphthyl acetate (III) is assigned, this being formed, it is suggested, by acetylation of the intermediate

compound (II). On hydrolysis, the acetyl compound (III) yields presumably 2 : 4-diphenyl- $\alpha$ -naphthol, m. p. 143—144°. Oxidation of (III) yields the same products as the oxidation of (I). L. F. H.

**Action of Grignard Reagent on Amino-acids. V. Wandering of Acyl Groups in Amino-alcohols and Glycols.** F. BETZIECHE (*Z. physiol. Chem.*, 1925, **146**, 227—240).—The *N*-benzoyl derivatives of amino-alcohols, on treatment with concentrated sulphuric acid in the cold or on boiling with 20% hydrochloric acid, yield basic substances which, on long keeping, revert to the original *N*-benzoyl derivative. With tertiary alcohols of the type  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CR}_2 \cdot \text{OH}$ , the reaction takes place readily when R is methyl and ethyl (e.g.,  $\beta$ -*N*-benzamido-*tert*-butyl alcohol), and less readily or not at all with the corresponding  $\alpha$ -phenyl and  $\alpha$ -benzyl derivatives. The basic substances obtained could not be purified, but were apparently mixtures of the benzoic acid ester base, formed by wandering of the benzoyl group from the amino to the hydroxyl group of the alcohol, with oxazoline derivatives formed secondarily from this base. On treatment of the *N*-benzoyl derivatives of the amino-alcohols with concentrated sulphuric acid and sodium nitrite, benzoyl derivatives are obtained which are stable towards oxidising agents; this indicates a wandering of the benzoyl group from the amino group of the original compound to the secondary hydroxyl of the newly formed glycol.

C. R. H.

**Derivatives of  $\delta$ -o-Aminobenzoylvaleric Acid.** M. J. PATERSON and S. G. P. PLANT (*J. Chem. Soc.*, 1925, **127**, 1797—1799).—The acid of m. p. 129° obtained by Perkin and Plant (T., 1923, **123**, 678) is proved to be  $\delta$ -o-aminobenzoylvaleric acid by its conversion by diazotising and boiling into  $\delta$ -o-hydroxybenzoylvaleric acid (von Braun, A., 1923, i, 104).  $\delta$ -o-Acetamidobenzoylvaleric acid has m. p. 153°; after boiling with potassium hydroxide solution it gives on acidifying a small, colourless precipitate of  $\gamma$ -4-hydroxy-2-methylquinoline-3-butyric acid, m. p. 241°.  $\delta$ -o-Formamidobenzoylvaleric acid has m. p. 160°.

F. R.

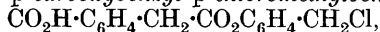
**Benzoylhydroperoxide [Perbenzoic Acid]. Preparation and Application to Organic Synthesis.** H. HIBBERT and C. P. BURT (*J. Amer. Chem. Soc.*, 1925, **47**, 2240—2243).—Benzoylhydroperoxide may be obtained in 90% yield by the addition, with much stirring, of a 10% solution of sodium ethoxide in alcohol to benzoyl peroxide in ether suspension at  $-5^\circ$ . The aqueous solution of the sodium salt is decomposed by adding it slowly to a slight excess of sulphuric acid at  $0^\circ$ , the reverse procedure resulting in the decomposition of the product. The benzoylhydroperoxide is extracted with chloroform and in this solution, dried at  $0^\circ$  with sodium sulphate, is stable for several days. It may be determined by the addition of an excess of acidified potassium iodide solution to the extract and titration with sodium thiosulphate. Styrene is obtained in 88% yield by the thermal decomposition of phenylethyl phenylacetate at 315—320°, and on treatment

with a 10% excess of the benzoylhydroperoxide solution yields, after 24 hrs., styrene oxide in 75% yield. J. W. B.

**Salts of certain Aromatic Carboxylic Acids and their Solubility.** F. EPHRAIM and A. PFISTER (*Helv. Chim. Acta*, 1925, **8**, 369—383; cf. this vol., i, 896).—An investigation of the solubilities in water of 67 metallic salts of benzoic, *p*-nitrobenzoic, *p*-chlorobenzoic, *p*-hydroxybenzoic, *p*-methoxybenzoic, and cinnamic acids. The salts of benzoic acid are, with few exceptions, more soluble than those of the corresponding para-substituted derivatives, decrease in solubility being least marked in the hydroxy-acid salts. In the cinnamic acid series, solubility decrease is very much more marked. The following new salts are described, the figures in brackets giving the number of molecules of water of crystallisation: *benzoates* of strontium (1), cobalt (2 and 4), and copper (4), and a complex copper salt,  $(\text{PhCO}_2)_2\text{Cu} \cdot \text{Ph} \cdot \text{CO}_2\text{H} \cdot \frac{1}{2}\text{H}_2\text{O}$ ; *p*-nitrobenzoates of strontium (8), magnesium (6), copper (1), cobalt (6), nickel (8), manganese (6), cadmium (2), silver (anhyd.); *p*-chlorobenzoates of strontium (4), lead (2), zinc (2), nickel (4), cobalt (4), manganese (2), cadmium (2), and copper (2); *p*-hydroxybenzoates of strontium (1), cobalt (7), nickel (7), and manganese (8); cinnamates of magnesium (4), cobalt (2), nickel (2), and copper (anhyd.). In the following cases, the number of molecules of water of crystallisation differs from that given in the literature: benzoates of calcium (2), magnesium ( $3\frac{1}{2}$ ), and zinc (1); *p*-nitrobenzoates of calcium (6) and barium (anhyd.); barium *p*-chlorobenzoate (1); *p*-hydroxybenzoates of silver (3), cadmium (7), and copper (7); *p*-methoxybenzoates of barium (1), calcium (3), zinc (1), cadmium (1), copper (6), and nickel (6); and manganese cinnamate (2).

M. J.

**New Substituted Benzyl Esters.** C. BARKENBUS and J. B. HOLTZCLAW (*J. Amer. Chem. Soc.*, 1925, **47**, 2189—2192).—When sodium  $\omega$ -chloro-*p*-toluate is boiled in neutral aqueous solution it is converted into *p*-carboxybenzyl *p*-chloromethylbenzoate,



m. p.  $221^\circ$ , which is hydrolysed quantitatively in slightly alkaline solution to  $\omega$ -hydroxy-*p*-toluic acid. The hydrolysis of  $\omega$ -chloro-*p*-toluic acid with dilute sodium hydroxide solution also yields this product, ether formation (cf. Gunther, A., 1890, 977) being minimised by avoiding an excess of the base. On heating with acetyl chloride this yields *p*-carboxybenzyl acetate ( $\omega$ -acetoxy-*p*-toluic acid), m. p.  $123$ — $124^\circ$ , but attempts to prepare the corresponding benzoate gave only a mixture from which the pure product could not be isolated. The chlorination of *o*- and *p*-toluonitriles to yield respectively *o*- and *p*-cyanobenzyl chlorides is best carried out at temperatures of  $140$ — $150^\circ$  and  $120$ — $130^\circ$ , respectively, instead of at the b. p. of the nitrile (cf. Mellinghoff, A., 1890, 239). When heated with sodium acetate or benzoate solutions at  $100$ — $110^\circ$  for 5 hrs., *o*-cyanobenzyl chloride yields respectively *o*-cyanobenzyl acetate, b. p.  $180$ — $182^\circ/24$  mm., and benzoate, m. p.  $54$ — $55^\circ$ , but



all attempts to hydrolyse the cyano group lead to the production of phthalide.

J. W. B.

**Condensation of Nitriles with Thioamides. V. Action of Sulphur Monochloride on Thioamides.** S. ISHIKAWA (*Sci. Papers Inst. Phys. Chem. Res.*, 1925, **3**, 147—154; cf. this vol., i, 917).—In correction of Chakravarti (T., 1923, **123**, 964), it is shown that sulphur monochloride reacts with thiobenzamide to give, not benziminosulphide, but dibenzenzylazosulphime (2 : 5-diphenyl-1 : 3 : 4-thiodiazole), or, when the reaction is carried out in cold ethereal solution, a mixture of dibenzenzylazosulphime with benziminoisothiobenzamide,  $\text{CPh}(\text{:NH})\text{C}\cdot\text{N}:\text{CPh}\cdot\text{SH}$  (main product). Similarly, *p*-thiotoluamide yields *p*-toluiminoisothio-*p*-toluamide, m. p. 108°, yellowish-red (hydrochloride, m. p. 161°), and *di-p*-toluenylazosulphime (2 : 5-*di-p*-tolyl-1 : 3 : 4-thiodiazole), m. p. 129°;  $\alpha$ -thionaphthamide yields red  $\alpha$ -naphthiminoisothio- $\alpha$ -naphthamide, and *di- $\alpha$ -naphthenylazosulphime* (2 : 5-*di- $\alpha$ -naphthyl*-1 : 3 : 4-thiodiazole), m. p. 129°. Thioacetamide yields no recognisable product. Sulphur monochloride reacts with thiobenzanilide, yielding benzphenyliminophenylthiobenzamide,  $\text{C}_{26}\text{H}_{20}\text{N}_2\text{S}$ , benzanilide, and aniline, whilst thioacetanilide yields acetanilide, aniline, and an unstable red substance.

B. F.

**Action of Keten on Hydroxybenzoic Acids and their Esters.** J. VAN ALPHEN (*Rec. trav. chim.*, 1925, **44**, 838—840; cf. this vol., i, 80).—Although keten does not react with phenol in ethereal solution, it acetylates salicylic acid quantitatively. Methyl salicylate, *p*-hydroxybenzoic acid, and ethyl *m*-hydroxybenzoate are acted on more slowly, whilst *m*-hydroxybenzoic acid and ethyl *p*-hydroxybenzoate are unaffected. In this respect, the *o*- and *m*-esters therefore have a common difference from the *p*-isomeride.

G. M. B.

**Bromo Derivatives of *p*-Methoxycinnamic Acid.** K. V. HARIHARAN and J. J. SUDBOROUGH (*J. Indian Inst. Sci.*, 1925, **8A**, 189—219; cf. T., 1903, **83**, 666, 1153; A., 1923, i, 336, 926).—Ethyl *p*-methoxycinnamate is extracted in 30% yield from the oil of the rhizomes of *Kaempferia galanga*, and is readily hydrolysed by alkali. On treating ethyl  $\alpha\beta$ -dibromo- $\beta$ -*p*-methoxyphenylpropionate with alcoholic potassium hydroxide, a mixture of isomeric  $\alpha$ -bromo-*p*-methoxycinnamic acids, m. p. 185° (85%) and 103° (15%), respectively, separated by means of their barium salts, is obtained. It is suggested that the acid of m. p. 103° is  $\alpha$ -bromo-*p*-methoxyallo-cinnamic acid, as it is readily transformed into the acid of m. p. 185° by sunlight, by bromine in chloroform solution, and by sulphuric acid. On treatment of methyl  $\alpha\beta$ -dibromo-*p*-methoxyphenylpropionate with alcoholic potash, 60% of the acid of m. p. 185° and 38% of the acid of m. p. 103° are obtained. By the action of alcoholic potassium hydroxide on the free dibromo-acid are obtained  $\omega$ -bromo-*p*-methoxystyrene and a bromo-*p*-methoxycinnamic acid, m. p. 123°, of unknown constitution, which gives a dibromide, probably  $\alpha\beta\beta$ -tribromo-*p*-methoxyphenylpropionic acid, m. p. 145°.

The three monobromo-acids on treatment with potassium hydroxide lose hydrobromic acid in the following order of increasing velocity: (m. p.) 102°, 185°, 123°, giving mainly *p*-methoxyphenylpropionic acid in good yield. Treatment with dimethylaniline of the dibromo-esters and -acid gives similar results to potassium hydroxide. On heating with water the dibromo-acid yields *o*-bromo-*p*-methoxystyrene and a small amount of *p*-methoxycinnamic acid.  $\beta$ -Bromo-*p*-methoxyallocinnamic acid, m. p. 145°, and  $\beta$ -bromo-*p*-methoxycinnamic acid, m. p. 139°, are obtained by treatment of an aqueous suspension of *p*-methoxyphenylpropionic acid with hydrogen bromide at 0°. The *allo*-acid is stable towards sodium carbonate at the ordinary temperature, whereas the other acid is readily decomposed, yielding *p*-methoxyphenylacetylene, carbon dioxide, and hydrogen bromide. On treatment with bromine in chloroform solution, both acids yield carbon dioxide, hydrogen bromide, and a product, m. p. 90—91°, probably  $\alpha\beta$ -dibromo-*p*-methoxystyrene. If the temperature is maintained at 25° during the passage of the hydrobromic acid into the *p*-methoxyphenylpropionic acid, *p*-anisyl methyl ketone and a yellow solid, m. p. 169—170°, probably tri-*p*-anisylbenzene, are obtained. If the hydrobromic acid be passed into the *p*-methoxyphenylpropionic acid in benzene suspension, the  $\alpha$ -bromo-acid, m. p. 185°, and the  $\alpha$ -bromo-*allo*-acid, m. p. 145°, are obtained. From the reactions studied the increased reactivity due to the introduction of the *p*-methoxy group is confirmed (cf. Angeli, A., 1924, i, 626).

L. F. H.

### Preparation of Anthracene-2-thioglycol-3-carboxylic Acid.

SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 103647; from *Chem. Zentr.*, 1925, i, 2411).—Anthracene-2-thioglycol-3-carboxylic acid, a lemon-yellow powder, is prepared by reduction of the corresponding anthraquinone derivative with zinc and ammonia (cf. Brit. Pat. 210413).

G. W. R.

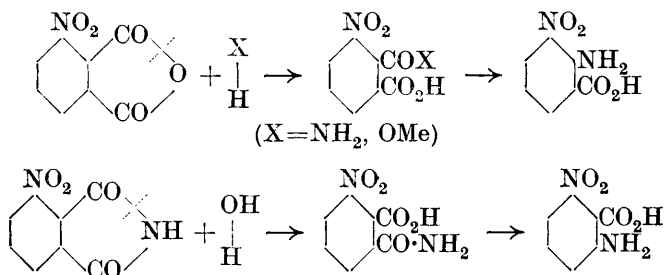
### *cis*- and *trans*-cycloHexane-1 : 3-dicarboxylic Acids.

**Separation of the *trans*-Acid into its Optically Active Components.** J. BÖESEKEN and A. E. J. PEEK (*Rec. trav. chim.*, 1925, 44, 841—850).—According to Sachse's theory and in view of evidence already obtained of rings of six or more members lying in more than one plane (cf. A., 1921, i, 843), a third isomeride of *cis*- and *trans*-cyclohexane-1 : 3-dicarboxylic acids is conceivable, but it has now been found that, if it exists, it is readily converted into the other forms and cannot be isolated. The *trans* configuration of the second known isomeride, m. p. 148°, has been confirmed by its resolution into its optically active components, the *strychnine* salt, 1A21B, crystallising first from alcohol. *d*- and *l*-*trans*-cycloHexane-1 : 3-dicarboxylic acids, m. p. 134°, have  $[\alpha]_D^{25} +23.46'$  and  $-23.10'$ , respectively, in 2.2% aqueous solution. The solubilities of the *dl*-, the *d-trans*-, and the *cis*-acids at 25° are 13.26, 43.10, and 22.30 g. per litre of water, respectively. The *trans*-(*dl*)- acid has an electrolytic dissociation constant  $K^{25} 3.45 \times 10^{-5}$ , the *cis*-acid  $K^{25} 5.34 \times 10^{-5}$ . The *cis*-acid could not be resolved.

G. M. B.

**Esterification.** B. V. BHIDE and J. J. SUDBOROUGH. (See i, 1127.)

**Preparation of Phthalamic Acids and their Conversion into Anthranilic Acids.** E. CHAPMAN and H. STEPHEN (*J. Chem. Soc.*, 1925, 127, 1791—1797).—Phthalamic acid can be prepared (a) by the action of water on phthalimide, and (b) by the action of ammonia on phthalic anhydride. By reaction (b) good yields of phthalamic acid and 4:5-dibromophthalamic acid were obtained from the corresponding anhydrides, and, further, by the action of sodium hypochlorite on the amic acids, the corresponding anthranilic acids were readily prepared. 3-Nitrophthalic anhydride by reaction (b) gave exclusively 3-nitrophthalamic acid, from which 3-nitroanthranilic acid was obtained in 90% yield, whilst 3-nitrophthalimide by reaction (a) gives almost exclusively 6-nitrophthalamic acid.



4-Nitrophthalic anhydride by reaction (b) gave an inseparable mixture of 4- and 5-nitrophthalamic acids, shown by conversion into the corresponding anthranilic acids to be in the proportion of 2 to 3, whereas 4-nitrophthalimide by reaction (a) gives the same mixture in the proportion 4 to 1. In both the examples investigated, therefore, the amic acid produced in larger amount by reaction (b) is produced in smaller yield by reaction (a) and *vice versa*.

4:5-Dibromo-2-acetamidobenzoic acid has m. p. 240°; 3-nitro-2-acetamidobenzoic acid, m. p. 180—181°. F. R.

#### Anhydrides of N-Carboxylic Derivatives of $\alpha$ -Amino-acids.

I. F. WESSELY (*Z. physiol. Chem.*, 1925, 146, 72—90).—Glycine-carboxylic anhydride on exposure to moist air during 4 days is decomposed almost quantitatively into an insoluble anhydride,

$\left[ \begin{array}{c} \text{CH}_2 \\ \diagup \text{CO} \end{array} \text{NH} \right]_n$ , apparently identical with that described by Leuchs (A., 1906, i, 236). In concentrated aqueous solution, an insoluble anhydride is still formed, but in diminishing amounts as the dilution increases, until in very dilute solution glycine is almost exclusively formed. It is not certain whether the insoluble anhydride formed in concentrated aqueous solution is identical with Leuch's anhydride or is another high-molecular peptide. The length of the chain in the peptide produced possibly increases with

the concentration of the glycinecarboxylic anhydride. The decomposition is accelerated by heating; in no case was complete solution of the anhydride obtained at 0°. The same decomposition takes place in the presence of other amino-acids, but the difficulty of isolating pure substances from the reaction mixture hinders its detection. Indirect proof of the reaction is afforded by the formation of carbon dioxide and *N*-phenylglycylglycine, m. p. 148°, on warming the anhydride of phenylglycine-*N*-carboxylic acid with glycine in aqueous solution. With very dilute hydrochloric acid (0.001*N*), glycinecarboxylic anhydride affords the insoluble anhydride; with 0.1*N* or stronger acid glycine formation is almost quantitative. The extent of glycine formation is also proportional to the amount of acid present. *N*-Sodium hydroxide solution leads to quantitative glycine formation, but with weaker alkali (0.1 and 0.01*N*) side reactions yielding peptides take place (cf. Mohr, A., 1909, i, 420). With 25% aqueous ammonia, phenylglycine-*N*-carboxylic anhydride reacts with loss of carbon dioxide, forming the amide of phenylglycine, m. p. 136° (cf. Leuchs, A., 1907, i, 770). The ethyl ester and the anilide were similarly obtained (Fuchs, A., 1922, i, 1152). Ethylamine affords the *ethylamide* of phenylglycine, m. p. 53—54°. The *piperidide*, m. p. 102—103°, and *methylanilide*, m. p. 118°, are similarly obtained, but tertiary amines do not react and the anhydride appears to be a suitable reagent for the detection of primary and secondary amines in tertiary amines. With ethyl aminoacetate, the anhydride affords the *ethyl* ester of *N*-phenylglycylglycine, m. p. 88°, from which the *N*-phenylglycylglycine is obtained on treatment with sodium hydroxide. Similarly, the ethyl ester of *l*-tyrosine in chloroform at the ordinary temperature yields the *ethyl* ester of *N*-phenylglycyl-*l*-tyrosine, m. p. 155—156°. Similarly, reactions, with evolution of carbon dioxide, take place with formamide, aminoethyl alcohol, and aminoacetaldehyde-acetal, but not with mercaptans. With pyridine, reaction takes place with evolution of carbon dioxide and formation of high-molecular insoluble substance. The anhydride of phenylalanine-*N*-carboxylic acid reacts similarly although more slowly. R. B.

### Synthesis of Aldehydes. H. STEPHEN.—(See i, 1131.)

**An Anhydride (Ether) of a Ketone Hydrate. Benzyl- $\beta$ -phenylethylsuccinic Acids.** J. BOUGAULT (*Compt. rend.*, 1925, **181**, 247—248).—The constitution of the dibasic acid, m. p. 170°, previously described, obtained from an acid amide having the properties of an anhydride of a hydrated ketone (this vol., i, 921), is now confirmed by its synthesis from methyl  $\beta$ -phenylethylsuccinate, which condenses with benzaldehyde in the presence of sodium and ether, the reaction product yielding on hydrolysis  $\alpha$ -benzylidene- $\alpha'$ -( $\beta$ -phenylethyl)succinic acid, m. p. 161°. Acetic anhydride converts the acid into an *anhydride*, m. p. 100°, whilst on reduction with sodium amalgam it yields the acid, m. p. 170°, previously described. The latter is accordingly  $\alpha$ -benzyl- $\alpha'$ -( $\beta$ -phenylethyl)succinic acid. A short treatment with acetic anhydride

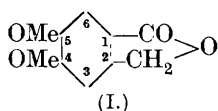
at 100° yields an *anhydride*, m. p. 78°, from which the original acid is regenerated on hydrolysis. Prolonged reaction with acetic anhydride (24 hrs.) at 100°, yields an *anhydride*, m. p. 74°, which on hydrolysis gives an isomeric *acid*, m. p. 125°. Both acids are racemic, but can be resolved with strychnine.  $\beta$ -Phenylethylsuccinic acid was obtained by condensing cinnamaldehyde with malonic acid, reducing the cinnamylidenemalonic acid with sodium amalgam, and warming with alkali, whereby  $\gamma$ -phenylpropylenemalonic acid is formed. The methyl ester of this acid on warming with sodium cyanide yields methyl  $\beta$ -cyano- $\delta$ -phenyl-*n*-valerate, from which  $\beta$ -phenylethylsuccinic acid is produced on hydrolysis.

R. B.

**Nitration of *m*-Meconine.** J. N. RAY and R. ROBINSON (*J. Chem. Soc.*, 1925, **127**, 1618—1623).—An electronic interpretation is given of the neutralisation of the directive power of methoxyl by a nitro group in the *o*- or *p*-position (see Jones and Robinson, T., 1917, **111**, 905), which also explains the failure of the

ester group,  $\text{R}-\text{O}-\text{C}=\text{O}$ , to exhibit marked carbonyl reactivity,

and of the amide group,  $\text{NH}_2-\text{C}=\text{O}$ , to function as a strong basic centre (the arrows symbolise the tendency of bivalent oxygen and trivalent nitrogen to increase the covalency at their single bindings, and of doubly linked oxygen and nitrogen to decrease the covalency). The carbonyl group of phthalide, on the other hand, is more



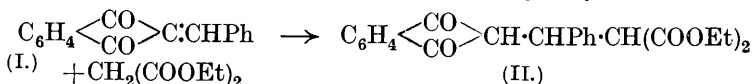
activating than that of an ordinary ester group, i.e., the  $-\text{CO}-\text{O}-$  complex here is less self-satisfying. Accordingly, *m*-meconine (I) should on nitration yield the 6-nitro derivative owing to neutralisation of the directive power of the 4-methoxyl by the active carbonyl. This is actually found to be the case and is inexplicable except on the basis of the electronic conception of valency.

An improved method of preparing *m*-meconine, m. p. 155° (cf. Edwards, Perkin, and Stoye, J., 1925, **127**, 198), is described. Nitration with nitric acid (*d* 1.42) at 0° yields 6-nitro-4 : 5-dimethoxyphthalide, m. p. 183—184°, which condenses with cotarnine (cf. Hope and Robinson, T., 1911, **99**, 1163; P., 1911, **27**, 229) to give *anhydrocotarnine-6-nitro-4 : 5-dimethoxyphthalide*, m. p. 200° (decomp.). 6-Amino-4 : 5-dimethoxyphthalide, m. p. 158°, obtained by reduction of the nitro compound with stannous chloride, is converted by Sandmeyer's method into 6-bromo-4 : 5-dimethoxyphthalide, m. p. 223°, the orientation of which is proved by its identity with the 6-bromo-*m*-meconine prepared from 2-bromoveratric acid, m. p. 200° (from 2-aminoveratric acid by the Sandmeyer reaction), and formaldehyde.

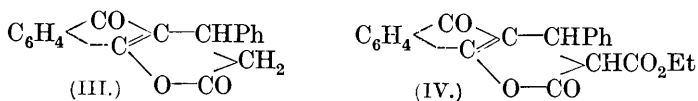
C. H.

**Additive Character of Heterogeneous Conjugated Systems.** M. JONESCU (*Bull. Soc. chim.*, 1925, [iv], **37**, 913—916).—By the condensation of 2-benzylidenediketohydrindene (I), with ethyl malonate in the presence of piperidine, *ethyl phenyl-2-diketohydrindenyl-*

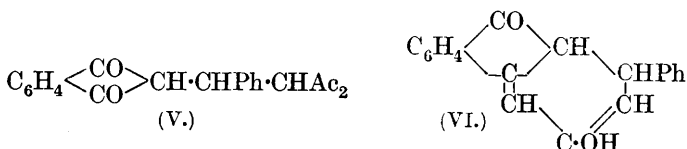
*methoxymalonate*, m. p. 108° (II), is obtained. If the condensation is carried out in the presence of sodium ethoxide, the corresponding *acid ester*, m. p. 112°, is obtained; this is readily hydrolysed to the *acid*,



m. p. 169°, which breaks down on fusion to give  $\beta$ -phenyl- $\beta$ -2-diketohydrindenylpropionic acid, m. p. 173°. The diester and acid ester,



on heating, yield a *lactone*, yellow, m. p. 106°. Cold sulphuric acid converts the diester and acid ester into the *lactone* (III), and the



diacid is converted by heat or treatment with acids into the *lactone*, (IV), m. p. 154°. Acetylacetone condenses with 2-benzylidenediketohydrindene, giving  $\beta$ -acetyl- $\alpha$ -phenyl- $\alpha$ -2-diketohydrindenylbutan- $\gamma$ -one (V), m. p. 111°, which when heated with acetyl chloride yields a mixture of 3-hydroxy-1-phenyl-dihydrofluorenone (VI), m. p. 200°, and 3-hydroxy-1-phenylfluorenone, yellow, m. p. 266°.

Acetylacetone reacts with benzoquinone under the same conditions, giving diacetyldihydroxyindacene, represented by (VII) or a tautomeric form thereof, green, m. p. 300° (decomp.), dissolving in alkalis giving a violet solution. The formation of these compounds is explicable on Thiele's theory of conjugated valencies.

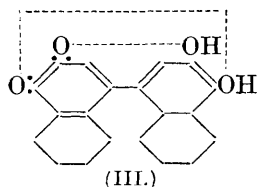
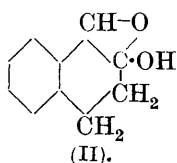
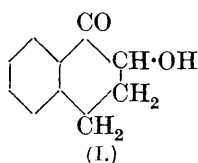
L. F. H.

### Therapeutic Compounds [Mercuri Compounds of Phenols].

WELLCOME FOUNDATION, LTD., T. A. HENRY, and T. M. SHARP (Brit. Pat. 237735).—When 2-acetoxymercuri-3-hydroxybenzaldehyde (T., 1922, **121**, 1059) is dissolved in warm *n*-hexoic acid and the solution allowed to cool, there separates 3-hydroxybenzaldehyde-2-mercuri-*n*-hexoate,  $\text{OH} \cdot \text{C}_6\text{H}_3(\text{CHO}) \cdot \text{Hg} \cdot \text{O} \cdot \text{CO} \cdot \text{C}_5\text{H}_{11}$ , m. p. 140°. In a similar manner are prepared the corresponding -*n*-octoate, m. p. 130—131°, the -*laurate*, m. p. 131—133°, -*myristate*, m. p. 130°, decomp. 200°, -*oleate*, m. p. 110—115°, and -*chaulmoograte*, m. p. 135°. By the action of mercuric acetate on *p*-tert.-butylphenol in alcohol in presence of acetic acid, 4-hydroxy-tert.-butylbenzene-3:5-dimercuri-acetate, decomp. 224°, is formed, which can be converted by lauric acid into the corresponding -*dimercurilaurate*, m. p. 120°. These

compounds containing higher acyl groups have the advantage of being soluble in oils. E. H. R.

**Hydrogenated Naphthalenes. VI.  $\alpha$ -2-Hydroxy-1-ketotetrahydronaphthalene and  $\beta$ -Naphthaquinol. Autoxidation of Polyhydric Phenols.** F. STRAUS, O. BERNOULLY, and P. MAUTNER (*Annalen*, 1925, **444**, 165—194; cf. this vol., i, 1138).— $\alpha$ -2-Acetoxy-1-ketotetrahydronaphthalene, m. p. 74·5—75°, b. p. 180°/20 mm., is obtained, together with  $\alpha$ - and  $\beta$ -naphthols, when 2-bromo-1-ketotetrahydronaphthalene (m. p. 40°, b. p. 124°/0·5—1·0 mm.; cf. Straus and Rohrbacher, A., 1921, i, 171) is boiled with glacial acetic acid and sodium acetate. The free 2-hydroxy-1-ketotetrahydronaphthalene (I), m. p. 36—36·5°, b. p. 93°/0·1 mm., is obtained by hydrolysing the above acetyl derivative with aqueous methyl-alcoholic potassium carbonate in absence of oxygen or air. It reduces Fehling's solution and becomes brown when kept. Both the hydroxytetralone and its acetyl derivative yield  $\beta$ -naphthol when warmed with mineral acids, possibly through tautomerisation to the cyclic derivative (II). The direct action of alkalis on 2-bromo- $\alpha$ -tetralone affords  $\alpha$ -tetralone (1-ketotetrahydronaphthalene), to-



gether with coloured products. Silver oxide and potassium formate are without action, whilst piperidine, in presence of air or oxygen, yields *piperidino-1-ketotetrahydronaphthalene* (bimolecular),  $C_{30}H_{38}O_2N_2$ , m. p. 242·5—243° (decomp.), which is decomposed by alkalis with formation of  $\alpha$ -tetralone. In alkaline solution, 2-hydroxy- $\alpha$ -tetralone undergoes autoxidation in presence of atmospheric oxygen, with successive formation of  $\beta$ -naphthaquinol, 3:4:3':4'-tetrahydroxy-1:1'-dinaphthyl, dinaphthylquinhydrone (III), and naphthalinic acid (2-hydroxy- $\alpha$ -naphthaquinone), each of which, except the quinhydrone, can be isolated by using the appropriate proportion of oxygen.

$\beta$ -Naphthaquinol forms a *monohydrate*, m. p. 58—60°, which yields the anhydrous material, m. p. 102·5—103°, when dried over calcium chloride or in a vacuum over sulphuric acid, or when crystallised from ligroin or carbon disulphide. 3:4:3':4'-Tetrahydroxy-1:1'-dinaphthyl (cf. Stenhouse and Groves, *Annalen*, 1878, 194, 208; Bamberger, A., 1923, i, 1142) has m. p. 205—210°. The *tetramethyl ether*, m. p. 145—147°, b. p. 200—220°/0·67 mm., is described. Dinaphthylquinhydrone (cf. Stenhouse and Groves, *loc. cit.*) has m. p. 252° after sintering at 245°, and decomposes at 255°.

The rate of absorption of oxygen by the hydroxytetralone is reduced when the initial amount of oxygen present is increased,

indicating that the end-product of the oxidation is in part produced by reactions not involving the formation of the above intermediates.

F. G. W.

**Relation between Chemical Constitution and Pungency. Synthesis of the Reduction Products of Zingerone and Di- $\beta$ -4-hydroxy-3-methoxyphenylethyl Ketone.** H. NOMURA and S. HOTTA (*Sci. Rep. Tōhoku Imp. Univ.*, 1925, **14**, 119—125; cf. Nomura and Nozawa, A., 1918, i, 438).—A study of the reduction products of zingerone ( $\beta$ -4-hydroxy-3-methoxyphenylethyl methyl ketone) shows that the presence of the carbonyl group in the side chain is not essential to its pungent taste, although it has some effect. On reduction with sodium and boiling absolute alcohol, zingerone yields  $\beta$ -4-hydroxy-3-methoxyphenylethylmethylcarbinol, b. p. 196—197°/17 mm. (diacetyl derivative, b. p. 209.5—210.5°/15.5 mm.), whilst the Clemmensen method (amalgamated zinc and concentrated hydrochloric acid) yields the hydrocarbon,  $\alpha$ -4-hydroxy-3-methoxyphenyl-*n*-butane, b. p. 141—142°/13.5 mm. (benzoyl derivative, m. p. 92.5—93°). Both products have a pungent taste similar to zingerone. Condensation of vanillin and acetone in the presence of hydrochloric acid, *d* 1.18, yields *di*-4-hydroxy-3-methoxystyryl ketone, yellow, m. p. 141.5—142.5° (monohydrate, m. p. 115.5—119.5°), which on reduction either with hydrogen and platinum black or sodium amalgam and water yields *di*- $\beta$ -4-hydroxy-3-methoxyphenylethyl ketone, colourless, m. p. 89.5—90.5° (dibenzoyl derivative, m. p. 129—130°), which is almost tasteless in the solid state, but slightly pungent in alcoholic solution. On methylation with methyl sulphate, this yields *di*- $\beta$ -3 : 4-dimethoxyphenylethyl ketone, colourless, m. p. 83.5—84.5°, oxime, m. p. 138.5—139.5°. J. W. B.

**Condensation of Vanillin with Methyl Ethyl Ketone.** J. ICHIKAWA (*Sci. Rep. Tōhoku Imp. Univ.*, 1925, **14**, 127—129; cf. preceding abstract).—Vanillin condenses with methyl ethyl ketone in the presence of sodium hydroxide to produce 4-hydroxy-3-methoxystyryl ethyl ketone, m. p. 91—92°, which on reduction with hydrogen and platinum-black yields  $\beta$ -4-hydroxy-3-methoxyphenylethyl ethyl ketone, b. p. 187—188°/11.5 mm., which has a pungent taste. When dry hydrogen chloride is used as the condensing agent, a divanillylidene derivative of methyl ethyl ketone is formed, which darkens at 255°, instead of the expected  $\alpha$ -vanillylidene-ethyl methyl ketone. J. W. B.

**Synthesis of the Homologues of Zingerone.** H. NOMURA and S. HOTTA (*Sci. Rep. Tōhoku Imp. Univ.*, 1925, **14**, 131—141).—The homologues of zingerone are synthesised by the condensation of vanillin with various alkyl methyl ketones in the presence of sodium hydroxide, followed by the reduction of the unsaturated product with sodium amalgam in aqueous suspension. The condensation proceeds less readily as the molecular weight of the ketones increases. The following new compounds are obtained in this manner from the appropriate ketone :  $\beta$ -4-hydroxy-3-methoxyphenylethyl ethyl ketone, m. p. 36—37°, b. p. 201—204°/28 mm.



(Ichikawa, preceding abstract, gives 187—188°/11.5 mm.), *benzoyl* derivative, m. p. 118—119°; this on methylation gives  $\beta$ -3:4-dimethoxyphenylethyl ethyl ketone, m. p. 26.5—27.5°, b. p. 183—184°/12 mm., *oxime*, m. p. 120—120.5°, *semicarbazone*, m. p. 143—144°; 4-hydroxy-3-methoxystyryl *n*-propyl ketone, faint yellow, m. p. 82.5—83.5°;  $\beta$ -4-hydroxy-3-methoxyphenylethyl *n*-propyl ketone, m. p. 44.5—45°, b. p. 198°/14 mm., *benzoyl* derivative, m. p. 107.5—108.5°;  $\beta$ -3:4-dimethoxyphenylethyl *n*-propyl ketone, b. p. 198—199°/17 mm., *oxime*, m. p. 94.5—95.5°; 4-hydroxy-3-methoxystyryl *n*-butyl ketone, faint yellow, m. p. indefinite 66—100° (contains approximately 1 mol. of water);  $\beta$ -4-hydroxy-3-methoxyphenylethyl *n*-butyl ketone, m. p. 47.5—48°, b. p. 213—214°/23 mm., *benzoyl* derivative, m. p. 91—91.5°;  $\beta$ -3:4-dimethoxyphenylethyl *n*-butyl ketone, b. p. 205—206°/20 mm., *oxime*, m. p. 111—112°; 4-hydroxy-3-methoxystyryl isobutyl ketone, faint yellow, m. p. 78—79°, b. p. 233—234.5°/20 mm.;  $\beta$ -4-hydroxy-3-methoxyphenylethyl isobutyl ketone, b. p. 210°/19 mm., *benzoyl* derivative, m. p. 81.5—82.5°,  $\beta$ -3:4-dimethoxyphenylethyl isobutyl ketone, b. p. 202°/17 mm., *oxime*, m. p. 114—114.5°, *semicarbazone*, m. p. 123.5—124.5°;  $\beta$ -4-hydroxy-3-methoxyphenylethyl *tert*-butyl ketone, m. p. 76—80°, b. p. 196.5—198°/16 mm., *benzoyl* derivative, m. p. 57.5—58°;  $\beta$ -3:4-dimethoxyphenylethyl *tert*-butyl ketone, m. p. 46.5—47.5°, *oxime*, m. p. 114.5—115.5°, *semicarbazone*, m. p. (after drying under reduced pressure) 127—128°. The isomeric 4-hydroxy-3-methoxyphenylethyl butyl ketones containing the *n*-, *iso*-, or *tert*-butyl groups are all equally pungent. J. W. B.

**Preparation of Zingerone.** H. NOMURA (*Sci. Rep. Tōhoku Imp. Univ.*, 1925, **14**, 143—144).—Zingerone may be obtained in 76% yield by the reduction of 4-hydroxy-3-methoxystyryl methyl ketone by sodium amalgam in aqueous suspension. J. W. B.

**Synthesis of a Homologue of Zingerone, 4-Hydroxy-3-methoxyphenylethyl *n*-Amyl Ketone.** J. MURAI (*Sci. Rep. Tōhoku Imp. Univ.*, 1925, **14**, 144—145; cf. preceding abstracts).—Vanillin condenses with methyl *n*-amyl ketone to yield 4-hydroxy-3-methoxystyryl *n*-amyl ketone, m. p. 50—50.5°, which on reduction with sodium amalgam in aqueous suspension yields  $\beta$ -4-hydroxy-3-methoxyphenylethyl *n*-amyl ketone, m. p. 37.5—38°, b. p. 196—197°/5.5 mm. (*benzoyl* derivative, m. p. 79.5—80°), and on methylation yields  $\beta$ -3:4-dimethoxyphenylethyl *n*-amyl ketone, b. p. 192°/5 mm., *oxime*, m. p. 97.5—98°. J. W. B.

**Synthesis of *m*-Hydroxyphenylethyl Methyl Ketone and  $\beta$ -3-Hydroxy-4-methoxyphenylethyl Methyl Ketone (*iso*Zingerone).** J. MURAI (*Sci. Rep. Tōhoku Imp. Univ.*, 1925, **14**, 149—154).—By the condensation of *m*-nitrobenzaldehyde and acetone in the presence of sodium hydroxide, reduction of the *m*-nitrostyryl methyl ketone (cf. Vorländer, A., 1897, i, 272) to the amino compound by ferrous sulphate and ammonia (cf. Miller and Rhode, A., 1890, 1138), and replacement of the amino group by hydroxyl, *m*-hydroxy-

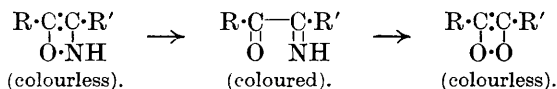
styryl methyl ketone (cf. Nomura and Nozawa, A., 1918, i, 438), is obtained. On reduction, it yields  $\beta$ -*m*-hydroxyphenylethyl methyl ketone, m. p. 85.5—86°, benzoyl derivative, b. p. 222—223°/4.5 mm., semicarbazone of benzoyl derivative, m. p. 162—162.5°. *iso*Vanillin condenses with acetone in the presence of hydrochloric acid (*d* 1.18), and the product by reduction yields  $\beta$ -3-hydroxy-4-methoxyphenylethyl methyl ketone (*isozingerone*), b. p. 159—160°/4 mm., benzoyl derivative, b. p. 235—236°/4 mm., semicarbazone of benzoyl derivative, m. p. 140—140.5°. *iso*Zingerone is more pungent than *m*-hydroxyphenylethyl methyl ketone, the pungency of the latter being increased by the presence of the methoxy group in the para-position to the side chain.

J. W. B.

**Hydroxybenzils.** J. T. MARSH and H. STEPHEN (*J. Chem. Soc.*, 1925, 127, 1633—1637).—The preparation of eight colourless di- and tri-hydroxybenzils by an extension of the Hoesch reaction to acyl cyanides is described. The products do not show ketone reactions, nor do they undergo the benzilic acid transformation; a peroxide structure is therefore suggested. No pure stable coloured forms have been obtained.

By treatment of acid chlorides and dry pyridine in anhydrous ether solution with pure hydrogen cyanide (cf. Claisen, A., 1898, i, 423), the following acyl cyanides were prepared: Benzoyl cyanide, m. p. 32°; *o*-methoxybenzoyl cyanide, m. p. 56°, b. p. 161°/12 mm.; *p*-methoxybenzoyl cyanide, m. p. 63—64°, b. p. 150°/12 mm.; 3:4:5-trimethoxybenzoyl cyanide, m. p. 136—137°; cinnamoyl cyanide (cf. Claisen and Moritz, A., 1881, 154), m. p. 114—115°. In the preparation of methoxy- and trimethoxy-benzoyl chlorides, heating with thionyl chloride for more than  $\frac{1}{2}$  hr. leads to demethylation.

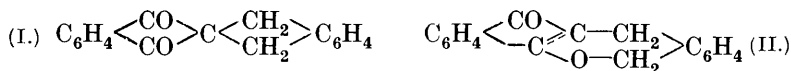
The acyl cyanides condense with resorcinol or phloroglucinol in dry ether saturated with hydrogen chloride, giving colourless ketimines, which are converted by boiling sodium acetate solution (or more slowly by dilute hydrochloric acid) into the benzils, the solutions passing through golden-brown to pale yellow:



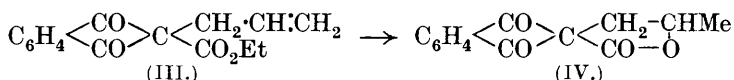
The following benzils are described: 2:4-Dihydroxybenzil, m. p. 239° (diacetate, m. p. 159°); 2:4-dihydroxy-2'-methoxybenzil, m. p. 223° (diacetate, m. p. 144°); 2:4-dihydroxy-4'-methoxybenzil, m. p. 234° (diacetate, m. p. 178.5°); 2:4-dihydroxy-3':4':5'-trimethoxybenzil, m. p. 257° (diacetate, m. p. 155°); 2:4:6-trihydroxybenzil, m. p. 287° (triacetate, m. p. 248°); 2:4:6-trihydroxy-2'-methoxybenzil, m. p. 235° (triacetate, m. p. 135°); 2:4:6-trihydroxy-4'-methoxybenzil, m. p. 262° (triacetate, m. p. 241°); 2:4:6-trihydroxy-3':4':5'-trimethoxybenzil, m. p. 187° (triacetate, m. p. 258°). All these hydroxybenzils darken some degrees below their m. p.

C. H.

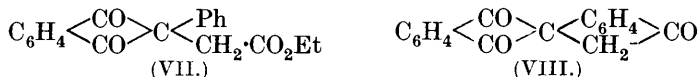
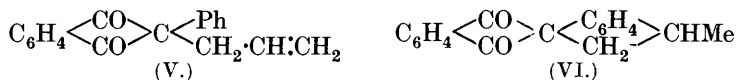
**Colour of Spirans.** D. RADULESCU (*Bull. Soc. chim.*, 1925, [iv], **37**, 916—918).—The spiro-carbon atom does not play the part of a chromophor (cf. Schlenk and Blum, A., 1923, i, 1235; Radulescu, A., 1923, i, 1211, A., 1924, i, 58, 215). From this consideration and from its stability towards alkali and its reactions with phenylhydrazine etc., it is concluded that the substance described by Fecht (A., 1907, i, 906) as xylylenediketohydrindene (I) has in



reality the constitution (II). By the action of hydrobromic acid on ethyl 2-allyldiketohydrindene-2-carboxylate (III), the *spiran* (IV),



m. p. 120—121°, *bromo* derivative, m. p. 154°, is obtained. On treating the hydrobromide of 2-phenyl-2-allyldiketohydrindene (V)



with aluminium bromide the *spiran* (VI), m. p. 129—131°, is obtained, and (VII) yields the *spiran* (VIII), m. p. 170—171°, on treatment with sulphuric acid. All these substances are colourless.

L. F. H.

### Preparation and Properties of Naphthaquinonearylimines.

R. LANTZ and A. WAHL (*Bull. Soc. chim.*, 1925, [iv], **37**, 890—901).—An account of work already published (this vol., i, 820, 911). In addition,  $\beta$ -naphthaquinone-1-o-methoxyanil is described, obtained by the oxidation of 1-o-anisidino- $\beta$ -naphthol. 2-Hydroxy- $\alpha$ -naphthaquinonedianil (*loc. cit.*) is capable of existing in the tautomeric form, 4-anilino- $\beta$ -naphthaquinone-1-anil.

L. F. H.

### Wandering of the Acetyl Group during Methylation.

O. KUBOTA and A. G. PERKIN (*J. Chem. Soc.*, 1925, **127**, 1889—1896).—A reinvestigation of the action of diazomethane on 2-acetylalizarin has shown that although a small amount of the 1-methyl ether is always formed (cf. Oesch and Perkin, *Proc. Chem. Soc.*, 1914, **30**, 213) the main product of the reaction is 2-methoxy-1-acetoxyanthraquinone, obtained in 80% of the theoretical amount. Similarly, 2 : 3-Diacetylanthragallol when methylated gave as chief product a *diacetylanthragallol 2-monomethyl ether* (yellow prismatic needles, m. p. 152—154°), which on hydrolysis gave a substance which dissolved in alkalis with a red colour and must therefore be *anthragallol 2-monomethyl ether* (yellow, microscopic needles, m. p.

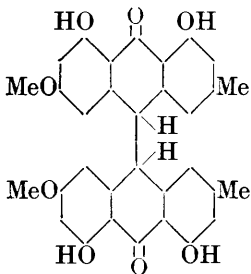
218—220°), since the alkali solutions of the 1- and 3-methyl ethers are blue or bluish-violet. From the filtrate anthragallol 1-methyl ether was isolated. In the methylation of 3 : 7 : 3' : 4'-tetra-acetyl-quercetin no migration of the acetyl group was observed. A sparingly soluble quercetin monomethyl ether was obtained as final product which resembled, but was not identical with rhamnetin. Since by decomposition with alcoholic potassium hydroxide it yielded phloroglucinol monomethyl ether the substance was evidently *quercetin 5-methyl ether* (m. p. 305—308°; *tetra-acetyl* derivative, m. p. 202—204°; *monopotassium* salt, lemon-yellow needles). As quercetin forms a similar salt the reactive hydroxyl in salt formation is not situated in the 5-position. The methylation of this hydroxyl group has no influence on the tinctorial property of quercetin, and as quercetin and rhamnetin dye alike, evidently the phloroglucinol hydroxyl groups of quercetin do not affect its tinctorial property. F. R.

### Reduction Products of the Hydroxyanthraquinones. VI.

A. G. PERKIN and G. YODA (*J. Chem. Soc.*, 1925, **127**, 1884—1888).—The impure dihydroxydianthraquinone obtained by Perkin and Haller (A., 1924, i, 300) has now been prepared in good yield from tetra-acetyldihydroxydianthranol. The latter substance on treatment in pyridine solution with iodine and boiling with acetic anhydride gives 3 : 6'-*diacetoxydianthraquinone*; the m. p. after repeated crystallisation from acetic anhydride remained constant at 293—295°, but was raised to 314—316° by recrystallisation from tetrachloroethane. On exposure to light in benzene solution, the substance slowly changed into diacetoxynaphthodianthrone. Alkaline hydrolysis of diacetoxydianthraquinone yielded 3 : 6'-*dihydroxydianthraquinone*, pale yellow, blackening at 280°, no definite m. p. It gives a yellow solution with alkalis, and a maroon-coloured liquid with sulphuric acid. A solution of the substance in alcohol on exposure to light deposited crystals which on acetylation gave diacetoxynaphthodianthrone and a little diacetoxyhelianthrone. By oxidation with alkaline ferricyanide and acetylation, diacetoxyhelianthrone was obtained. *Dibenzoyldihydroxydianthraquinone*, yellow, darkens at 295°, m. p. 301—302°. Methylation of dihydroxydianthraquinone gave *dimethoxydianthraquinone*, m. p. 297—299°. When its acetone solution is evaporated in daylight the substance becomes rapidly converted into dimethoxynaphthodianthrone and dimethoxyhelianthrone. F. R.

[**Composition of**] **Chrysarobin**. R. EDER and F. HAUSER (*Arch. Pharm.*, 1925, **263**, 436—451; cf. this vol., i, 948, and Tutin and Clewer, T., 1912, **101**, 290).—Dehydroemodinanthranol monomethyl ether, (A),  $C_{32}H_{26}O_8$ , m. p. 270° (after darkening at 265°), is insoluble in cold 2% sodium hydroxide solution but in a 5% solution gives a yellow solution which becomes darker. Its solution in pyridine or aniline, when boiled, becomes green, then brown, and finally red. The amorphous substance recovered from this treatment undergoes autoxidation in alkaline solution to

give dark brown needles of emodin monomethyl ether, m. p. 205°, which is also the sole product of oxidation of A by chromic anhydride in glacial acetic acid solution. Reduction of A by zinc and acetic acid gave emodinanthrone monomethyl ether. Acetylation requires carefully regulated conditions and yields the *tetra*- or *penta*-acetyl derivative, m. p. 233—234°. The mol. wt. of A is established by cryoscopic examination of A and of its acetyl and benzoyl derivatives in molten camphor; and the annexed formula is proposed for it (cf. dianthrone, H. Meyer, A., 1913, i, 62).



The yellow non-autooxidisable constituent of chrysarobin, ararobinol,  $C_{30}H_{22}O_6$ , m. p. 224—225° (after darkening at 218°), is difficult to purify, being unstable in solution and developing colour and fluorescence. It is oxidised by chromic anhydride to chrysophanic acid, m. p. 193°, and reduced by means of zinc and acetic acid to chrysophanic acid anthrone, m. p. 203°, readily oxidised in alkaline solution to chrysophanic acid. A *penta*- or *tetra*-acetyl derivative of ararobinol is described, m. p. 235—236° (with previous darkening), the mol. wts. confirming the new formula proposed. From these facts it appears that ararobinol is related to chrysophanic acid anthrone as the substance A is related to emodinanthrone monomethyl ether. These four substances give characteristic colour changes, when warmed with concentrated sulphuric acid, which emphasise their close relationship. The substance termed "dihydroararobinol," m. p. 180°, isolated by Tutin and Clewer from the products of a Zeisel reaction, is now shown to be chrysophanic acid anthrone. G. M. B.

**Camphane Series. XL. Constitution of Manasse's Hydroxycamphor.** M. O. FORSTER and P. P. SHUKLA (*J. Chem. Soc.*, 1925, 127, 1855—1860).—Camphorquinone reduced hot with zinc and acetic acid or with aluminium amalgam in the cold gave a crude product from which by recrystallisation Manasse's "α"-hydroxycamphor, m. p. 203—205°, was obtained (A., 1903, i, 45). Conversion into the methyl ether and hydrolysis gave the corresponding "β"-hydroxycamphor, m. p. 215° (*loc. cit.*). By treatment of the crude product and specimens of the "α" and "β" modifications with magnesium methyl iodide there was obtained in each case the quantitative amount of methane for one hydroxyl group, whilst the methyl ether did not react with the Grignard reagent. Evidently therefore the "α"- and "β"-hydroxycamphors cannot be represented by the conventional formulæ, and even such an equilibrium as  $-CH(OH) \cdot CO- \rightleftharpoons -C(OH) : C(OH)-$  is precluded. Further, the "β" modification gave with phthalic anhydride a *camphoryl hydrogen phthalate* (rectangular plates, m. p. 164—165°), whilst the "α" modification by similar treatment gave a product, m. p. 152—156°, which was resolved into a mixture of the foregoing substance with an isomeric *camphoryl*

*hydrogen phthalate* (needles, m. p. 147°). Following a suggestion of Karrer and Takashima (this vol., i, 940) that the solid methyl ether is a *cycloacetal*, the following constitutions are proposed for the methyl ether (I) and the "β"-hydroxycamphor (II). The "α" modification is probably the latter substance associated with



a variable amount of the stereoisomeride in which the hydroxyl group and hydrogen atom occupy the alternate plane.

It has not been possible to decide whether hydrolysis of the two camphoryl hydrogen phthalates leads to the respective parents, because, on following the hydrolysis polarimetrically, there is indication of concurrent mutarotation in the hydroxycamphor regenerated. F. R.

**Chenopodium Oil. II. The Hydrocarbon Fraction.** T. A. HENRY and H. PAGET (*J. Chem. Soc.*, 1925, **127**, 1649—1659; cf. T., 1921, **119**, 1714).—Nelson's terpene tetrabromide (*J. Amer. Chem. Soc.*, 1920, **42**, 1204), obtained by bromination of the hydrocarbon fraction of chenopodium oil, is shown to be derived most probably from  $\Delta^2:8(9)$ -*p*-menthadiene. The presence also of *l*-limonene and possibly of *n*-butylene-ββ-oxide in the oil is demonstrated.

The first runnings of the hydrocarbon fraction yielded an oil, b. p. 64—78°,  $d_{15}^{15}$  0.837,  $n_D^{20}$  1.3968—1.3981,  $[\alpha]_D^{15}$  +0.10°, consisting probably of impure *n*-butylene βγ-oxide. Repeated fractionation of the main portion, b. p. 170—185°, gave nine fractions, all levorotatory and all containing α-terpinene. Nelson's tetrabromide, m. p. 117°, was obtained only from fractions 1—4 (b. p. 170—175.5°). From fractions 6—8 (b. p. 176—180°), together with the higher-boiling part of 4, α-terpinene was removed by means of Beckmann's chromic acid mixture (Henry and Paget, *loc. cit.*, 1717), leaving a mixture, the analysis of which corresponded with 40% of terpene and 60% of *p*-cymene, and from which 63% of *p*-cymene was isolated by oxidation with permanganate in acetone. This mixture, on bromination, gave *l*-limonene tetrabromide, m. p. 104°,  $[\alpha]_D^{16}$  —66.12°, obtained crystalline after distilling off most of the *p*-cymene in a vacuum. From the oxidation of the mixture with permanganate in acetone there was isolated with considerable difficulty an oily acid,  $\text{C}_9\text{H}_{14}\text{O}_5$ , b. p. 210°/34 mm. (sodium, barium, and silver salts described), which is probably the lactone of αε-dihydroxy-β-carboxymethylheptoic acid,

$\text{CHMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_2\cdot\text{CO}_2\text{H})\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , since further oxidation with chromic acid yields lævulic acid and acetic acids. When the oxidation of the mixture of *l*-limonene and *p*-cymene was performed in aqueous solution, the isolable products were cuminaldehyde (semicarbazone, m. p. 210°) and isopropenylbenzoic acid, m. p. 159—160°, from the cymene, and hydroxyterpenylic acid, m. p. 195°, and lævulic acid (semicarbazone,

m. p. 194°) from the limonene (commercial limonene similarly oxidised gave these two acids).

The terpene ("terpene A") corresponding with Nelson's tetrabromide could not be isolated. The tetrabromide from fractions 1—4 (see above) gave, by treatment with sodium methoxide, an oil,  $C_{10}H_{14}Br \cdot OMe$ , b. p. 115—118°/18 mm., and eventually *p*-cymene. This methyl ether was oxidised slowly by chromic acid or permanganate to *p*-tolyl methyl ketone and *p*-toluic acid.

A bromoacetoxylhydro-*p*-cymene,  $CH_2Br \cdot CMe(OAc) \cdot \overset{CH \cdot CH \cdot CMe}{\underset{CH_2 \cdot CH_2}{|}}$ , yielding on oxidation *p*-tolyl methyl ketone, terephthalic acid, and *p*-toluic acid, was obtained from the tetrabromide by the action of silver acetate.

Oxidation of the total hydrocarbon fraction by chromic acid yielded a keto-alcohol,  $C_{10}H_{16}O_2$ ,  $\overset{CHMe \cdot CO \cdot CH \cdot OH}{\underset{CH_2 \cdot CH_2 \cdot CH \cdot CMe \cdot CH_2}{|}}$ , b. p. 110—136°/15 mm. The semicarbazone, m. p. 157° (+AcOH) or 204° (dried at 120° in a vacuum), readily lost the elements of water to form an anhydro-base (acetate, m. p. 206°; picrate, m. p. 158°), as is characteristic of *o*-hydroxyketones. The mother-liquor from the preparation of the semicarbazone gave on dilution an oily  $\alpha$ -terpinene derivative, oxidisable by permanganate to a mixture of *anti*- and *para*- $\alpha\delta$ -dihydroxy- $\alpha$ -methyl- $\delta$ -isopropyladipic acid, m. p. 189°. In addition to the keto-alcohol, the chromic acid oxidation gave dimethylacetylacetone (semicarbazone, m. p. 201°) and *p*-tolyl methyl ketone. The keto-alcohol could not be obtained by oxidation of terpinene, *d*-limonene, or *p*-cymene, and is thus most probably derived from terpene A.

Oxidation of the total hydrocarbon fraction with permanganate in acetone yielded, in addition to the products already mentioned as derived from terpinene and *p*-cymene, and *l*-limonene, a very small amount of a ketone,  $C_9H_{14}O$  (semicarbazone, m. p. 204°), which, if derived from terpene A, should be  $\Delta^2$ -tetrahydro-*p*-tolyl methyl ketone.

Terpene A may be identical with Tschugaev's isolimonene (A., 1905, i, 71) and Aschan's diprene (A., 1924, i, 1212). C. H.

**Action of Hydrogen Peroxide on Limonene.** J. SWORD (J. Chem. Soc., 1925, 127, 1632—1633).—Limonene (b. p. 175.5—176.5°,  $d^{15}_4$  0.8453,  $n^{15}_D$  1.4759,  $[\alpha]^{15}_D$  +96.89°) from oil of bitter orange, shaken for 14—18 days in glacial acetic acid with gradual addition of "perhydrol" (2 mols.), is oxidised, forming as main product  $\Delta^{8(10)}$ -*p*-menthen-1 : 2-diol, m. p. 67.5°, b. p. 140—143°/10 mm. (Priesschaev, A., 1910, i, 86), together with small amounts of terpin hydrate, m. p. 116—117°, and an oil (*p*-nitrobenzoate, m. p. 79°; dihydrobromide,  $C_{10}H_{16} \cdot 2HBr$ , m. p. 44—45°) which forms a monosodium derivative, and on distillation with steam yields an oil which no longer gives a *p*-nitrobenzoate. C. H.

**Terpenes. II. Synthesis of Diterpenes.** I. KONDAKOV and S. SAPRIKIN (Bull. Soc. chim., 1925, [iv], 37, 918—934).—From

consideration of the literature of the synthetic diterpenes (cf. Henry, T., 1901, **79**, 1144; Semmler, A., 1913, i, 742; 1909, i, 110, 171; Semmler and Rosenberg, A., 1913, i, 377; Semmler and Jonas, A., 1913, i, 742; Semmler and Jakubowicz, A., 1914, i, 973; Weber, A., 1902, i, 552; Uchida, A., 1916, i, 218; Frankforter and Poppe, A., 1913, i, 987; Brooks, A., 1918, i, 286; Bourchardat and Lafont, A., 1893, i, 223; Kondakov and Schindelmeiser, A., 1903, i, 350; Kursanoff, A., 1901, i, 553) it is concluded that the physical constants given are in a number of cases inaccurate, that all are probably optically inactive, and that no crystalline derivatives of the synthetic products can be obtained. The diterpenes obtained from caoutchouc and from  $\alpha$ -pinene by Semmler (*loc. cit.*) appear to be closely similar. L. F. H.

**Crystalline Form and Optical Properties of Cadinylenesulphochloride.** V. KARANDÉEV (*Bull. Acad. St. Pétersbourg*, 1915, [6], 1919—1926; from *Chem. Zentr.*, 1925, i, 2557).—Cadinylenesulphochloride (Lepeschkin) has. m. p. 101—102°. Its empirical formula is  $C_{15}H_{17}O_2SCl$ . It forms monoclinic crystals,  $a:b:c = 1.4665:1:1.2254$ ;  $\beta = 98^\circ 42'$ ; cleavage along the plane {110}. The plane of the optical axis is parallel to (010). The principal refractive indices are  $\alpha_D = 1.5028$ ,  $\beta_D = 1.6162$ ,  $\gamma_D = 1.7530$ ;  $\alpha_F = 1.5110$ ,  $\beta_F = 1.6350$ ,  $\gamma_F = 1.7856$ . G. W. R.

**Kachi-grass Oil.** B. S. RAO and J. J. SUDBOROUGH (*J. Indian Inst. Sci.*, 1925, **8A**, 9—27).—Kachi-grass oil (from *Cymbopogon caesioides*) resembles ginger-grass oil closely in properties and, like the latter, contains dipentene, limonene, geraniol, and perillal alcohol (A., 1911, i, 218). [Cf. B., 1925, 783.] G. M. B.

**Essential Oil of *Cyperus rotundus*.** B. S. RAO, P. B. PANICKER, and J. J. SUDBOROUGH (*J. Indian Inst. Sci.*, 1925, **8A**, 39—47).—Steam-distillation of the tubers of the Indian *Cyperus rotundus* yields 0.7% of an oil which differs appreciably from the Soudanese oil in physical constants. No pure substance was isolated from the oil, but there are present at least two sesquiterpenes, two or more alcohols, probably tertiary, and large quantities of neutral substances of high b. p. G. M. B.

**Indian Essential Oils.** B. S. RAO, J. J. SUDBOROUGH, and H. E. WATSON (*J. Indian Inst. Sci.*, 1925, **8A**, 143—188).—The yields and physical constants of a large number of known essential oils are recorded as obtained from Indian plants. The roots of a camphor tree yielded 7.9% of an oil giving 25% of camphor on steam-distillation. The oil contained only 0.2% of safrole. An East Indian oil of fennel contained 6% of fenchone, and also borneol. [Cf. B., 1925, 782.] G. M. B.

**Indian Essential Oils. XIII. Essential Oil from a New Species of *Andropogon* Occurring in the Etawah District, U.P.** J. L. SIMONSEN (*Indian Forest Rec.*, 1924, **10**, 153—165).—The flower heads of a new species of *Andropogon* yield on steam distillation 0.4—0.5% of an oil containing: *d*- $\Delta^4$ -carene; *d*-cadinene; *d*-caryo-



phyllene; *d*-piperitol, b. p. 165—170°/200 mm.,  $d_{30}^{30}$  0.911,  $n_D^{30}$  1.474,  $[\alpha]_D^{30} +46^\circ$ , which on dehydration yields  $\alpha$ -terpinene; a sesquiterpene alcohol,  $C_{15}H_{24}O$ , b. p. 165—167°/16 mm.,  $d_{30}^{30}$  0.9497,  $n_D^{30}$  1.5000,  $[\alpha]_D^{30} +8.5^\circ$ ; and *n*-hexoic, *n*-octoic, and palmitic acids (from the ester fraction). The genetic and stereochemical relationships of *d*- $\Delta^4$ -carene, *d*-piperitol, and *d*-piperitone are discussed. B. F.

**Chemical Composition of *Asperula odorata* (Woodruff). Extraction and Properties of a New Glucoside, Asperuloside.** H. HÉRISSEY (*J. Pharm. Chim.*, 1925, [viii], 2, 177—185; cf. Bourquelot and Hérisséy, A., 1920, i, 586; Herboth, this vol., i, 760).—By extraction of *Asperula odorata* with boiling alcohol and recrystallisation of the extract from ethyl acetate, 0.05% of a new glucoside, *asperuloside*, colourless, m. p. 126—127° (corr.),  $[\alpha]_D -204.4^\circ$ ,  $M$  409, is obtained. It is free from nitrogen, and on hydrolysis with acids or emulsin yields 43—45% of dextrose and a brown precipitate, *asperuligenol*. L. F. H.

### Nature of the Reaction between Tannin and Carbohydrates.

**I. Comparative Study of the Interaction of Tannin with Gelatin and Certain Carbohydrates.** H. B. STOCKS and C. V. GREENWOOD (*J. Soc. Leather Trades Chem.*, 1925, 2, 315—322).—Tragasol, a galacto-mannan, is precipitated by gallotannic acid in the same way as gelatin and albumin over a range of  $p_H$  values, but no precipitation occurs at  $p_H$  4.0, the corresponding figure for gelatin being about  $p_H$  8.0. Tragasol films absorb gallotannic acid readily from solutions of various concentrations and combine with it. Gelatin films absorb solutions of gallotannic acid but do not combine with the tannin. Tragasol and gelatin when present together in solution are precipitated by means of gallotannic acid as a complex containing gelatin, tragasol, and gallotannic acid. D. W.

**Tannins and Similar Substances. XX. Conversion of Cyanidin into Catechin.** K. FREUDENBERG, H. FIKENTSCHER, M. HARDER, and O. SCHMIDT (*Annalen*, 1925, 444, 135—145; cf. this vol., i, 602).—The *pentamethyl ethers* of *d*- and *l*-epicatechin, m. p. 103—104°,  $[\alpha]_{578}^{18} \pm 84^\circ$  in tetrachloroethane, were prepared from the respective penta-acetyl-*d*- and *l*-epicatechins (cf. Freudenberg, Böhme, and Beckendorf, A., 1921, i, 576) by five successive methylations with methyl sulphate. The *racemic* mixture, m. p. 113—114°, which affords a *monobromo* derivative, m. p. 138—139°, is obtained by the addition of 2 mols. of hydrogen to cyanidin chloride pentamethyl ether, m. p. 160° (cf. Pratt and Robinson, this vol., i, 422), in alcoholic solution in presence of platinum-sponge. Cyanidin chloride is reduced similarly by hydrogen, in methyl-alcoholic hydrogen chloride solution, in presence of platinum-sponge at 0°, to *dl*-epicatechin, special precautions being necessary to prevent condensation of the latter, under the influence of the mineral acid, to tannins and tannin-red.

F. G. W.

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**Echitamine.** J. A. GOODSON and T. A. HENRY (*J. Chem. Soc.*, 1925, **127**, 1640—1648).—Echitamine,  $C_{22}H_{28}O_4N_2$ , occurs in the bark of various *Alstonia* (Hesse, A., 1880, 447). From *A. congensis* bark a yield of 0.03—0.34% (according to district of origin) of echitamine hydrochloride, identical with the alkaloid from *A. scholaris*, has been obtained; from an acidified alcoholic solution of the total alkaloids, echitamine hydrochloride, m. p. 295° (corr., decomp.),  $[\alpha]_D^{25} -58^\circ$ , separates on keeping. The hydrobromide, m. p. 268° (anhydrous, corr., decomp.),  $[\alpha]_D^{25} -43.5^\circ$  (hydrated salt), hydriodide, m. p. 267°, sulphate, decomp. 275°, *nitrate*, m. p. 127° (+2H<sub>2</sub>O, corr., decomp.), and *picrate*, decomp. 98° (+24H<sub>2</sub>O), are described.

Echitamine contains one methoxyl, one methylimino, and two hydroxyl groups [*diacetate hydrochloride*, m. p. 271° (corr., decomp.)]. The free base, which could not be obtained crystalline, is hydrolysed by dilute alkali at 120°, giving *demethylechitamine*,  $C_{21}H_{26}O_4N_2$ , m. p. 290° (air-dry, corr., decomp.) or 268° (dry, corr., decomp.), which is the carboxylic acid corresponding with the methyl ester, echitamine. The *hydrochloride*, m. p. 306° (corr., decomp.), is acid to litmus, whereas that of echitamine is neutral. By the action of nitric acid on echitamine *nitrate* there is formed a red *base*,  $C_{22}H_{26}O_4N_2(NO_2)_2$ , decomp. 156° (+4H<sub>2</sub>O) or 184° (dry). This base still retains the ester group of echitamine. The red colour changes sharply to yellow on neutralisation with acid. Echitamine forms a *nitroso* derivative, m. p. 157° (decomp.). Distilled with soda-lime or 50% aqueous potassium hydroxide, echitamine gives a mixture containing an indole derivative, together with methyl alcohol, methylamine, and another base. Both echitamine and demethylechitamine give an intense blue coloration with Hopkins and Cole's glyoxylic reagent for tryptophan.

From the ether and chloroform extracts obtained in the isolation of echitamine, and from the mother-liquors after separation of the crude hydrochloride, there is isolated a *lactone*,  $C_9H_{14}O_3$ , m. p. 74—77° (air-dry, corr.) or 103° (dry, corr.),  $[\alpha]_D^{25} +49.9^\circ$  (air-dry, in water) or +56.4° (dry, in water). This substance contains no methoxyl or methylenedioxy group, but forms a *sodium salt*,  $C_9H_{15}O_4Na$ , and a *monoacetyl* derivative. C. H.

**Picrates of the Opium Alkaloids.** C. W. MAPLETHORPE and N. EVERS (*Pharm. J.*, 1925, **115**, 137—139).—Tables are given of the m. p. and solubilities in water, alcohol, and acetone at 20° of various alkaloid picrates. The following m. p. (all corrected) are new, or differ considerably from earlier determinations: *picrate* of morphine, 163—165°; of thebaine, 217°; of narcotine, 174°; of narceine, 195°; of cryptopine, 161—163°; of xanthaline, 212.5°. B. F.

**New Isomerism in the Isatin Series.** G. HELLER and R. FUCHS (*J. pr. Chem.*, 1925, [ii], **110**, 283—288; cf. A., 1917, i, 219).—Interaction of silver isatin and benzoyl chloride in benzene at 100° yields  $\alpha$ -isatol. A parallel experiment at the ordinary temperature (8 days) yields isatin,  $\alpha$ -isatol, and  $\beta$ -isatol, m. p. 162—

163.5°. Better yields are obtained by the use of silver isatin prepared in the cold. When the reaction is carried out in ether at 30°, no  $\alpha$ -isatol is formed. The new isomeride is unstable towards solvents, giving rise to amorphous products after long boiling in benzene. The crystalline product, m. p. 177—180°, obtained by a similar change in glacial acetic acid, is not homogeneous, since extraction with ethyl acetate yields a fraction, m. p. 175—177°. The  $\alpha$ - and  $\beta$ -isomerides have the same molecular weight and are very similar in their reactions. The  $\beta$ -compound is, in general, more soluble than the  $\alpha$ -compound, into which it is partly transformed by prolonged keeping or by heating with alcohol. Structural difference is shown, however, by the fact that the  $\beta$ -compound gives the indophenin reaction. Its constitution is as yet uncertain.

In continuation of the Hantzsch controversy, the author contends that the latter's "isatoid," obtained by the action of glacial acetic acid on the reaction product of silver isatin and benzoyl chloride, is the secondary decomposition product mentioned above and is, accordingly, not homogeneous. M. J.

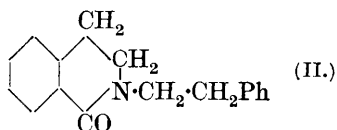
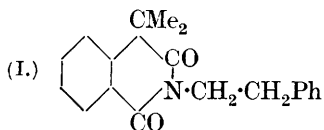
**isoQuinoline Derivatives. IX. Preparation and Reduction of isoQuinoline and its Derivatives.** R. FORSYTH, C. I. KELLY, and F. L. PYMAN (*J. Chem. Soc.*, 1925, **127**, 1659—1667).—A method for the isolation of pure *isoquinoline* from "crude pyridine bases" through the acid sulphate is described (cf. Harris and Pope, T., 1922, **121**, 1029) by which a yield of 4% of pure *isoquinoline*, from the "heavy quinoline bases," b. p. 230—255°, is obtained. Reduction of pure *isoquinoline* with tin and hydrochloric acid in alcohol affords tetrahydro*isoquinoline* in a yield of 96.4% of the theoretical. 1-Benzyl*isoquinoline*, m. p. 55—56°, b. p. 222°/18 mm. [hydrochloride, m. p. (2H<sub>2</sub>O) below 100°, m. p. (anhydrous) 185—187°], is best prepared by heating 1-benzyl*isoquinoline* methiodide at 20—30 mm. pressure until removal of methyl iodide is complete (cf. Decker and Pschorr, A., 1904, i, 926). On reduction as above it yields 1-benzyl-1 : 2 : 3 : 4-tetrahydro*isoquinoline*, a viscous oil [hydriodide (H<sub>2</sub>O), m. p. 167—168.5° (anhydrous); *picrate*, yellow, m. p. 166—167°], in 81% yield. 1-Benzyl*isoquinoline* methiodide affords similarly 1-benzyl-2-methyl-1 : 2 : 3 : 4-tetrahydro*isoquinoline* in 86% yield. Condensation of aminoacetal with veratraldehyde at 100° affords *veratrylidene-aminoacetal*, pale yellow, m. p. 61—62°. On reduction with sodium and alcohol, this yields *veratrylaminoacetal*, b. p. 208°/15 mm. (cf. Rügheimer and Schön, A., 1909, i, 605), which affords 6 : 7-dimethoxy*isoquinoline*, m. p. 93° [hydrochloride, (+3H<sub>2</sub>O), m. p. 221° (decomp.) (anhydrous); *methiodide*, buff-coloured, m. p. about 226° (decomp.)], when treated with arsenic pentoxide and sulphuric acid. Reduction of 6 : 7-dimethoxy*isoquinoline* with tin and hydrochloric acid in alcohol affords a 94% yield of 6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydro*isoquinoline*, m. p. 80—130°, which absorbs carbon dioxide from the air and was not obtained free from carbonate (*hydrochloride*, m. p. 262°; *picrate*, yellow, m. p. 202—203°). 6 : 7-Dimethoxy*isoquinoline* methiodide affords

similarly an 82% yield of 6:7-dimethoxy-2-methyl-1:2:3:4-tetrahydroisoquinoline (cf. Pyman, T., 1915, **107**, 176). In none of the above reductions were by-products of the pavine type obtained (cf. Pyman, *loc. cit.*).

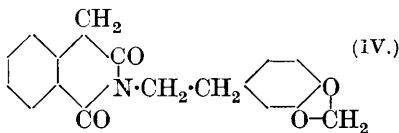
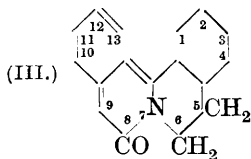
F. G. W.

**Synthetical Experiments in the isoQuinoline Group. V. Synthesis of Substances Allied to Oxyberberine.** R. D. HAWORTH, W. H. PERKIN, jun., and H. S. PINK (*J. Chem. Soc.*, 1925, **127**, 1709—1723).— $\beta$ -Phenylethylamine is conveniently prepared by converting  $\beta$ -phenylpropionyl chloride into the amide by treatment with ammonia in benzene, and treating the recrystallised amide with sodium hypochlorite (cf. Decker, A., 1913, i, 272).  $\beta$ :3:4-Dimethoxyphenylpropionic acid is obtained by condensing veratraldehyde with malonic acid in pyridine solution in presence of piperidine, and reducing the resulting 3:4-dimethoxycinnamic acid with sodium amalgam (cf. Perkin and Robinson, T., 1907, **91**, 1079).

2- $\beta$ -Phenylethylhomophthalimide, m. p. 128—129°, obtained by heating  $\beta$ -phenylethylamine with homophthalic acid at 180°, is converted into 1:3-dichloroisoquinoline (cf. Gabriel, A., 1886, 812) when heated with phosphorus oxychloride at 140—150°. When treated with methyl iodide in alkaline aqueous alcoholic solution, it yields 2- $\beta$ -phenylethyl-4:4-dimethylhomophthalimide (I), m. p. 60—61°, whilst electrolytic reduction in alcoholic sulphuric acid solution affords 2- $\beta$ -phenylethyl-dihydroisoquinolone (II), m. p.

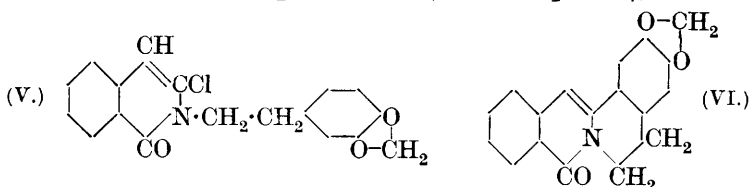


77—78°, together with 2- $\beta$ -phenylethyl-1:2:3:4-tetrahydroisoquinoline, liquid (*hydrochloride*, m. p. 227—229°). When 2- $\beta$ -phenylethylhomophthalimide is heated with aqueous sodium hydroxide, N- $\beta$ -phenylethylhomophthalamic acid, m. p. 122—123°, is produced. When the *methyl* ester of the latter, m. p. 74—75°, obtained by heating the silver salt with methyl iodide in dry ether, is boiled with phosphorus oxychloride in toluene, *oxyisoprotoberberine* (III), yellow, m. p. 134°, is obtained in small yield. 2-Homopiperonylhomophthalimide (IV), m. p. 156—157°, and 2-homopiperonyl-4:4-dimethylhomophthalimide, m. p. 126—127°, are obtained as above from homopiperonylamine. When (IV) is boiled with phosphorus

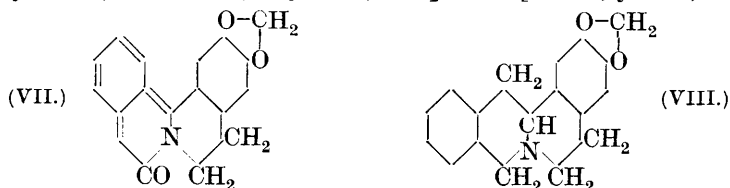


oxychloride in toluene, 3-chloro-2-homopiperonyl-1-isoquinolone (V) is produced. No condensation product is obtained by boiling

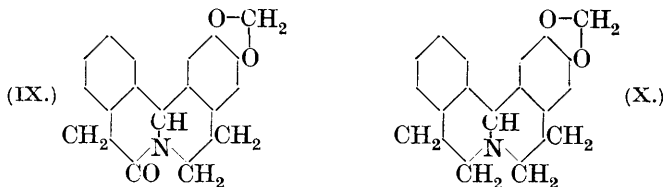
the latter with copper powder in quinoline. *N*-Homopiperonyl-homophthalamic acid, m. p. 158—159° (*amide*, m. p. 216°), is obtained



by hydrolysing (IV) with aqueous sodium hydroxide. The *methyl ester*, m. p. 95—96°, affords 2 : 3-methylenedioxyoxyprotoberberine (VI), m. p. 180°, when boiled with phosphorus oxychloride in toluene, together with 2 : 3-methylenedioxyoxyisoprotoberberine (VII), orange (hydrated) or scarlet (anhydrous), m. p. 225° [*acetate*, yellow, m. p.



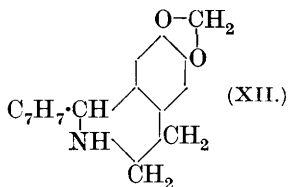
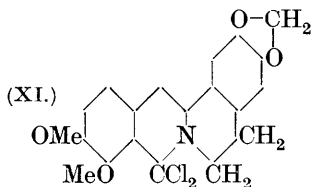
250° (decomp.)]. The former is reduced electrolytically as above to 2 : 3-methylenedioxytetrahydroprotoberberine (VIII), m. p. 128—129° [*hydrochloride*, m. p. 270° (decomp.)]; *picrate*, m. p. 208—210° (decomp.)], whilst the latter affords similarly 2 : 3-methylenedioxy-dihydroisoprotoberberine (IX), nodules, m. p. 196—197° (from alcohol), or needles, m. p. 203—204° (from dilute acetic acid), together with 2 : 3-methylenedioxytetrahydroisoprotoberberine (X), syrup (*hydrochloride*, decomp. at 260°; *picrate*, m. p. 216—217°).



2-Homopiperonyl-6 : 7-dimethoxyhomophthalimide [see (IV)], yellow, m. p. 178—179°, and the *dimethyl* derivative [see (V)], m. p. 151°, are described. Treatment of the former with phosphorus oxychloride in boiling toluene affords 3-chloro-2-homopiperonyl-6 : 7-dimethoxy-1-isoquinolone [see (V)], yellow, m. p. 163—164°, whilst hydrolysis with sodium hydroxide yields *N*-homopiperonyl-4 : 5-dimethoxyhomophthalamic acid, m. p. 181—182°. When the *methyl ester*, m. p. 136°, of the latter is boiled with phosphorus oxychloride in toluene, oxy- $\psi$ -berberine is obtained (cf. Haworth, Perkin, and Rankin, A., 1924, i, 1098), together with a salt of a *dichloro* derivative [see (XI), below], orange-yellow, m. p. 204—205° (decomp.), which on subsequent hydrolysis with sodium hydroxide yields oxy- $\psi$ -berberine. Treatment of oxyberberine

with phosphorus oxychloride affords methyl*nor*oxyberberine (cf. Faltis, A., 1910, i, 698; Bland, Perkin, and Robinson, T., 1912, **101**, 262; Perkin, Rây, and Robinson, this vol., i, 695) and a *chloro* derivative to which the structure (XI) must be assigned, as it is converted by ammonia into *iminoberberine*, m. p. not below 280° (*hydrochloride*, m. p. similar), which is hydrolysed to oxyberberine with aqueous sodium hydroxide.

N-Phenylacetylhomopiperonylamine (cf. Decker, *loc. cit.*), yields 6 : 7-methylenedioxy-1-benzyl-3 : 4-dihydroisoquinoline when boiled with phosphorus oxychloride in toluene. Reduction of the latter with zinc and sulphuric acid yields 1-benzyl*nor*hydrohydrastinine (XII), m. p. 64—66° (*hydrochloride*, m. p. 110°; *picrate*, m. p. 184—185°). Treatment of the latter with formaldehyde and formic acid



in a sealed tube at 180° affords the N-methyl derivative, *benzylhydrohydrastinine*, a syrup [*hydrochloride*, m. p. 174—175° (decomp.)]. 2 : 3-Methylenedioxydihydroprotoberberine, yellow, m. p. 128—129° (*hydrochloride*, yellow, m. p. 250°; *picrate*, orange, m. p. 254—255°), is obtained by boiling the formyl derivative of benzyl*nor*hydrohydrastinine with phosphorus oxychloride in toluene. On reduction with zinc and sulphuric acid, it yields the above 2 : 3-methylenedioxytetrahydroprotoberberine (VIII). Oxidation of the latter in alcoholic solution with iodine in presence of sodium acetate, followed by treatment of the product in aqueous suspension with sulphur dioxide, affords 2 : 3-methylenedioxyprotoberberinium iodide, yellow, m. p. not below 300°, from which the *chloride*, m. p. not below 250°, is obtained by digestion with silver chloride in aqueous suspension. Treatment of the latter with aqueous 50% potassium hydroxide yields 2 : 3-methylenedioxydihydroprotoberberine and 2 : 3-methylenedioxyoxyprotoberberine. F. G. W.

**Preparation of Di-iodohydroxyquinolines.** F. PASSEK (D.R.-P. 411050; from *Chem. Zentr.*, 1925, i, 2412).—The following new compounds are mentioned : 5 : 7-di-iodo-8-hydroxyquinoline, greenish-yellow, m. p. 200—250° (decomp.); 5 : 8-di-iodo-6-hydroxyquinoline, greyish-yellow, m. p. 191°. G. W. R.

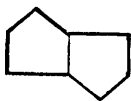
**Preparation of Derivatives of 2-Phenylquinoline-4-carboxylic Acid.** J. D. RIEDEL, AKT.-GES. (D.R.-P. 411051; from *Chem. Zentr.*, 1925, i, 2412).—The following new compounds are mentioned : tertiary *bismuth* 2-phenylquinoline-4-carboxylate; primary *bismuth* 2-phenylquinoline-4-carboxylate. G. W. R.

**Polynuclear Heterocyclic Aromatic Types. II. Some Anhydronium Bases.** J. W. ARMIT and R. ROBINSON (*J. Chem. Soc.*, 1925, **127**, 1604—1618).—As a restriction on the cyclic con-

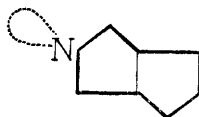
jugation theory, it is suggested that the number of electrons must be such that sextets (represented in the formulæ below by the central ring) can be formed in each ring. Applying this restriction, the existence of a nucleus, in fusion with other rings, containing a pentamethine ring, of type (I) remains possible, whilst types (II) and (III) cannot satisfy this condition (cf. Armit and Robinson,



(I)

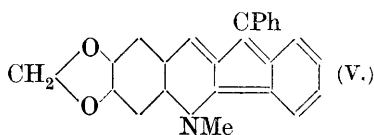
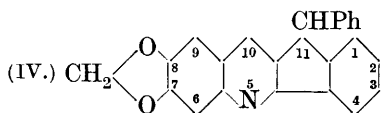


(II)

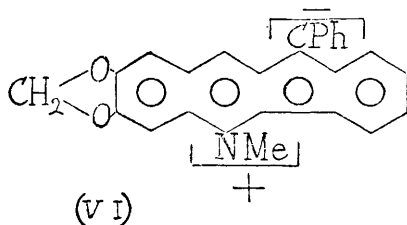


(III)

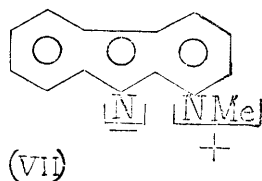
T., 1922, **121**, 828). 6-Aminopiperonal condenses with 3-phenylindone in presence of potassium hydroxide to form 7 : 8-methylenedioxy-11-phenylindoloquinoline (IV), red, m. p. 245—246° [*hydrochloride*, yellow, decomp. 247°; *picrate*, yellow, decomp. 236°; *methosulphate*, yellow, m. p. 233°; *methiodide*, yellow, m. p. 241—242° (decomp.)]. Decomposition of the methosulphate with hot aqueous potassium hydroxide affords *anhydro*-7 : 8-methylenedioxy-11-phenylindoloquinoline *methohydroxide*, green, m. p. 246° after darkening at 226° and decomposing progressively [*picrate*, yellow, m. p. 226° after sintering at 221°]. The structure of this compound is probably intermediate between (V) and (VI); the former



cannot be stable as the right-hand benzene ring is not aromatic, nor can the latter since it is a dipole. Similar considerations apply to the structures of analogous compounds described below. The term *anhydronium bases* is suggested for compounds of this type. The *methiodide* of the above anhydro base, yellow, affords a methohydroxide, orange, when decomposed with potassium hydroxide, a second anhydro base not being formed.



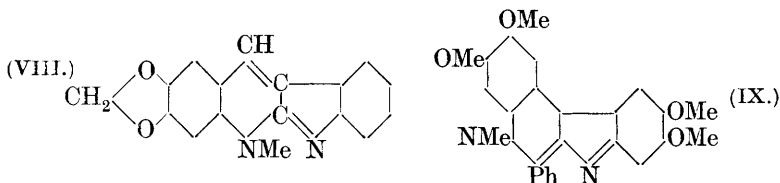
(VI)



(VII)

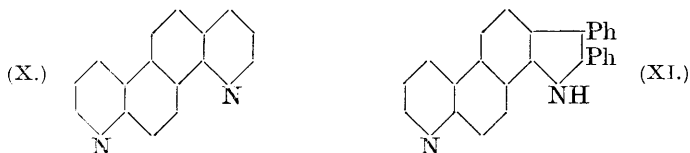
3-Carboline (Lawson, Perkin, and Robinson, A., 1924, i, 562) affords a *methosulphate*, which, when decomposed with potassium

hydroxide, yields **3-methyl-3-isocarboline** (VII), yellow, m. p. 140°. **6-Aminopiperonal** condenses with oxindole in methyl-alcoholic solution in presence of potassium hydroxide, with formation of



**6'-aminopiperonylideneoxindole**, orange, decomp. at 226° (*picrate*, darkens at 235°, m. p. not below 300°). The *methosulphate* (**6'-methylaminopiperonylideneoxindole methyl hydrogen sulphate**), yellow, darkens at 289°, m. p. not below 300°, yields **10:11-anhydro-7:8-methylenedioxyquinindoline-10-methohydroxide** (VIII), orange, m. p. 244°, when treated with potassium hydroxide. **Py-N-Methylphenyldiveratroisoharmyrene** (IX), scarlet, m. p. 264° (decomp.) after darkening above 140° (*methiodide*, yellow, m. p. 266°), is obtained when *phenyldiveratroharmyrene methosulphate*, orange-yellow, is treated with sodium hydroxide. In aqueous or alcoholic solution, the anhydro base reverts to the methohydroxide.

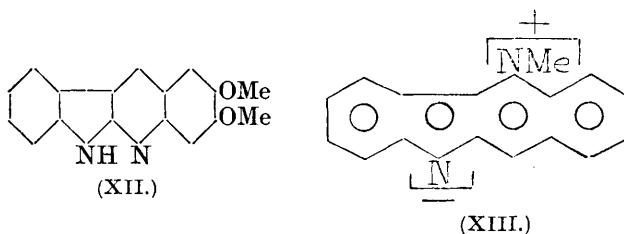
Anhydronium bases in the 4- and 5-carboline series have been previously described (Perkin and Robinson, T., 1919, **115**, 951; Kermack, Perkin, and Robinson, *ibid.*, 1922, **121**, 1877; Robinson and Robinson, A., 1924, i, 666; Robinson and Thornley, A., 1924, i, 1349). The following compounds were prepared to examine the influence of further separation of the nitrogen atoms. Nitro- $\beta$ -naphthaquinoline (cf. Claus and Bessler, A., 1898, i, 331) is reduced, when aqueous sodium sulphide solution is added to its solution in boiling aniline, to amino- $\beta$ -naphthaquinoline, m. p. 158°, which yields, by Skraup synthesis, **1:6-naphthadiquinoline** (X), m. p. 183.5—184.5° [*sulphate*, m. p. 268° (indistinct) after darkening above 250°], the latter being also obtained similarly from 1:6-naphthylenediamine. These syntheses serve to orient the nitro group in the above nitro derivative. When amino- $\beta$ -naphthaquinoline, its dihydrochloride, and benzoin are heated together at 180—190°, **5:6-(2:3-diphenylindolo)(6:7)-quinoline** (XI), decomp. at 298° [*acetate* (+H<sub>2</sub>O), decomp. above 300°], is



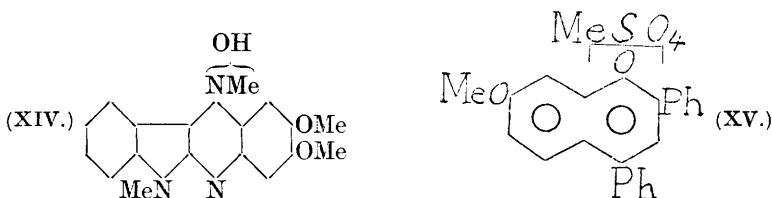
obtained, the *methosulphate* of which (yellow, turning scarlet at about 165°) yields, on treatment with alcoholic potassium hydroxide, a crimson, crystalline *precipitate*, m. p. 225° (decomp.). **2:3-Dimethoxyindophenazine** (XII), yellow, m. p. 284° [*hydrochloride*, m. p. 290° (decomp.)]; *picrate*, yellow, m. p. 254°, is



obtained by reducing 4:5-dinitroveratrole with zinc dust and acetic acid, and adding an acetic acid solution of isatin to the resulting reaction mixture (cf. Schunk and Marchlewski, A., 1896, i, 96).



When the *methosulphate*, m. p.  $247^{\circ}$ , is decomposed with hot potassium hydroxide, 2:3-dimethoxy-5(or 11)-methylisoindo-phenazine (XIII), scarlet, m. p.  $261^{\circ}$  after sintering at  $257^{\circ}$  [*methiodide*, m. p.  $205^{\circ}$  (decomp.)], is obtained, whilst the corresponding *methohydroxide*, yellow, m. p.  $278^{\circ}$ , is formed if the action of potassium hydroxide on the above methosulphate is carried out in the cold. *Dimethoxymethylisoindo-phenazine dimethosulphate*, orange, m. p.  $238^{\circ}$ , obtained by boiling the anhydro base with methyl sulphate in benzene, affords, on treatment with hot potassium hydroxide, 2:3-dimethoxy-6-methylindophenazine-11(or 5)-methohydroxide (XIV), yellowish-orange, m. p.  $164^{\circ}$ . Treatment of the latter with methyl



sulphate in benzene, followed by decomposition of the product with potassium hydroxide, affords a *compound*, m. p.  $85^{\circ}$ , apparently an isomeride of the base of m. p.  $164^{\circ}$ .

7-Methoxy-4-phenylflavylum methosulphate (XV), yellow, m. p.  $179^{\circ}$ , is obtained by treating anhydro-7-hydroxy-2:4-diphenylpyranol(1:4) with methyl sulphate in benzene. The corresponding *ferrichloride* has m. p.  $191^{\circ}$  (cf. Crabtree, Robinson, and Turner, T., 1918, 113, 877).

As the formation of an anhydronium base invariably involves a redistribution of charge (unless the positive and negative centres of the dipole are so powerfully basic and acidic that the substance is a true betaine) the system connecting the charged centres must be electrically conducting, which will only be the case when it is conjugated, and can be represented on the classical valency theory by alternate single and double bonds.

F. G. W.

**Alkylallylbarbituric Acids.** E. H. VOLWILER (*J. Amer. Chem. Soc.*, 1925, 47, 2236—2240).—By the action of allyl bromide on

the appropriate monoalkylbarbituric acids (cf. Fischer and Dilthey, A., 1905, i, 35) the following 5-alkyl-5-allylbarbituric acids were prepared: *n*-butylallyl, m. p. 128° (cf. Layraud, Fr. Pat. 1922, 541997, gives 118°), isobutylallyl, 137—138·5°, diallyl, *n*-propylallyl, m. p. 133—134·5°, isopropylallyl, m. p. 137·5—138·5°, sec.-butylallyl, m. p. 108—110°, isoamylallyl, m. p. 118—119·5°, ethylallyl, m. p. 158—159·5°; and their physiological action was compared with that of known dialkylbarbituric acids. The replacement of an alkyl group by an allyl group frequently leads to an increase in effectiveness as an hypnotic together with a lower degree of increase of toxicity, the ratio of the minimum effective dose to the minimum lethal dose (white rats) increasing in the order given above.

J. W. B.

**Action of Chromic Acid on Indigotin.** L. EYMER (*Rev. gén. Mat. Col.*, 1925, 29, 225—226).—The accelerating influence exerted by oxalic acid in the oxidation of indigotin by means of chromic acid as described by Prudhomme (A., 1903, ii, 430) is ascribed to the action of ozone, which is formed, together with chromium chromate, as a result of the reduction of the chromic acid by the oxalic acid. The effect of the oxalic acid is destroyed by the addition of hydrogen peroxide, since the latter immediately combines with the ozone formed, thereby liberating oxygen.

A. J. H.

**2-Pyridylpyrrole.** A. E. TSCHITSCHIBABIN and I. G. BYLINKIN (*J. Russ. Phys. Chem. Soc.*, 1924, 55, 100—105).—The authors have attempted to synthesise an isomeride of nicotine, namely, 2-[2-pyridyl]-*N*-methylpyrrolidine. Three stages of this synthesis have been carried out, the process followed being similar to that used in Pictet's nicotine synthesis.

*N*-2-Pyridylpyrrole is prepared by the dry distillation of a mixture of 2-aminopyridine with mucic acid and aluminium oxide. Attempts were made to improve the yield by addition of glycerol, but high-melting products were obtained, from which the separation of pyridylpyrrole proved very difficult. The *N*-2-pyridylpyrrole was separated from the unchanged 2-aminopyridine by benzoylating the latter, instead of acetylation as employed by Pictet for the isolation of *N*-3-pyridylpyrrole.

*N*-2-Pyridylpyrrole, b. p. 123°/11 mm., 250°/748 mm. (*picrate*, m. p. 141°), gives an intense blue pine shaving test. Its solution in hydrochloric or sulphuric acid is colourless in the cold but becomes purple-red when heated. On passing its vapour through a glass tube at a dull red heat, 2-[2-pyridyl]pyrrole, m. p. 87—88° (*picrate*, m. p. 221°), is obtained. It gives a blue pine shaving test. When methylated it yields *N*-methyl-2-[2-pyridyl]pyrrole (*α*-nicotyrine), b. p. 149—150° (*picrate*, m. p. 138—139°). It is a colourless liquid with a characteristic odour and on keeping becomes dark red.

E. R.

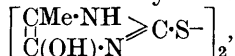
**4- and 5-Nitro-1 : 2-dimethylglyoxalines.** V. K. BHAGWAT and F. L. PYMAN (*J. Chem. Soc.*, 1925, 127, 1832—1836).—Nitration of 1 : 2-dimethylglyoxaline with mixed acid at 100° gives

4-nitro-1 : 2-dimethylglyoxaline, m. p. 182—183° (corr.) [*hydrochloride*, m. p. 215° (decomp.)], in 20% yield, together with 10% of the 5-nitro compound, m. p. 138—139° (corr.) [*hydrochloride*, m. p. 195° (decomp.; corr.); *picrate*, m. p. 162—163°]. By methylation of 4(5)-nitro-2-methylglyoxaline with methyl sulphate the same compounds result in yields of 1.1% and 57%, respectively. They give with methyl iodide the same 4(5)-nitro-1 : 2 : 3-trimethylglyoxaliniium iodide, m. p. 195—196° (decomp.; corr.), which by dry distillation in a vacuum is converted into the 4-nitro-1 : 2-dimethylglyoxaline (67% yield). Neither 4- nor 5-nitrodimethylglyoxaline condenses with benzaldehyde. Reduction of the 5-nitro compound with stannous chloride gives ammonia, methylamine, glycine, and a base,  $C_5H_{10}N_2$  [*picrate*, m. p. 142.5° (corr.)]. 5(4)-Bromo-4(5)-nitro-2-methylglyoxaline is converted by ammonium sulphide into 4(5)-nitro-5(4)-thiol-2-methylglyoxaline, m. p. about 260° (decomp.; corr.) [ammonium salt darkens at 190°; *hydrochloride*, m. p. about 260° (decomp.; corr.)]. 4(5)-Nitro-1 : 3 : 5(4)-trimethylglyoxaliniium iodide, m. p. 134—135° (corr.; dried at 100°), may be obtained either from 5-nitro-1 : 4-dimethylglyoxaline or from 4-nitro-1 : 5-dimethylglyoxaline. 5-Nitro-1 : 4-dimethylglyoxaline hydrochloride decomposes at 188° (corr.). C. H.

**Condensation of Dihydroxyacetone and of Methylglyoxal with Thiocarbamide.** B. SJOLLEMA and L. SEEKLES (*Rec. trav. chim.*, 1925, **44**, 827—837).—Thiocarbamide reacts with methylglyoxal in cold aqueous solution in presence of sulphuric acid or with dihydroxyacetone in alcohol at 120° to produce the 5-methyl-2-thiohydantoin, m. p. 164°, obtained by Johnson (A., 1912, i, 390) from alanine and ammonium thiocyanate (*silver salt* described). Dilute sulphuric acid converts it into a white *polymeride*, turning brown and decomposing above 270°, which probably arises from the tautomeric form

$$\begin{array}{c} \text{CH}_2\text{:C} \text{---} \text{NH} \\ | \\ \text{CH(OH) \cdot NH} \end{array} \text{ > CS}$$


(cf. Davidson, this vol., i, 583). Hydrogen peroxide produces the same polymeride together with acetamide and acetylcarbamide. Oxidation by yellow mercuric oxide yields a *disulphide*,



coloured above 240° and decomp. 260°, which is reduced only with great difficulty by the use of alkaline sodium sulphite to the thiol. By the action of nitric acid on the thiohydantoin, nitropyruvic ureide (cf. this vol., i, 584), m. p. 236° (decomp.), is formed. G. M. B.

**Syntheses of Heterocyclic Nitrogen Nuclei. I. Pyrazole-carboxylic Acids by Condensation of Aldehydephenylhydrazones with Ethyl Acetoacetate.** G. MINUNNI (*Gazzetta*, 1925, **55**, 502—539).—Pyrazolecarboxylic acids are obtained by condensing an aliphatic or aromatic aldehydephenylhydrazone with ethyl acetoacetate in the presence of a little zinc chloride. This

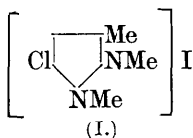
dehydrating agent, which, so far, is the only satisfactory one met with, tends to resinify both the phenylhydrazone and the reaction products and with acetaldehyde and propaldehyde, owing to this effect, the method fails. The reaction is carried out between 120° and 135° and, in order to reduce the resinification, as quickly as possible. The ester is crystallised from alcohol or other solvent, or, if uncrystallisable, it is hydrolysed to the free acid.

[With G. LAZZARINI and S. D'URSO.]—The preparation and properties of the following compounds are described:—1-Phenyl-5-methyl-3-n-hexylpyrazole-4-carboxylic acid, m. p. 100—101° (decomp.); ethyl ester uncrystallisable. 1:3-Diphenyl-5-methylpyrazole-4-carboxylic acid, m. p. 193—194° (decomp.); ethyl ester, m. p. 105° (cf. Knorr and Blank, A., 1885, i, 810). 1-Phenyl-3-m-nitrophenyl-5-methylpyrazole-4-carboxylic acid, m. p. 207—208° (decomp.); ethyl ester, m. p. 105·5—106·5°. 1-Phenyl-3-p-nitrophenyl-5-methylpyrazole-4-carboxylic acid, m. p. 209·5—210° (decomp.); ethyl ester, m. p. 107—108°. 1-Phenyl-3-o-hydroxyphenyl-5-methylpyrazole-4-carboxylic lactone (1-phenyl-5-methylpyrazocoumarin), m. p. 182—183°. 1-Phenyl-3-o-hydroxyphenyl-5-methylpyrazole-4-carboxylic acid, m. p. 160° (decomp.) (above its m. p. this compound passes with loss of water into the lactone, m. p. 182°). 1-Phenyl-3-p-anisyl-5-methylpyrazole-4-carboxylic acid, m. p. 177—178°; ethyl ester, m. p. 88—89°. 1-Phenyl-3-mp-methylenedioxyphenyl-5-methylpyrazole-4-carboxylic acid, m. p. 203—204° (decomp.); ethyl ester, m. p. 97—98°. 1-Phenyl-3-p-tolyl-5-methylpyrazole-4-carboxylic acid, m. p. 202—203°; ethyl ester, m. p. 94—95°. W. E. E.

### Isomeric Relationships in the Pyrazole Series. III.

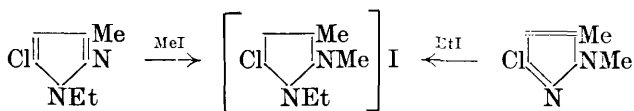
**5-Chloro-3-methylpyrazole and its Derivatives.** K. VON AUWERS and F. NIEMEYER (*J. pr. Chem.*, 1925, [ii], **110**, 153—203; cf. this vol., i, 585).—3-Methylpyrazol-5-one, m. p. 218—219° (cf. Curtius and Jay, A., 1889, [393], yields 5-chloro-3-methylpyrazole, m. p. 118—119°, b. p. 138°/15 mm. (hydrochloride, m. p. 137°), in 80% yield when heated with 1·5 mols. of phosphorus oxychloride at 144° (cf. Michaelis and Lachwitz, A., 1910, i, 641; Bosz, *Diss.*, Rostock, 1909). When heated in alkaline solution with methyl sulphate, 5-chloro-3-methylpyrazole affords a mixture of 5-chloro-1:3-dimethylpyrazole, b. p. 157—158°,  $d_4^{20}$  1·134,  $n_{D}^{20}$  1·4866 (perchlorate, hygroscopic, m. p. 148—149°), and 3-chloro-1:5-dimethylpyrazole, m. p. 46—47°, b. p. 210—212°,  $d_4^{20}$  1·0819,  $n_{D}^{20}$  1·47285 (perchlorate, m. p. 173—174°), the latter preponderating. Treatment of the silver salt with methyl iodide in ether at 100° yields the two dimethyl derivatives in approximately equal proportions, a similar mixture being also obtained when 5-chloro-3-methylpyrazole is treated with ethereal diazomethane. The action of methyl iodide on the sodium salt in absolute ether yields exclusively the 1:5-dimethyl derivative, but if moisture is present a small proportion of the 1:3-dimethyl compound is also produced (cf. Rojahn, A., 1922, i, 1183). 1:3-Dimethylpyrazol-5-one, m. p. 117°, b. p. 130°/19 mm. (picrate, m. p. 206°) (cf. Knorr, A., 1894, i, 545;

Hadank, *Diss.*, Rostock, 1908), obtained by warming ethyl acetoacetate with an aqueous solution of methylhydrazine, is converted into 5-chloro-1:3-dimethylpyrazole when heated with phosphorus oxychloride at 140—150° for 10 hrs. Treatment of either of the above chlorodimethylpyrazoles with methyl iodide and methyl alcohol at 100° yields 5-chloro-1:2:3-trimethylpyrazolium iodide



(I), m. p. 235—236° or 243—247° in an open tube, and 208—210° or about 220° in a closed tube, depending on the rate of heating (cf. Michaelis and Lachwitz, *loc. cit.*). Addition of methyl bromide proceeds similarly, the product having m. p. about 240° (cf. Lachwitz, *Diss.*, Rostock, 1908, 35). The additive products obtained when 5-chloro-4-bromo-1:3-dimethyl- and 3-chloro-4-bromo-1:5-dimethylpyrazole (cf. Rojahn, *loc. cit.*) are heated with methyl bromide at 100° have m. p. 199° and 201—203°, respectively, and are apparently identical. Treatment of (I) with sodium hydroxide in aqueous alcohol affords 1:2:3-trimethylpyrazol-5-one (1-methylantipyrene), whilst digestion with silver chloride yields the corresponding pyrazolium chloride. Methylation of 3-methylpyrazol-5-one with methyl iodide at 100° also affords 1-methylantipyrene, together with; a trace of 1:3-dimethylpyrazol-5-one, whilst methyl *p*-toluenesulphonate and alkali yield 1-methylantipyrene and 1:5-dimethylpyrazol-3-one, m. p. 172—173° (*picrate*, m. p. 192°) (cf. Rojahn, *loc. cit.*). 1-Methylantipyrene was synthesised from ethyl acetoacetate and dimethylhydrazine. It is converted by phosphorus oxychloride at 140° into 5-chloro-1:2:3-trimethylpyrazolium chloride, m. p. 252°, apparently identical with Michaelis and Lachwitz' "1-methylantipyrene chloride."

When 5-chloro-3-methylpyrazole is treated in aqueous alkaline or alcoholic sodium ethoxide solution with ethyl bromide, 5-chloro-3-methyl-1-ethylpyrazole, b. p. 167°,  $d_4^{20}$  1.0906,  $n_D^{20}$  1.4814 (*perchlorate*, hygroscopic, m. p. 99°), and 3-chloro-5-methyl-1-ethylpyrazole, b. p. 217°,  $d_4^{20}$  1.117,  $n_D^{20}$  1.4931 (*perchlorate*, m. p. 138—139°), are produced in about equal proportions. Treatment with ethyl iodide at 100° affords a similar mixture, quaternary salts not being formed. Treatment of the above chloromethylethylpyrazoles at 100° with methyl iodide yields 5-chloro-2:3-dimethyl-1-ethylpyrazole, m. p. 184—185° (open tube), m. p. 182—183° (closed tube) (*perchlorate*, m. p. 191—194°), and 3-chloro-2:5-dimethyl-1-ethylpyrazole, m. p. similar (*perchlorate*, m. p. 208—213°). The same compounds are obtained by the action of ethyl iodide on 5-chloro-2:3-dimethyl- and 3-chloro-2:5-dimethylpyrazole, indicating that the halogen atom is not attached directly to nitrogen, but ionically to the whole molecule, the production of the same quaternary salt from the two series of derivatives being formulated as follows:



5-Chloro-3-methyl-1 : 2-diethylpyrazolium iodide is obtained when either of the above chlorodimethylpyrazoles is heated with ethyl iodide and alcohol at 140—150°.

Treatment of 5-chloro-3-methylpyrazole, or of its sodium salt in alcohol or ether, with benzyl chloride affords mixtures of varying proportions of 5-chloro-1-benzyl-3-methylpyrazole, b. p. 146°/13 mm.,  $d_4^{20}$  1.161,  $n_D^{20}$  1.5556 (hydrochloride, solid; 4-bromo derivative, b. p. 183°/13 mm.), and 3-chloro-1-benzyl-5-methylpyrazole, b. p. 177—180°/13 mm.,  $d_4^{20}$  1.173,  $n_D^{20}$  1.5625 (4-bromo derivative, m. p. 62—63°, b. p. 195°/13 mm.) (cf. Bosz, Rojahn, *loc. cit.*). 3-Chloro-2-benzyl-1 : 5-dimethylpyrazolium iodide, m. p. 215—216°, is obtained by the action of benzyl iodide on 3-chloro-1 : 5-dimethylpyrazole, or of methyl iodide on 5-chloro-1-benzyl-3-methylpyrazole, 5-chloro-2-benzyl-1 : 3-dimethylpyrazolium iodide, m. p. 214—215°, being obtained similarly. 3-Methylpyrazol-5-one and benzyl chloride afford, when heated at 180—240°, two compounds, m. p. 142—143° and 154—155°, respectively, whilst the sodium salt and benzyl chloride in alcohol yield 1-benzyl-3-methylpyrazol-5-one, together with 1-benzyl-5-methylpyrazol-3-one, m. p. 224—226°. The former yields 5-chloro-1-benzyl-3-methylpyrazole when treated with phosphorus oxychloride, but the latter is decomposed by this reagent.

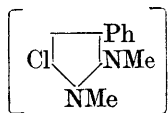
When heated, the above quaternary pyrazolium salts are decomposed into pyrazoles and alkyl halides. By analogy with corresponding decompositions in the chloroglyoxaline series (cf. Sarasin, A., 1924, i, 1115), the alkyl group is removed from the nitrogen atom adjacent to the halogen-substituted carbon atom, unless the other alkyl group possesses very weak affinity, as, for example, benzyl or allyl. Thus 5-chloro-1 : 2 : 3-trimethyl-, -2 : 3-dimethyl-1-ethyl-, and -2 : 3-dimethyl-1-benzyl-pyrazolium iodides all yield 3-chloro-1 : 5-dimethylpyrazole. The decomposition of 5-chloro-2-benzyl-1 : 3-dimethylpyrazolium iodide affords benzyl iodide and 3-chloro-1 : 5-dimethylpyrazole, the latter being apparently formed by isomerisation of the primary product, 5-chloro-1 : 3-dimethylpyrazole, in the nascent state, although the latter, once isolated, forms a perfectly stable compound. 5-Chloro-1 : 3-dimethyl-2-ethylpyrazolium iodide yields 3-chloro-5-methyl-1-ethylpyrazole when heated.

F. G. W.

**Isomeric Relationships in the Pyrazole Series. IV. Alkyl Derivatives of 3-Phenylpyrazol-5-one, and Alkyl and Acyl Derivatives of 5(3)-Chloro-3(5)-phenylpyrazole.** K. VON AUWERS and H. MAUSS (*J. pr. Chem.*, 1925, [ii], **110**, 204—234).—1 : 5-Dialkylpyrazoles are apparently incapable of existence (Auwers and Broche, A., 1923, i, 151), whilst their 3-chloro derivatives exist and are more stable than the corresponding 5-chloro-1 : 3-dialkyl isomerides (cf. preceding abstract). The changes in stability brought about by the replacement of the 3(5)-methyl group by the larger, more negative phenyl group are the subject of the following investigation.

Alkylation of 3-phenylpyrazol-5-one in aqueous methyl-alcoholic alkaline solution with methyl *p*-toluenesulphonate (cf. Rojahn, A.,

1922, i, 1184) affords 5-methoxy-3-phenylpyrazole, m. p. 106—106.5°, together with 1-methyl-5-pyrazol-3-one, m. p. 161°, and 3-phenyl-1-methylpyrazol-5-one (isonitroso compound, reddish-yellow). 3-Phenyl-4-methylpyrazol-5-one, m. p. 213—214.5°, is obtained when methyl benzoylacetate is warmed with hydrazine hydrate and alcohol. It yields 5-chloro-3-phenyl-4-methylpyrazole, m. p. 115—116° [hydrochloride, m. p. 140—150° (decomp.)], when heated with phosphoryl chloride and benzene at 200°. 3-Chloro-5-phenyl-1-methylpyrazole, m. p. 76°, is obtained by the action of phosphoryl chloride on the above 5-phenyl-1-methylpyrazol-3-one. 5-Chloro-3-phenylpyrazole (cf. Michaelis and Rassmann, A., 1907, i, 246) has b. p. 183—186°/12 mm. On methylation with methyl iodide or methyl sulphate at 100°, it yields 5-chloro-3-phenyl-1-methylpyrazole, m. p. 62°; the action of methyl iodide on the sodium salt in dry toluene affords 3-chloro-5-phenyl-1-methylpyrazole, m. p. 76°, whilst diazomethane, sodium ethoxide and methyl iodide, methyl sulphate and alkali, and the silver salt and methyl iodide, all afford a mixture of the 5- and 3-chloro derivatives, which can be separated by passing hydrogen chloride into a solution of the mixture in dry ether, when the hydrochloride of the 5-chloro derivative crystallises out. Rojahn's product (*loc. cit.*) is apparently a mixture. No indications could be obtained that the two isomerides are mutually interconvertible. 5-Chloro-3-phenyl-1 : 2-dimethylpyrazolium iodide (I)



(cf. Michaelis and Dorn, A., 1907, i, 246) is obtained when either of the above chlorophenylmethylpyrazoles is heated with methyl iodide at 100°. On distillation, it loses methyl iodide with formation of the 3-chloro-5-phenyl-1-methylpyrazole. The further action of methyl iodide on the 5-chloro isomeride affords 5-iodo-3-phenyl-1 : 2-dimethylpyrazolium iodide, m. p. 189—190° (cf. Michaelis and Pasternack, A., 1899, i, 941). Ethylation of 5-chloro-3-phenylpyrazole with ethyl iodide at 100° affords 5-chloro-3-phenyl-1-ethylpyrazole, b. p. 160—161°/18 mm. (hydrochloride, m. p. 88—92°; hydrobromide), whilst ethyl iodide and sodium ethoxide yield a mixture of the latter and 3-chloro-5-phenyl-1-ethylpyrazole, b. p. similar, which does not form a hydrochloride. The action of methyl iodide on the 3-chloro-1-ethyl derivative yields a substance, m. p. 194—195° (decomp.).

When heated with benzyl chloride at 140—170°, 5-chloro-3-phenylpyrazole yields 5-chloro-3-phenyl-1-benzylpyrazole, m. p. 53—54° (hydrochloride, m. p. 107—108°), together with a trace of 3-chloro-5-phenyl-1-benzylpyrazole, m. p. 67—68°, which does not form a hydrochloride. The latter forms a larger proportion of the product when the benzylation is carried out in presence of alcoholic sodium ethoxide.

Treatment of 5-chloro-3-phenylpyrazole with acetyl chloride at 100°, or at 0° in presence of pyridine, of its silver salt with acetyl chloride in ether, or of its sodium salt with acetyl chloride in dry toluene, yields a mixture of the following acetyl derivatives, which can only be separated mechanically by taking advantage of the difference of crystal forms: 5-chloro-1-acetyl-3-phenylpyrazole,

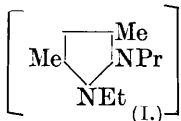
rhombs, m. p. 69—70°, and 3-chloro-1-acetyl-5-phenylpyrazole, fine needles, m. p. 75—76°. Benzoyl chloride at 100° yields similarly an *N*-benzoyl derivative, m. p. 89—90°, whilst *o*-nitrobenzoyl chloride, at 130—170°, yields two isomerides, m. p. 111—113° and 188—189°, to which the constitutions 5-chloro-3-phenyl-1-(*o*-nitrobenzoyl)-, and 3-chloro-5-phenyl-1-(*o*-nitrobenzoyl)pyrazole, respectively, are provisionally assigned. The action of *o*-nitrobenzoyl chloride on the silver salt in ether yields the derivative of m. p. 111—113° exclusively, whilst the sodium salt in toluene affords a mixture of the two.

Acetylation of 5-chloro-3-methylpyrazole with acetyl chloride at 100° or the b. p. of the mixture, or in pyridine, or by the action of acetyl chloride on the sodium or silver salt, yields always the same *N*-acetyl derivative, m. p. 20—21°, b. p. 198—200° (cf. Michaelis and Rojahn, A., 1917, i, 480), save that in an isolated experiment indication was obtained that a labile isomeride, b. p. 135—136°, was first produced, which passes to the higher-boiling modification on redistillation. *N*-Benzoyl-, m. p. 36—37°, b. p. 300—302°, *N*-(*m*-nitrobenzoyl)-, m. p. 125—125.5°, and *N*-(*o*-nitrobenzoyl)-, m. p. 139—140°, derivatives of 5-chloro-3-methylpyrazole were also prepared, isomerides not being obtained in these cases. F. G. W.

### Isomeric Relationships in the Pyrazole Series. V. *N*-Alkyl and *N*-Acyl Derivatives of Methylpyrazoles. K. VON AUWERS and W. DANIEL (*J. pr. Chem.*, 1925, [ii], 110, 235—263; cf. preceding abstracts).—3 : 5-Dimethyl-1-ethylpyrazole, b. p. 172—173°, $d_4^{20}$ 0.931, $n_{D}^{20}$ 1.4699 (*picrate*, m. p. 128—129°), and 3 : 5-dimethyl-1-propylpyrazole, b. p. 189—191°, $d_4^{20}$ 0.924, $n_{D}^{20}$ 1.4717 (*picrate*, m. p. 102—103°), were prepared by the action of the appropriate alkyl bromides on 3 : 5-dimethylpyrazole. When the former is heated with propyl iodide, or the latter with ethyl iodide, at 140°, the same 3 : 5-dimethyl-1(2)-ethyl-2(1)-propylpyrazole (I), m. p. 106°, is obtained. This yields a *periodide*, m. p. 70—71°, and decomposes when heated above its m. p. at 15—20 mm. pressure into ethyl and propyl iodides and 3 : 5-dimethyl-1-propyl- and 3 : 5-dimethyl-1-ethylpyrazole, a preponderance of the former being in accordance with the stronger affinity of the propyl group. 3-Methyl-1-allylpyrazole, b. p. 174—175° (*picrate*, m. p. 106—108°), yields, when heated with methyl iodide at 100°, 2 : 3-dimethyl-1-allylpyrazolium iodide, which affords, on distillation, 1 : 3-dimethylpyrazole. 1-Benzyl-3-methyl-2-allylpyrazolium iodide, m. p. 153—154°, yields 3(5)-methyl-1-allylpyrazole on distillation, together with a small proportion of 3-methyl-1-allylpyrazole.

Condensation of *n*-amylacetylacetylene,  $d_4^{20}$  0.873,  $n_{D}^{20}$  1.4489 (cf. Moureu and Delange, A., 1901, i, 14), with semicarbazide yields the semicarbazone, m. p. 89—90°, a pyrazole derivative not being produced. Treatment of the above ketone with hydrazine hydrate in ether-alcohol affords 3-methyl-5-amylpyrazole, b. p. 260—265°, b. p. 152°/11 mm.

Ethyl 3-methylpyrazole-1-carboxylate, b. p. 102—104°, obtained by





heating 3-methylpyrazole with ethyl chloroformate, loses carbon dioxide when heated at 200°, 3-methyl-1-ethylpyrazole being formed, together with some 3-methylpyrazole. When heated at 100° with methyl iodide, it is converted into 1:2:3-trimethylpyrazolium iodide. *isoAmyl 3-methylpyrazole-1-carboxylate*, b. p. 135—137°, obtained similarly, yields 3-methylpyrazole when heated, some resinification also taking place. *Ethyl 3:5-dimethylpyrazole-1-carboxylate*, m. p. 36—38°, b. p. 106—107°/11 mm., is obtained similarly, and also by condensing acetylacetone with ethyl hydrazinecarboxylate. Acetophenone affords, with the latter reagent, the *carb-ethoxyhydrazone*, m. p. 120—120·5°. 3-Methyl-1-acetylpyrazole, m. p. 29—30°, b. p. 70—71°/10 mm., and 3-methyl-1-benzoylpyrazole, b. p. 155—157°/14 mm. (*perchlorate*, m. p. 161—162°), are described.

The *benzoylhydrazones* of *crotonaldehyde*, m. p. 158—159°, of  $\alpha$ -*bromocrotonaldehyde*, m. p. 151°, decomposing rapidly when kept in air, and of *cinnamaldehyde*, m. p. 192—194°, were prepared, but none of these could be converted into the expected benzoylpyrazoles. 3-Methyl-1-o-nitrobenzoylpyrazole, m. p. 120°, is described.

*Benzoxymethyleneacetonesemicarbazone*, m. p. 178—179°, is converted, by digestion with cold alcoholic sulphuric acid, into 3-methylpyrazole-1-carboxylamide, m. p. 127—128°, which is also produced by the action of ammonia on 3-methylpyrazole-1-carboxyl chloride, m. p. 117—119°, obtained by the action of carbonyl chloride on 3-methylpyrazole in ether. Treatment of the above amide with ammoniacal silver solution affords the *silver* salt of 3-methylpyrazole, which is reconverted into the amide on treatment with carbamyl chloride. 4-Bromo-3-methylpyrazole-1-carboxylamide, m. p. 146—147°, is described. The above amide has the same m. p. as that synthesised by Viguier (A., 1913, i, 444) from semicarbazide and  $\beta$ -ethoxycrotonaldehyde diethylacetal, a reaction which should lead to the isomeric 5-methyl-1-carboxylamide. When this condensation is carried out in cold aqueous solution, the product has m. p. 116—118°, but is converted into the isomeride of m. p. 127—128° when boiled in benzene solution. It therefore represents 5-methylpyrazole-1-carboxylamide. 4-Bromo-5-methylpyrazole-1-carboxylamide, m. p. 150—151°, is described. Treatment of  $\beta$ -ethoxycrotonaldehyde diethylacetal with *p*-nitrophenylhydrazine affords the *p*-nitrophenylhydrazone of *tetrolaldehyde*, yellow, m. p. 157—158°. F. G. W.

**Tetrahydroindazoles.** K. VON AUWERS, L. VON SASS, and W. WITTEKINDT (*Annalen*, 1925, **444**, 195—220; cf. A., 1924, i, 325).—The synthesis of tetrahydroindazoles from *cyclohexanone* through the hydroxymethylene derivative has been applied to mono- and di-methylcyclohexanones. A methyl group *para* to carbonyl exerts no directive influence on the course of the synthesis of alkylated indazoles. A methyl group *ortho* to carbonyl favours the formation of 2-alkylindazoles, whilst two methyl groups *meta* to carbonyl favour the production of 1-alkyl derivatives.

The *benzoate*, m. p. 96—97°, and the *anilide*, m. p. 150·5—151° (*oxime*, m. p. 130—131°), of 1-methyl-3-hydroxymethylenecyclohexan-4-one (cf. Sen-Gupta, T., 1915, **107**, 1361) are described.

1 : 3-Dimethyl-4-hydroxymethylenecyclohexan-5-one, pale yellow, b. p.  $92^{\circ}/10$  mm.,  $d_4^{20}$  1.019,  $n_D^{20}$  1.4958 (benzoate, m. p.  $87-88^{\circ}$ ), was obtained from the corresponding cyclohexanone by treatment with sodium and ethyl formate. Whilst the above 1-methyl derivative changes, when kept for a few weeks in a closed vessel, into a viscous, black mass from which only 50% of the original material is recoverable by distillation under diminished pressure, the 1 : 3-dimethyl derivative shows only slight darkening in 12 months. When treated with semicarbazide acetate (1 equivalent) in aqueous-alcoholic solution, 1-methyl-3-hydroxymethylenecyclohexan-4-one yields 5-methyltetrahydroindazole-2-carboxylamide as a mixture of two isomerides, the *labile* form, m. p.  $158^{\circ}$  (starting with bath at  $150^{\circ}$ ), being converted into the *stable* variety, m. p.  $170^{\circ}$ , when heated between these temperatures. The *labile* form is produced exclusively when semicarbazide hydrochloride is used. The *semicarbazone* of the benzoxymethylene ketone, m. p. (varying with rate of heating)  $188-193^{\circ}$ , is described. When two equivalents of semicarbazide, either as base or acetate, are applied, the hydroxymethylene derivative affords a mixture of the *stable* (*labile*?) carboxylamide and the *disemicarbazone*, m. p.  $230-235^{\circ}$  (decomp.) after melting at  $206^{\circ}$  and resolidifying. 1 : 3-Dimethyl-4-hydroxymethylenecyclohexan-5-one is similarly converted by semicarbazide acetate into 4 : 6-dimethyltetrahydroindazole-2-carboxylamide, m. p.  $133-134^{\circ}$  (*labile* form), with subsequent resolidification to the *stable* form, m. p.  $151-152^{\circ}$ , which is otherwise only obtainable using semicarbazide hydrochloride. The *semicarbazone* of the benzoxymethylene ketone, m. p.  $190^{\circ}$ , was prepared. The *disemicarbazone* of the hydroxymethylene ketone has m. p.  $228-232^{\circ}$  (*stable* form, also obtained by crystallising from water) after melting at  $188-191^{\circ}$  (*labile* form) and resolidifying. The *anilide*, a yellow oil, b. p.  $218-220^{\circ}/23$  mm., is obtained from the hydroxymethylene ketone and aniline and is converted by semicarbazide acetate into the above *disemicarbazone*.

5-Methyl-4 : 5 : 6 : 7-tetrahydroindazole, m. p.  $74-75.5^{\circ}$ , b. p.  $168^{\circ}/20$  mm. (*picrate*, m. p.  $156-157^{\circ}$ ), and 4 : 6-dimethyl-4 : 5 : 6 : 7-tetrahydroindazole, m. p.  $76-77^{\circ}$ , b. p.  $151-152^{\circ}/10$  mm. (*picrate*, m. p.  $167-168^{\circ}$ ), were prepared by hydrolysis of the above respective carboxylamides with hydrochloric acid. Condensation of 1-methyl-3-hydroxymethylenecyclohexan-4-one with phenylhydrazine base, or of the benzoate with phenylhydrazine acetate, yields 2-phenyl-5-methyl-4 : 5 : 6 : 7-tetrahydroindazole, m. p.  $68-69^{\circ}$  (*perchlorate*, m. p.  $158-160^{\circ}$ ). Phenylhydrazine hydrochloride and the free hydroxymethylene derivative yield similarly 1-phenyl-5-methyl-4 : 5 : 6 : 7-tetrahydroindazole, m. p.  $62.5-63.5^{\circ}$ , b. p.  $193^{\circ}/15$  mm. (*perchlorate*, m. p.  $109-111^{\circ}$ ), whilst phenylhydrazine acetate yields a mixture of the two phenyl derivatives. 1 : 3-Dimethyl-4-benzoxymethylenecyclohexan-5-one yields a *phenylhydrazone*, m. p.  $103-106^{\circ}$  after turning brown at  $101^{\circ}$ , which is converted by warm 30% sulphuric acid into 2-phenyl-4 : 6-dimethyl-4 : 5 : 6 : 7-tetrahydroindazole, a yellow oil, b. p.  $194^{\circ}/13$  mm.,  $d_4^{16.6}$  1.0625,  $n_D^{16.6}$  1.58445 (*perchlorate*, m. p.  $199-200^{\circ}$  after softening at  $192^{\circ}$ ). Both the

free hydroxymethylene derivative and its benzoate react with phenylhydrazine base to form a *diphenylhydrazone*, m. p. 171—172° (decomposing when kept), which yields, on treatment with sulphuric acid, a mixture of 1-phenyl-4:6-dimethyl-4:5:6:7-tetrahydroindazole, m. p. 71—72°, b. p. 187°/13 mm.,  $d_4^{20.5}$  1.0660,  $n_{\text{He}}^{20.5}$  1.57555 (supercooled liquid),  $d_4^{99.7}$  1.0096,  $n_{\text{He}}^{99.7}$  1.54329 (*perchlorate*, m. p. 177—178°), with the above 2-phenyl derivative, in the proportion of 1:3. The free hydroxymethylene derivative and phenylhydrazine hydrochloride yield similarly, at 100°, a mixture in which the 1-phenyl derivative preponderates.

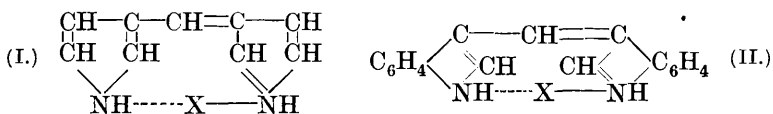
2-Benzyl-5-methyl-4:5:6:7-tetrahydroindazole, yellow, viscous, b. p. 203°/21 mm. (*picrate*, m. p. 132—133°), was obtained by the action of benzylhydrazine acetate on 1-methyl-3-benzoxymethylenecyclohexan-4-one, and also from 5-methyl-4:5:6:7-tetrahydroindazole and benzyl chloride. A trace of the 1-benzyl derivative (*picrate*, m. p. 110—111°) was also obtained by using benzylhydrazine hydrochloride instead of the acetate. 2-Benzyl-4:6-dimethyl-4:5:6:7-tetrahydroindazole, m. p. 36—37.5°, b. p. 201.5—202°/12 mm.,  $d_4^{61}$  1.0423,  $n_{\text{He}}^{61}$  1.55556 (*picrate*, m. p. 172°), was obtained analogously to the above 2-benzyl derivative, whilst the corresponding tetrahydroindazole and benzyl chloride yield a product containing 33% of the 1-benzyl-4:6-dimethyl derivative, yellow, b. p. 191—192°/13 mm.,  $d_4^{17.4}$  1.0407,  $n_{\text{He}}^{17}$  1.54391, which does not form a *picrate*.

Treatment of 5-methyl-4:5:6:7-tetrahydroindazole with ethyl bromide and sodium ethoxide yields 5-methyl-1-ethyl-4:5:6:7-tetrahydroindazole, b. p. 124°/22 mm. (*picrate*, m. p. 113—114°), and 5-methyl-2-ethyl-4:5:6:7-tetrahydroindazole, b. p. 121°/16 mm. (*picrate*, m. p. 152—153°). In absence of sodium ethoxide, the 2-ethyl derivative is formed exclusively at 100°. 4:6-Dimethyl-1-ethyl-4:5:6:7-tetrahydroindazole, b. p. 121—123°/15 mm.,  $d_4^{15.4}$  0.9753,  $n_{\text{He}}^{15.4}$  1.50232 (*picrate*, m. p. 114—115°), and 4:6-dimethyl-2-ethyl-4:5:6:7-tetrahydroindazole, b. p. 118—118.5°/13 mm.,  $d_4^{15.5}$  0.9716,  $n_{\text{He}}^{15.5}$  1.49915 (*picrate*, m. p. 139—141°), were obtained similarly. Ethyl 4:6-dimethyl-4:5:6:7-tetrahydroindazole-2-carboxylate, m. p. 63°, b. p. 182—182.5°/20 mm., obtained by treating the indazole with ethyl chloroformate and pyridine, loses carbon dioxide at 200° with formation of the above 2-ethyl derivative. 2:5-Dimethyl-4:5:6:7-tetrahydroindazole, b. p. 114°/14 mm. (*picrate*, m. p. 170—171°), was obtained by condensing 1-methyl-3-benzoxymethylenecyclohexan-4-one with methylhydrazine acetate. 1:4:6-Trimethyl-4:5:6:7-tetrahydroindazole, b. p. 118—119°/12 mm.,  $d_4^{19.8}$  0.9886,  $n_{\text{He}}^{19.8}$  1.50115 (*picrate*, m. p. 146—147°), and 2:4:6-trimethyl-4:5:6:7-tetrahydroindazole, b. p. 124°/12 mm.,  $d_4^{25.4}$  0.9823,  $n_{\text{He}}^{25.4}$  1.49728 (*picrate*, m. p. 174—175°), were obtained analogously, but the latter is better prepared by condensing 1:3-dimethyl-4-methoxymethylenecyclohexan-5-one, b. p. 117°/13 mm., with  $\alpha$ -methylsemicarbazide, and hydrolysing the resulting methylsemicarbazone, a yellow, viscous oil, with 30% sulphuric acid. Methyl 4:6-dimethyl-4:5:6:7-tetrahydroindazole-2-carboxylate, m. p. 74—75°, b. p. 167—168°/15 mm., loses carbon dioxide

at 175—190°, with formation of the above 2:4:6-trimethyl derivative.

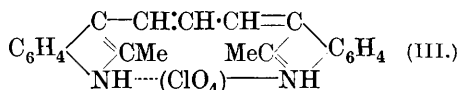
F. G. W.

**Homologous "Vinylene-" Indole and Pyrrole Dyes.** W. KÖNIG (*Z. angew. Chem.*, 1925, **38**, 743—748).—The absorption spectra and tinctorial characters of substances of the type  $\text{R}'\text{R}''\text{N}[\text{CR}]_{2n-1}\text{NR}'''\text{R}'\text{X}$  are studied, in particular the cases where the groups  $\text{R}'$  form closed rings (indole or pyrrole) with the end carbon atoms of the polymethine chain. For these is proposed a system of nomenclature similar to those suggested by Friedländer for the indigoid series and by König for the cyanines. The two simplest pyrrole (I) and indole (II) parent substances are named, respectively, "pyrroflavin" and "indorhodin," the iso-



merides being distinguished by numerical prefixes, 2:2', 2:3', and 3:3'. The vinylene homologues are indicated by the prefix *strepto-mono-*, *-di-*, *-tri-*, etc. *-vinylene*.

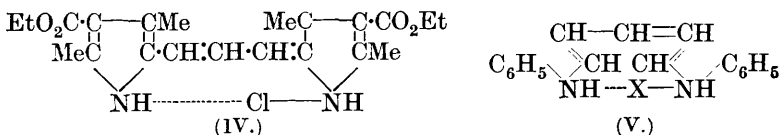
3:3'-streptomonoVinylene-2:2'-dimethylindorhodinium perchlorate (III) is obtained in about 60% yield when 2-methylindole is



heated at 100° for 1 hr. with propiolacetal,  $\text{CH}:\text{C}:\text{CH}(\text{OEt})_2$ , and excess of perchloric acid. It explodes feebly above 280°, and shows absorption maxima in alcohol at 555, 400, and 340  $\mu\mu$ . The *chloride* dyes tannin-mordanted cotton reddish-violet; the *bromide* is also described. The free base, m. p. above 250°, gives with sodium ethoxide a *sodium* salt, which shows bands at 560, 395, and 320  $\mu\mu$ . The close approximation of these bands to those of the perchlorate is noteworthy.

3:3'-streptomonoVinylene-2:2':5:5'-tetramethylindorhodinium perchlorate (as III) is similarly prepared from 2:5-dimethylindole and propiolacetal or  $\beta$ -ethoxyacetaldehydeacetal, and shows absorption maxima about 5  $\mu\mu$  higher than for the lower homologue. The *sodium* salt is obtained from it by the action of concentrated aqueous sodium hydroxide.

2:2'-streptomonoVinylene-4:4'-dicarbethoxy-3:3':5:5'-tetramethylpyrroflavinium chloride (IV), m. p. 211°, results when ethyl



2:4-dimethylpyrrole-3-carboxylate is heated with propiolacetal in alcoholic hydrogen chloride solution (yield 80%). It dyes tannin-

mordanted cotton violet, and shows an absorption band at 567  $\mu\mu$ . The free base gives a sodium salt with a band at 568  $\mu\mu$ .

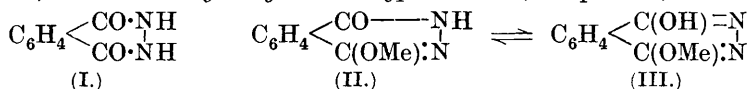
The original paper includes a table of fifteen polymethine dyes (chiefly from unpublished work) with their absorption maxima and shades on tannin-mordanted cotton. A comparison of the polymethine dye (V) with the closely-related indorhodin (II) shows the marked bathochromic effect of ring-closure. The result of lengthening the methine chain is to move the absorption bands 70—100  $\mu\mu$  towards the violet for each additional vinylene group, with a corresponding deepening of the shade on tannin-mordanted cotton by about 20 units of the Ostwald scale. C. H.

### Decomposition of Pyrazolines by Spontaneous Oxidation.

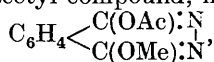
R. LOCQUIN and R. HEILMANN (*Compt. rend.*, 1925, **181**, 120—122).—The decomposition of pyrazolines in the presence of copper oxide into nitrogen and unsaturated hydrocarbons first observed by Maire (*Bull. Soc. chim.*, 1908, [iv], **3**, 278; A., 1908, i, 290) is found to proceed also in the absence of the catalyst, the amount of nitrogen evolved varying from 0.5 to 5.0% of the theoretical. The ready oxidation of pyrazolines (Curtius and Wirsing, A., 1895, i, 248) by air or oxygen is confirmed. When dry oxygen is bubbled through 2 : 2 : 4-trimethylpyrazoline cooled in ice, there are formed nitrogen, water, and the corresponding unsaturated ketone, mesityl oxide. With pyrazolines of higher molecular weight the products are nitrogen and the corresponding saturated ketone. Thus 2-methyl-4-isopropylpyrazoline gives methyl isoamyl ketone, b. p. 144° (semicarbazone, m. p. 142—143°), and 2-methyl-4-isobutylpyrazoline yields methyl isohexyl ketone, b. p. 163—165° (semicarbazone, m. p. 152—153°). Similar results are obtained by using ferricyanide or hydrogen peroxide in place of oxygen. In all cases the reaction is far from integral, high-boiling basic products being formed. C. H.

### Constitution of Phthalhydrazide.

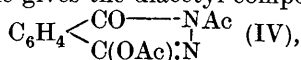
D. RADULESCU and V. GEORGESCU (*Bull. Soc. chim.*, 1925, [iv], **37**, 881—890).—The compound obtained by Mihailescu and Florescu (A., 1924, i, 1070) by the action of hydrazine on phthalic anhydride is identical with the purified products obtained by Rothenburg (A., 1894, i, 285) and by Försterling (A., 1895, i 354) and has m. p. 332—334° when pure. It behaves as a monobasic acid and does not react with aldehydes, and the constitution assigned to it is (I). When methylated, it affords 4-hydroxy-1-methoxyphthalazine, m. p. 232°, existing



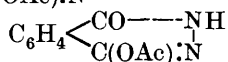
in the tautomeric forms (II) and (III), and 1 : 4-dimethoxyphthalazine, m. p. 77°,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C(OMe)} \cdot \text{N} \\ \diagdown \text{C(OMe)} \cdot \text{N} \end{array}$ . The monomethoxy derivative yields an acetyl compound, m. p. 141°,



dissolving in mineral acids. When acetylated with acetic anhydride alone phthalhydrazide gives the diacetyl compound,



obtained by Mihailescu and Florescu (*loc. cit.*), but in the presence of sodium acetate the acetylation product is the stable *diacetyl* compound,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{C}(\text{OAc}) \text{:} \text{N} \\ \text{C}(\text{OAc}) \text{:} \text{N} \end{array}$ . The constitution



is assigned to the monoacetyl compound obtained by the hydrolysis of (IV). When treated with phosphorus pentachloride and oxychloride, phthalhydrazide is converted into 4-chloro-1-hydroxyphthalazine, m. p. 274°, and an impure *dichloro* compound. Phosphorus pentasulphide converts phthalhydrazide into 1:4-dithiophthalazine, yellow, m. p. 262—265°, and a *substance*, m. p. 175—177°, containing sulphur. L. F. H.

**Different Coupling Tendencies of the Principal Aromatic Nuclei with Diazo Compounds.** G. R. LEVI (*Atti Congr. naz. Chim. Ind.*, 1924, 271—274; from *Chem. Zentr.*, 1925, i, 2305—2306; cf. this vol., i, 436).—Certain diarylamines were coupled with diazosulphanilic acid (*a*) in hydrochloric acid solution, and (*b*) in potassium acetate solution. By reduction to the diamines, the structure of the resulting diazo compounds was determined, whereby the coupling affinity of the different nuclei for diazo compounds was shown to be in the order  $\alpha$ -naphthyl >  $\beta$ -naphthyl > phenyl. The following new compounds are mentioned: *phenyl-1-naphthylene-1:4-diamine*, m. p. 148°; *phenyl-2-naphthylene-1:2-diamine*, m. p. 137°;  $\alpha$ -naphthyl-1-naphthylene-1:4-diamine (*acetyl* compound, m. p. 219°); *s.- $\alpha$ - $\beta$ -dinaphthazine*, m. p. 243°;  $\beta$ -naphthyl-2-naphthylene-1:2-diamine (*acetyl* compound, m. p. 214°).

G. W. R.

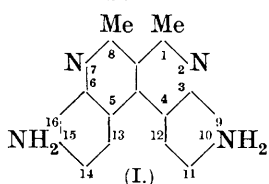
**Synthetical Experiments in the Naphthyridine Groups.** J. M. GULLAND and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 1493—1503).—2:6-Dimethylcinchomeronimide (cf. Mumm and Hüneke, A., 1918, i, 183) is conveniently prepared by heating the acid with carbamide (cf. Herzog, A., 1919, i, 536; Lawson, Perkin, and Robinson, A., 1924, i, 562) at 225—230°. When treated with cold sodium hypobromite solution it is converted into 3-amino-2:6-dimethylisonicotinic acid, pale yellow (+5H<sub>2</sub>O), m. p. (anhydrous) 295° after darkening at 285° [*hydrochloride* (+2H<sub>2</sub>O), yellow, m. p. 253—255° after darkening; *copper* salt, yellow, m. p. not below 315°]. When the hydrochloride is heated with soda-lime in a stream of hydrogen, 3-amino-2:6-lutidine, m. p. 122°, a strong base with a characteristic odour (*monohydrate*, m. p. about 70—75°; *hydrochloride*, m. p. 235°) distils over. This can be diazotised and coupled with phenol, yielding 3-p-hydroxybenzeneazo-2:6-lutidine, orange, m. p. 240° (decomp.) [*hydrochloride*, m. p. 239—240° (decomp.)]. Methylation by the method of Pyman (T., 1918, 113,

227) affords the *o*-methyl ether, red, m. p. 81—82°, resolidifying on cooling to a yellow mass [*hydrochloride*, orange, m. p. 183—185° (decomp.)]. Attempts to carry out a semidine transformation on this substance were unsuccessful.

Attempts to obtain a 1 : 7-naphthyridine derivative from 3-amino-2-methylcinchoninic acid (Lawson, Perkin, and Robinson, *loc. cit.*) by applying Camps' synthesis of 2 : 4-dihydroxyquinoline from anthranilic acid (A., 1900, i, 310) failed (cf. also Seide, this vol., i, 72). 3-Amino-2-methylcinchoninic acid is not esterified when its solution in methyl alcohol is saturated with hydrogen chloride and heated. Methyl 3-amino-2-methylcinchoninate, yellow, m. p. 83—84° (acetyl derivative, yellow, m. p. 169°), is obtained by esterification in presence of sulphuric acid. When the amino-acid is boiled with acetic anhydride and sodium acetate, 3-acet-amido-2-methylcinchoninic acid (+1.5H<sub>2</sub>O), m. p. 286° (anhydrous), is obtained, together with anhydro-3-acetamido-2-methylcinchoninic acid, m. p. 199—200°, which yields the acetamido derivative when boiled with water or alkali. Treatment of the latter with methyl alcohol and sulphuric acid affords a substance, C<sub>24</sub>H<sub>22</sub>O<sub>5</sub>N<sub>4</sub>·4H<sub>2</sub>O, m. p. 217° (decomp.), whilst boiling with concentrated hydrochloric acid yields a yellow substance, m. p. 234—235°. The latter possesses no basic properties; both are soluble in aqueous sodium carbonate. 1-Keto-2-phenyl-3 : 5-dimethyl-1 : 2-dihydro-2 : 4 : 6-naphthaisotriazine, C<sub>9</sub>H<sub>4</sub>MeN <  $\begin{matrix} \text{CO-NPh} \\ | \\ \text{N=CMe} \end{matrix}$ , yellow, m. p. 235°,

is obtained when the above anhydro derivative is boiled with aniline.

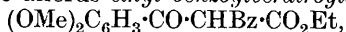
2 : 4 : 2' : 4'-Tetranitrodiphenylmethane (cf. Schöpff, A., 1894, i, 598) is obtained in 70% yield by adding molten diphenylmethane (53 g.) to a stirred solution of potassium nitrate (128 g.) in sulphuric acid (360 g.) at below 25°, a further equal amount of potassium nitrate being then added and the mixture shaken on the steam-bath for 30 mins. Tetranitrobenzophenone is obtained in 72% yield by oxidation of the tetranitrodiphenylmethane with chromic acid in sulphuric acid solution (cf. Städel, A., 1883, 990). 2 : 4 : 2' : 4'-Tetra-aminobenzophenone, yellow, m. p. 202°, is obtained by reducing the tetranitro derivative, in suspension in acetic acid, with tin and hydrochloric acid. When heated above its m. p. it loses ammonia, with formation of diaminoacridone. Treatment with aqueous nitrous acid produces a brown precipitate, the solution containing a diazonium salt. 10 : 15-Diamino-1 : 8-dimethyl-dibenzocopyrine (I), decomp. at 305°, m. p. not below 340° (tri-



hydrochloride is obtained, together with a *hydrochloride*, dark red, changing, with loss in weight, at 130° to a purplish-brown mass

with green reflex, soluble in water with green fluorescence, and diazotisable.

Condensation of ethyl veratrate with acetophenone in ether in presence of metallic sodium yields *benzoylveratroylmethane*, yellow, m. p. 67°, isolated as the *copper* salt, green, m. p. 250°. Condensation of veratroyl chloride with ethyl benzoylacetate in presence of sodium ethoxide affords *ethyl benzoylveratroylacetate*,



m. p. 125—126°, which yields, on hydrolysis with ammonia, benzamide and ethyl veratroylacetate, together with veratramide, veratric acid, and acetophenone.

The following stilbene derivatives were prepared in an attempt to obtain 2:6-naphthyridine derivatives by the dehydration of *oo*-diacylaminostilbenes. 2:4-Dinitro-3':4'-methylenedioxystilbene, salmon coloured, m. p. 180°, obtained by heating together piperonal and 2:4-dinitrotoluene in presence of piperidine, yields the corresponding 4-nitro-2-amino compound, dark red, m. p. 213° (cf. Thiele and Escales, A., 1901, i, 689), on reduction with stannous chloride in acetic acid; reduction with hydrogen sulphide in presence of ammonia affords an isomeric base. Reduction of 2:4-dinitrostilbene with hydrogen sulphide in aqueous-alcoholic ammonia solution affords 2-nitro-4-aminostilbene (cf. Thiele and Escales, *loc. cit.*). Nitrostilbenediazonium hydrogen sulphate can be isolated in crystalline form and yields 4-iodo-2-nitrostilbene, yellow, m. p. 105°, when treated with aqueous potassium iodide. Similar reduction of 2:4-dinitro-2':3'-dimethoxystilbene, yellow, m. p. 165°, prepared as above from 2:3-dimethoxybenzaldehyde, affords 2-nitro-4-amino-2':3'-dimethoxystilbene, orange, m. p. 121—122°. 2:4-Dinitro-3':4'-dimethoxystilbene, maroon-red, m. p. 143°, affords the 2:4:6'-trinitro derivative, yellow, m. p. 192°, on treatment with nitric acid in acetic acid. 2:4-Dinitro-2'-hydroxystilbene, light brown, m. p. 179—181°, and 2:4-dinitro-4'-hydroxy-3'-methoxystilbene, vermilion, m. p. 193°, are described. F. G. W.

**Oxidation of isoBarbituric Acid.** D. DAVIDSON and O. BAUDISCH (*J. Biol. Chem.*, 1925, **64**, 619—623).—When oxidised by potassium ferricyanide, isobarbituric acid gives 4:4'-di-iso barbituric acid,  $\text{C}_8\text{H}_6\text{O}_6\text{N}_4$ , yellow rhombic plates, m. p. above 310°; with alkalis it forms red salts, which, in presence of excess of alkali, show green fluorescence; on further oxidation with bromine it gives diuracil-4:4'-indigotin ("urindigo"),  $\text{C}_8\text{H}_4\text{O}_6\text{N}_4$ , a scarlet substance, m. p. above 310°. C. R. H.

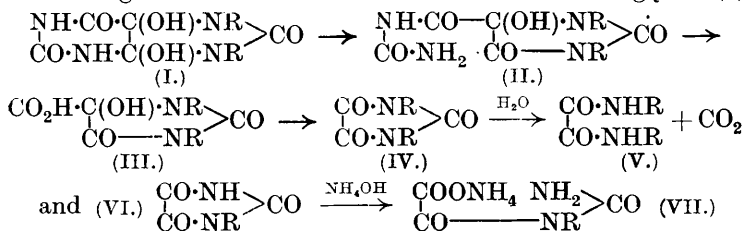
**Action of Alkali on Substituted Uric Acids. II. 9-Phenyl-1:3:7-trimethyluric Acid.** E. S. GATEWOOD (*J. Amer. Chem. Soc.*, 1925, **47**, 2175—2181; cf. A., 1924, i, 218).—The primary decomposition product obtained by the action of sodium hydroxide (2N) on 9-phenyl-1:3:7-trimethyluric acid at 100° is 3-phenyl-1-methylhydantoylmethylamide, m. p. 163—164° (together with methylamine and carbon dioxide), which on further decomposition with alkali yields 3-phenyl-1-methylhydantoin, and on oxidation with hydrogen peroxide yields 5-hydroxy-3-phenyl-1-methylhydantoyl-



*methylamide* (+1H<sub>2</sub>O), m. p. 195—196°, becoming anhydrous when dried at 100°. This is hydrolysed by alkali to mesoxalic acid, methylamine, and αβ-phenylmethylcarbamide. Ethyl aminomalonate (cf. Johnson and Nicolet, A., 1914, i, 328) condenses with phenylcarbimide to yield *ethyl phenylureidomalonate*, m. p. 112—114° (*dimethylamide*, m. p. 225°), but it was not found possible to convert this into ethyl 3-phenylhydantoincarboxylate, boiling with 20% hydrochloric acid converting it into 3-phenylhydantoin. Dimethyluramil condenses with allylcarbimide in the presence of *N*-potassium hydroxide solution to yield 1:3-*dimethyl-9-allyl-ψ-uric acid*, m. p. 190° (decomp.), which when boiled with concentrated hydrochloric acid is converted into 1:3-*dimethyl-9-allyluric acid*, not melting below 280°. Phenylmethylhydantoic acid has m. p. 150° (cf. Paal and Ganser, A., 1895, i, 224, give 102°). J. W. B.

**Action of Alkali on Substituted Uric Acids. III. 1:3:7:9-Tetramethyluric Acid and 1:3:9-Trimethyluric Acid.** E. S. GATEWOOD (*J. Amer. Chem. Soc.*, 1925, 47, 2181—2189).—The data concerning the relative acidity of the hydrogen atoms in uric acid (cf. Biltz and Herrmann, A., 1921, i, 691) and their stability towards *N*-potassium hydroxide solution are correlated, and it is shown that the decomposition of substituted uric acids by alkalis depends (1) on the salt-forming power of the acid, the least acidic being the most unstable; (2) whether the substituent is in the pyrimidine or glyoxaline ring, the former being the first one attacked, and hence substitution in position 1 increases the instability more than in position 7. The primary decomposition product is the same in all cases, viz., the hydantoylmethylamide, but on further decomposition tetrasubstituted uric acids yield hydantoins, whilst 1:3:9-trisubstituted acids yield carbamides. Tetramethyluric acid is instantly decomposed by boiling alkali, yielding methylamine, carbon dioxide, and 1:3-dimethylhydantoylmethylamide (cf. Biltz, A., 1910, i, 522), whilst 1:3:9-trimethyluric acid is readily decomposed, giving methylamine, carbon dioxide, and 3-methylhydantoylmethylamide (cf. Biltz, A., 1913, i, 1376), which is hydrolysed by sodium hydroxide to methylamine, oxalic acid, and methylcarbamide. Attempts to isolate an intermediate product indicative of the point at which the uric acid molecule is first ruptured were unsuccessful. J. W. B.

**Oxidation of Uric Acid Glycols.** K. H. SLOTTA (*J. pr. Chem.*, 1925, [ii], 110, 264—272).—The author deduces, from collected data, the following mechanism for the breakdown of uric acid glycols (I):

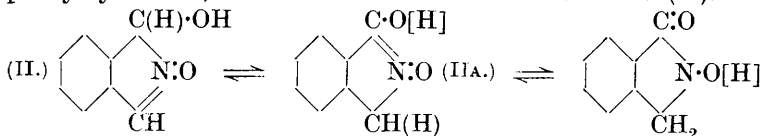


The formation of hydroxyhydantoylcarbamide (II) (cf. Biltz and Topp, A., 1911, i, 693) is followed by loss of the side-chain with production of the corresponding carboxylic acid (III). Formation of this compound is inferred from the production of hydantoin by hydriodic acid reduction of uric acid glycols (cf. Biltz and Heyn, A., 1912, i, 589) and from their oxidation in mineral acid solution to parabanic acids (IV) and (VI) (cf. Biltz and Schauder, A., 1924, i, 569). The breakdown process is carried further by oxidation in neutral solution, when ammonium carbonate formed by hydrolysis of the side-chain reacts with the parabanic acids as they arise. Unsubstituted and monoalkylparabanic acids yield, in presence of weak alkali, salts of oxaluric acid (VII) (cf. Menshutkin, A., 1874, 1889), whereas dialkylparabanic acids give symmetrical dialkyloxamides (V) (cf. Behrend and Fricke, A., 1903, i, 739). The author is unable to detect intermediate products in the oxidation of the unsubstituted glycol, the 9-alkyl-, and 7:9-dialkyluric acid glycols with hydrogen peroxide in the cold, but obtains ammonium oxalurate, ammonium alkyloxalurate, and symmetrical dialkyloxamides, respectively. The formation of these compounds must be regarded as an indication of the intermediate production of parabanic acids in the breakdown of uric acid glycols. M. J.

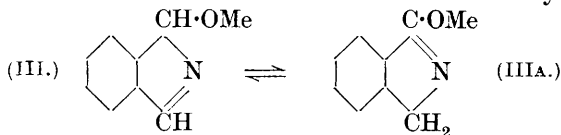
**Tautomerism of Dyads. IV. Evidence of the Tautomeric Mobility of Oximes.** J. P. GRIFFITHS and C. K. INGOLD (*J. Chem. Soc.*, 1925, **127**, 1698—1708).—1-Hydroxy-2:3-benzoxazine (I), m. p. 114—115°, is obtained when a methyl-alcoholic solution of phthalaldehyde is treated with aqueous hydroxylamine, and the reaction mixture extracted with ether after a few minutes. When treated with semicarbazide or *p*-nitrophenylhydrazine, this yields *phthalaldehyde-1-oxime-2-semicarbazone*, m. p. 235° (decomp.), and *phthalaldehyde-1-oxime-2-p-nitrophenylhydrazone*, m. p. 175° (decomp.), respectively, the formation of these derivatives affording evidence of the tautomeric relationship between phthalaldehyde-monoxime (IA) and the ring compound (I), and illustrates the structural analogy of the latter with the reducing sugars. When boiled with methyl alcohol, preferably in presence of a trace of

of the latter indicating a greater stability of the ring phase in the above tautomerisation.

1(or 3)-*Hydroxyisoindole-2-oxide* (II), m. p. 181°, is obtained as in the preparation of (I), the proportions in which (I) and (II) are formed in this reaction being apparently fortuitous, except that alkalis and high temperature favour the production of (II). Conversion of (I) into (II) can be effected by allowing the former to remain in solution in solvents other than alcohols and ketones, or by digesting it with sodium carbonate, a change which probably proceeds by ring closure of the second oxime form (IB). Treatment of (II) with *p*-nitrophenylhydrazine affords the above *p*-nitrophenylhydrazone, a reaction consistent with structure (II). The



formation of a sodium salt (yellow) and an iron salt (intense violet) is evidence for the existence of the tautomeric form (IIA) (cf. also Ingold and Piggott, T., 1922, 121, 2381), whilst further tautomerisation to (IIB) (cf. Bamberger, A., 1922, i, 770) is indicated by the formation of *N*-methoxyphthalimidine, m. p. 74°, when the *isoindole oxide* is treated with methyl iodide in presence of sodium methoxide. The *N*-methoxy derivative yields phthalimidine on reduction with tin and hydrochloric acid, whilst on oxidation with potassium permanganate a mixture of phthalimide and hydroxyisoindole oxide is obtained. 1(or 3)-*Methoxyisoindole-2-oxide*, derived from (II) or (IIA), m. p. 52° after softening at 48°, is obtained as a by-product in the above methylation. On reduction with zinc dust and ammonium chloride in methyl-alcoholic



solution it affords *o*-methylphthalimidine (III) or (IIIA), m. p. about 40° (not recrystallised), whilst oxidation with permanganate yields phthalimide.

F. G. W.

**Stereoisomeric Azo-dyes.** G. T. MORGAN and D. G. SKINNER (*J. Chem. Soc.*, 1925, 127, 1731—1742).—The diphenyl-βγ-diamino-*n*-butane obtained by heating βγ-dibromo-*n*-butane with aniline (cf. Trapezonzjanz, A., 1893, i, 79) is a mixture of *dl*-(I),  $\text{Me·CH·NHPH}$ , and *meso*-(II),  $\text{Me·CH·NHPH}$ , isomerides. The

former, greatly preponderating, is separated by repeated crystallisation of the picrate, m. p. 136—137° (from benzene), or the sulphate, m. p. 182° (from alcohol); the latter can be obtained by conversion of the residual diamines into the *mesonitrosoamine*, m. p. 125°, with subsequent reduction to the diamine and final recrystallisation of the *mesosulphate*, m. p. 206°.

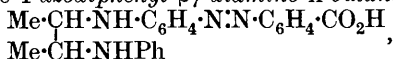
When coupled with benzene-*p*-diazoniumsulphonate, (I) affords *dl-di-4'-sulphobenzenedis-4-azodiphenyl-βγ-diamino-n-butane*, dark red, decomp. at 194° (*potassium* salt, orange). The aqueous dye-bath does not develop optical activity, but when glacial acetic acid is used as solvent (cf. Porter and Ihrig, A., 1923, i, 1027) the bath assumes slight lævorotation after 72 hrs. The *distrychnine* salt, yellow, decomp. at 179°,  $[\alpha]_{6513}^{17}$  —308·3° in alcohol, affords, on treatment with aqueous potassium carbonate, the *l-potassium* salt,  $[\alpha]_{6563}^{17}$  —206°. The more soluble fractions of the strychnine salt were viscid and did not yield the *d-potassium* salt. The *cinchonidine* salt, decomp. at 176°, is resolvable by fractional crystallisation into the salts of the *d*- and *l*-acids,  $[\alpha]_{6563}^{18}$  —272° and  $[\alpha]_{6563}^{17}$  —58·4°, respectively, from which the above *l-potassium* salt,  $[\alpha]_{6563}^{16·8}$  —176·1°, and the *d-potassium* salt,  $[\alpha]_{6563}^{18}$  +167·8°, respectively, are obtained by the action of potassium carbonate. The *morphine* salt, charring at 184°, *cinchonine* salt, decomp. at 192°, and the noncrystalline *dibrucine* and *codeine* salts are described. *meso-Di-4'-sulphobenzenedis-4-azodiphenyl-βγ-diamino-n-butane* (*potassium* salt) is obtained similarly from (II). This acid and its salts are more stable and less soluble than the above racemoid compounds. The rates of absorption of the above *d*-, *dl*-, *l*-, and *meso*-dyes by wool are in the order named, although the differences are too slight for direct optical measurement of preferential absorption.

*dl-trans-2'-Carboxybenzene-4-azodiphenyl-βγ-diamino-n-butane* (III),  

$$\text{Me}\cdot\text{CH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$$

$$\text{NHPH}\cdot\text{CHMe}$$
 dark red, decomp. at

113°, obtained from (I) and diazotised anthranilic acid, does not develop optical activity in the course of dyeing wool. The *strychnine* salt, decomp. at 121°, yields the salt of the *l*-acid,  $[\alpha]_{6708}^{19}$  —80·5°, on repeated crystallisation. Decomposition of the latter with ammonium carbonate affords the corresponding *ammonium* salt,  $[\alpha]_{6708}^{16}$  —43·7°. Salts of the *d*-acid could not be isolated. *dl-cis-2'-Carboxybenzene-4-azodiphenyl-βγ-diamino-n-butane* (IV),



red, decomp. at 116°, is obtained similarly from (II). The above *cis*- and *trans-dl*-forms are absorbed by wool at practically the same rates from the dye-bath. The *trans-l*-form is absorbed more slowly, the differences observed being considerably greater than in the case of the above sulphonic derivatives.

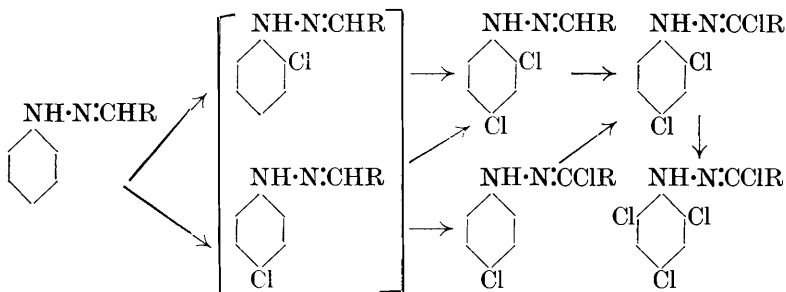
*dl*-Diphenyl-βγ-diamino-*n*-butane does not yield simple sulphonic acids when treated with oleum or chlorosulphonic acid. F. G. W.

***p*-Arsinobenzeneazophthaleins.** W. G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1925, 47, 2244—2249).—By the addition of a solution of *p*-arsinobenzenediazonium chloride to an equivalent quantity of a phthalein in alkaline solution, coupling takes place, probably in the *o*-position to the phenolic hydroxyl group, the product being a mixture of the unchanged phthalein and its mono- and di-arsinobenzeneazo derivatives, which may be resolved by fractional precipitation from an aqueous alkaline solution with alcohol. From

the appropriate phthalein the following are obtained: *o*-4-*arsinobenzeneazo*- and *o*:*o'*-*di*-4-*arsinobenzeneazo-phenolphthalein*; *o*-4-*arsinobenzeneazo*- and *o*:*o'*-*di*-4-*arsinobenzeneazo-phenoltetrachlorophthalein*; *o*-4-*arsinobenzeneazo*- and *o*:*o'*-*di*-4-*arsinobenzeneazo-fluorescein*; *o*-4-*arsinobenzeneazo*- and *o*:*o'*-*di*-4-*arsinobenzeneazo-dibromofluorescein*. Phenolsulphonephthalein yielded a mixture which was not readily separated. All the products are coloured, amorphous powders, the introduction of one or two *p*-*arsinobenzeneazo* groups into a colourless phthalein producing an orange or a brown coloration (cf. Sen and Sett, A., 1924, i, 336). The products are trypanocidally inactive and are not indicators. J. W. B.

**Synthesis of Arylazoaldoximes.** T. K. WALKER (*J. Chem. Soc.*, 1925, 127, 1860—1863).—The action of diazonium salts and nitrous acid on monoalkylated malonic acids results in a nearly quantitative yield of arylazoalkylformaldoximes:  $\text{CHR}(\text{CO}_2\text{H})_2 + \text{N}_2\text{Ar}\cdot\text{OH} \rightarrow \text{CO}_2\text{H}\cdot\text{CR}\cdot\text{N}\cdot\text{NHAr} \rightarrow \text{OH}\cdot\text{N}\cdot\text{CR}\cdot\text{N}\cdot\text{NAr}$ . *Benzeneazobenzylformaldoxime*, m. p.  $144^\circ$  (*phenylcarbamate*, m. p.  $154^\circ$ ; *benzoate*, m. p.  $144$ — $145^\circ$ ), is prepared by adding a solution of benzylmalonic acid and sodium acetate to a diazobenzene solution, and after 5 mins. adding a cooled 2% aqueous solution of nitrous acid. It is also prepared by treating phenylpyruvic acid phenylhydrazone (obtained by coupling ethyl benzylacetoacetate with diazotised aniline and hydrolysing the resulting ester) with nitrous acid. *p*-*Tolueneazoallylformaldoxime*, m. p.  $93^\circ$ , is similarly obtained from *p*-diazotoluene, and *p*-*tolueneazobenzylformaldoxime*, m. p.  $144^\circ$  (crystallographic measurements recorded; *phenylcarbamate*, m. p.  $152$ — $153^\circ$ ), from *phenylpyruvic acid p*-tolylhydrazone, m. p.  $158^\circ$  (*ethyl ester*, m. p.  $72^\circ$ ). Benzeneazobenzaldoxime is obtained with difficulty by the action of nitrous acid on phenylglyoxylic acid phenylhydrazone, m. p.  $163^\circ$ . C. H.

**Action of Halogens on *m*- and *p*-Nitrobenzaldehydephenylhydrazones.** F. D. CHATTAWAY and A. J. WALKER (*J. Chem. Soc.*, 1925, 127, 1687—1698; cf. Chattaway, T., 1908, 93, 852; 1909, 95, 958, 1065; Bülow and Huss, A., 1918, i, 314).—When excess of chlorine is passed into a chloroform suspension of *m*- or *p*-nitrobenzaldehydephenylhydrazone, the reaction takes the following course, each nuclear chlorination being probably preceded by chlorination of the  $\alpha$ -imino group ( $\text{R}=\text{C}_6\text{H}_4\cdot\text{NO}_2$ ):



The monochloro compounds have not been isolated. The action of bromine in acetic acid is similar but less energetic, and tribromination of the nucleus does not occur. Bromo-*m*- and -*p*-nitrobenzaldehyde-2:4:6-tribromophenylhydrazones are, however, easily prepared by direct bromination of the 2:4:6-tribromophenylhydrazones, and this method may also be used for the preparation of other  $\omega$ -bromo-halogenated hydrazones. The dibromo- $\omega$ -bromides were previously obtained by Ciusa and Vecchiotti (A., 1916, i, 437).

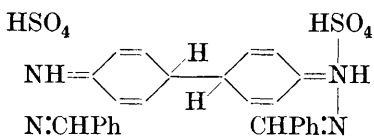
The  $\omega$ -halogen derivatives react with sodium acetate in boiling acetic acid, forming  $\alpha$ -acetyl- $\beta$ -nitrobenzoyl derivatives of the halogenated phenylhydrazines, and with aqueous-alcoholic ammonia to give hydrazidines,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{NHAr}$ . Hydrolysis of the acetylated products gives *m*- and *p*-nitrobenzoic acids entirely free from halogen. The constitution is further confirmed by synthesis from nitrobenzoylarylhiazines and acetic anhydride. The following new compounds are described (the two *m*. *p*. refer respectively to the *m*-nitro and the *p*-nitro derivatives):

$\omega$ -Chloro-*m*- and -*p*-nitrobenzaldehydearylhydrazones: *p*-chlorophenyl, *m*. *p*. 130° (impure), and 213°; 2:4-dichlorophenyl, *m*. *p*. 158°, and 199°; 2:4:6-trichlorophenyl, *m*. *p*. 157°, and 164°.  $\omega$ -Bromo-*m*- and -*p*-nitrobenzaldehydearylhydrazones; *p*-bromophenyl, *m*. *p*. 146.5°, and 224°; 2:4-dibromophenyl, *m*. *p*. 179°, and 214°; 2:4:6-tribromophenyl, *m*. *p*. 173° (*m*-nitro); *p*-chlorophenyl, *m*. *p*. 133° (*m*-nitro).  $\alpha$ -Acetyl- $\beta$ -*m*- and -*p*-nitrobenzoylarylhiazines; *p*-chlorophenyl, *m*. *p*. 167° (*p*-nitro); *p*-bromophenyl, *m*. *p*. 169—170° (*p*-nitro; *m*-nitro compound amorphous); 2:4-dichlorophenyl, *m*. *p*. 155—156°, and 158°; 2:4-dibromophenyl, *m*. *p*. 169°, and 201—202°; 2:4:6-trichlorophenyl, *m*. *p*. 143°, and 121°; 2:4:6-tribromophenyl, *m*. *p*. 180° (*m*-nitro). *m*- and *p*-Nitrobenzenylarylhiazidines; *p*-chlorophenyl, *m*. *p*. 150° (*m*-nitro); *p*-bromophenyl, *m*. *p*. 145°, and 155° [*hydrochlorides*, *m*. *p*. 200° (decomp.), and 210° (decomp.)]; 2:4-dichlorophenyl, *m*. *p*. 154° (*m*-nitro) [*hydrochloride*, *m*. *p*. 220° (decomp.)]; 2:4-dibromophenyl, *m*. *p*. 182° (decomp.), and 175° [*hydrochlorides*, *m*. *p*. 225° (decomp.), and 200° (decomp.)]; 2:4:6-trichlorophenyl, *m*. *p*. 194°, and 157° [*hydrochlorides*, *m*. *p*. 230° (decomp.), and 260° (decomp.)].

The following substances were prepared in order to confirm the structure of the above compounds: *Acetyl-m-nitrobenzaldehyde-2:4:6-trichloro- and -tribromo-phenylhydrazones*, *m*. *p*. 204°, and 230°, respectively;  $\beta$ -nitrobenzoyl-2:4:6-trichlorophenylhydrazines, *m*. *p*. 205° (*meta*), and 203° (*para*);  $\beta$ -*m*-nitrobenzoyl-2:4-dichlorophenylhydrazine, *m*. *p*. 196°;  $\beta$ -nitrobenzoyl-2:4-dibromophenylhydrazines, *m*. *p*. 210° (*meta*), and 227° (*para*). These nitrobenzoyl compounds are converted by phosphorus pentachloride into  $\omega$ -chloro-nitrobenzaldehydearylhydrazones. C. H.

**Colours Produced by the Action of Sulphuric Acid on Some Hydrazones.** F. D. CHATTAWAY, S. J. IRELAND, and A. J. WALKER (*J. Chem. Soc.*, 1925, 127, 1851—1855).—Intense blue

colorations are observed when the aldehyde or ketone compounds of 4:4'-dihydrazinodiphenyl, of *p*-iodophenylhydrazine, and of 4-iodo-2-methylphenylhydrazine are dissolved in concentrated sulphuric acid. These are probably due to the formation of quinonoid



salts, e.g., annexed formula. In the case of the nitrobenzylidene derivatives, quinonoid alkali salts of the *aci*-isomerides are possible, and intense colorations are here produced also by alcoholic potassium

hydroxide. The *o*-nitro derivative gives a green, the *m*-nitro a brown, and the *p*-nitro a blue indistinguishable from the colour in sulphuric acid.

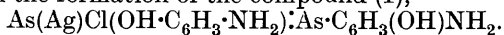
The following diphenylene-4:4'-dihydrazones are described (all decompose at the m. p.; the colours in sulphuric acid are indicated in brackets): *benzaldehyde*, m. p. 283° (cobalt-blue); *salicylaldehyde*, m. p. 264° (indigo-blue); *anisaldehyde*, m. p. 248° (bright green); *cinnamaldehyde*, m. p. 253° (sap-green); *acetophenone*, m. p. 250° (heliotrope); *benzophenone*, m. p. 145° (violet); *pyruvic acid*, m. p. 225° (orange-red, becoming magenta in a few seconds); *o*-nitrobenzaldehyde, m. p. 247° (cobalt-blue); *m*-nitrobenzaldehyde, m. p. 257° (cobalt-blue); *p*-nitrobenzaldehyde, m. p. 275° (cobalt-blue). *o*-, *m*-, and *p*-Nitrobenzaldehyde-*p*-iodophenylhydrazones and 4-iodo-2-methylphenylhydrazones give transiently a yellow colour in sulphuric acid, quickly changing to intense cobalt-blue. With *o*- and *m*-iodophenylhydrazones only yellow or orange solutions are obtained in sulphuric acid, but with alcoholic potassium hydroxide the usual green (*o*-nitro) and blue (*p*-nitro) result. C. H.

**Chemical Tests of Arsenobenzenes, especially the "DM Index."** A. PATTA (*Boll. Chim. Farm.*, 1925, **64**, 417—424).—[Cf. B., 1925, 826.] T. H. P.

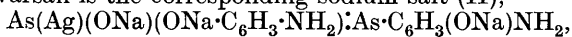
**Synthesis of *N*:*N'*-Dimethylenesulphonates of *o*-, *m*-, and *p*-Diaminoarsenobenzene.** H. KASHIMA (*J. Amer. Chem. Soc.*, 1925, **47**, 2207—2211).—An improved method for the preparation of *o*-aminophenylarsinic acid (cf. Benda, A., 1912, i, 63) is the reduction of the corresponding nitro compound by means of 4% sodium amalgam and methyl alcohol. By reduction of *o*-, *m*-, and *p*-aminophenylarsinic acids with hypophosphorous acid, using potassium iodide as a catalyst, are obtained 2:2'-diaminoarsenobenzene (cf. Fichter and Elkind, A., 1914, i, 444), 3:3'-diaminoarsenobenzene, yellow powder (*dihydrochloride* described), and 4:4'-diaminoarsenobenzene, whilst the first of these compounds is also obtained by the direct reduction of *o*-nitrophenylarsinic acid with sodium hyposulphite. These compounds condense with formaldehyde and sodium hydrogen sulphite (cf. Voegtlin and Johnson, A., 1923, i, 70) to yield the corresponding 2:2'-, 3:3'-, and 4:4'-diaminoarsenobenzene *N*:*N'*-dimethylenesulphonates. J. W. B.

**Arseno-metallic Compounds. IV. Silver Salvarsan.** A. BINZ, H. BAUSCH, and E. URBSCHAT (*Z. angew. Chem.*, 1925, **38**, 740—743; cf. *ibid.*, 1923, **36**, 551).—The constitutions suggested by

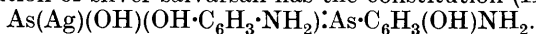
Ehrlich and Karrer (A., 1916, i, 95), Binz, Bauer, and Hallstein (A., 1920, i, 401), and Gray (T., 1923, **123**, 635) fail to account for the properties of silver salvarsan. It is not a colloidal solution of silver chloride, hydroxide, or oxide in salvarsan, since it gives no trace of nitrogen when treated with hydrazine hydrate. The compound of salvarsan with cupric chloride, on addition of sodium hydroxide, gives a precipitate insoluble in alkalis instead of soluble sodium salvarsan and colloidal copper hydroxide. The two "isomerides" of silver salvarsan (Binz and Ludwig, A., 1923, i, 161) are found to be due to the incomplete expulsion of the acid radical when sodium carbonate is used in place of sodium hydroxide, resulting in the formation of the compound (I),



Silver salvarsan is the corresponding sodium salt (II),



whilst the brown precipitate obtained by passing carbon dioxide into a solution of silver salvarsan has the constitution (III),



Since this is a derivative of arsenic acid, it should be more strongly acid than salvarsan base, as is, in fact, the case, whereas according to Ehrlich and Karrer's co-ordination structure (*loc. cit.*) it should be more basic. The formation of silver salvarsan by an oxidative addition of silver nitrate without production of metallic silver is an unusual reaction, but silver salvarsan itself shows unusual behaviour in giving a silver mirror only in the presence of atmospheric oxygen. This is probably analogous to the formation of silver iodide and not silver chloride by the action of iodine, indicating that the silver and the chlorine atoms are already separated in the monosilver chloride (I).

The following compounds are described: 4:4'-Dihydroxy-3:3'-diaminoarsenobenzene monosilver chloride (I); 4:4'-dihydroxy-3:3'-diaminoarsenobenzene monosilver hydroxide (III); 4:4'-dihydroxy-3:3'-diaminoarsenobenzene monosilver chloride dihydrochloride, dinitrate, and sulphate, obtained either from (I) or from an alkaline solution of (III) by the action of the appropriate acid.

C. H.

**Arylselenoglycollic Acids.** G. T. MORGAN and W. H. PORRITT (*J. Chem. Soc.*, 1925, **127**, 1755—1759).—Arylselenomercaptans, prepared by Taboury's method (A., 1903, i, 748) from magnesium aryl halides and selenium, condense with sodium chloroacetate in aqueous-alcoholic solution to form arylselenoglycollic acids, which, unlike the thioglycollic acids, show no tendency to cyclise by alkaline fusion or by treatment with sulphuric acid. They are oxidised by 25% hydrogen peroxide to arylselenoxyglycollic acids,  $\text{Ar}\cdot\text{SeO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , and combine with halogens directly to form additive compounds.

*Phenylselenoglycollic acid* has m. p. 40°, b. p. 160°/750 mm. (potassium and copper salts described). *p-Bromophenylselenoglycollic acid*, m. p. 127° (sodium, silver, and copper salts described), is converted by hydrogen peroxide into *p-bromophenylselenoxy-*



*glycollic acid*, m. p. 187° (*sodium, potassium, ammonium, and copper salts* described), and with bromine in dry chloroform yields a *dibromide*, decomp. 120—130°, and a *tetrabromide*, decomposing when warmed. *p-Tolylselenoglycollic acid*, m. p. 98° (*sodium, potassium, ammonium, and copper salts* described), may similarly be converted into *p-tolylselenoxyglycollic acid*, m. p. 165°, and *p-tolylselenoglycollic acid dibromide*, decomp. 90—100°, and *tetrabromide*, decomposing on warming. The selenoxy-acids and the di- and tetra-bromides liberate iodine from aqueous potassium iodide.

C. H.

**Preparation of Mercury Derivatives of Phenols Substituted in the Nucleus.** SACCHARIN-FABRIK AKT.-GES. VORM. FAHLBERG, LIST, & CO. (D.R.-P. 410969; from *Chem. Zentr.*, 1925, i, 2407).—The following new compounds are mentioned: *sodium mercurisulphophenoxide*,  $C_6H_4(ONa) \cdot HgSO_3Na$ ; *sodium mercurisulphotolyxide*; *cresolmercurisulphonic acid*; *phenolmercurisulphonic acid*.  
G. W. R.

**Aromatic Derivatives of Germanium.** G. T. MORGAN and H. D. K. DREW (*J. Chem. Soc.*, 1925, 127, 1760—1768).—When germanium tetrabromide is treated in dry ether with a large excess (36 mols.) of magnesium phenyl bromide there are obtained *tetra-phenylgermane*,  $GePh_4$ , m. p. 230—231°, volatile without decomposition, and *triphenylgermanium bromide*, m. p. 138°, together with less phenylated products. With 8 mols. of the reagent in chloroform, there are also isolated a little *triphenylgermanium oxide*, m. p. 182—183°, obtained more easily from the bromide by boiling with silver nitrate, and *phenylgermanonic* or *germanibenzoic acid*,  $Ph \cdot GeO_2H$ . Triphenylgermanium bromide becomes the main product when 5 mols. of Grignard reagent are used, and from the residual oil (chiefly diphenylgermanium dibromide), after hydrolysis with silver nitrate there are isolated (i) a *compound*, m. p. 277—278°, probably  $3GePh_2O, (GePhO)_2O$ , (ii) *tetra-anhydrotetrakisdi-phenyl-germanediol*,  $O \langle \begin{smallmatrix} GePh_2 \cdot O \cdot GePh_2 \\ GePh_2 \cdot O \cdot GePh_2 \end{smallmatrix} \rangle O$ , m. p. 218°, (iii) an amorphous *compound*, m. p. 260°, also obtainable by hydrolysis of the oily bromide prepared from (ii) by the action of hydrobromic acid, (iv) triphenylgermanium oxide, and (v) *trianhydrotetrakisdi-phenyl-germanediol*,  $(HO \cdot GePh_2 \cdot O \cdot GePh_2)_2O$ , m. p. 149° (crystallographic measurements by T. V. BARKER are recorded for the tri- and tetra-anhydro compounds). By the action of "molecular" sodium in xylene, triphenylgermanium bromide is converted into *hexaphenyldigermene*, m. p. 340°, which gives no indication of dissociation in solution. The determination of germanium in these compounds is described. As a by-product of the action of aqueous-alcoholic silver nitrate on the lower phenylated products there was obtained an intensely yellow and more soluble form of *p-nitrophenol*, m. p. 106—112°, consisting probably in part of an *aci-isomeride*.

The oxygenated germanium compounds resemble the corre-  
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spending silicon compounds, but show less tendency to form syrups, colloids, and infusible mixtures.

C. H.

**Bile Pigments. IX.** H. FISCHER and G. NIEMANN (*Z. physiol. Chem.*, 1925, **146**, 196—218).—The preparation of mesobilirubin from bilirubin (A., 1924, i, 1092) has been simplified and the yield improved by carrying out the hydrogenation in the boiling water-bath instead of in the cold. From the mesobilirubin so obtained there was prepared a copper salt,  $C_{26}H_{30}O_7N_3Cu$ , prisms, m. p. above  $350^\circ$ ; on treatment with 5 mols. of bromine in chloroform and acetic acid, mesobilirubin gives, in small yield, a bromo derivative. The by-product in the preparation of mesobilirubin obtained by Fischer (A., 1915, i, 148) has m. p.  $300^\circ$ ; it could not be esterified, and on oxidation with nitric acid it gave methylethylmaleimide. The condensation product of mesobilirubin with benzaldehyde (A., 1924, i, 1092) remained unchanged on attempted hydrogenation in presence of platinum and on heating at  $195^\circ$  with sodium methoxide; on reduction with hydriodic acid in glacial acetic acid, it gave a crystalline product which titrated as a monobasic acid (M, 387), could not be esterified, showed no optical activity, and on oxidation with nitric acid gave an acid fraction which was probably benzoic acid and an alkaline fraction (unidentified). The results suggest that the effect of the hydriodic acid was to reduce the hydroxyl group of bilirubinic acid.

Oxidation of bilirubin with nitric acid gave a product of which the elementary composition and molecular weight were in close agreement with those of methylvinylmaleimide; on reduction of this substance with hydrogen and palladium, however, a product was obtained which had m. p.  $58-60^\circ$  and was not identical with methyl-ethylmaleimide. In this connexion, an attempt was made to synthesise vinylmaleic anhydride by condensation of ethylene dibromide with ethyl acetoacetate, and subsequent formation of the cyanohydrin of ethyl bromoethylacetoacetate, hydrolysis, and elimination of hydrogen bromide; there was obtained instead, however, by the condensation of 2 mols. of ethyl acetoacetate with 1 mol. of ethylene dibromide, a substance which, with phenylhydrazine, gave *bis*-(1-phenyl-4-methylpyrazolyl)ethane,  $C_{22}H_{22}O_2N_2$ .

Mesobilirubinogen was not affected by fermentation with yeast.

An alcoholic extract of *Penicillium claveriaeformis*, Solms, contained a pigment which showed an absorption spectrum closely similar to, but not identical with, that of the porphyrins.

C. R. H.

### Superposition of the Phenomena of Dissociation and Selective Adsorption in the Case of Proteolytic Diastases.

L. HUGONENQ and J. LOISELEUR (*Compt. rend.*, 1925, **181**, 149—151).—Diazotisation or condensation with formaldehyde does not diminish the proteolytic activity of pepsin, but the same treatment (or acetylation) of proteins prevents their digestion by pepsin. The converse holds in the case of trypsin; reagents which attack the amino group destroy the activity of the trypsin, but do not affect the digestibility of proteins by trypsin. Synthetic peptides

(benzoylglycylglycine, glycylglycine ethyl ester, diketopiperazine) behave analogously. Pepsin may thus be represented as  $P \cdot \text{CO}_2\text{H}$ ; the negative organic ion associates itself with the  $\text{Na}^+$  of sodium chloride, leaving the  $\text{Cl}^-$  to exercise its action on the amino group of the protein. A converse explanation holds in the case of trypsin,  $T \cdot \text{NH}_2$ .

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C. H.

## Biochemistry.

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**Hæmocyanin. I. Dissociation Curves of the Oxyhæmocyanin in the Blood of some Decapod Crustacea.** E. STEDMAN and (MRS.) E. STEDMAN (*Biochem. J.*, 1925, **19**, 544—551).—The affinity of hæmocyanin for oxygen in the blood of *Maia*, *Palinurus*, *Cancer*, and *Homarus* is the same. The dissociation curves of the oxyhæmocyanin present in the blood of the above species are plotted from determinations of the oxygen capacities of blood equilibrated with oxygen at various tensions. It is suggested that the hæmocyanins from these animals are identical, and that they are capable of exercising respiratory functions in a manner similar to hæmoglobin.  
S. S. Z.

**Direct Method of Measuring the Osmotic Pressure of Hæmoglobin.** G. S. ADAIR.—(See ii, 965.)

**Re-formation of Methæmoglobin. I. Experiments in Vitro.** K. SAKURAI (*Arch. exp. Path. Pharm.*, 1925, **107**, 287—315).—When a large part of the pigment of fresh defibrinated blood is converted by the addition of a small amount of amyl nitrite into methæmoglobin, a spontaneous re-formation of oxyhæmoglobin takes place on keeping, the course of which is followed by means of oxygen capacity measurements. Re-formation is complete in 2 days (bacterial action being excluded), but it is never complete if the amount of nitrite exceeds 0.05%. In the presence of liver or lung pulp, complete re-formation takes place in 24 hrs. Muscle and spleen pulp accelerate, but to a less extent, and re-formation is not complete. Addition of sodium thiosulphate also accelerates, but the rate is not affected by addition of sodium succinate or of sodium chloride or by passing a stream of air, hydrogen, or nitrogen. Chloroform, used as an antiseptic, does not disturb the process. The acceleration of re-formation is supposed to be due to the reducing action of the pulp added.  
P. W. C.

**Determination of Calcium in Blood.** R. V. STANFORD and A. H. M. WHEATLEY (*Biochem. J.*, 1925, **19**, 710—714).—Calcium in blood and blood products may be determined with a probable error of  $\pm 5\%$  by precipitating the proteins with trichloroacetic acid, precipitating the calcium as calcium oxalate in certain conditions as to  $p_H$ , and then dissolving the latter in acid and

titrating with permanganate. The calcium content of blood, plasma, and corpuscles is given. S. S. Z.

**Determination of Phosphorus Compounds in Blood.** R. V. STANFORD and A. H. M. WHEATLEY (*Biochem. J.*, 1925, **19**, 697—705).—The inorganic phosphates are determined by treating the fluid with trichloroacetic acid and filtering. To the filtrate potassium dihydrogen phosphate, acid molybdate, quinol, and sodium sulphite are added. The phosphorus is then determined colorimetrically against a standard. For the determination of total phosphorus the fluid is first oxidised with concentrated sulphuric and nitric acids and subsequently neutral molybdate is used instead of acid molybdate. For the determination of lipin phosphorus, the fluid is treated with a mixture of alcohol and ether and filtered. After evaporating the solvents from the filtrate it is submitted to the same treatment as for total phosphorus. S. S. Z.

**Distribution of Phosphorus Compounds in Blood.** R. V. STANFORD and A. H. M. WHEATLEY (*Biochem. J.*, 1925, **19**, 706—709).—The results of five blood analyses are tabulated. The relative quantities of the various types of phosphorus compounds are fairly constant. S. S. Z.

**Interferometric Studies. I. Determination of the Refractive Index and Protein Content of Blood-serum by the Interferometer.** L. BELTZ and E. KAUFMANN (*Z. klin. Med.*, 1925, **101**, 409—428; from *Chem. Zentr.*, 1925, i, 2586).—The concentration and protein contents of small amounts of blood plasma may be conveniently and accurately determined by means of the interferometer. Mixtures of potassium and sodium chloride solutions and of the protein and salts of blood-serum show additive relationships. G. W. R.

**Determination of Sugar in Small Quantities of Blood.** D. G. C. TERVAERT (*Biochem. J.*, 1925, **19**, 541—543).—A modification of Shaffer and Hartmann's method (*A.*, 1921, ii, 417). S. S. Z.

**Reducing Substances of the Blood.** A. HILLER, G. C. LINDER, and D. D. VAN SLYKE (*J. Biol. Chem.*, 1925, **64**, 625—638).—Determinations of reducing substances in normal blood by the methods of Hagedorn and Jensen (*A.*, 1923, ii, 265, 440) and of Folin and Wu (*A.*, 1920, ii, 337), after preliminary removal of dextrose either by yeast fermentation or by spontaneous glycolysis, give results equivalent to 0.01—0.03% of dextrose. The amount of these residual reducing substances is generally high in cases of glomerulonephritis with nitrogen retention; by administration of insulin to rabbits it is possible to reduce the fermentable sugar of the blood to zero without affecting the other reducing substances. C. R. H.

**Urea Determinations on Small Quantities of Blood.** J. PATTERSON (*Biochem. J.*, 1925, **19**, 601—603).—The blood is received in potassium dihydrogen phosphate, and treated with urease.

The ammonia formed is collected in 0.01*N*-sulphuric acid. A mixture of methyl-red and methylene-blue is used as indicator. Accurate results can be obtained with 0.2—0.5 c.c. of blood.

S. S. Z.

**Determination of Uric Acid in Blood Plasma.** M. DELAVILLE and C. JONES (*Compt. rend. Soc. Biol.*, 1925, **92**, 522—524; from *Chem. Zentr.*, 1925, i, 2586).—Removal of the proteins of blood plasma by means of metaphosphoric acid results in too low values being found for uric acid in the filtrate. If, however, the boiling liquid is treated with 3% sulphuric acid and submitted to ultra-filtration after cooling, satisfactory values may be obtained, using the phosphotungstic acid colorimetric method.

G. W. R.

**Use of Quinhydrone Electrode for Determination of  $p_H$  of Serum.** G. E. CULLEN and E. BILLMANN (*J. Biol. Chem.*, 1925, **64**, 727—738).—The quinhydrone electrode (Billemann, A., 1921, ii, 372) can be used conveniently for the determination of  $p_H$  of blood-serum provided that the latter is quite free from hæmoglobin.

C. R. H.

**Use of the Glass Electrode in Biochemistry.** P. T. KERRIDGE (*Biochem. J.*, 1925, **19**, 611—617).—Two glass electrodes, requiring only 0.5 c.c. of liquid, are described.

S. S. Z.

**Micro-electrode for Determination of Hydrogen-ion Concentration.** J. H. BODINE and D. E. FINK (*J. Gen. Physiol.*, 1925, **7**, 735—740).—The apparatus consists of a small pyrex glass bulb, fitted with side tube for the supply of hydrogen, and ending below in a capillary, into which the solution to be tested is drawn by capillarity until it just makes contact with a platinum wire electrode. The whole is mounted in the tube of a microscope, which can be lowered until the end of the capillary makes contact with the potassium chloride solution contained in a U-tube fixed to the microscope stage. Into the other arm of the U-tube dips a calomel electrode. The apparatus is easily cleaned, and determinations are quickly made with an accuracy of 0.02 to 0.05  $p_H$ , using 0.015 to 0.02 c.c. of fluid. It is therefore suitable for use with the blood and body fluids of small insects.

H. P. M.

**Micro-Method for Titrating the Bicarbonate in Plasma.** E. H. LEPPER and C. J. MARTIN (*Biochem. J.*, 1925, **19**, 573—580).—The blood is collected, from a free puncture of the skin, in a specially constructed tube containing a few crystals of oxalate and a little liquid paraffin, and is centrifuged. The plasma is then introduced into a flask from a micro-burette and the carbon dioxide removed by shaking until by inverting the flask over a tube the contents match a standard tube containing sodium dihydrogen phosphate of  $p_H$  7.07.

S. S. Z.

**Effect of X-Rays on the Acid-Base Equilibrium of Blood.** P. PAGNIEZ, F. COSTE, and I. SOLOMON (*Compt. rend. Soc. Biol.*, 1925, **92**, 489—491; from *Chem. Zentr.*, 1925, i, 2570).—Normal individuals submitted to the action of X-rays of medium penetrative

power (dose=500 *R*) showed alkalosis of the blood in 83% of cases. The average change in  $p_H$  was 4.7%, the maximum change being 20%. The alkalosis thus obtained was independent of the part submitted to radiation, appeared generally 1 hr. after treatment, and persisted occasionally for 24 hrs. G. W. R.

**Colloidal Theory of Hæmolysis.** F. HERRMANN and M. ROHNER (*Arch. exp. Path. Pharm.*, 1925, **107**, 192—237).—A distinction is made between hæmolysis due to osmotic action and that due to solution of the lipoid-protein corpuscular envelope. Solution of the hæmoglobin may also play a part. In hæmolysis by ammonium salts, the Hofmeister anion series is followed, whilst in the case of mercury salts, those which most readily form complex compounds are the most intensely hæmolytic. A study of the resistance of the corpuscles of different animals to the two main types of hæmolysis shows that, as the size of the corpuscles increases, the resistance to hypotonic solutions increases, whilst that to lecithin diminishes. The integrity of the corpuscular envelope depends on the maintenance of the ratio of "dispersive" to "aggregative" forces ( $d/s$ ) within certain limits. Lecithin causes hæmolysis by increasing the "dispersive" or "adsorptive" forces, whilst hypotonicity, salts, etc. hæmolyse by promoting imbibition and coagulation. The two types of hæmolytic agent are mutually antagonistic and inhibitory. Cholesterol inhibits both types of action and appears to stabilise the lipoid phase. H. P. M.

**Changes in Conductivity of Red Cell Suspensions during Hæmolysis.** E. PONDER and W. W. TAYLOR (*Biochem. J.*, 1925, **19**, 552—558).—The liberation of electrolyte from red cells during hæmolysis by water is proportional to the percentage number of cells hæmolysed and is complete when hæmolysis is complete. In complement-amboceptor hæmolysis the full amount of electrolyte does not appear to be liberated. This is due to some of the electrolyte passing out of the cells combined with hæmoglobin, from which it can be split off by the addition of saponin and also, to some extent, by heating. S. S. Z.

**"Third Component" or Heat-stable Factor of Complement.** H. R. WHITEHEAD, J. GORDON, and A. WORMALL (*Biochem. J.*, 1925, **19**, 618—625).—Zymin, like yeast, inactivates the complement activity of guinea-pig serum. Both substances act as more efficient inactivators if they are previously heated in normal saline or in the dry condition at 100° for  $\frac{1}{2}$  hr. The complement activity can be restored by the addition of serum previously heated at 56°. Kaolin and charcoal do not inactivate serum. S. S. Z.

**Presence of Argon in Living Cells.** A. PICTET, W. SCHERRER, and L. HELFER (*Compt. rend.*, 1925, **181**, 236—238).—The traces of argon produced (cf. this vol., i, 865) in the fermentation of dextrose are now shown to be present in the yeast. The following quantities of argon are present in 1 g. of the tissues (dried) named: yeast, 0.28—0.31 c.c.; sheep's brain, 0.86 c.c.; coagulated ox-blood,

0.84 c.c. Since neither fibrin nor hæmoglobin obtained from ox-blood contains argon, the presence of the latter in the blood clot is not due to superficial absorption. Possibly the argon is occluded in the cells and escapes when these are ruptured. R. B.

**Determination of Very Small Amounts of Lead in Animal Tissues.** H. BERNHARDT.—(See ii, 1003.)

**Determination of Chlorine in Small Amounts of Tissue.** E. URBACH and P. FANTL (*Wiener klin. Woch.*, 1925, **38**, 384—385; from *Chem. Zentr.*, 1925, i, 2325). G. W. R.

**Fatty Acids in Subcutaneous Fat of Man.** H. C. ECKSTEIN (*J. Biol. Chem.*, 1925, **64**, 797—806).—The abdominal subcutaneous fat of man contains, on the average, 0.37% of unsaponifiable matter (0.24% of cholesterol) and 94.6% of fatty acids, of which 63.6% are unsaturated. Fractionation of the unsaturated acids by distillation of their methyl esters, and subsequent determinations of iodine values and analysis of bromine additive products, gave evidence of the presence of acids containing two, three, and four double bonds. The saturated acids probably include traces of lauric acid and about 1% of myristic acid. The proportions of saturated and unsaturated fatty acids are approximately the same as in blood and fæces. C. R. H.

**Adipocere.** A. TSCHIRCH and H. GFELLER (*Chem. Umschau*, 1925, **32**, 181—183).—The low iodine value (7.7—10.8) for adipocere indicates that it is formed by the hydrogenation of the unsaturated acids of human fat. The acid value (188—197) and the m. p. (62°) are higher than for human fat. The presence of cholesterol was noted. The bearing of these facts on the formation of petroleum from organic deposits is briefly discussed. H. P. M.

**Synthesis of the Histones of the Thymus Gland.** K. FELIX (*Z. physiol. Chem.*, 1925, **146**, 103—121).—The product obtained by digestion of the histones of the thymus gland with pepsin and hydrochloric acid is divided by precipitational methods into five fractions, and determinations of free amino and carboxyl groups and of methylatable nitrogen are carried out. Digestion does not appear to liberate free amino and carboxyl groups to any great extent. Lysine is set free, but not in sufficient amount to explain the very great increase in methylatable nitrogen, which probably results from the increase of free guanidine groups. These methylate along with the free amino groups on treatment with methyl sulphate. It would appear, therefore, that the fragments into which the histones are decomposed by digestion are bound together by linkings between the guanidine groups. P. W. C.

**Bile Pigments. IX.** H. FISCHER and G. NIEMANN.—(See i, 1198.)

**Liberation of Adsorbed Substances from Proteins. A Function of the Bile Salts.** I. S. M. ROSENTHAL (*J. Pharm. Expt. Ther.*, 1925, **25**, 449—457).—Rose-Bengal, bromosulphthalein



(dyes excreted in the bile), and bilirubin, have been shown by ultra-filtration experiments to be completely bound *in vitro* by the blood proteins, but to be liberated from this combination by sodium taurocholate. Phenolsulphonephthalein, which circulates in the blood partly bound to the proteins, is also liberated by bile salts, so that *in vitro* it becomes entirely diffusible. Sodium taurocholate increases the permeability of collodion membranes to dyes.

C. P. S.

**Phosphatide and Total Phosphorus Content of Human and Cow's Milk.** A. F. HESS and F. D. HELMAN (*J. Biol. Chem.*, 1925, **64**, 781—796).—Cow's milk contains about four times as much total phosphorus and twice as much lipid phosphorus as human milk; the latter usually contains a higher percentage of lipid phosphorus in the early period (two weeks after birth) than later. No definite relation could be shown to exist between the fat and lipid phosphorus content of milk.

C. R. H.

**Chemical Constituents of Camel's Urine.** B. E. READ (*J. Biol. Chem.*, 1925, **64**, 615—617).—The 24-hr. urine of a camel contained 8.7 g. of total nitrogen; there was no ammonia, very slight traces of urea, 9.24 g. of total creatinine, 39.0 g. of hippuric acid, 4.7 g. of purine bases, and 7.99% of chlorides.

C. R. H.

**Determination of Acetoacetic Acid and  $\beta$ -Hydroxybutyric Acid in Urine.** M. W. GOLDBLATT (*Biochem. J.*, 1925, **19**, 626—632).—The urine is precipitated with basic lead acetate and ammonia and to an aliquot portion of the filtrate sulphuric acid is added. Through the heated mixture a current of air is aspirated. The distillate is received in *N*/50-iodine and sodium hydroxide. Hydrochloric acid is then added and the mixture is titrated with *N*/200-sodium thiosulphate, which gives the acetoacetic acid and acetone content. The residue in the distilling flask is then oxidised with potassium dichromate and the distillate is treated similarly to that above, whence the  $\beta$ -hydroxybutyric acid content is calculated. The determination of  $\beta$ -hydroxybutyric acid in dilutions containing less than 1 mg. per c.c. gave a yield of 65—68% and for dilutions of 1—2 mg. per c.c. 70—75%.

S. S. Z.

**Determination of Ammonia and Ammonium Salts in Urine.** A. YOVANOVITCH (*Compt. rend. Soc. Biol.*, 1925, **92**, 520—522; from *Chem. Zentr.*, 1925, i, 2586—2587).—Urine (2 c.c.) is treated with sufficient lithium carbonate solution to give an alkaline reaction. The ammonia is then distilled with steam in a vacuum at 40—50° into 5—10 c.c. of 1/70—1/20*N*-hydrochloric acid. After distilling for 5 mins., the excess of acid is titrated, using methyl-red as indicator, carbon dioxide being first removed (by boiling).

G. W. R.

**Cholesterol Secretion in the Urine.** I. J. A. GARDNER and H. GAINSBOROUGH (*Biochem. J.*, 1925, **19**, 667—671).—Cholesterol exists in urine in free and ester forms and as a compound only

hydrolysable by strong acids. In cases of parenchymatous nephritis accompanied by cholesterolaemia, there is an increased excretion of all forms of cholesterol. In highly albuminous urine, the cholesterol in free and ester forms is almost wholly precipitated with the proteins on boiling with very dilute acetic acid. This precipitated cholesterol has the same ratio of ester to total cholesterol as is found in plasma. The cholesterol compound which is hydrolysable by acids remains in solution after precipitation in approximately the same quantity as the total other forms in the whole urine. It is suggested that this compound is cholesterol ethereal sulphate.

S. S. Z.

**Determination of Small Amounts of Reducing Sugars in Urine.** F. WOKES (*Pharm. J.*, 1925, **115**, 127—131).—The following modification of the micro-blood-sugar method of Cole ("Practical Physiological Chemistry," 6th edition, p. 253) is used: To 20 c.c. of urine add 20 c.c. of a solution prepared by dissolving 220 g. of red mercuric oxide in 160 c.c. of concentrated nitric acid and 160 c.c. of water, adding 75 c.c. of *N*-sodium hydroxide, diluting to 1 litre, and filtering. Then add solid sodium hydrogen carbonate to alkalinity, filter, and to 10 c.c. of the filtrate add a slight excess of sodium sulphide solution. Dilute to 100 c.c. and filter. By qualitative tests it is possible to find, from a table given, the amount of filtrate to use in order that the determination may be carried out on a solution containing 0.0002—0.0015% of reducing sugar, which range gives the greatest accuracy. To the amount of filtrate thus determined, add 3 c.c. of a solution containing, in 250 c.c., 20 g. of potassium hydrogen carbonate, 30 g. of potassium carbonate (anhydrous), 0.875 g. of copper sulphate, and 0.075 g. of potassium iodate. Dilute to 23 c.c., boil for 8 mins., run in 5 c.c. of dilute sulphuric acid, cool to 20°, add 2 drops of 10% potassium iodide, and titrate with *N*/200 sodium thiosulphate, using a micro-burette. The results agree within 5%.

B. F.

**Glucose [Dextrose] Content of Normal Urine.** G. S. LUND and C. G. L. WOLF (*Biochem. J.*, 1925, **19**, 538—540).—When normal urine is fermented with yeast no production of carbon dioxide can be detected by the differential manometer of Barcroft. Dextrose is, therefore, absent from normal urine.

S. S. Z.

**Excretion of Purine Derivatives in Dogs.** E. LANGFELDT and J. HOLMSEN (*Biochem. J.*, 1925, **19**, 717—723).—In dogs on a fat diet the percentage of the total nitrogen excreted as allantoin nitrogen is fifteen times higher than in man. Both allantoin and uric acid excretion in dogs increases when protein is given. In three dogs kept on the same diet of milk and bread *ad libitum*, the uric acid and allantoin excretion varied with the individuals. From comparisons of the "uricolytic index" (percentage of allantoin nitrogen on the sum of uric acid nitrogen and allantoin nitrogen) of the various animals it is concluded that the oxidation of uric acid also varied with the individual animals.

S. S. Z.

**Elimination of Benzoic Acid and Benzoates from the Body.**

F. BORDAS, FRANÇOIS-DAINVILLE, and ROUSSEL (*Compt. rend.*, 1925, **181**, 304—306; cf. A., 1914, i, 457; 1915, i, 744; 1919, i, 424; 1924, i, 685).—After ingestion of repeated doses of sodium benzoate, elimination of the acid from the body is not complete until three days after the last dose. This retention of benzoates renders their use as a food preservative dangerous. L. F. H.

**Absorption Coefficient of Mesobilirubinogen and Coproporphyrin.**

G. NIEMANN (*Z. physiol. Chem.*, 1925, **146**, 181—195).—The absorption spectrum has been examined of preparations of the condensation product of mesobilirubinogen (urobilinogen) with *p*-dimethylaminobenzaldehyde. The absorption coefficient was found to be 0.0000099315 at the point of maximum absorption ( $\lambda=556$ ); a knowledge of this constant makes it possible to obtain absolute values for the concentration of urobilinogen in mixtures such as faeces by the spectrophotometric method of Charnass (A., 1909, i, 820). Urobilinogen could not be isolated in crystalline form from faeces, nor could a crystalline preparation of its condensation product with *p*-dimethylaminobenzaldehyde be obtained. The absorption spectra of coproporphyrin and Kämmerer's porphyrin in ethereal solution are sufficiently different from one another with regard to the bands in the red to enable one to be detected spectroscopically in the presence of the other; this is not the case with their esters. C. R. H.

**Metabolism of Carcinoma Cells.**

O. WARBURG (*Klin. Woch.*, 1925, **4**, 534—536; from *Chem. Zentr.*, 1925, i, 2316—2317).—Metabolism in carcinoma cells is similar to that of the aerobic lactic acid bacillus, being partly fermentative and partly oxidative in character. Carcinoma cells are distinguished by their fermentative activity from embryonic tissue and from resting and growing epithelium, the metabolism of which is, on the balance, oxidative. The fermentative metabolism of the carcinoma cell is qualitatively and quantitatively equivalent to the decomposition phase in embryonic metabolism. The equilibrium between decomposition and oxidation in carcinoma cells is displaced towards the side of decomposition. G. W. R.

**Comparison of the Polarimeter and Copper Reduction Values of Dextrose Solutions [in the presence of Phosphate, Insulin, and Liver Extract].**

H. L. WHITE.—(See ii, 1006.)  
**Nature of Dextrose in the Blood of Healthy Men.** C. LUNDSGAARD and S. A. HOLBOELL (*Compt. rend. Soc. Biol.*, 1925, **92**, 387—389; from *Chem. Zentr.*, 1925, i, 2385).—The blood of healthy men after treatment with sodium fluoride was dialysed for 1.5 hrs. and the optical rotation and reducing action were determined in the dialysate. The values found for  $[\alpha]_D$  varied from  $+16^\circ$  to  $+40^\circ$ , or appreciably below the values required for  $\alpha\beta$ -dextrose. After keeping the dialysate for 48 hrs., the value for  $\alpha\beta$ -dextrose was reached. It is concluded that  $\alpha\beta$ -dextrose is not present in blood. G. W. R.

**Nature of Dextrose in the Blood of Diabetics before and after Injection of Insulin.** C. LUNDGAARD and S. A. HOLBOELL (*Compt. rend. Soc. Biol.*, 1925, **92**, 395—397; from *Chem. Zentr.*, 1925, i, 2385; cf. preceding abstract).—The dialysate from the blood of diabetics shows after 1.5 hrs. an optical rotation corresponding with that for  $\alpha\beta$ -dextrose, and no change occurs after keeping for 48 hrs. Only two exceptions were found in thirteen cases. Two hrs. after injection of insulin, the dialysate behaves as that from normal blood. Dialysates from the blood in harmless glycosurias are similar to those from normal blood. It is concluded that in diabetes normal dextrose is not changed into forms with lower optical rotation. In order that insulin can restore the ability to change normal dextrose into other forms, the co-operation of some unknown substance in muscle is required.

G. W. R.

**Nature of Dextrose in Different Physiological Fluids.** C. LUNDGAARD and S. A. HOLBOELL (*Compt. rend. Soc. Biol.*, 1925, **92**, 398—399; from *Chem. Zentr.*, 1925, i, 2385; cf. preceding abstracts).—The optical behaviour of cerebrospinal fluid, oedema fluid, and pleural exudate is similar but even more marked than that of the dialysate from blood. The sugar of these fluids cannot be  $\beta$ -dextrose. The lower optical rotations of these fluids as compared with blood dialysates may be due either to a change of "neodextrose" into  $\alpha\beta$ -dextrose during the dialysis of blood, or a higher concentration of "neodextrose" in the fluids than in blood.

G. W. R.

**"Uricolytic Index" of Diabetic Dogs.** E. LANGFELDT and J. HOLMSEN (*Biochem. J.*, 1925, **19**, 724—726).—The "uricolytic index" (cf. i, 1205) decreases when nucleic acid is fed to diabetic dogs. This indicates a diminished power to destroy uric acid.

S. S. Z.

**Is Glycolysis Diminished in Diabetic Blood?** H. BIERRY, F. RATHERY, and R. KOURILSKY (*Compt. rend. Soc. Biol.*, 1925, **92**, 480—482; from *Chem. Zentr.*, 1925, i, 2571).—In defibrinated diabetic blood, treated aseptically at 38°, there is a continuous disappearance of free sugar. The intensity of the glycolysis depends on the sugar content and on the individual blood. The protein sugar may increase or decrease during glycolysis, but the total sugar content decreases. The effect of insulin on glycolysis is the same for normal as for diabetic blood.

G. W. R.

**Sodium, Potassium, and Calcium in Blood after Ovariectomy and in the Menopause.** A. BLANCHETIÈRE (*Compt. rend. Soc. Biol.*, 1925, **92**, 491—493; from *Chem. Zentr.*, 1925, i, 2571).—After ovariectomy and in the menopause there was in several cases an absolute increase in blood calcium, a decrease in the potassium content relative to the sodium content, and a decrease in the alkali content relative to the alkaline-earth content.

G. W. R.

**Hydrogen Carbonate of the Plasma and Hydrogen-ion Concentration of the Blood of Guinea-pigs Suffering from Scurvy.** E. H. LEPPER and S. S. ZILVA (*Biochem. J.*, 1925, **19**, 581—588).—There are large variations in the amount of hydrogen carbonate in the plasma of normal guinea-pigs; the hydrogen-ion concentration shows only slight variations. The titratable alkali of the plasma of guinea-pigs suffering from scurvy is on the average at a lower level than that of normal guinea-pigs. This is due to the deficiency of sodium and potassium salts of organic acids in the scurvy-producing diet. The addition of sodium citrate to the diet restores the normal hydrogen carbonate content of the plasma, but does not influence the onset of scurvy. An increase in the hydrogen-ion concentration of the blood of guinea-pigs suffering from scurvy was not observed. Scurvy is therefore not caused by acidosis.

S. S. Z.

**Metabolic Processes in *Ascaris lumbricoides*.** W. K. SLATER (*Biochem. J.*, 1925, **19**, 604—610).—The worms require oxygen for their normal metabolism, although they are capable of prolonged existence in the absence of air by reducing their movements to a minimum.

S. S. Z.

**Metabolism of Cold-blooded Animals. I.** K. Hsü (*Z. Biol.*, 1925, **83**, 45—52).—The nitrogen metabolism of frogs is investigated during starvation and during feeding with mealworms. An attempt to keep frogs in nitrogen equilibrium under different conditions by feeding with mealworms is only successful for a short time owing to incomplete digestion of the worms. The influence of temperature on metabolism is considered.

P. W. C.

**Acetylation of Amino-acids in the Animal Body.** F. KNOOP and J. G. BLANCO (*Z. physiol. Chem.*, 1925, **146**, 267—275).—After administration of the racemic acetyl derivatives of phenylglycine, phenylalanine (m. p. 151°), and phenyl- $\alpha$ -aminobutyric acid (m. p. 149°), the unoxidised acid excreted in the urine invariably consisted for the greater part of the *l*-isomeride. In the case of phenylalanine, at least, this indicates that the acetyl derivative of the naturally-occurring isomeride is the less readily metabolised and is evidence against the supposition that acetylation may be an intermediate step in the metabolism of amino-acids.

C. R. H.

**Organic Phosphorus and Calcium of the Blood Plasma during the Development of Callus in Fracture.** S. SATANOVSKI (*Compt. rend. Soc. Biol.*, 1925, **92**, 826—827; from *Chem. Zentr.*, 1925, i, 2452—2453).—The phosphorus content of the plasma of dogs increases by 1 mg. per 100 c.c. on the third day after a fracture, rises for 1 month, and after 5—6 weeks returns to normal. The calcium content is practically unaffected.

G. W. R.

**Bone Growth. II. Changes in Calcium, Magnesium, and Phosphorus of Bone during Growth. III. Changes in Composition of Ash.** F. S. HAMMETT (*J. Biol. Chem.*, 1925, **64**, 685—692, 693—696; cf. this vol., i, 1001).—II. Growth capacity

curves for total ash, calcium, and phosphorus in the bones of growing rats are almost identical; that for magnesium indicates a retardation at the 50th day.

III. The ash of bones of growing rats shows an increase in the calcium percentage and a decrease in that of magnesium and of phosphorus, the changes being complete at the conclusion of puberty (75th day).  
C. R. H.

**Calcification. I. Solubility Product of Secondary and Tertiary Calcium Phosphate. II. Delayed Equilibrium between the Calcium Phosphates and its Biological Significance.** L. E. HOLT, jun., V. K. LA MER, and H. B. CHOWN. **III. Equilibria Concerned with Calcification of Bone.** L. E. HOLT, jun. (*J. Biol. Chem.*, 1925, **64**, 509—565, 567—578, 579—587).—I. Titration curves at 38° of phosphoric acid with calcium hydroxide were obtained and the precipitates and solutions at the different stages analysed for calcium and phosphorus; continuous shaking for at least 10 days was carried out after each addition of calcium hydroxide to allow the attainment of complete equilibrium. The form of the curves so obtained was similar to that reported by Wendt and Clarke (A., 1923, ii, 417). The Ca : P ratio of the precipitates indicated that these consisted of secondary calcium phosphate when the calcium hydroxide added was between 1·07 and 1·11 equivalents, of tertiary calcium phosphate when 1·2—3·0 equivalents were added, and of a more basic substance (? hydroxyapatite, cf. Bassett, A., 1908, ii, 675) when more than 3·0 equivalents were added. By mathematical treatment of the equations defining the three dissociation constants of phosphoric acid and of that relating the total molecular concentration of phosphorus to the sum of the concentrations of ionised and non-ionised phosphoric acid, there are derived expressions for the concentrations of the different phosphate ions in terms of the  $p_H$ , the total phosphorus concentration, and the three dissociation constants; thus  $[PO_4'''] = [P]k_1k_2k_3/[H^+]^3 + [H^+]^2k_1 + [H^+]k_1k_2 + k_1k_2k_3$ . It was therefore possible to calculate the solubility product constants of secondary and tertiary calcium phosphate from the titration curve data. Calculated thus the solubility constant of tertiary calcium phosphate exhibited marked but constant differences at different points on the curve, which could be correlated with the varying concentrations of primary phosphate ions in the solution. The experiments were extended to solutions to which were added neutral salts (*e.g.*, sodium chloride and magnesium sulphate); the presence of these greatly increased the solubility of the calcium phosphate, the magnitude of the effect of the added salt increasing with the valency of its component ions. The theory of Debye and Hückel (A., 1923, ii, 724; 1924, ii, 386; Brönsted and La Mer, A., 1924, ii, 306) was applied to the solubility data obtained, and curves were plotted showing the relation between the stoichiometric solubility product and the square root of the ionic strength of the solution; extrapolation of such curves to zero ionic strength gave the solubility product at infinite dilution; for tertiary calcium phosphate

this was  $10^{-32.5}$  and for secondary calcium phosphate  $10^{-6.4}$  at  $38^{\circ}$ . In blood-serum, the solubility product for tertiary calcium phosphate was  $10^{-26}$  and in presence of the inorganic salts alone of blood-serum  $10^{-27.2}$ . The authors discuss the results of Kugelmass and Shohl (A., 1924, ii, 235) and point out that their own experiments indicate that the  $p_H$  at which the maximum buffer effect is exerted by calcium depends on the solubility product of calcium phosphate (and hence on the other salts in solution); e.g., in presence of 0.1*M*-sodium chloride the maximum buffer effect is at  $p_H$  5.6, whilst in presence of 0.1*M*-magnesium sulphate it is at  $p_H$  6.4.

II. A solution was prepared by adding 2.13 equivalents of calcium hydroxide to a solution of phosphoric acid, the solution was kept at  $38^{\circ}$  with occasional shaking, and samples were withdrawn from time to time for determination of  $p_H$  and content of calcium and phosphorus. The data so obtained indicated that the solution was supersaturated with respect to secondary calcium phosphate for a short time only, subsequently becoming much under-saturated; with respect to tertiary calcium phosphate, however, it remained super-saturated for many days. The slowness of the precipitation of the latter salt is explained as being due in part to the transitory precipitation of secondary calcium phosphate and in part to the fact that the actual precipitation of tertiary calcium phosphate may be a reaction of the fifth order. Normal blood-serum is super-saturated with tertiary calcium phosphate to the extent of 200%; although this calcium phosphate is not precipitated on shaking such serum alone, precipitation does take place if the serum is shaken in contact with solid calcium phosphate.

III. Recalculation, in the light of the preceding papers, of data obtained by previous workers, shows that the solubility product of tertiary calcium phosphate in the blood-serum is markedly reduced during active rickets, although even in this condition the serum remains supersaturated.

C. R. H.

**Effect of Ultra-violet Light on the Mineral Metabolism of the Lactating Animal.** J. B. ORR, H. E. MAGEE, and J. M. HENDERSON (*Biochem. J.*, 1925, **19**, 569—572).—In three balance experiments on lactating goats it was found that irradiation by a carbon arc lamp reduced the quantity of calcium excreted in the faeces; the urinary excretion remained practically constant.

S. S. Z.

**Influence of Small Quantities of Potassium Iodide on the Assimilation of Nitrogen, Phosphorus, and Calcium in the Growing Pig.** F. C. KELLY (*Biochem. J.*, 1925, **19**, 559—568).—Small amounts of iodine, as potassium iodide, added to cereal rations of young growing pigs, lead to increased assimilation and retention of nitrogen and phosphorus. Evidence of an increased retention of calcium was less definite. The amount of iodine required varies with the individual animals.

S. S. Z.

**Effects of Parathyroid Feeding on Calcium and Creatine Metabolism.** D. WOODMAN (*Biochem. J.*, 1925, **19**, 595—600).—Administration of extracts of parathyroid has no effect on the weight

of adult rats or on the growth of young ones. The treatment has no effect on creatine metabolism as measured by muscle creatine, but causes an alteration in the ratio of creatinine to creatine excreted, resulting in the elimination of more creatine and less creatinine. Parathyroid feeding and injections have no effect on the deposition of calcium in bone. S. S. Z.

**Effect of Insufficient Feeding with Carbohydrates and Protein on the Excretion of Creatine and Creatinine.** W. PALLADIN (*Bull. Acad. St. Pétersbourg*, 1916, [6], 1129—1137; from *Chem. Zentr.*, 1925, i, 2573).—Creatine appears in the urine of dogs on a carbohydrate-free diet, but when very large amounts of protein are given it disappears, probably because the excess protein yields carbohydrate in the body. Creatine is found in the urine with a diet containing no protein when the carbohydrate portion of the ration falls below 12%, calculated on energy value. G. W. R.

**Hyperglycæmia Produced by Glycerol.** C. VOEGTLIN, J. W. THOMPSON, and E. R. DUNN (*J. Biol. Chem.*, 1925, 64, 639—642).—Oral or intra-peritoneal administration of glycerol to fasting rabbits produces a marked rise in the blood-sugar concentration, which reaches its greatest height in about 1 hr.; determinations of total solids show that there is no concentration of the blood. C. R. H.

**Urinary Excretion of Tartrates following Administration to Animals.** G. E. SIMPSON (*J. Pharm. Exp. Ther.*, 1925, 25, 459—466).—Sodium *d*-tartrate, injected subcutaneously, was eliminated in the urine of cats, dogs, and rabbits to the same extent, up to 88% being recovered. The amount recovered after oral administration was less, and was considerably smaller in the case of rabbits than of dogs. These differences may perhaps be ascribed to greater bacterial destruction in the intestine of the rabbit. Animals receiving subcutaneous doses at wide intervals developed a tolerance with continued ability to excrete the toxic substance; the opposite was true of animals which received doses at short intervals. C. P. S.

**Pharmacological Behaviour of Malic Acid and its Salts.** F. P. UNDERHILL and G. T. PACK (*J. Pharm. Exp. Ther.*, 1925, 25, 467—485).—Magnesium malate, the most efficient laxative among the malic salts, is about as efficient as magnesium hydroxide. The minimum lethal dose of neutral sodium malate is 1.5 g. per kg. (tartrate 1.0 g.) for the rabbit, and 3.5 g. per kg. (tartrate 3.0) for the rat; 1 g. per kg. is non-toxic to dogs. Injection of malates may be followed by albuminuria, but without severe acute nephritis. C. P. S.

**Permeability and Physiological Action of Compounds of the Choline Group.** E. WERTHEIMER and H. PAFFRATH (*Pflüger's Archiv*, 1925, 207, 254—268; from *Chem. Zentr.*, 1925, i, 2382).—The permeability of living membranes shows great seasonal variation. Skin membranes of winter frogs are much more permeable



to choline than those of summer frogs. The physiological effect varies inversely with the rate of diffusion through living membranes in the case of choline, stearylcholine, formylcholine, propionylcholine, acetylcholine, trimethylammonium bromide, physostigmine, chloroacetylcholine, pilocarpine, and histamine. This regularity does not hold for dead membranes. Adrenaline increases the permeability for choline and similar compounds.

G. W. R.

**Intravenous Silver Therapy. II. Influence of Body Electrolytes on the Solubility of Silver Salts.** K. VON NEERGAARD (*Arch. exp. Path. Pharm.*, 1925, **107**, 316—348).—The greatest concentration of silver ions obtainable in presence of physiological electrolytes is shown mathematically and potentiometrically to be of the order of  $10^{-9}N$  or 1/10,000 mg. Ag per litre. This low order of magnitude is determined almost entirely by the concentration of chlorine ion. Administration of bromides and iodides or, under pathological conditions, the presence of ionised sulphur diminishes still further the silver-ion concentration. Silver, in addition, forms a sodium silver chloride complex, the concentration of which is also determined by the presence of  $Cl'$ . The maximum possible concentration of this salt is shown to be about 1 mg. per litre. Therapeutically, owing to the smallness of the dose, the saturation capacity is not reached, ionised silver chloride being first formed, but with higher doses more and more of the complex salt results. The degree of fineness of the colloidal particles of silver chloride does not show any real influence on the molecular solubility.

P. W. C.

**Application of the Law of Mass Action to the Course of Enzyme Action.** S. G. HEDIN (*Z. physiol. Chem.*, 1925, **146**, 122—129).—A number of enzyme reactions are discussed and an attempt to determine, by application of the law of mass action, the amount of free enzyme compared with the amount combined with substrate is regarded as unsatisfactory, some reactions having a velocity proportional to the amount of substrate, whilst in others the amount of combined or active enzyme is proportional to the total amount of enzyme.

P. W. C.

**Inhibition of *Cypridina* Luminescence by Light.** E. N. HARVEY (*J. Gen. Physiol.*, 1925, **7**, 679—685).—The luminescence of the luciferin-luciferase solution secreted by *Cypridina* is inhibited by illumination with a carbon arc, but partly returns in the dark. The ultra-violet has very little effect, and the greatest inhibitory action is produced by radiations between 4600 and 3800 Å., which region includes some of the radiations emitted by the luminescent solution. The inhibitory action is on the luciferin, the luciferase being unaffected. Other chemiluminescences studied were found not to be inhibited by light.

H. P. M.

**Polarised Light and Starch Grains.** W. N. JONES (*Ann. Bot.*, 1925, **39**, 651—653).—The evidence on which Baly and Semmens base their conclusions that exposure to polarised light accelerates hydrolysis of starch grains by diastase and causes

hydrolysis in the absence of the enzyme (cf. this vol., i, 12) is criticised. "The effect figured as due to hydrolysis brought about by exposure to polarised light is quite unlike that ordinarily induced by diastase. . . . If starch grains mounted in water are subjected to sudden slight pressure, results exactly comparable to those figured can be produced." Negative results were obtained on repeating the experiments of Baly and Semmens under conditions such that the starch grains could not be subjected to accidental pressure.  
C. T. G.

**Taka-esterase. Comparison with Pancreatic Lipase and Hepatic Esterase.** R. WILLSTÄTTER and H. KUMAGAWA (*Z. physiol. Chem.*, 1925, **146**, 151—157).—The esterase contained in taka-diaastase differs in its properties from both pancreatic lipase and hepatic esterase; it is most active at  $p_H$  8.6, is unaffected by the presence of calcium oleate or sodium oleate, is inhibited by albumin and by albumin together with calcium oleate, and hydrolyses the esters of mandelic acid much more readily than tributyrin; towards the esters of mandelic, phenylmethoxyacetic, phenylchloroacetic, and tropic acids it exhibits stereochemical specificity, its behaviour in this respect being similar to that of hepatic esterase (A., 1924, i, 1144).  
C. R. H.

**Determination of Pepsin in Gastric Juice.** I. BOAS (*Deut. med. Woch.*, 1925, **51**, 511—512; from *Chem. Zentr.*, 1925, i, 2327).—For the approximate determination of pepsin in gastric juice a cube of macaroni of known composition and weight is acted on. As it is digested, a certain amount of starch is liberated; this is determined and taken as a measure of the pepsin content.

G. W. R.

**Pepsin Determinations on Gastric Juice by the Method of Boas.** P. HIRSCH-MAMROTH and H. RINDFLEISCH (*Deut. med. Woch.*, 1925, **51**, 512—513; from *Chem. Zentr.*, 1925, i, 2327; cf. preceding abstract).—Small variations in the pepsin content of gastric juice may be readily shown by the method of Boas. The presence of blood in the gastric juice renders the method useless.

G. W. R.

**Xanthine Oxydase. VI. A Cell Oxidation System Independent of Iron.** M. DIXON and S. THURLOW (*Biochem. J.*, 1925, **19**, 672—675).—In the case of xanthine oxydase molecular oxygen seems to act as a direct acceptor of hydrogen in the system without being activated by iron, since the activity of the enzyme is not inhibited by cyanide or pyrophosphate; nor does the addition of iron accelerate the reaction.

S. S. Z.

**Nitrogenous Equilibrium of the Yeast Cell.** H. VON EULER and V. SANDBERG (*Z. physiol. Chem.*, 1925, **146**, 290—299).—During yeast fermentation of dextrose there was found an increase in the total and amino nitrogen of the yeast, a decrease in the total and amino nitrogen of the medium, no change in the total nitrogen, and a decrease in the amino nitrogen of the whole system, indicating

a synthesis of nitrogenous substances; no change was observed in the tyrosine content of the yeast. C. R. H.

**Alcoholic Fermentation. XI. Acids Resulting from Yeast Fermentation in Presence of Calcium Carbonate.** S. KOSTYTSCHEV and L. FREY (*Z. physiol. Chem.*, 1925, **146**, 276—285).—Among the products of rapid fermentation of sucrose, in a medium containing calcium carbonate, but free from nitrogenous substances, there were isolated succinic, malic, and acetic acids. It is suggested that aspartic acid may lose ammonia to give oxalacetic acid, which may be converted by carboxylase into carbon dioxide and acetaldehyde, the latter being either reduced to ethyl alcohol or oxidised to acetic and oxalic acids; alternatively, the oxalacetic acid might be reduced to malic acid. This scheme would also account for the occurrence of malic and oxalic acids in plants. C. R. H.

**Increase of Invertase Content of Yeast.** R. WILLSTÄTTER, C. D. LOWRY, jun., and K. SCHNEIDER (*Z. physiol. Chem.*, 1925, **146**, 158—180).—The increased content of invertase in yeast, following repeated fermentations of strong sugar solutions, observed by Meisenheimer and others (*A.*, 1913, i, 1139; 1915, i, 358), takes place to a greater extent in presence of minimal amounts of sucrose. The most favourable results (an increase of 8—15 times in the invertase concentration) were obtained by the slow addition of 20% sucrose solution to a suspension of yeast in an inorganic medium; the optimum temperature is 27°, but variations in temperature from 20° to 32° and of  $p_H$  from 4.5 to 7.0 do not exert great influence on the reaction. Better results were obtained with relatively fresh yeast than with that which had been used repeatedly in the brewery. Dextrose could be substituted for sucrose without affecting the results, but maltose gave less increase of invertase. Yeast treated in this manner showed a slight increase in its content of maltose, but no change in that of  $\beta$ -glucosidase or protease or in its fermenting power. C. R. H.

**Capacity of Fresh Yeast to Ferment Galactose after Preliminary Treatment with this Sugar and the Constancy of this Property.** H. VON EULER and T. LÖVGREN (*Z. physiol. Chem.*, 1925, **146**, 44—62).—The authors' top yeast *R* by preliminary treatment with galactose develops the power of fermenting this sugar. Such treatment causes the capacity of the yeast to ferment dextrose to fall in the ratio 55:30, whilst its power to ferment galactose never attains 50% of that for dextrose. Yeast treated with galactose retains its power of fermenting this sugar for a long time after it has been returned to its original substrate, dextrose. P. W. C.

**Kinetics of the Cleavage of Peptides by Yeast Enzymes.** A. FODOR and C. EPSTEIN (*Kolloid-Z.*, 1925, **37**, 168—178).—A continuation of previous researches on the velocity of polypeptide cleavage by macerated yeast juice (cf. *Fermentforsch.*, 1916, **1**, 533). The results obtained when the enzyme is used in the following media—(i) the original juice, (ii) a kaolin adsorbate of the juice,

and (iii) a glycine elutriate of this adsorbate—are compared and discussed.  
N. H. H.

**Nature of the Peptide-cleaving Enzyme of Yeast Macerates.** A. FODOR, A. BERNFELD, and R. SCHÖNFELD (*Kolloid-Z.*, 1925, **37**, 32—37; 159—168).—A direct separation of the enzyme-carrier from the chief mass of the phosphoprotein of macerated yeast is possible, but the solutions obtained have only a weak activity. Adsorption on kaolin and elution with glycine solutions give active solutions containing only minute traces of protein. The enzyme-carrier is a very unstable colloid. After a second adsorption and elution, the activity falls to one-half in 24 hrs. The most active fraction from fractional precipitation with acetone corresponds in composition with the phosphoprotein obtained by acid precipitation. A method for preparing a solution of the enzyme, free from detectable quantities of protein and phosphoric acid, is given in which adsorption by kaolin is followed by elution of the adsorbate with 2.5% glycine solution.  
E. M. C. and N. H. H.

**Formation of Acetylmethylcarbinol and 2:3-Butylene-glycol in the Fermentation of Sugars by Alcohol Yeasts and True Lactic Acid Bacteria.** A. J. KLUYVER and H. J. L. DONKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 314—317).—Whilst the carbinol and glycol have long been known to be formed by some microbes, the yeasts and true lactic acid bacteria do not normally yield them, and also generally yield no free hydrogen, being therefore regarded as favouring oxidation of acetaldehyde with simultaneous removal of hydrogen by the protoplasm (stage C, following abstract). If a compound which can act as a hydrogen acceptor, e.g., methylene-blue or sulphur, be added in the ordinary yeast fermentation of dextrose, this is reduced and the glycol and carbinol are formed. Lævulose acts in the same way both with yeast and lactic acid bacteria.  
S. I. L.

**The Unity in the Chemistry of the Fermentative Sugar Dissimilation Processes of Microbes.** A. J. KLUYVER and H. J. L. DONKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 297—313).—A general scheme put forward for the fermentative decompositions of the hexoses by microbes embraces the stages: (A) Conversion to 2 mols. of a hypothetical intermediate product  $C_3H_6O_3$ ; (B) transformation of this into (1) lactic acid and (2) formic acid and acetaldehyde; (C) oxidation of the products B(2) to carbon dioxide and acetic acid, respectively, with simultaneous reduction of protoplasm; (D) condensations of acetaldehyde, forming acetylmethylcarbinol and butyric acid, and of acetic acid, yielding carbon dioxide and acetone, and (E) regeneration of protoplasm from the reduction product formed in (C), with simultaneous reductions, yielding alcohols, glycerol, and other products. The microbes concerned are divided according to the products formed in fermentation into eight groups, and the stages of decomposition allocated between these on the basis of the known data. This characterisation is in accordance with the natural grouping.  
S. I. L.

**Adjustment of  $p_H$  of Culture Media under Sterile Conditions.**

L. M. CHRISTENSEN and E. I. FULMER (*Ind. Eng. Chem.*, 1925, **17**, 935).—The unit of apparatus consists of a 2-litre flask connected without stopcock to the burette. Air is admitted through soda-lime and U-tubes containing glass beads with just enough sulphuric acid to fill the bottom of the tube. A glass shield keeps out any organisms while the reagent is being added. Three such units are required (for acid, alkali, and water). The titration curve for the medium is found from the  $p_H$  values with known amounts of acid and water, and the desired adjustment made. [Cf. *B.*, 1925, 820.]

D. G. H.

**Acetone-producing Organisms.**

G. J. FOWLER and V. SUBRAMANYAN (*J. Indian Inst. Sci.*, 1925, **8 A**, 71—83).—Spores of the acetone bacillus developed in maize culture, and preserved in sealed tubes, retain their vitality for at least 7 years. The organism grows best on cereal mash, the insoluble vegetable protein of the grain being essential to its healthy metabolism. Post-fermentation changes in acidity and percentage of acetone are mainly due to bacterial activity. These organisms are widespread in nature and are associated especially with the presence of starch in seeds, tubers, or leaves.

G. M. B.

**Mahua Flowers as Raw Material for the Acetone Fermentation Process.**

A. G. GOKHALE (*J. Indian Inst. Sci.*, 1925, **8 A**, 84—87).—Mahua flowers have been successfully fermented by the acetone process, and the optimum conditions have been determined in detail. [Cf. *B.*, 1925, 777.]

G. M. B.

**Bacterium Producing Ethyl Butyrate.**

C. BIDAULT and S. BLAIGNAN (*Compt. rend. Soc. Biol.*, 1925, **92**, 416—417; from *Chem. Zentr.*, 1925, i, 2314).—A bacterium was isolated from pickling brine which resembled *Bacillus faecalis alkaligenes*. It produces ethyl butyrate in the presence of air.

G. W. R.

**Fermentation Products of Mannitol-Forming Bacteria.**

H. R. STILES, W. H. PETERSON, and E. B. FRED (*J. Biol. Chem.*, 1925, **64**, 643—654).—Four strains of mannitol-forming bacteria have been obtained from fermenting cereal infusions; when the pentoses were fermented the products were acetic and lactic acids. Mannitol was produced by all strains from levulose, by three of them from sucrose, and by two from raffinose, the other products being acetic and lactic acids, carbon dioxide, and (from raffinose) ethyl alcohol. Dextrose, galactose, and lactose were fermented in varying degrees to ethyl alcohol, carbon dioxide, and lactic acid; the lactic acid in almost all cases was inactive. One of the strains was able to produce volatile acid from calcium lactate and slowly to decompose mannitol with production of acetic and lactic acids.

C. R. H.

**Possible Rôle of Pyruvic Acid in Bacterial Growth.**

J. H. QUASTEL (*Biochem. J.*, 1925, **19**, 641—644).—Experimental evidence points to the probability that pyruvic acid or some very

closely allied substance derived from the compounds forming the source of nutritive carbon in the medium, is the first organic molecule entering into the protoplasmic synthesis of bacteria. S. S. Z.

**Dehydrogenations Produced by Resting Bacteria. II.** J. H. QUASTEL and M. D. WHETHAM (*Biochem. J.*, 1925, **19**, 645—651).—A record is given of the behaviour of a number of amino-acids, sugars, and related substances in the presence of resting *Bacillus coli* as the activating source and of methylene-blue as the hydrogen acceptor. The relative reducing powers of some of the donors are tabulated. S. S. Z.

**Dehydrogenations Produced by Resting Bacteria. III.** J. H. QUASTEL and W. R. WOOLDRIDGE (*Biochem. J.*, 1925, **19**, 652—659).—*Bacillus alkaligenes* possesses feeble activating powers, its reducing action being greatest with formic, lactic,  $\alpha$ - and  $\beta$ -hydroxy-butyric acids. It does not oxidise fumarates, malates, aspartates, nitrates, or chlorates. Its power of activating sugars is very slight. *B. prodigiosus* possesses powerful activating properties, which appear in the cases of fumarates, malates, and aspartates to be greater than those of *B. coli*. It activated all the sugars tested, its effects with sucrose, arabinose, and dulcitol being relatively weak. *B. proteus* is less powerful than *B. prodigiosus* or *B. coli* in activating fumarates, malates, or aspartates as hydrogen acceptors. The action on nitrates and chlorates is similar in all three organisms. Of the sugars tested only dextrose and lævulose are activated to any extent. The mechanism in *B. prodigiosus* and *B. proteus* which activates fumarates, nitrates, and chlorates is thermolabile. S. S. Z.

**Anaërobic Growth of Bacteria.** J. H. QUASTEL and M. STEPHENSON (*Biochem. J.*, 1925, **19**, 660—666).—*Bacillus alkaligenes* is incapable of anaërobic growth in the presence of nitrate or fumarate. *B. proteus* can grow anaërobically in the presence of nitrate and certain hydrogen donators, but not in the presence of fumarates and these donators; *B. coli* and *B. prodigiosus* can grow anaërobically on nitrate, fumarate, malate, or aspartate with glycerol (or in some cases lactate) as hydrogen donator. This points to the fact that anaërobic growth takes place when the organism is capable of activating some constituent of the medium as a hydrogen acceptor (see preceding abstract). S. S. Z.

**Sulphur Bacteria.** L. G. M. BAAS-BECKING (*Ann. Bot.*, 1925, **39**, 613—650).—An ecological study of communities of sulphur bacteria containing a large variety of forms. Endothiobacteria (*i.e.*, forms which deposit soluble liquid sulphur inside the cells) need a certain amount of light and occur within 20 cm. of the surface in alkaline water containing hydrogen sulphide. They are almost independent of the salt concentration, which may vary from 0.05% to 7.5%, and of the oxygen content of the water. Evidence is given indicating that the hydrosulphide ion and not free hydrogen sulphide is used by these organisms as a source of energy. The mechanism of the formation of sulphur in the cells is discussed. C. T. G.

**Conversion of Sulphur into Sulphate by Micro-organisms of the Soil.** G. GUITTONNEAU (*Compt. rend.*, 1925, **181**, 261—262).—By methods previously described (this vol., i, 766), the author has now obtained from soil cultures a micro-organism which is capable of transforming thiosulphates into sulphates. The new micro-organism has very little action on sulphur itself, whilst the organisms previously described are incapable of converting thiosulphate into sulphate. Where both organisms are present the final product is, however, sulphate, but in the presence of large quantities of ammonium succinate the conversion of thiosulphate into sulphate is inhibited, and the thiosulphate accumulates.  
R. B.

**Rôle of Auxiliary Pigments in the *Cyanophyceæ*.** A. RICHTER (*Bull. Acad. St. Pétersbourg*, 1916, [6], 1115—1128; from *Chem. Zentr.*, 1925, i, 2568—2569).—Phycocyanin and carotin in blue-green algæ do not act as assimilators of carbon dioxide.  
G. W. R.

**Calcium Requirements of Algæ and Fungi.** O. LOEW (*Biol. Zentr.*, 1925, **45**, 122—125; from *Chem. Zentr.*, 1925, i, 2312).—There is no sharp distinction between algæ and fungi in their relationships to calcium. Certain of the lower algæ can grow in the absence of calcium, whilst in the higher fungi a supply of calcium is necessary. Reagents, such as oxalates, which precipitate calcium are without harmful effect on organisms which do not require calcium. Certain fungi may grow vegetatively in the absence of calcium but require calcium for spore formation.  
G. W. R.

**Adrenaline Secretion during Starvation.** S. OGAWA (*Arch. exp. Path. Pharm.*, 1925, **107**, 171—179).—The adrenaline secretion in rabbits is determined by means of the Trendelenburg frog preparation on samples of blood taken, without anæsthetic, from the vena cava in the neighbourhood of the suprarenal vein. The adrenaline content of the suprarenal glands is determined colorimetrically by means of mercuric chloride and sodium acetate. An increased adrenaline secretion is observed during the first few days of starvation, followed by a progressive diminution in the secretion accompanied by a reduction in the adrenaline content of the glands.  
H. P. M.

**Product with Insulin Action.** W. STIX (*Z. physiol. Chem.*, 1925, **146**, 143—146).—Formol titration, bromination, esterification, etc. of an insulin solution were attempted with inconclusive results.  
P. W. C.

**Insulin. I. Is Insulin an Unstable Sulphur Compound?** J. J. ABEL and E. M. K. GEILING (*J. Pharm. Exp. Ther.*, 1925, **25**, 423—448).—A commercial preparation, "Iletin" (Lilly), is repeatedly precipitated by pyridine from its aqueous or acetic acid solution. From the mother-liquors, by further fractionation, all but a trace of hypoglycæmic activity can be removed, leaving about 35—40% of the total material. Crystalline amino-acids

and a very slightly active protein-like substance have been isolated. The substances insoluble in pyridine are then extracted with 90% phenol, and the insulin is precipitated from the phenol solution by addition of excess of distilled water. The precipitate is dissolved in dilute acetic acid and reprecipitated by pyridine. Finally, it is several times dissolved in dilute acetic acid and precipitated by addition of saturated sodium chloride solution. The product so obtained is evaluated at 40 or more rabbit units per mg., whereas the original material was 8—12 units per mg. This active insulin is inactivated by boiling for a short time with 0.1N-sodium carbonate, whereby the mode of combination of part, if not all, of the sulphur is altered, enabling it subsequently to be liberated by acid in the form of hydrogen sulphide. No ammonia is liberated by this treatment. The inert fractions obtained during the purification contain very little of this labile sulphur, the content of which appears to be directly proportional to the hypoglycæmic activity. Phosphorus is not a constituent of insulin. C. P. S.

**Distribution of Insulin in the Organs of Normal and Depancreatized Dogs.** M. NOTHMANN (*Arch. exp. Path. Pharm.*, 1925, **108**, 1—63).—The organs of normal animals contain insulin identical in all respects with pancreatic insulin, but 2 to 5 days after depancreatization the liver only contains insulin. The insulin in all organs other than the liver is therefore derived from the pancreas. The function of the hepatic insulin of the diabetic is possibly the conversion into glycogen of lævulose, which is known to be metabolised by the diabetic. E. C. S.

**Variations in the Hydrogen-ion Concentration of the Blood under Different Conditions. I. Effect of Single Administrations of Nutrient Substances. II. Effect of Insulin and other Organ Extracts.** A. GIGON (*Z. ges. exp. Med.*, 1925, **44**, 95—106; 107—115; from *Chem. Zentr.*, 1925, 2315—2316).—I. The normal  $p_H$  of the blood of healthy fasting men at rest is 7.24—7.35. After drinking 1 litre of water while fasting, there was a marked decrease in the  $p_H$  of the blood for at least 3 hrs., the urine showing a corresponding increase in  $p_H$ . Administration of 100 g. of dextrose or lævulose caused a decrease in  $p_H$ , after 10—30 min. in the case of dextrose, later in the case of lævulose. In both cases, the urine became slightly more acid. Caseinogen was without effect. Olive oil increased alkalinity. Hydrochloric acid rendered the blood more acid without affecting the reaction of the urine. The action of sodium hydrogen carbonate in raising  $p_H$  is more marked in the urine than in the blood. Dextrose and lævulose, both orally and subcutaneously, have similar effects in rabbits. Sucrose and physiological salt solution are without effect. Olive oil given subcutaneously raises the  $p_H$  more markedly than when given orally. Oral administration of sodium hydrogen carbonate causes a marked rise in blood  $p_H$ .

II. Insulin administered to rabbits in doses insufficient to cause convulsions does not appreciably affect the  $p_H$  of the blood. Larger doses cause a temporary increase in blood  $p_H$  during the convulsions.



The acidifying effect of injections of dextrose or adrenaline is not observed after administration of insulin. Disodium hydrogen phosphate and sodium dihydrogen phosphate lower the  $p_H$  of the blood slightly and antagonise the effect of insulin on blood  $p_H$ . Protein-free liver extract raises, whilst protein-free lung extract lowers, the  $p_H$  of the blood. G. W. R.

**Biochemical Determination of Insulin.** F. WYSS (*Compt. rend.*, 1925, **181**, 327—328).—A method of determining the potency of insulin preparations based on certain chemical properties is suggested. L. F. H.

**Vitamin Content of *Cortex limonis*, B.P.** S. G. WILLIMOTT and F. WOKES (*Pharm. J.*, 1925, **115**, 164—168).—Experiments with rats indicate that the *flavedo* (outer rind) of lemon contains appreciable amounts of vitamin. B. F.

**Formation of Vitamin-A during Germination of Seeds.** W. STEPP (*Z. Biol.*, 1925, **83**, 94—98).—When wheat is allowed to germinate and then dried by warming, the seeds contain no noteworthy amount of vitamin-A. If, however, animals, maintained on a diet causing keratomalacia, have germinated wheat added to their diet, they improve but do not increase in weight. It appears, therefore, that germination of wheat causes the production of enough vitamin-A to prevent keratomalacia, but not sufficient to increase the weight of the animal. P. W. C.

**Growth Factors.** V. H. VON EULER and E. ERIKSON (*Z. physiol. Chem.*, 1925, **146**, 241—246).—Purified commercial glycerol, both before and after irradiation, was able to promote growth in rats deprived of vitamin-A. It is thought that this result is due to the presence in the glycerol of an active substance derived from the original fat and not destroyed in the process of preparation. Samples of irradiated ivory-nut oil, when kept in stoppered dark-walled flasks, retained most of their growth-promoting activity for 3—4 months. C. R. H.

**Jendrassik Reaction for Vitamin-B.** N. BEZSSONOFF (*J. Biol. Chem.*, 1925, **64**, 589—590). V. E. LEVINE (*ibid.*, 591—593).—Polemical (cf. Bezssonoff, A., 1924, i, 588; Levine, this vol. i., 108). C. R. H.

**Basal Vitamin-B-free Diet of Drummond and Watson.** A. L. BACHARACH (*Biochem. J.*, 1925, **19**, 638—640).—If the lemon juice is eliminated from the above diet, cessation of growth is secured in about 7 days. S. S. Z.

**Blood-sugar Levels of Rats Fed with Complete Diets and Diets Deficient in Vitamin-B.** P. EGGLETON and L. GROSS (*Biochem. J.*, 1925, **19**, 633—637).—The rate of absorption of dextrose from the alimentary tract is unaffected by vitamin-B deficiency. The elimination of vitamin-B from the diet of the rat causes a gradual removal of glycogen from the liver. S. S. Z.

**Antiscorbutic Fraction of Lemon Juice.** III. S. S. ZILVA (*Biochem. J.*, 1925, **19**, 589—594).—Unlike basic lead acetate, which

precipitates the antiscorbutic factor from lemon juice quantitatively, normal lead acetate does not precipitate it at all. The behaviour of these two precipitating reagents towards the antiscorbutic factor in swede juice is the same as to that in lemon juice. Small quantities of amino and amide nitrogen are present in certain concentrated antiscorbutic fractions. They, however, form only a part of the total nitrogen content, which is of the order of 1—2 mg.%. There is no connexion between the amide nitrogen and the antiscorbutic activity of lemon juice. S. S. Z.

**Vitamin Deficiency and Pernicious Anæmia.** N. R. DHAR (*Chem. Zelle Gewebe*, 1925, **12**, 225—227).—Pernicious anæmia is thought to be due to deficiency of vitamin-*B* and -*C*. E. C. S.

**Formation of Vitamin-D in Germinating Seeds.** W. STEPP (*Z. Biol.*, 1925, **83**, 99—101).—A series of experiments, similar to those already described (cf. i., 1221), indicate that vitamin-*D* is not formed during the germination of seeds. P. W. C.

**Effect of Wounding on the Respiration of Plants.** W. PALLADIN (*Bull. Acad. Sci. St. Pétersbourg*, 1917, [6], 1507—1514; from *Chem. Zentr.*, 1925, i, 2567).—Stems of cactus, peas, and bulbs of *Amaryllis vittata* develop more carbon dioxide after being cut. The respiration of cactus stems and pea seeds which have been frozen and thawed is also increased by wounding. Injury thus increases the amount of the respiratory enzymes. Potatoes contain more solanine after being wounded. Respiration of the roots of carrots is scarcely increased by wounding. Freezing results in the formation of dark colouring matters. As chromogens exert an adverse effect on respiration, the observed inhibitory effect of freezing on the respiration of carrot roots may be understood. Injury thus increases respiratory ferments, hydrogen acceptors (chromogens), and stimulators (solanine). G. W. R.

**Development and Distribution of Chlorophyll in Roots of Flowering Plants Grown in the Light.** D. POWELL (*Ann. Bot.*, 1925, **39**, 503—513).—The roots of most plants, when grown in water or culture solution exposed to bright light, develop chlorophyll. The particular group of cells in which chlorophyll appears varies in different species but is constant for a given species. The distribution of the plastids is not affected by illumination. In the case of *Pisum sativum*, conditions which favour assimilation in the shoot also favour development of chlorophyll in the root. C. T. G.

**Diurnal Changes in Acidity of *Bryophyllum calycinum*.** F. G. GUSTAFSON (*J. Gen. Physiol.*, 1925, **7**, 719—728).—Parallel changes are observed in the hydrogen-ion concentration and in the total (titratable) acidity of the juice expressed from *Bryophyllum calycinum* at different times of the day. There is a shift towards the alkaline side during the hours of daylight, with a return to the original state during the night. The decrease in acidity is most marked on bright days, whilst in darkness the acidity increases for the first few days. After this, the total acidity slowly diminishes,

although the  $p_H$  remains almost constant. Temperature and the presence of oxygen appear to be of minor importance. The changes only take place in the living plant, and the acidity of the expressed juice does not alter on keeping, or even on boiling. H. P. M.

**Plant Yield and Intensity of External Factors—Mitscherlich's "Wirkungsgesetz."** G. E. BRIGGS (*Ann. Bot.*, 1925, 39, 475—502).—A criticism of Mitscherlich's treatment of the data used in formulating his law expressing the relation between plant yield and the intensity of the external factors governing growth. In the case of manures, the exact intensity of the factor ( $x$ ) cannot be measured directly, since there is a certain quantity in the seed and in the soil, and the crucial data giving the yields for very small values of  $x$  are missing and difficult to obtain. With the figures actually available, the agreement of calculated and observed results has little significance, and various values can be assigned to the "Wirkungsfaktoren" which will give figures agreeing fairly closely with the experimental data. The results can also be fitted with equations of a quite different type from that adopted by Mitscherlich. Further, the evidence for the assumption that the relationship between yield per pot and the intensity of an external factor is independent of the number of plants per pot is inadequate; it is probable also that errors occur in eliminating extra plants from pots after germination. The application of Mitscherlich's equation in conjunction with the results of pot-culture experiments to the determination of the effect of the addition of manure in the field is inadmissible, since the range of the roots and the amount of nutrients available in the field are unknown. The attempt to formulate a law of plant yield based on our present knowledge can have little physiological significance. C. T. G.

**Formation of Starch from Arabinose by Plants.** M. POLONOVSKI and F. MORVILLEZ (*Compt. rend. Soc. Biol.*, 1925, 92, 443—445; from *Chem. Zentr.*, 1925, i, 2312—2313).—Bean seedlings and colourless potato shoots were, after sterilisation, placed in nutrient solutions (Sachs) to which 0—5% of arabinose and dextrose, respectively, were added. The solutions were aerated with air free from carbon dioxide. The experiments were carried out partly in light and partly in darkness and showed that whilst neither dextrose nor arabinose sufficed for normal nutrition, yet varying amounts of starch were formed from arabinose. The greatest formation of starch occurred in the dextrose solutions. G. W. R.

**Decomposition of Oxalic Acid by Plants.** W. PALLADIN and E. LOVTSCHINOVSKAJA (*Bull. Acad. Sci. St. Pétersbourg*, 1916, [6], 937—948; from *Chem. Zentr.*, 1925, i, 2567—2568).—The decomposition of oxalic acid by wheat meal and wheat bran, respectively, was determined by measuring the amount of carbon dioxide formed. Oxidation is more energetic by the latter, which also decomposes neutral potassium oxalate. When the oxygen of the air is replaced as hydrogen acceptor by methylene-blue, oxidation of oxalic acid no longer occurs. Atmospheric oxygen cannot be replaced by

potassium nitrate, formate, or hydrogen peroxide. Among reducing agents, resorcinol first increases and then decreases oxidation of oxalic acid. Pyrogallol and quinol strongly inhibit oxidation. The inhibition by reducing agents is attributed to their effect on peroxydase. Emulsin has a slightly favourable effect. No oxidation is effected by an aqueous extract of bran. The action of zymin is inhibited by oxalic acid. The respiration of the wheat embryo is unaffected by neutral potassium oxalate. G. W. R.

**Absorption of Ultra-violet Light by Plants.** W. PALLADIN and E. HÜBBENET (*Bull. Acad. Sci. St. Pétersbourg*, 1917, [6], 1007—1036; from *Chem. Zentr.*, 1925, i, 2569).—Aqueous acid extracts from etiolated roots and stems show a very weak absorption of ultra-violet light. The extracts from flowers and from etiolated leaves show an appreciable absorption. G. W. R.

**Behaviour of the Alkaloids of Alkaloid-containing Seeds during Germination.** T. SABALITSCHKA and C. JUNGGERMANN (*Pharm. Zentr.*, 1925, 66, 474—477, 501—506).—A diffusion of alkaloids from the seeds of *Lupinus luteus*, *Datura stramonium*, *Trigonella fenum graecum*, and *Strychnos nux vomica* during germination under normal conditions does not take place but occurs only when the amount of water for germination is so large as to be injurious to the seed. Alkaloids cannot be regarded either during germination or in the growing plant primarily, if at all, as a means of protection. P. W. C.

**Dynamics of Assimilation of Potassium [by Plants] from Mineral Silicates.** J. M. DOBRESCU-CLUY (*Chem. Erde*, 1925, 2, 83—102).—Applying the methods and formula worked out by Mitscherlich to studies of the relative availability to plants of the potassium in various mineral silicates, it was found that the use of water saturated with carbon dioxide as a solvent gave figures which were in direct disagreement with the results of pot experiments with the same minerals. When, however, dilute hydrochloric acid was used as the solvent, the figures obtained agreed well with the vegetation experiments. The four minerals—biotite, phonolith, muscovite, and orthoclase—are in the order named in regard both to the solubility of the potassium present in hydrochloric acid and to its availability to plants, the difference in these respects between biotite and orthoclase being very marked. The more weathered the mineral, the greater is the facility with which the potassium can be assimilated. Water saturated with carbon dioxide is very suitable for work on the availability of phosphoric acid, but it is not to be expected that the same solvent should be equally applicable to the study of other plant nutrients. C. T. G.

**Carbon Dioxide Content of the Soil Air as a Factor in the Absorption of Inorganic Elements by Plants.** F. W. PARKER (*Soil Sci.*, 1925, 20, 39—44; cf. A., 1924, i, 811).—Neither addition of carbon dioxide to the soil air nor its removal (by continuous aspiration) appreciably affected the yield of oats, rape, or crimson clover grown in pots. In the absence of phosphatic fertiliser, the

phosphorus content of the plants was slightly increased by addition of carbon dioxide, but there was no indication of any increase in the availability of added rock phosphate. The treatments did not influence either the calcium or total ash content of the plants, except in the case of oats, where addition of carbon dioxide increased and its removal decreased the percentage of ash. C. T. G.

**Anthocyanins.** P. M. NIKIFOROVSKI (*Z. physiol. Chem.*, 1925, 146, 91—97).—A reaction claimed to be specific for anthocyanins is described and employed for their classification. Aqueous alcoholic (50%) extracts of anthocyanins from a large number of wild and garden flowers give with 0.5—5% aluminium chloride solution a red or blue colour, the difference in colour being apparently determined by the number of free hydroxyl groups in the pigment.

P. W. C.

**Chemical Composition of the Bark of the Purgative Buckthorn (*Rhamnus cathartica*, L.).** M. BRIDEL and C. CHARAUX (*Ann. Chim.*, 1925, [x], 4, 79—120).—A full account of work already published (this vol., i, 621, 636, 690).

S. K. T.

**Constituents of the Marking Nut: "*Semecarpus anacardium*," Linn.** D. S. NAIDU (*J. Indian Inst. Sci.*, 1925, 8 A, 129—141).—Extraction of the pericarp of this nut with light petroleum yields 9.2% of a corrosive oil containing pyrocatechol, a new phenol *anacardol*,  $C_{18}H_{30}O$  ( $d_{15}^{25}$  0.9693,  $n_D^{25}$  1.5078, *picrate*, m. p. 100—101°), to which the corrosive properties are due, and two phenolic acids,  $C_{16}H_{15}O_3 \cdot CO_2H$ , m. p. 196—200° (*barium salt insoluble*, *pentabromo derivative*, m. p. 160—161°), and  $C_{14}H_{13}O_3 \cdot CO_2H$ , m. p. 210—215° (*barium salt soluble*). The fined oil from the kernels of the nut resembles that from cashew-kernels.

G. M. B.

**Seeds of *Mercurialis*.** P. GILLOT (*J. Pharm. Chim.*, 1925, [viii], 2, 129—131).—The following is the percentage composition of the seeds of *Mercurialis annua*, L., *M. perennis*, L., and *M. tomentosa*, L., respectively: water, 6.8, 8.58, 6.72; fat, 38.05, 26.45, 35.62; proteins, 13.55, 19.43, 15.25; cellulose, 31.91, 39.55, 33.13; reducing sugar, 0.09, 0.30, 0.07; hydrolysable sugar, 1.29, 1.49, 0.97; starch, 0.39, 0.01, 0.97; ash, 7.92, 4.10, 8.24. The seeds give, on pressing or extraction with light petroleum, oils resembling linseed oil in composition. [Cf. *B.*, 1925, 813.]

B. F.

**Cereals. IV. Amino-acids and Polypeptides in the Ungerminated Rye Kernel.** S. L. JODIDI and J. G. WANGLER (*J. Agric. Res.*, 1925, 30, 989—994).—Polypeptides and amino-acids occur in the ungerminated rye kernel. Since the ungerminated kernels of wheat, oats, and maize also contain these substances, it is suggested that they are normal constituents of the ungerminated kernel of other cereals such as rice, sorghum, etc.

O. O.

**Unpleasant Taste of *Radix primulae*.** L. KOFLER and M. BRAUNER (*Arch. Pharm.*, 1925, 263, 424—430).—There is a substance or mixture of substances in the root of *Primula veris* and

*P. elatior*, distinct and separable from saponin, and responsible for the unpleasant taste of the root. G. M. B.

**Proteins of Bark of Locust Tree (*Robinia pseudacacia*). I. Enzymes Associated with the Proteins ; Composition and Properties of the Albumin.** D. B. JONES, C. E. F. GERSDORFF, and O. MOELLER (*J. Biol. Chem.*, 1925, **64**, 655—671).—Successive extractions of the dried inner bark of the common locust tree with water, 10% sodium chloride, 70% alcohol, and 0.5% sodium hydroxide removed 65% of the total nitrogen. For the preparation of the proteins, the material was extracted with 10% sodium chloride to which was added sufficient sodium hydroxide to keep the reaction neutral; from the filtered solution there was precipitated by dialysis a *globulin* and from the filtrate from the latter, by half-saturation with ammonium sulphate, an *albumin*, the yields being 1.38% and 2.52%, respectively, of the original material. The globulin preparations had the power of hydrolysing amygdalin and carbamide. The purified albumin has C 54.52%, H 6.83%, N 14.77%, S 0.8%; arginine 4.39, histidine 1.74, lysine 5.45, cystine 1.37, tyrosine 6.27, tryptophan 4.18, aspartic acid 7.72, and glutamic acid 4.48%; it is precipitated by 44% saturation with ammonium sulphate and is coagulated on heating at 62—63°. C. R. H.

**Proteins of the Cotton Seed.** D. B. JONES and F. A. CSONKA (*J. Biol. Chem.*, 1925, **64**, 673—683).—Pulverised cotton-seed meal was extracted first with benzene to remove fats, then with 10% sodium chloride, and finally with 0.2% sodium hydroxide; the latter extract contained a small amount (0.73% of the meal) of a *glutelin*. From the sodium chloride extract there separated, on heating, two distinct precipitates, at 62° and at 85°, which, however, appeared to be of identical composition, and yielded an ash containing 57.29%  $P_2O_5$ . By 23% saturation of the sodium chloride extract with ammonium sulphate a precipitate of  $\alpha$ -*globulin* was produced; the mother-liquor from this was diluted and treated with ammonium sulphate to 74% saturation, which gave a precipitate of  $\beta$ -*globulin*; the  $\alpha$ -globulin coagulated at 95—97°, the  $\beta$ -globulin at 92—93°; no marked difference in the nitrogen distribution could be observed between the two specimens. By treatment with alcohol of the mother-liquors obtained in the purification of the globulins by dialysis there was precipitated a protein containing 16.57% of a pentose. No evidence of the presence of a nucleic acid in the cotton-seed meal was obtained. C. R. H.

**Pectic Substance in Beech Wood.** M. H. O'DWYER (*Biochem. J.*, 1925, **19**, 694—696).—A pectic substance corresponding with pectic acid was obtained from beech wood by extraction with hot dilute ammonium oxalate and precipitation with hydrochloric acid. There is evidence that this substance is not confined to the tertiary layer in the cell-wall. S. S. Z.

**Pectic Substances of Plants. III. Nature of Pectinogen and its Relation to Pectic Acid.** F. W. NORRIS and S. B. SCHRYVER (*Biochem. J.*, 1925, **19**, 676—693).—Pectinogen is obtained by extracting the cell-wall substance with warm 0.5% ammonium oxalate or oxalic acid. Its composition, especially with regard to methoxyl content, varies considerably. The influence of the source, the extractive, and the period of extraction on the product have been studied. The shorter the period of extraction the more nearly does the composition of the resulting pectinogen correspond with that of pectinogen as it occurs in the cell-wall, although the yield is not theoretical. Alkalis such as lime-water convert pectinogen into pectic acid, which is precipitated. In addition to methyl alcohol, a substance similar to hemicellulose is found in the alkaline filtrate. The composition of this substance is not constant. Substances of the general type described as hemicelluloses may also be obtained by direct extraction of the cell-wall substance with sodium hydroxide or by similar treatment after extraction of pectinogen. It is concluded that pectinogen occurs in the plant as a methylated pectic acid in loose combination with metallic ions such as calcium, and that it has one of its four carboxyl groups unmethylated. S. S. Z.

**Toxins. II. Croton.** P. KARRER, F. WEBER, and J. VAN SLOOTEN (*Helv. Chim. Acta*, 1925, **8**, 384—392; cf. A., 1924, i, 690).—The extraction from croton seeds and purification of croton are described. The results of experiments on the hæmolysing power of the toxin towards rabbit-blood-corpuscles and on its agglutinating power towards those of sheep are given. Positive results under the conditions employed were obtained in each case, in a preparation made from 5 c.c. of blood with 0.01 mg. of toxin. The adsorbing capacities of kaolin, basic aluminium sulphate, and aluminium hydroxide for croton were studied by investigation of the hæmolysing and agglutinating power of the recovered adsorbates. Kaolin adsorbs only a very small quantity of a less toxic constituent. Basic aluminium sulphate and aluminium hydroxide adsorb the more toxic constituents. Attempts to concentrate the hæmolysing and agglutinating principle by fractional adsorption failed to give a product of power equal to that of the original croton. A complete analysis by the methods of Dakin, Hausmann, and Van Slyke of the amino-acids after hydrolysis of the protein is given. M. J.

**Decay of the Xylem of the Apple caused by *Polystictus versicolor*, Fr.** R. G. SMITH (*Phytopathology*, 1924, **14**, 114—118).—All the constituents except lignin are attacked, the reductions being greatest in the alcohol-soluble non-sugars, hexosan-yielding hemicelluloses, cellulose, and starch. CHEMICAL ABSTRACTS.

**Detection of Small Quantities of Lactic Acid in Fruit [Tomato] Juice as Calcium Lactate.** A. BORNTRÄGER.—(See ii, 1007.)

**Effect of Concentrated Solutions of Poisons on Plant Cells.** W. ARZICHOVSKI and O. SCHELJAKIN (*Bull. Acad. Sci. St. Pétersbourg*, 1916, [6], 1043—1062; from *Chem. Zentr.*, 1925, i, 2569).—When preparations of the leaves of *Begonia rex* are immersed in different acids of strength varying from saturation to 0.125*N*, the cell protoplasm contracts into one or more spheres but again fills the cells when the preparations are placed in water. The more often alternate immersion in acids and water is repeated, the less injurious is the effect of the acids. The least injurious acids are sulphuric, hydrochloric, and phosphoric acids, followed by acetic, oxalic, and citric acids. Nitric and chromic acids are more injurious. No plasmolysis is produced by silver nitrate but a precipitate is formed with the cell sap. Copper salts cause plasmolysis and precipitation; formaldehyde, calcium chloride, potassium nitrate, and sodium nitrate cause plasmolysis only. The cells are killed by phenol.  
G. W. R.

**Predominance of Activity of Anaërobic Nitrogen-fixing Bacteria in the Soil.** G. TRUFFAUT and N. BEZSSONOFF (*Compt. rend.*, 1925, **181**, 165—167).—In comparative experiments, in which (i) air or (ii) nitrogen only was supplied to suspensions of soil in dextrose solution containing calcium carbonate to neutralise the soil acidity, with or without addition of mineral food, the fixation of nitrogen was found to be nearly twice as much in anaërobic as in aërobic conditions. The rôle of *Azotobacter* and other aërobic nitrogen-fixers has probably been exaggerated in the past (cf. also Winogradsky, A., 1894, ii, 200).  
C. H.

**Adsorption of Dyes by Soils.** J. A. WILKINSON and W. HOFF (*J. Physical Chem.*, 1925, **29**, 808—815).—The adsorption of dyes by soils and clays has been studied in acid and in alkaline solutions. The effect of the presence of acid and alkali on the adsorption of acid and basic dyes is similar to that observed in the dyeing of fibres (cf. Bancroft, A., 1914, ii, 178, 250, 436). Evidence of base exchange between the dyes and the basic elements in the soil was obtained.  
F. G. S.

**Use of the Quinhydrone Electrode for Determination of  $p_H$  in Soils.** C. BRIOUX and J. PIEN (*Compt. rend.*, 1925, **181**, 141—143).—The quinhydrone electrode (Biilmann, A., 1924, i, 819) has considerable advantages over the hydrogen electrode in simplicity and rapidity, and for most soils it is equally accurate (cf. Christensen and Jensen, *Int. Mitt. Bodenkunde*, 1924, **14**, 1—26). Discrepancies, due possibly to interaction between soil constituents and the quinhydrone, are observed with certain soils, but these disappear when the soil suspensions are previously centrifuged, except in 3 of the 37 soils examined. The  $p_H$  values are in all cases slightly higher than by the hydrogen electrode, since the rapidity of the determination diminishes the diffusion of potassium chloride into the soil suspension.  
C. H.



**Influence of the Soil Reaction on Absorption of Phosphorus and of Potassium in Presence of Various Phosphatic Manures.**

A. NEMEC and M. GRACANIN (*Compt. rend.*, 1925, **181**, 194—196).—The amounts of phosphorus and of potassium absorbed by seedlings of rye from soils of  $p_H$  5.0, 6.2, and 7.1 containing various phosphates are larger for the more acid soil. The actual amounts absorbed are greatest with a superphosphate present. G. M. B.

**Heat of Wetting of Soils Dried at Different Temperatures and the Force with which Soils Absorb Water.**

G. J. BOUYOUKOS (*Soil Sci.*, 1925, **20**, 67—72).—The heat of wetting of soils increases with the temperatures at which they are dried, reaching a maximum in soils dried at about 107°. The amount of moisture which is effective in producing the heat of wetting is small (1.4—12.1%), and of this only a very small part, driven off at 107°, is responsible for the greater part of the heat evolved. Assuming the heat of wetting to be due mainly to adsorption and compression of the water film, the force of adsorption can be calculated and amounts to a very high value. C. T. G.

**Factors Influencing the Heat of Wetting of Soil Colloids.**

G. J. BOUYOUKOS (*Soil Sci.*, 1925, **19**, 477—482; cf. this vol., i, 348).—When the colloidal material extracted from soil is ignited, it no longer evolves any heat on wetting, even when ground finely enough to stay in suspension in water for 24 hrs. This is also the case with ferric hydroxide and silica gels. It is suggested that the reactivity of soil colloids is a function not only of size of particles, but also of the physical condition. The wide variations in the heat of wetting of the colloids in different soils may be partly accounted for by the extent to which decomposition has proceeded and the consequent condition of the surface of the particles, whether porous, smooth, or vitrified. There is also some evidence of a relationship between heat of wetting of soil colloids and their chemical composition. Heat of wetting is probably “a manifestation of the water undergoing a change in its state of aggregation, possibly from a liquid to a solid or semi-solid phase.” C. T. G.

**Clays as Soil Colloids.** A. F. JOSEPH (*Soil Sci.*, 1925, **20**, 89—94).—By repeated centrifuging and shaking, practically the whole of the clay fraction of soils was obtained in the colloidal condition. Thus the inorganic colloid content of most soils is apparently identical with the clay content, as determined by mechanical analysis. There is a satisfactory correlation between the chemical composition and the properties of clays of diverse origins, the data given being the silica-alumina ratio, the “imbibitional” water-holding capacity (cf. Fisher, A., 1924, i, 819), and the rate of evaporation, measured by Keen’s method (cf. *J. Agric. Sci.*, 1914, **6**, 456). C. T. G.

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## Organic Chemistry.

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**"Cracking" of Paraffins.** A. WILLIAMS-GARDNER (*Fuel*, 1925, 4, 430—440).—Decomposition of ethane begins at 550°, the main products being methane and ethylene. At higher temperatures, the ethylene is hydrogenated, yielding methane, and at the same time decomposes slightly to hydrogen and carbon. Aromatic compounds are formed between 700° and 850° by polymerisation of ethylene; methane itself decomposes into its elements above 850°. At no period is acetylene present in any appreciable quantity, nor does it play an important part in the decomposition reactions.

A. C. M.

**Petroleum. II. Action of Sodium Hypochlorite on Sulphur Compounds of the Types found in Petroleum Distillates.** S. F. BIRCH and W. S. G. P. NORRIS (*J. Chem. Soc.*, 1925, 127, 1934—1944).—Dilute hypochlorite solutions containing no free alkali oxidise quantitatively organic sulphides to sulphones, disulphides to sulphonic and sulphuric acids, and mercaptans to sulphonic acid, disulphide, and sulphuric acid. Hydrogen sulphide is oxidised with precipitation of sulphur and formation of some sulphuric acid, but thiophen and sulphur remain unattacked.

B. W. A.

**Method and Laboratory Apparatus for Dehydrating Alcohol.** H. GUINOT (*Bull. Soc. chim.*, 1925, [iv], 37, 1008—1013).—An apparatus is described which is capable of yielding 1 litre per hr. of anhydrous alcohol from 95% alcohol. The alcohol (1.5 litres) is distilled from a 3-litre flask surmounted by a fractionating column of 6 cm. internal diam. carrying 30 plates 2.6 mm. apart, and a condenser, both of which are connected by cocks with the dehydrator. At first, the condensed liquid is caused to flow back to the top of the fractionating column and benzene is delivered into the column, near the top, in portions of 50 c.c. When the temperature at the top of the column remains steady at 65°, corresponding with the b. p. of a ternary mixture of constant composition, the distilled liquid is run into the dehydrator, which is filled with glass Raschig rings, and traversed by a counter-current of potassium carbonate solution ( $d$  1.542) at the rate of about 340 c.c. per hr. About 1360 c.c. of the ternary mixture flows through the dehydrator in the same time, and the issuing liquid is delivered to the top of the column. As soon as a thermometer placed 6 plates above the flask shows a slight fall in temperature (2°), the benzene delivery is stopped and hydrated alcohol fed into the column at the desired rate, whilst absolute alcohol distils from the flask by a second tube. The pressure in the distilling flask is regulated by a small manometer. An increase in the rate of feed decreases slightly

the strength of the alcohol obtained; at 2 litres per hr. the strength of the alcohol is 99.6%. R. B.

**Chloro-ethers. II. Preparation of Some New Chloro-ethers and Alkoxyethyl Esters.** J. W. FARREN and H. R. FIFE [with F. E. CLARK and C. E. GARLAND] (*J. Amer. Chem. Soc.*, 1925, 47, 2419—2423).—In continuation of earlier work (A., 1917, i, 316), the following chloro-ethers have been obtained in yields of 50—85% by a modification of Wedekind's method (A., 1903, i, 456), in which the hydrogen chloride was removed by a current of hydrogen at the end of the reaction and the ether distilled in a current of the same gas: chloromethyl ethyl ether, b. p. 81—82°,  $d_4^{20}$  1.0263,  $n$  1.0282; chloromethyl isopropyl ether b. p. 97—98°,  $d_4^{20}$  0.9790,  $n$  1.4592 (cf. Stappers, A., 1905, i, 261); chloromethyl sec.-butyl ether, b. p. 121—123°,  $d_4^{20}$  0.9751,  $n$  1.4205; cyclohexyl chloromethyl ether, b. p. 183—185°,  $d_4^{20}$  1.0432,  $n$  1.4713, and chloromethyl  $\beta$ -chloroethyl ether, b. p. 145—147°,  $d_4^{20}$  1.2817,  $n$  1.4952. Some of the *s*-dichlorodimethyl ether is also formed in the reaction, but tends to revert to chloromethyl alcohol, in accordance with the ready hydrolysis of  $\alpha$ -chloro-ethers. With the sodium salts of fatty acids, these chloromethyl ethers give the corresponding alkoxy-methyl esters in yields of 60—90%. The following esters are described: ethoxymethyl formate, b. p. 114—116°,  $d_4^{20}$  1.0343,  $n$  1.3900; ethoxymethyl acetate, b. p. 128—129°,  $d_4^{20}$  0.9932,  $n$  1.3903; ethoxymethyl propionate, b. p. 145—146°,  $d_4^{20}$  0.9711,  $n$  1.4000; ethoxymethyl butyrate, b. p. 160—162°,  $d_4^{20}$  0.9656,  $n$  1.4050; isopropoxymethyl formate, b. p. 124—126°,  $d_4^{20}$  1.0000,  $n$  1.3910; isopropoxymethyl acetate, b. p. 133—135°,  $d_4^{20}$  0.9502,  $n$  1.3890; isopropoxymethyl propionate, b. p. 147—149°,  $d_4^{20}$  0.9444,  $n$  1.3980; isopropoxymethyl butyrate, b. p. 164—166°,  $d_4^{20}$  0.9432,  $n$  1.4001; sec.-butoxymethyl formate, b. p. 147—148°,  $d_4^{20}$  0.9477,  $n$  1.4020; sec.-butoxymethyl acetate, b. p. 156—158°,  $d_4^{20}$  0.9319,  $n$  1.4035; sec.-butoxymethyl propionate, b. p. 164—166°,  $d_4^{20}$  0.9291,  $n$  1.4075; sec.-butoxymethyl butyrate, b. p. 177—178°,  $d_4^{20}$  0.9283,  $n$  1.4085. Chloromethyl  $\beta$ -chloroethyl ether yields a formate, b. p. 184—188°, which was not obtained pure. R. B.

**Hypochlorous Esters and the Problem of the Polarity of Valencies.** J. F. DURAND and R. NAVES (*Bull. Soc. chim.*, 1925, [iv], 1147—1155).—Ethyl hypochlorite reacts vigorously with dilute hydrochloric acid, yielding chlorine and ethyl alcohol. With hydrobromic acid, the reaction is less violent and, at 0°, the primary products are alcohol and bromine chloride, converted by ethylene into  $\beta$ -chloro- $\alpha$ -bromoethane. Hydriodic acid reacts violently, but ethylene in this case yields a mixture of ethylene dichloride and  $\beta$ -chloro- $\alpha$ -iodoethane, thus indicating the primary formation of iodine chloride, which probably decomposes,  $3\text{ICl} \rightarrow \text{ICl}_3 + \text{I}_2$ . Bromine under ordinary conditions reacts with explosive violence. The formation of ethyl alcohol and ethyl acetate in the spontaneous decomposition of ethyl hypochlorite (Taylor, McMullin, and Gammal, this vol., i, 501) is accompanied by the liberation of chlorine (cf.

this vol., i, 1054), probably through the action of the hydrogen chloride produced in the primary decomposition,  $\text{EtOCl} \rightarrow \text{Me}\cdot\text{CHO} + \text{HCl}$ . The above decompositions are regarded as supporting a polar structure for ethyl hypochlorite, in which the chlorine is positive and the group  $-\text{OCl}$  functions as in hypochlorous acid and chlorine monoxide. Ethyl hypochlorite thus behaves rather as chlorine ethoxide than as an ester of hypochlorous acid and is analogous to Schutzenberger's chlorine acetate. R. B.

**Trithioacetaldehydes and the Mechanism of their Transformations.** E. FROMM and L. ENGLER (*Ber.*, 1925, 58, [B], 1916—1924).— $\alpha$ -Trithioacetaldehyde is converted by iodine in anhydrous ether into  $\alpha$ -trithioacetaldehyde di-iodide,  $\text{C}_6\text{H}_{12}\text{S}_3\text{I}_2$ , m. p. 76—78°, which is converted by water, potassium hydroxide, alcohol, or acetone into  $\beta$ -trithioacetaldehyde, but by solid silver acetate in the presence of ether into  $\alpha$ -trithioacetaldehyde. Similarly,  $\beta$ -trithioacetaldehyde di-iodide, prepared from its components in glacial acetic acid, is transformed by silver acetate into  $\beta$ -trithioacetaldehyde. The reaction is suitable for the detection of  $\alpha$ - and  $\beta$ -trithioacetaldehyde in their mixtures. More highly iodinated trithioacetaldehydes could not be prepared.  $\alpha$ -Trithioacetaldehyde is converted by the theoretical amount of hydrogen peroxide in the presence of glacial acetic acid into  $\alpha$ -trithioacetaldehyde trisulphoxide,  $\text{C}_6\text{H}_{12}\text{O}_3\text{S}_3$ , m. p. 184°, whereas  $\beta$ -trithioacetaldehyde yields  $\beta$ -trithioacetaldehyde trisulphoxide, m. p. 153°. The products could not be re-converted into the respective initial materials, since the only reducing agent available for the purpose (hydriodic acid) causes isomerisation of the aldehydes. Either trisulphoxide passes on further oxidation into the known trisulphone, isomerism disappearing at this stage. The  $\alpha$ - and  $\beta$ -trisulphoxides are converted by potassium hydroxide into trithioacetaldehyde disulphoxide sulphide,  $\text{C}_6\text{H}_{12}\text{O}_2\text{S}_3$ , m. p. 255° (decomp.) after darkening at 220°, which is reduced by hydriodic acid to  $\beta$ -trithioacetaldehyde and oxidised by an excess of hydrogen peroxide to trithioacetaldehyde trisulphone.

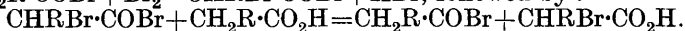
Treatment of  $\gamma$ -trithioacetaldehyde (Mann and Pope, T., 1923, 123, 1178) with iodine in anhydrous ether affords  $\alpha$ -trithioacetaldehyde di-iodide, from which, by treatment with pure silver acetate,  $\alpha$ -trithioacetaldehyde is obtained; on oxidation, it yields homogeneous  $\alpha$ -trithioacetaldehyde trisulphoxide. Contrary to the statement of Mann and Pope, it can be separated by cautious crystallisation from acetone into  $\alpha$ - and  $\beta$ -trithioacetaldehyde.  $\gamma$ -Trithioacetaldehyde appears to be a mixture of 2 parts of  $\alpha$ - with 1 part of  $\beta$ -trithioacetaldehyde.

The mechanism of the conversion of the labile into the stable thioaldehydes is uncertain, but it is not sufficient that the ring should be opened at one point and then be again closed. It is more probable that the molecule is completely broken into its units, which subsequently reunite to yield the isomeric form. Evidence in favour of this view is found in the observation that either  $\alpha$ - or  $\beta$ -trithioacetaldehyde is converted by sulphur chloride into the unimolecular  $\alpha\alpha'$ -dichlorodiethyl sulphide, and that the

latter is transformed by hydrogen sulphide into  $\alpha$ -trithioacetaldehyde.  
H. W.

**Isolation of Natural Crystalline Lecithin.** H. H. ESCHER (*Helv. Chim. Acta*, 1925, 8, 686—691).—The author has isolated three crystalline forms of lecithin from egg-yolk. The egg-yolk or ox brain (5—10 kg.) is exhaustively extracted with boiling chloroform or alcohol and the phosphatides in the extract are separated from fatty materials by precipitation of the freshly prepared extract with acetone. The precipitated phosphatides are freed from the adhering solvent and treated with absolute alcohol (5 litres for 1 kg.), which, at the ordinary temperature, leaves a sparingly soluble fraction (kephalin), a further fraction (sphingomelin) separating at 0°. The alcoholic extract is cooled to  $-35^\circ$  for 24 hrs. and pure lecithin (75% of phosphatides) remains in the alcohol. It is freed from alcohol and dissolved in anhydrous ether, which on cooling to  $-30^\circ$  deposits a snow-white sludge. The form of lecithin least soluble in ether is obtained as a snow-white, hygroscopic powder, m. p.  $244-245^\circ$ , iodine number 50, corresponding with 1.5 double linkings. From the mother-liquors two other crystalline preparations were isolated, the iodine values corresponding with 2.5 and 3.5 double linkings, respectively. For details of the preparation the original paper must be consulted. J. W. B.

**Reaction of Bromine with Aliphatic Acids. Catalytic Effect of Acyl Halides.** H. B. WATSON (*J. Chem. Soc.*, 1925, 127, 2067—2082).—Halogen acids have a specific catalytic effect on the  $\alpha$ -bromination of fatty acids, but the effect of acetic anhydride, various acid chlorides, and especially of acid bromides is far more powerful. With acetic anhydride and with acetyl chloride, a short period of acceleration is followed by a constant value for  $k_1$ , but with acid bromides  $k_1$  (although of a slightly lower value, due to perbromide formation) is constant throughout. The facts suggest that the peculiar effect of acid bromides is due to the reaction:  $\text{CH}_2\text{R}\cdot\text{COBr} + \text{Br}_2 = \text{CHBr}\cdot\text{COBr} + \text{HBr}$ , followed by:



The action of acid chlorides may be explained on a somewhat similar basis. The catalytic effect of small quantities of phosphorus may well be due to the formation of some acid bromide by this reagent, whilst halogen acids may owe their smaller effect to the undetected equilibrium  $\text{R}\cdot\text{CO}_2\text{H} + \text{HX} \rightleftharpoons \text{R}\cdot\text{COX} + \text{H}_2\text{O}$ , since added water lowers the velocity of the reaction considerably.

B. W. A.

**Separation of Carbon Monoxide in Organic Molecules.** A. MAILHE (*Caoutchouc et Gutta-Percha*, 1925, 22, 12785—12788; cf. A., 1922, i, 985; 1923, i, 458, 800; 1924, i, 623; this vol., i, 503).—Aliphatic acid chlorides are decomposed in contact with metallic nickel at  $400^\circ$ , primarily into carbon monoxide and alkyl chloride, the latter then decomposing into hydrogen chloride and alkylene. The gases evolved in the decomposition, under these conditions, of acetyl, propionyl, isobutyryl, and isovaleryl chlorides

contain, in addition to the appropriate alkylene, small proportions of hydrogen and carbon dioxide, and, except in the case of acetyl chloride, 10—20% of methane, the proportion of the latter increasing as the series is ascended. Aromatic acid chlorides undergo similar decomposition into carbon monoxide and aryl chloride, the latter resisting further change. Decomposition of benzoyl chloride in contact with nickel at 400° affords, in addition to chlorobenzene, about 5% of benzil.

F. G. W.

**Preparation of Acetic Anhydride.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 411519, addn. to D.R.-P. 396696; from *Chem. Zentr.*, 1925, ii, 92).—The wash liquids used to retain the acetyl chloride carried away by hydrogen chloride from the reaction mixture are acetic acid or anhydride, or a mixture of the two.

A. C.

**Hydroxylamine Salts of Organic Acids.** R. E. OESPER and M. P. BALLARD (*J. Amer. Chem. Soc.*, 1925, 47, 2424—2427).—The following hydroxylamine salts have been obtained by neutralisation in alcoholic solution: *propionate*, m. p. 56—57°; *isobutyrate*, m. p. 98—99°; *valerate*, m. p. 67°; *aminoacetate*, m. p. 77—78°; *myristate*, m. p. 69—70°; *benzoate*, m. p. 113° (cf. Gluud and Kempf, *T.*, 1913, 103, 1532); *o-chlorobenzoate*, m. p. 104·5°; *m-chlorobenzoate*, m. p. 144°; *p-chlorobenzoate*, m. p. 130°; *o-bromobenzoate*, m. p. 99°; *m-bromobenzoate*, m. p. 139°; *p-bromobenzoate*, *o-aminobenzoate*, m. p. 95—96°; *o-toluate*, m. p. 105°; *m-toluate*, m. p. 83°; *p-toluate*, m. p. 128°; *p-aminobenzoate*, m. p. 103°; *cinnamate*, m. p. 119° (cf. Posner, *A.*, 1912, i, 453); *hydrocinnamate*, m. p. 84—85°; *salicylate*, m. p. 141°; *phenylacetate*, m. p. 83°; *mandelate*, m. p. 125°; *hippurate*, m. p. 68°; *o-phthalate*, m. p. 134·5°; *benzenesulphonate*, m. p. 98—107°. The yellow *o-nitrobenzoate*, m. p. 133°, *m-nitrobenzoate*, m. p. 137°, and *p-nitrobenzoate*, m. p. 146° (*monohydrate*, m. p. 143°), were obtained from hydroxylamine sulphate and the corresponding barium salt. Butyric, lactic, hydroxybutyric, and thioacetic acids yielded viscous oils which quickly underwent dehydration, yielding the corresponding hydroxamic acid, a change characteristic of the hydroxylamine salts of fatty acids on heating above their m. p. With the propionate and valerate, the change takes place slowly at the ordinary temperature. Hydroxylamine salts of aromatic acids when heated yield ammonium salts or amides. Solubility details are given.

R. B.

**Thallous Salts of Lauric and Myristic Acid.** D. HOLDE and K. TAKEHARA (*Ber.*, 1925, 58, [B], 1788—1791; cf. Holde and Selim, this vol., i, 504).—*Thallous myristate*, m. p. 120—123°, and *thallous laurate*, m. p. 125—126°, have been prepared by the method recorded previously (*loc. cit.*) and their solubility in 50% alcohol at 19—20° and 25° has been measured. The salts appear too freely soluble to allow a satisfactory separation of them from thallous oleate or linoleate by the process used for the higher saturated fatty acids (*loc. cit.*); this appears to be the case also with hexoic acid.

H. W.

**Oxidation Products of Oleic Acid. II. Degradation of Dihydroxystearic Acid.** A. LAPWORTH and E. N. MOTTRAM (*J. Chem. Soc.*, 1925, 127, 1987—1989; cf. *B.*, 1925, 728).—Oxidation of dihydroxystearic acid at the ordinary temperature with potassium permanganate in dilute alkaline solution yields suberic, *n*-octoic, and oxalic acids, the last being a primary degradation product, due to a splitting between the  $\eta\theta$  and  $\iota\lambda$  carbon atoms. When the oxidation is carried out in a hot solution (Edmed, T., 1898, 73, 628), suberic and azelaic acids are the main products.

B. W. A.

**Polymerisation of Fatty Oils. IV.** J. MARCUSSEN (*Z. angew. Chem.*, 1925, 38, 780—782; cf. this vol., i, 356).—The mol. wt. of the fatty acids contained in wood oil and linseed oil gels, determined by Rast's camphor method and cryoscopically in glacial acetic acid, is in the neighbourhood of 500, showing the acids to be bimolecular. The view that autoxidation of fats leads to the formation of ketoxy-acids is disproved by the observation that "blown" cotton-seed oil contains acids having an acetyl value of about 290, which remains unchanged after reduction of the acids. They also have a mol. wt. about 700. The probable stages in the formation of these "oxidised" fatty acids are discussed.

W. T. K. B.

**Chaulmoogra Oil. I.** T. HASHIMOTO (*J. Amer. Chem. Soc.*, 1925, 47, 2325—2333).—By using an improved distillation apparatus, the final 10—15% of the ethyl esters of the fatty acids obtained from chaulmoogra oil have been distilled without appreciable decomposition at bath temperatures not exceeding 190° and 0.01—0.05 mm. Hydrolysis and fractionation of the fatty acids with light petroleum, alcohol, and acetone yields a brown resin insoluble in organic solvents, an acid,  $C_{36}H_{60}O_6$ , m. p. 113.5°, iodine value 42.51 (*silver salt*), for which the name *taraktogenic acid* is proposed; an acid, m. p. 77°, precipitated by alcohol, possibly, arachidic acid, chaulmoogric acid, *isogadoleic acid*,  $C_{20}H_{38}O_2$ , m. p. 65.5—66°, iodine value 78.13 (*silver salt*), a resinous substance insoluble in acetone, a liquid acid, *paralinoleic acid*,  $C_{18}H_{32}O_2$ , b. p. 112—113°/0.038 mm., m. p. —11.6°,  $d_{15}^{15}$  0.9129,  $n_D^{20}$  1.46195, with lactonic properties and an iodine value varying greatly with the time of reaction, and a white *solid*, m. p. about 52°, probably an acid. Examination of the first 80—85% of the ethyl esters distilling confirmed the results of Power (T., 1904, 85, 838; 1905, 87, 884; 1907, 91, 557) and Dean (A., 1921, i, 91). The chaulmoogra oil used in the investigation was obtained from the seeds of *Taraktogenus Kurzii*, and had the constants: m. p. 22—23°,  $d_{25}^{25}$  0.9503,  $[\alpha]_D + 50.7^\circ$ , iodine value 104.8, yielding on hydrolysis fatty acids, m. p. 43—45°, iodine value 110.12,  $[\alpha]_D + 52.1^\circ$ , neutralisation value 205.0, and saponification value 257.5 (due to the presence of paralinoleic acid). R. B.

**Bromination of Lactic Acid and Calcium Lactate in the Presence of Light.** J. C. GHOSH and K. BASU (*J. Indian Chem. Soc.*, 1925, 2, 39—48).—The velocity of the photobromination of lactic acid and calcium lactate (cf. Ciusa and Piergallini, A., 1914,

ii, 604) for light of different wave-lengths is determined. In the case of lactic acid the unimolecular reaction constants are somewhat irregular, possibly due to the impurities in the lactic acid used. In the dark, the observed reaction velocity is about two-thirds that found when photocatalysis is employed, and it is shown that four quanta of energy activate 1 mol. of bromine, and therefore Einstein's law of photochemical equivalence does not appear to hold. Much more regular results were obtained using calcium lactate, which could be purified by crystallisation. In this case, the dark reaction accounts for three-quarters of the observed velocity and the constants for a unimolecular reaction are much more regular. Increase in the concentration of the bromine relative to the calcium lactate tends to make the constants irregular, whilst a relative increase in the concentration of the calcium lactate considerably increases the velocity constants, which still remain regular; hence bromine is the photoactive molecule and calcium lactate the acceptor, so that in the former case the reaction tends to degenerate into a zero molecular one, whilst in the latter the reaction velocity is increased owing to the greater opportunity for the activated bromine molecules, during their period of excitation, to collide with the calcium lactate molecules. On applying Einstein's law to this case, it is found that when the concentration of the calcium lactate is small (0.03*N*) about two quanta are necessary for the transformation of 1 mol., but when it is increased to 0.06*N*, only one quantum is necessary (cf. Noddack, A., 1921, ii, 568).

J. W. B.

**Reduction of the Group  $-\text{CH}(\text{OH})\cdot\text{CCl}_3$ .** I. A. N. MELDRUM and R. L. ALIMCHANDANI.—(See i, 1272.)

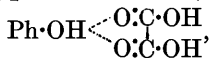
**Uranyl Oxalate.** A. COLANI (*Bull. Soc. chim.*, 1925, [iv], 37, 856—861).—By heating uranyl oxalate at 100° for 24 hrs. the trihydrated compound is converted into the monohydrate, and undergoes no further change at that temperature. The monohydrate is found to rehydrate very easily. These results are in agreement with those of Ebelman (*Ann. Chim. Phys.*, 1842, 5, 191) and Courtois (A., 1914, i, 802). The contradictory results of Oechsner de Coninck and Raynaud (A., 1912, i, 535) are imputed to the presence of alkali or alkaline-earth metals in their uranyl oxalate. The solubility of the oxalate in water, from 11° to 100°, and in mineral acids at 20° has been investigated. The compound is stable in dilute acids, easily decomposed by concentrated acid. The solubility curve of the oxalate in oxalic acid shows no indication of the formation of the hydrogen oxalate. With alkaline salts, a strong inclination to form double salts is shown, the compound  $\text{UO}_2\text{C}_2\text{O}_4\cdot\text{NH}_4\text{Cl}\cdot\text{H}_2\text{O}$  being obtained with ammonium chloride. With sodium chloride the double oxalate,  $\text{Na}_2(\text{UO}_2)_4(\text{C}_2\text{O}_4)_5\cdot 11\text{H}_2\text{O}$ , is formed.

L. L. B.

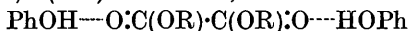
**Intermediate Compounds formed during the Esterification of Oxalic Acid with Phenols.** F. FEIGL and R. KOBILIANSKY (*Ber.*, 1925, 58, [B], 1483—1488).—Phenols readily yield compounds



with oxalic acid of the type,  $\text{PhOH} \cdots \text{O}:\text{C}(\text{OH})\cdot\text{CO}_2\text{H}$  or



$\text{PhOH} \cdots \text{O}:\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{O} \cdots \text{HOPh}$ , and



(R=Me or Ph). Union is considered to occur by means of the subsidiary valencies of the phenolic hydrogen atom and the carbonyl oxygen atom, since phenolic ethers do not form such compounds, whereas they are obtained from oxalic esters. The molecular compounds pass into oxalic esters when treated with a suitable dehydrating agent. The following compounds are described:  $\text{C}_2\text{O}_4\text{H}_2\cdot\text{PhOH}$ , m. p.  $98^\circ$ , from a molten mixture of phenol and oxalic acid;  $\text{C}_2\text{O}_4\text{H}_2\cdot 2\text{PhOH}$ , m. p.  $127^\circ$ ; diphenyl oxalate, m. p.  $130^\circ$ ;  $\text{C}_2\text{O}_4\text{Ph}_2\cdot 2\text{PhOH}$ , m. p.  $106^\circ$ ;  $\text{C}_2\text{O}_4\text{Me}_2\cdot 2\text{PhOH}$ , m. p.  $123^\circ$ ;  $\text{C}_2\text{O}_4\text{H}_2\cdot 2\text{C}_{10}\text{H}_{17}\cdot\text{OH}$ , m. p.  $155^\circ$ ; *di-ar-tetrahydro- $\beta$ -naphthyl oxalate*, m. p.  $149^\circ$ ;  $\text{C}_2\text{O}_4\text{Me}_2\cdot 2\text{C}_{10}\text{H}_{11}\cdot\text{OH}$ , m. p.  $147^\circ$ ;  $\text{C}_2\text{O}_4\text{Ph}_2\cdot 2\text{C}_{10}\text{H}_{11}\cdot\text{OH}$ , m. p.  $122^\circ$ ;  $\text{C}_2\text{O}_4\text{H}_2\cdot 2\text{C}_{10}\text{H}_7\cdot\text{OH}(\beta)$ , m. p.  $167^\circ$ ;  $\text{C}_2\text{O}_4\text{H}_2\cdot 2\text{C}_{10}\text{H}_7\cdot\text{OH}(\alpha)$ , m. p.  $163^\circ$ ; *di- $\beta$ -naphthyl oxalate*, m. p.  $189^\circ$ ;  $\text{C}_2\text{O}_4\text{H}_2\cdot \text{C}_6\text{H}_4\text{Me}\cdot\text{OH}(p)$ , m. p.  $56^\circ$ ; *di-p-tolyl oxalate*, m. p.  $147^\circ$ ;  $\text{C}_2\text{O}_4\text{H}_2\cdot \text{C}_6\text{H}_4(\text{OH})_2(p)$ , m. p.  $197^\circ$ .  
H. W.

#### Thermal Decomposition of Acetyl Succinyl Peroxide.

E. BRUNNER (*Helv. Chim. Acta*, 1925, 8, 651—654).—Persuccinic acid (cf. Clover and Houghton, A., 1904, i, 707) reacts with acetic anhydride at the ordinary temperature to yield *acetyl succinyl peroxide*,  $\text{AcO}\cdot\text{O}\cdot\text{CO}\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$ , m. p.  $72\text{--}75^\circ$ , decomp.  $120^\circ$ , which on thermal decomposition yields carbon dioxide and butyric acid, thus confirming the view of Fichter and Krummenacher (cf. A., 1918, i, 369) that the intermediates in the Kolbe electrochemical synthesis of hydrocarbons are peroxides and peracids. J. W. B.

**Stereochemical Studies. VIII. Optically Active  $\alpha\alpha'$ -Dibromoadipic Acids.** B. HOLMBERG and E. MÜLLER (*Ber.*, 1925, 58, [B], 1601—1604).— $\alpha\alpha'$ -Dibromoadipic acid, m. p.  $191\text{--}193^\circ$  after softening at  $185^\circ$ , is converted by *l*-phenylethylamine into *l*-phenylethylammonium hydrogen  $\alpha\alpha'$ -dibromoadipate, m. p.  $97\text{--}99^\circ$ , but the process affords no indication of the resolvability of the acid. On the other hand,  $\alpha\alpha'$ -dibromoadipic acid, m. p.  $138\text{--}139^\circ$ , is resolved by the alternate use of *d*- and *l*-phenylethylamine into *l*- $\alpha\alpha'$ -dibromoadipic acid, m. p.  $151\text{--}153^\circ$ ,  $[\alpha]_D -65.1^\circ$  (in alcohol), and *d*- $\alpha\alpha'$ -dibromoadipic acid, m. p.  $151\text{--}153^\circ$ ,  $[\alpha]_D +66.3^\circ$  (in alcohol), from which an *r*-acid, m. p.  $143\text{--}144^\circ$ , is obtained. The optical homogeneity of the active acids is not definitely established, but the stereochemical configuration of the inactive acids is elucidated. H. W.

#### Electrosynthesis of *n*-Duotriacontanedicarboxylic Acid.

D. A. FAIRWEATHER (*Proc. Roy. Soc. Edin.*, 1925, 45, 283—285).—Diethyl hexadecanedicarboxylate, obtained by electrolysis of sodium ethyl sebacate, was half hydrolysed with sodium hydroxide in cold dilute alcoholic solution; addition of hydrochloric acid

precipitated *ethyl hydrogen hexadecanedicarboxylate*, m. p.  $71^{\circ}$  (silver salt). A 20% solution of the sodium salt in 10% alcohol was electrolysed at  $70-75^{\circ}$ , whereby a solid ester, m. p.  $62^{\circ}$ , was obtained which was separated by ether into a mixture, m. p.  $30-35^{\circ}$ , and *ethyl n-duotriacontanedicarboxylate*, m. p.  $80^{\circ}$ . *n-Duotriacontanedicarboxylic acid*,  $C_{32}H_{64}(CO_2H)_2$ , has m. p.  $123^{\circ}$  (corr.). R. A. M.

**Action of Yeast on Glycidic Acids.** R. KUHN and F. EBEL (*Ber.*, 1925, 58, [B], 1447—1449).—*cis*- and *trans*-Oxidoethylene- $\alpha\beta$ -dicarboxylic acids (Kuhn and Ebel, this vol., i, 780) appear to be decomposed in the presence of yeast into carbon dioxide and oxido-ethylenemonocarboxylic acid. The latter compound has not been isolated from the products of the reaction and its production is assumed, since it is non-fermentable by the yeasts used and acetaldehyde is not formed during the fermentation. H. W.

**Transformations of a New Type.** J. BÖESEKEN (*Ber.*, 1925, 58, [B], 1470—1473).—The conversion of *cis*-oxidoethylenedicarboxylic acid into *r*-tartaric acid (cf. Kuhn and Ebel, this vol., i, 780) is not the first recorded instance of quantitative transission of a ring system, since a similar instance has been described by Böeseken and van Loon (*A.*, 1920, i, 837). Kuhn and Ebel's view that transission of a ring system (*e.g.*, the reduction of the sugars) is always possible appears to be too general, since they overlook the necessity of at least one of the atoms of the ring which condition the steric configuration being thereby involved. On the other hand, Meisenheimer's assumption (*A.*, 1922, i, 152) that the groups developed by ring opening must necessarily be spatially proximate is untenable in this general form. H. W.

**Configuration of the Malic Acids.** A. SONN and W. ROSINSKY (*Ber.*, 1925, 58, [B], 1688—1690).—*r*-Chloromalic acid can be resolved into its optical antipodes by brucine in aqueous alcoholic solution; *d*-chloromalic acid, m. p.  $153^{\circ}$ ,  $[\alpha]_D^{20} +14.0^{\circ}$  in water,  $[\alpha]_D^{20} +16.2^{\circ}$  in acetone, *brucine l-chloromalate* ( $+3H_2O$ ), m. p. (anhydrous)  $191-192^{\circ}$ , and *l*-chloromalic acid,  $[\alpha]_D^{20} -7.55^{\circ}$ , are described. *d*-Chloromalic acid is converted by hot water into *d*-tartaric acid and is reduced by zinc to *d*-malic acid. The corresponding actions of *l*-chloromalic acid are described. H. W.

**Incorrect Application of Biological Agents in Organic Chemistry.** C. B. VAN NIEL and F. V. HOOFT (*Ber.*, 1925, 58, [B], 1606—1610).—Attention is directed to the non-homogeneous nature of yeast and a number of instances are cited from the literature in which incorrect results have been obtained in its use owing to the presence of foreign organisms. In general, the fermentability of a substance by yeast can be regarded as established only when the period of action is so short (not exceeding 8—10 hrs.) that foreign organisms cannot materially increase.

The supposed fermentability of the ketogluconic acid obtained by the action of bromine on dextrose, to carbon dioxide and arabinose has led Hönig and Tempus (*A.*, 1924, i, 712) to regard it as an  $\alpha$ -ketonic acid, and the supposed identity of this acid with that

obtained by Bertrand (A., 1904, ii, 760) by biochemical oxidation of dextrose has led Pringsheim ("Zuckerchemie," 1925, p. 230) to regard the latter acid also as  $\alpha$ -ketonic. It is shown, however, that Bertrand's acid is not fermentable by pure yeast cultures; the fermentation observed by Hönig and Tempus is due probably to bacteria the action of which is not restricted to  $\alpha$ -ketonic acids.

H. W.

### Occurrence of *d*-Glycuronic Acid in Vegetable Fibres.

C. G. SCHWALBE and G. A. FELDTMANN (*Ber.*, 1925, 58, [B], 1534—1539).—The presence of *d*-glycuronic acid in bleached straw is established by the isolation of the cinchonine salt, m. p. 202°,  $[\alpha]_D +139.9^\circ$ . Its amount, as determined by the carbon dioxide evolved on treatment with hydrochloric acid, is 1.07%.

H. W.

**Ring Formation in Additive Compounds. II. Constitution of Compounds of Stannic Chloride with Polycarboxylic Esters.** W. HIEBER and R. BECKER.—(See i, 1325.)

### Stereochemical Studies. IX. Dithiocarbomalic Acids.

B. HOLMBERG (*Ber.*, 1925, 58, [B], 1822—1833; cf. Holmberg, A., 1910, i, 361, 834; 1912, i, 130; Ahlqvist, A., 1919, i, 435).—The action of carbon disulphide on *l*-(-)-malic acid in alkaline solution proceeds comparatively slowly, so that carbonate and trithiocarbonate are produced in considerable amount, but the crude product of the reaction is transformed by ethyl bromide into *l*-(+)-ethyl dithiocarbomalic acid,  $\text{SEt}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 150—151° or 147—148° when rapidly or slowly heated,  $[\alpha]_D +28.2^\circ$  to  $+26.55^\circ$  in alcohol,  $+24.8^\circ$  in ethyl acetate,  $+33.5^\circ$  in acetone,  $+44.1^\circ$  in water; the *potassium hydrogen, barium, and aniline hydrogen* (m. p. 89—91°) salts are described. The configurative relationship of *l*-(+)-ethyl dithiocarbomalic acid to *l*-malic acid is also established by the conversion of the former into the latter. The acid becomes inactivated to a greater or less extent when heated by itself or in acid solution, but quantitative measurements are rendered impossible by extensive side reactions. When the potassium salt is heated in aqueous solution at 100°, mercaptans are evolved and somewhat racemised *l*-malic acid is produced. *dl*-Ethyl dithiocarbomalic acid, m. p. 161—162° or 163—164° (decomp.), according to the rate of heating, is obtained similarly from *dl*-malic acid; the *barium* and *aniline* (m. p. 85—87°) salts are described. The resolution of the acid by means of the active phenylethylamines proceeded very slowly.

*l*-(+)-Ethyl dithiocarbomalic acid is converted by dimethylamine in aqueous solution into *l*-(+)-dimethylthiocarbamylmalic acid,  $\text{NMe}_2\cdot\text{CS}\cdot\text{O}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. anhydrous 117—118.5° (decomp.), *monohydrate*, m. p. 75—78°,  $[\alpha]_D +50.9^\circ$  in alcohol,  $[\alpha]_D +28.55^\circ$  in water (for the anhydrous acid). The acid is converted by ice-cold ethyl alcohol and hydrogen chloride into the corresponding *ethyl ester*,  $[\alpha]_D +35.9^\circ$  in alcohol, which is transformed by ethyl bromoacetate in hot benzene into somewhat impure dextrorotatory ethyl bromosuccinate, which is also obtained directly

from the dextrorotatory free acid to which it can be hydrolysed. The acid therefore has the *l*-(+)-form and the dextrorotatory chloro- and iodo-succinic acids possess the *l*-configuration and the lævorotatory monohalogenosuccinic acids the *d*-configuration. *dl*-*Dimethylthiocarbamylmalic acid* has m. p. 116—117° (decomp.) when anhydrous, m. p. 76—78° as the *monohydrate*. *l*-(+)-*Diethylthiocarbamylmalic acid*, m. p. (anhydrous) 70—71°,  $[\alpha]_D +56.5^\circ$  in alcohol (*monohydrate*, m. p. 52.5—53.5°), and *dl*-*diethylthiocarbamylmalic acid*, m. p. 122—124° (decomp.), are described. H. W.

**Reduction of Aldehydes and Ketones.** H. MEERWEIN and R. SCHMIDT (*Annalen*, 1925, **444**, 221—238).—A practical method for the reduction of aldehydes and of certain ketones to alcohols is developed from the well-known Cannizzaro reaction and its modifications (Claisen, A., 1887, 574; Tischtschenko, A., 1907, i, 282, 284; Child and Adkins, A., 1924, i, 139). When an aldehyde is treated with aluminium ethoxide in absolute alcohol, the reaction takes the following course:  $R \cdot CHO + aOEt \rightleftharpoons R \cdot CH(Oal) \cdot OEt \rightarrow R \cdot CH_2 \cdot Oal + O \cdot CHMe$  ( $a = \frac{1}{3} Al$ ). During the first phase, the reaction of the mixture becomes more acid and a precipitate is sometimes observed. The second phase is analogous to the decomposition of benzaldehydeacetal into acetaldehyde and benzyl ethyl ether, and to the formation of aldehydes and hydrocarbons from ethers. Since the acetaldehyde may react with the new aluminium alkoxide, it must be removed as formed by means of a current of hydrogen or nitrogen or by distillation. The amount of aluminium ethoxide necessary depends on the nature of the aldehyde, but is usually about 30% of the weight of the latter. The method gives 80—90% yield in the course of a few days at the ordinary temperature, and is suitable for reduction even of  $\alpha$ -unsaturated aldehydes or of aldehydes containing halogen or nitro groups, but is less satisfactory with aminoaldehydes and hydroxyaldehydes, and fails with the acidic phenolaldehydes. A small amount of etherification or aldolisation occurs in some cases as a side-reaction. Only such ketones as easily form alkoxides are readily reduced by this method, e.g., trichloroacetone, trichloroacetophenone,  $\alpha$ -hydroxyketones,  $\alpha$ -diketones, and  $\alpha$ -keto-esters.

The alkylloxides of magnesium and calcium have practically no reducing action, probably because they are too strongly basic. Calcium ethoxychloride is without effect, but magnesium ethoxychloride at boiling temperature is as efficient as aluminium ethoxide.

The method has biochemical interest in that aldehydes and ketones readily reducible by phytochemical means are also reduced by the new method, and conversely.

The preparation of aluminium ethoxide by adding absolute alcohol, containing a little mercuric chloride and iodine, to a briskly boiling suspension of aluminium in xylene, and its application to the reduction of furfuraldehyde in cold alcohol to furfuryl alcohol (88% yield) and a little *furfuryl pyromucate*, b. p. 150—155°/14 mm., of butylchloral in boiling alcohol to  $\beta\beta\gamma$ -trichlorobutyl alcohol, m. p. 62° (92% yield), and of benzoin in boiling toluene to hydro-

benzoin (*dibenzoate*, m. p. 247°) and *isohydrobenzoin* (*dibenzoate*, m. p. 132—133°), are described.

Magnesium ethoxide, obtained by refluxing a mixture of absolute alcohol, containing 20% of xylene, with magnesium turnings and a little mercuric chloride and iodine, is converted by treatment with the calculated quantity of alcoholic hydrogen chloride or of alcoholic magnesium chloride into magnesium ethoxychloride. The latter is used for the reduction of cinnamaldehyde in boiling alcohol to cinnamyl alcohol, b. p. 126—130°/7 mm. (80% yield). It is not suitable for the reduction of halogenated aliphatic aldehydes—*e.g.*, chloral is decomposed into chloroform and ethyl formate. The yields obtained with a large number of other aldehydes and ketones are recorded.

C. H.

**[Behaviour of] Aldehydes and Ethylene Oxide in the Friedel-Crafts Synthesis.** A. SCHAARSCHMIDT, L. HERMANN, and B. SZEMZO.—(Cf. i, 1278.)

**Products of the Bromination of Paracetaldehyde.** A. STEPANOV, N. PREOBRASCHENSKI, and M. SCHTSCHUKINA (*Ber.*, 1925, **58**, [B], 1718—1723).—The action of bromine on freshly distilled paracetaldehyde at  $-15^{\circ}$  in diffused light followed by treatment of the product with a paste of crystalline sodium acetate and water leads to the production of *dibromoparacetaldehyde*,  $\text{O} < \text{CH}(\text{CH}_2\text{Br}) \cdot \text{O} > \text{CHMe}$ , m. p.  $57^{\circ}$ , b. p. 135—136°/14 mm., 126—127°/10 mm.; if the product of the bromination is treated with crystalline sodium acetate in the absence of water, tribromoparacetaldehyde, m. p. 103—104°, b. p. 176°/13 mm., 164—165°/8 mm., is the main product (cf. Hibbert and Hill, A., 1923, i, 439). Dibromoparacetaldehyde is decomposed when heated at  $155^{\circ}$  into acetaldehyde and bromoacetaldehyde, b. p. 104—105°/749 mm.,  $d_4^{20}$  1.8414,  $n_D^{20}$  1.4798 (*semicarbazone*, m. p.  $130^{\circ}$ ), which is readily obtained in this manner. Bromoacetaldehyde readily undergoes polymerisation to a substance  $(\text{C}_2\text{H}_3\text{OBr})_n$ , m. p. 136—138°, but the process may be delayed considerably by the addition of acetaldehyde. It is converted by 2 mols. of water into the *hydrate*,



m. p. 47—49°, and by excess of water into a *compound*, m. p. 60—62°. Monobromoacetaldehydediethylacetal has b. p. 57—58°.

H. W.

**Hydrogenation of Cyclic and Acyclic Aldazines and Ketazines by Aluminium Amalgam.** H. MAZOUREVITCH (*Bull. Soc. chim.*, 1925, [iv], **37**, 1155—1167).—The azines of both aliphatic and aromatic aldehydes and ketones on reduction with aluminium amalgam in neutral solution yield mainly primary amines. Secondary amines are formed in a few cases. *Phenylethylketazine*, m. p. 66—67°, yields  $\alpha$ -phenylpropylamine [*chloroplatinate*, m. p. 200—202° (decomp.), *chloroaurate*], accompanied by traces of a neutral substance, probably a hydrochloride. Propaldazine yields a mixture of propylamine and dipropylamine; *isobutaldazine* yields

mainly diisobutylamine (*oxalate*, m. p. 245—248°, subliming; *phenylcarbamate*, m. p. 104—106°) with isobutylamine and probably a little *s*-diisobutylhydrazine. *iso*Propylideneazine gives a mixture of isopropylamine and diisopropylamine. Diethylketazine yields almost entirely *n*-amylamine [the *chloroplatinate*, *hydrogen oxalate*, ( $\frac{1}{2}$ H<sub>2</sub>O), m. p. 122—124°, and *normal oxalate*, m. p. 218—220° (decomp.), are described].

Methylpropylketazine similarly yields  $\beta$ -aminopentane, and di-propylketazine,  $\delta$ -aminoheptane (*oxalate*). Benzylideneazine yields almost entirely benzylamine [*chloroplatinate*, m. p. 208—210° (when rapidly heated), decomp. 204—205°; *oxalate*, m. p. 200—202° (decomp.)], probably with traces of the hydrazone. R. B.

**Reduction of *s*-Dichloroacetone by Yeast.** H. K. SEN and C. BARAT (*J. Indian Chem. Soc.*, 1925, 2, 77—81).—Yeast reduces *s*-dichloroacetone to dichlorohydrin, the method being the same as that previously employed (cf. Sen, this vol., i, 337). With equimolecular proportions of dichlorohydrin and chloroformamide, the urethane is produced, but if 1 mol. excess of the chloroformamide is used the *allophanic* ester, NH<sub>2</sub>·CO·NH·CO<sub>2</sub>CH(CH<sub>2</sub>Cl)<sub>2</sub>, m. p. 182°, is obtained. An improved method for the oxidation of dichlorohydrin to *s*-dichloroacetone is described. J. W. B.

**Keto-enolic Tautomerism. V. Desmotropic  $\gamma$ -Methylacetylacetones.** H. P. KAUFMANN and J. LIEFE (*Ber.*, 1925, 58, [B], 1560—1563).—As in the case of ethyl diacetylsuccinate (A., 1923, i, 90), the discrepancies in the results of the determination of enol in  $\gamma$ -methylacetylacetone are due to the presence of water (in the iodide solution); they are not observed if alcoholic sodium iodide solution is used.

The homogeneous enolic form of  $\gamma$ -methylacetylacetone [ $\beta$ -hydroxy- $\gamma$ -methyl- $\Delta^{\beta}$ -penten- $\delta$ -one], m. p. +7°, is obtained by decomposing the sodium derivative of the ketone by dilute sulphuric acid in presence of ether. The homogeneous ketonic form could not be isolated by "aseptic distillation" (Meyer and Schoeller, A., 1920, i, 707); the distillate is not purely enolic, but the residue contains up to 93% of ketone. H. W.

**Configurational Relationships of the Sugars, Hydroxy-acids, Amino-acids, and Halogen Acids.** P. A. LEVENE (*Chem. Reviews*, 1925, 2, 179—216).

**Rate of Oxidation of Sugars by Permanganate.** R. KUHN and T. WAGNER-JAUREGG (*Ber.*, 1925, 58, [B], 1441—1447).—The hexose (5 g.), or the equivalent quantity of other type of sugar, is dissolved with *M*/15-phosphoric acid (10 c.c.), *M*/15-potassium dihydrogen phosphate (10 c.c.), and *N*/10-potassium permanganate (20 c.c.) in water to 100 c.c. at 18°. At intervals, 10 c.c. of the liquid are mixed with 15 c.c. of the mixture of phosphate solutions (1:1) and 1 c.c. of potassium iodide solution (10%), and the liberated iodine is titrated with *N*/10-thiosulphate. The time in minutes required to reduce the permanganate to 25% is termed

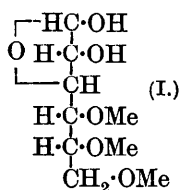
the "permanganate number" of the sugar. In general, the  $\beta$ -forms of the sugar react considerably more rapidly than the corresponding  $\alpha$ -forms, but the comparison of  $\alpha$ - and  $\beta$ -glucoses with  $\alpha$ - and  $\beta$ -mannoses indicates that reactivity towards permanganate is not governed in a simple manner by the relative positions of the hydroxy groups within the sugar molecule. Haworth and Law's observation (T., 1916, **109**, 1320) that lævulose reduces permanganate only after being preserved in acid solution could not be confirmed; there is thus no support for the hypothesis of the formation of a  $\gamma$ -fructose in acid solution. Pre-treatment of sugars with alkali followed by neutralisation of the solution induces increased activity towards permanganate (cf. Armstrong and Hilditch, T., 1919, **115**, 1410). The phenomenon is not, however, due to the establishment of an equilibrium between lævulose, dextrose, and mannose, since the sugar first named, which is most rapidly attacked by permanganate, also has its activity enhanced by treatment with alkali. The irreversible nature of the change in lævulose appears also to exclude the hypothesis that the effect is due to enolisation (cf. Armstrong and Hilditch, *loc. cit.*). Solutions of sucrose which have been subjected to rapid hydrolysis by invertase show only a slight diminution in the permanganate number, which is ascribed to  $\alpha$ -glucose; there appears to be no evidence of the production of a readily oxidisable lævulose of the amylen oxide type, so that either there is no difference between ordinary lævulose and that contained in sucrose, or the isomerisation of the latter form occurs so readily that it cannot be detected.

H. W.

**Methyl Derivatives of *d*-Glucose.** E. PACSU (*Ber.*, 1925, **58**, [B], 1455—1464).—*d*-Glucosediethylmercaptal is converted slowly by methyl ethyl ketone in the presence of anhydrous copper sulphate into a mixture of products from which *d*-glucosediethylmercaptal  $\gamma\delta$ -isobutylidene ether, m. p. 90—91°,  $[\alpha]_D^{25}$  —6.56° in *s*-tetrachloroethane,  $[\alpha]_D^{25}$  —117.58° in ethyl alcohol, can be isolated in small amount. It is not possible to isolate the diisobutylidene ether by means of its *p*-toluenesulphonate, but the crude mixture is readily methylated, and the product, after removal of the isobutylidene groups, affords monomethyl-*d*-glucosediethylmercaptal and trimethyl-*d*-glucosediethylmercaptal, m. p. 96° (instead of 73—74° recorded previously). The use of methyl ethyl ketone has no advantage over that of acetone (cf. Pacsu, A., 1924, i, 712). Monomethyl-*d*-glucosediethylmercaptal is converted by mercuric chloride in the presence of ethyl alcohol into the ethyl ether of monomethyl-*d*-glucose, from which  $\delta$ -monomethyl-*d*-glucose, m. p. 156—157° after softening at 149°,  $[\alpha]_D^{25}$  +18.57° to +61.92° (in water),  $[\alpha]_D^{25}$  +32.44° to +52.58° (in alcohol), is obtained by hydrolysis. The position of the methyl group in the molecule is established by the non-identity of the compound with the known  $\beta$ -,  $\gamma$ -, and  $\zeta$ -methylglucoses. The mutarotation of the sugar in aqueous solution appears to follow the law of a bimolecular reaction, possibly attributable to the displacement of the oxygen bridge with simultaneous production of  $\alpha$ - and  $\beta$ -forms. The methylglucose could

not be caused to condense with acetone; the corresponding *phenylosazone*, decomp. about  $198^{\circ}$ , according to the rate of heating, has  $[\alpha]_D^{15} -50.33^{\circ}$  to  $-34.84^{\circ}$  (in pyridine-alcohol).

Trimethylglucosidibenzylmercaptal is transformed by methyl alcohol and mercuric chloride followed by hydrolysis of the glucoside



into  $\delta\epsilon\zeta$ -trimethyl-d-glucose (I), which could be obtained only as an amorphous mass,  $[\alpha]_D^{15} +75.81^{\circ}$  (in alcohol),  $[\alpha]_D^{15} +65.94^{\circ}$  to  $+61.13^{\circ}$  (in water). The presence of the propylene oxide ring is deduced from the ability of the sugar to condense with acetone and to yield a *phenylosazone*, m. p.  $156-157^{\circ}$ ,  $[\alpha]_D^{15} -32.63^{\circ}$  to  $-15.46^{\circ}$  (in alcohol).

Treatment of monomethyl-d-glucosidibenzylmercaptal with mercuric chloride (1 mol.) in boiling absolute alcohol gives  $\delta$ -methyl- $\alpha$ -benzylthiogluco-side, m. p.  $136^{\circ}$ ,  $[\alpha]_D^{15} +249.61^{\circ}$  (in alcohol).

H. W.

**Fission of  $\gamma$ -Methylfructoside by Invertase. Configuration of Sucrose.** H. H. SCHLUBACH and G. RAUCHALLES (*Ber.*, 1925, 58, [B], 1842—1850).—It is pointed out that the prefix  $\gamma$  was first employed by E. Fischer to denote the derivative of a labile sugar, and that its use has since been extended to all the members of this class. The choice has proved somewhat unfortunate, since new structurally isomeric, and not stereoisomeric, forms are involved, and confusion has become complete since the discovery of stereoisomeric forms of the labile sugars which are designated  $\alpha$ - and  $\beta$ -compounds. It is therefore proposed to designate the labile sugars by the prefix *h* ( $\zeta\tau\epsilon\rho\sigma$ ).

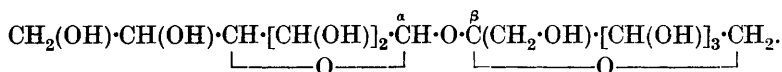
Since yeast invertase is active only towards sucrose and such sugars as are related to it by changes only in the glucose portion of the molecule, its activity towards *h*-methylfructoside may be expected. It is found that Menzies' *h*-methylfructoside (mainly a mixture of the two stereoisomeric  $\gamma$ -methylfructosides, cf. T., 1922, 121, 2238) is hydrolysed to a definite extent at about the same rate as sucrose. Observations of the change in specific rotation show that yeast invertase hydrolyses the  $\beta$ -*h*-methylfructoside and that, contrary to previous practice, it is to be regarded as a  $\beta$ -*h*-fructoinvertase. The portion which remains unhydrolysed is not, however, pure  $\alpha$ -*h*-methylfructoside, since it contains the normal methylfructosides present in the original mixture; from the specific rotations, the content of the normal compounds is calculated to be at least 6.7%. Hydrolysis follows much the same course at  $0^{\circ}$  as at  $30^{\circ}$ , so that the temperature coefficient of the isomerisation of *h*-fructose is not greatly different from that of the hydrolysis. Fischer's  $\gamma$ -methylfructoside (cf. Purdie and Paul, T., 1907, 91, 289) contains about 50% of *h*-methylfructosides.

The mixture of *h*-methylfructosides is hydrolysed as readily as sucrose by taka-invertase, the extent being greater than when yeast invertase is used. Taka-dia-stase appears therefore to contain, besides  $\beta$ -*h*-fructoinvertase, an enzyme which can hydrolyse



$\alpha$ -*h*-methylfructoside; this hypothesis is confirmed by the observation that the residue left after complete action of yeast invertase is further hydrolysed by taka-invertase. Kuhn's hypothesis (A., 1923, i, 1033) that the fructose portion of the sucrose molecule is attacked by yeast invertase and the glucose portion by taka-invertase cannot therefore be maintained, since either enzyme is active towards *h*-methylfructosides.

The established presence of glucose in the  $\alpha$ -form in sucrose has enabled Hudson to calculate the value,  $+17^\circ$ , for the fructose component. A closely similar value is derived by application of the theory of optical superposition to sucrose and  $\alpha\beta$ -trehalose which have the common  $\alpha$ -glucose component, but differ in respect of the fructose and  $\beta$ -glucose components. Hudson has been led to assume the presence of the (unknown)  $\alpha$ -fructose in sucrose, but this conception is not supported by the specific rotation of  $\alpha$ -fructose as calculated from its relationship to *d*-arabinose. These contradictions are removed by regarding the fructose component,  $[\alpha]_D +17^\circ$ , as  $\beta$ -*h*-fructose. The constitution and configuration of sucrose are best expressed by the formula :



H. W.

**Constitution of Lupeose.** N. CASTORO (*Gazzetta*, 1925, 55, 463—467; cf. A., 1909, ii, 754; Schulze, A., 1901, ii, 467).—In water, lupeose gives colloidal solutions and hence in this solvent the results of cryoscopic determinations of its molecular weight are too high. It has been shown to be a tetrasaccharide (Schulze, A., 1910, i, 610) composed of 2 mols. of *d*-galactose, 1 mol. of dextrose, and 1 mol. of a *d*-hexose (cf. A., 1911, i, 17), now shown to be lævulose. Lupeose (cicerose or  $\gamma$ -galactan) has  $\alpha_D +48^\circ$  to  $50^\circ$ .

W. E. E.

**Starch. XIV. Nitric Esters of the Polyamyloses.** H. PRINGSHEIM, J. LEIBOWITZ, and S. H. SILMANN (*Ber.*, 1925, 58, [B], 1889—1893).—Nitration of the polyamyloses leads in all cases to mixtures of more or less highly nitrated products; it is not possible to secure the quantitative formation of the trinitrates by use of a large excess of nitrating acid. The crude mixture of nitrates, invariably obtained in good yield, is separated into its components by fractional crystallisation from alcohol or acetic acid, although the process is complicated by the instability of the substances. The following compounds have been isolated in the homogeneous, well-crystallised form :  $\alpha$ -tetra-amylose octanitrate,  $[\text{C}_6\text{H}_8\text{O}_3(\text{NO}_3)_2]_4$ , m. p.  $204^\circ$  (decomp.),  $[\alpha]_D +96.4^\circ$  in nitrobenzene;  $\alpha$ -diamylose hexanitrate,  $[\text{C}_6\text{H}_7\text{O}_2(\text{NO}_3)_3]_2$ , m. p.  $206\text{--}207^\circ$  (decomp.),  $[\alpha]_D +79.7^\circ$  in ethyl acetate,  $+78.1^\circ$  in nitrobenzene (from  $\alpha$ -tetra-amylose or  $\alpha$ -diamylose);  $\beta$ -triamylose hexanitrate,  $[\text{C}_6\text{H}_8\text{O}_3(\text{NO}_3)_2]_3$ , m. p.  $203^\circ$ ,  $[\alpha]_D +122.4^\circ$  in nitrobenzene;  $\beta$ -triamylose nonanitrate,  $[\text{C}_6\text{H}_7\text{O}_2(\text{NO}_3)_3]_3$ , m. p.  $198^\circ$ ,  $[\alpha]_D +90.5^\circ$  in nitrobenzene. The production of a diamylose tetranitrate has been established, but

its isolation has not hitherto been possible. The most important result is the identification of both reaction products of the  $\beta$ -series as derivatives of triamylose by cryoscopic determinations of molecular weight. Both esters are obtained from the hexa- as well as from the tri-saccharide.

The difference in the behaviour of the  $\alpha$ - and  $\beta$ -polyamyloses, apart from the assured existence of triamylose, is sufficient to exclude the possibility of their formation from a common unit. The ready decomposition of the more complex polyamyloses with almost theoretical yields of fission products proves that the materials are polymerides in which the unit materials are united only by subsidiary valencies; closed structures such as suggested by Ling and Nanji (T., 1923, 123, 2666; this vol., i, 1011) appear to be excluded.

H. W.

**Cellulose. XVI. Crystalline Cellulose Acetates. II. K. HESS, G. SCHULTZE, and E. MESSMER** (*Annalen*, 1925, 444, 266—287; cf. this vol., i, 118).—The acetone-soluble cellulose acetate (Bayer's "cellite"), prepared on a large scale by treatment of cellulose triacetate with sulphuric and acetic acids, is shown to be a mixture of tri- and di-acetates in the approximate ratio 1 : 4, monoacetate being absent. Preparations having the same acetyl content may have varying rotatory power, although that of the triacetate obtained on acetylation of the mixture is always the same. This indicates the presence of varying proportions of the isomeric diacetates. The mixture of di- and tri-acetates can readily be crystallised from its solution in hot benzene-alcohol (1 : 1). The crystals are stable only in contact with the solvent, and when dry become amorphous. Like the triacetate crystals (*loc. cit.*), they give no X-ray line spectrum. This peculiarity is also shown by Wichmann's albumin crystals (A., 1899, i, 838; Katz, A., 1924, ii, 652). The crystallising power is due less to the individuality of the product than to its high temperature coefficient of solubility. That the crystalline acetate is derived from chemically intact cellulose is proved by the identity of the rotatory power curves (see following abstract) for the hydrolysed product and for pure natural cellulose. The existence in natural cellulose of more than one isomeride is rendered extremely improbable by the identity of the curves obtained for the hydrolysis products after 40 recrystallisations of the crystalline mixture and after prolonged fractional extraction with chloroform.

The acetone-soluble acetate, prepared by Ost's modification (Z. angew. Chem., 1919, 32, 69, 83) of the method of D.R.-P. 252706, contains the acetates of dextrose and cellobiose in addition to di- and tri-acetates of cellulose. The rate of acetylation varies very considerably with different cellulose preparations—1½ hrs. for Kahlbaum's defatted cotton, 2 hrs. for "linters II," 16 hrs. for "linters I," and more than 48 hrs. for mercerised "linters I." Mercerisation cannot thus be regarded as a depolymerisation. A further result of mercerisation is the much slower hydrolysis of triacetate in solution to diacetate.

The crude acetate may be purified by repeated precipitation from solution in hot benzene-alcohol. Crystallisation becomes apparent after six precipitations from this solvent and depends on (i) the purity of the product (freedom from sugars), (ii) the concentration of the solution (a 2% solution of well-crystallised product separates only in amorphous form), (iii) the rate of cooling (slow cooling is essential), (iv) the solvent (variation in the ratio of benzene to alcohol results in amorphous precipitates).

C. H.

**Cellulose. XVII. Characterisation of Cellulose Preparations.** K. HESS, E. MESSMER, and N. LJUBITSCH (*Annalen*, 1925, 444, 287—327; cf. Hess, *Naturwiss.*, 1924, 12, 1150).—It has earlier been shown (*loc. cit.* and this vol., i, 118) that the rotatory power of cellulose-cuprammonium solutions is strictly related to the concentration of copper and cellulose, and it has been possible to follow purifications and separations by means of the optical activity of the copper-complex compound. By plotting rotatory power against the copper or  $C_6H_{10}O_5$  concentration (in milliatoms or millimols. per 100 c.c.) a characteristic curve is obtained.

Wood cellulose containing 88—89% of alkali-resistant “ $\alpha$ -cellulose,” the alkali-soluble portion,  $\alpha$ -cellulose, and pure cotton cellulose all gave identical curves and must be regarded as a single chemical individual, the differences being attributable to physical causes (*e.g.*, differences in surface conditions). In a similar manner, the identity of American and Egyptian cotton celluloses is demonstrated and Venn’s conclusions (this vol., i, 887) are shown to be erroneous. The Egyptian cotton preparation was easily soluble in cuprammonium solutions and the solution showed a higher viscosity than was observed with any other variety of cellulose. Ramie cellulose, although it contains 5% of matter difficultly soluble in cuprammonium solutions, is nevertheless composed of chemically pure cellulose. Mercerisation is shown by the curves to be accompanied by a purification of the cellulose so treated.

The hydrocelluloses and cellulose dextrans give curves of the same type as that for pure cellulose, although the values are somewhat lower owing to the presence of hydrolytic products. They differ completely in character from the curves for sugars and their derivatives or for other polysaccharides.

C. H.

**Constitution of Pine Lignin. V.** P. KLASON (*Ber.*, 1925, 58, [B], 1761—1764; cf. A., 1920, i, 822; 1922, i, 324; 1923, i, 187; this vol., i, 371).—The action of saturated sulphur dioxide solution on lignin under the mildest possible conditions appears to lead to the formation of the acid,  $3C_{10}H_{10}O_3 \cdot H_2SO_3$ , isolated as the  $\beta$ -naphthylamine salt. More drastic treatment of the acid with sulphurous acid appears to lead ultimately to the sulphonic acid of simple coniferaldehyde (isolated as the  $\beta$ -naphthylamine salt).

Paracetaldehyde is converted by  $\beta$ -naphthylamine hydrochloride into the compound  $(CH_3 \cdot CHO)_3 + 2C_{10}H_9N \cdot 2H_2O$ . Paracinnamaldehyde is converted by sulphurous acid and subsequent treatment of the acid with  $\beta$ -naphthylamine into the salt  $(CHPh \cdot CH \cdot CHO)_3 + H_2SO_3 + C_{10}H_9N \cdot H_2O$ .

The comparatively ready fission of lignosulphonic acid to conifer-aldehydesulphonic acid indicates the improbability of an aldol-like union of the coniferaldehyde molecules in lignin. H. W.

**Preparation of Alicyclic Primary Amines by Reduction of Oximes with Active Aluminium.** H. MAZOUREVITCH (*Bull. Soc. chim.*, 1925, [iv], 37, 1033—1043).—Aliphatic oximes and phenylhydrazones are readily reduced by aluminium amalgam in aqueous alcoholic solution, yielding mainly primary amines, but the yields are lower than those obtained with sodium amalgam (Tafel, A., 1886, 939; 1889, 975), although the method has the advantage in experimental simplicity. The oximes give lower yields of amines, but much purer products than the phenylhydrazones. The reduction of the latter compounds may take place in two ways, either through the intermediate formation of a mixed arylalkylhydrazine, or through an alkylazine, formed by condensation of the hydrazone,  $2\text{CHR:N}\cdot\text{NHPh} \rightarrow \text{CHR:N}\cdot\text{N:CHR} + \text{NHPh}\cdot\text{NHPh}$ , the azine then undergoing reduction. The latter mode of reduction accounts for the formation of the secondary amines also sometimes observed. Thus acetonephenylhydrazone yields isopropylamine together with a little diisopropylamine; the corresponding oxime yields only isopropylamine. Similarly, the phenylhydrazone of methyl ethyl ketone yields isobutylamine and a fraction, b. p. 136—146°, consisting mainly of *s*-diisobutylhydrazine [*dithiocarbamide*, m. p. 145—146° (decomp.), *oxalate*, m. p. 144—145° (decomp.)]; the phenylhydrazone of methyl propyl ketone yields  $\beta$ -aminopentane, and of *n*-valeraldehyde *n*-amylamine, together with fractions of higher b. p. The phenylhydrazone of isovaleraldehyde yields isoamylamine together with a fraction, b. p. 173—175°, *s*-diisoamylhydrazine, giving an *oxalate*, m. p. 157—159° (decomp.), a *phenylthiocarbamide*, m. p. 148—149.5°, and a *phenylcarbamate*, m. p. 230—230.5° (decomp.). The phenylhydrazone of heptaldehyde yields heptylamine and a fraction, b. p. 271—275°, giving an *oxalate*, m. p. 205—207° (decomp.), a *phenylthiocarbamide*, m. p. 150—151°, and with phenylcarbimide,  $\beta\delta$ -*di-phenyl- $\alpha$ -heptylsemicarbazide*, m. p. 224—225° (decomp.). The fraction does not give a chloroplatinate and is probably *s*-phenylheptylhydrazine,  $\text{C}_7\text{H}_{15}\cdot\text{NH}\cdot\text{NHPh}$ . With oximes of the hydroaromatic series, the reduction scarcely takes place or follows an abnormal course. Camphoroxime only yields traces of bornylamine, whilst carvone derivatives yield carvylamine contaminated with many impurities. R. B.

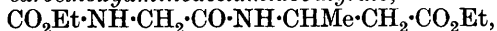
**Higher Fungi. XVIII. The Muscarine Question.** B. GUTH (*Monatsh.*, 1925, 45, 631—648).—The following salts of choline, which was prepared by condensing trimethylamine with ethylene oxide (cf. Wurtz, *Compt. rend.*, 1868, 65, 1015; 66, 772; Meyer and Hopff, A., 1921, i, 851), are described: *hydrochloride*; *chloroplatinate*, m. p. 242°; *chloroaurate*, m. p. 250°, impure preparations of which decompose on keeping, with deposition of gold; *mercuric iodide* double salt,  $\text{C}_5\text{H}_{14}\text{ONCl}\cdot 2\text{HgI}_2$ ; *mercuric chloride* double salt,  $\text{C}_5\text{H}_{14}\text{ONCl}\cdot\text{HgCl}_2$ , m. p. 170° after sintering at 168°.

which on recrystallisation from water is converted into the salt previously described by Mörner (A., 1897, ii, 222) and Gulewitsch (A., 1895, i, 196; 1898, i, 622). The *sulphate*, *phosphate*, *chromate*, *hydrogen tartrate*, *salicylate*, and *picrate* are difficult to crystallise and purify, and not suitable for analytical purposes. The salts obtained from the acids prepared in this way still give strong colorations with diphenylamine (cf. Weinhausen, A., 1919, i, 474; 1921, i, 192). When choline chloroaurate is dissolved in nitric acid ( $d$  1.52) and the solution evaporated to dryness, a crystalline product, apparently the *chloroaurate* of *homocholine* [?] *nitrite*,  $(\text{NMe}_3\text{Cl}\cdot\text{CH}_2\text{ONO})\text{AuCl}_3$ , is obtained. Choline chloroplatinate yields, when treated similarly, the chloroplatinate of choline nitrite, m. p.  $237^\circ$  (cf. Ewins, A., 1914, i, 665; Dale, A., 1914, i, 780; Nothnagel, A., 1893, i, 297). Cold, dilute, acidified potassium permanganate solution is without appreciable action on choline sulphate. At higher temperatures, betaine is produced (cf. Liebreich, *Ber.*, 1869, 2, 167). Trimethylammoniumacetal, obtained by condensing monochloroacetal with trimethylamine, forms a crystalline *hydrochloride*. The *chloroplatinate* and *chloroaurate* are well crystallised, but different samples vary considerably in appearance and m. p. Hydrolysis of the acetal with hydrochloric acid affords the betaine-aldehyde, the chloroplatinate of which,  $(\text{NMe}_3\text{Cl}\cdot\text{CH}_2\cdot\text{CHO})_2\text{PtCl}_4\cdot 3\text{H}_2\text{O}$ , exhibits varying crystalline forms, and different, apparently pure samples have m. p. between  $204^\circ$  and  $230^\circ$ . The chloroaurate exhibits similar variations (cf. Berlinerblau, A., 1884, 1056; Fischer, A., 1893, i, 300). The bases obtained from toadstools afford, when fractionally precipitated with chloroauric acid, a series of chloroaurates, all of which appear to be the choline salt in a more or less pure condition. The presence of muscarine in these bases could not be confirmed, and it is concluded that the "typical muscarine action" is not a pharmacological property of trimethylammonium bases. F. G. W.

**Isomerism of the N-Carbalkoxy Derivatives of Dipeptides which contain a  $\beta$ -Amino-acid.** H. LEUCHS and P. SANDER (*Ber.*, 1925, 58, [B], 1528—1534; cf. Leuchs and Manasse, A., 1907, i, 770; Leuchs and La Forge, A., 1908, i, 723).—The action of methyl chloroformate and sodium carbonate on *dl*- $\beta$ -aminobutyric acid leads to the production of  $\beta$ -carbomethoxyaminobutyric acid, m. p.  $90-91^\circ$  (corr.), which is converted by the successive action of thionyl chloride and ammonia into the corresponding *diamide*, m. p.  $141-142^\circ$ . The chloride reacts with ethyl anilinoacetate in ethereal solution, giving *ethyl*  $\beta$ -carbomethoxyaminobutyryl-N-phenylaminoacetate,  $\text{CO}_2\text{Me}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , m. p.  $94.5-95.5^\circ$ , which is converted by 1 mol. of alkali hydroxide into  $\beta$ -carbomethoxyaminobutyryl-N-phenylaminoacetic acid (ammonium salt), and by excess of alkali hydroxide into  $\beta$ -aminobutyryl-N-phenylaminoacetic acid. Similarly, *ethyl*  $\beta$ -carbomethoxybutyrylaminoacetate, m. p.  $100^\circ$ , is converted by gentle hydrolysis into  $\beta$ -carbomethoxybutyrylaminoacetic acid, m. p.  $135-136^\circ$  [corresponding *dimethyl* ester ( $\alpha$ -series), m. p.  $101-103^\circ$ ], and by methyl-

alcoholic ammonia into  $\beta$ -carbomethoxybutyrylaminoacetamide ( $\alpha$ -series), m. p. 118—119°; more drastic hydrolysis transforms it into the corresponding dibasic acid identified by conversion into the *dimethyl* ester,  $\text{CO}_2\text{Me}\cdot\text{NH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , m. p. 85° (corresponding *diamide*, m. p. 180—182° after slight gas evolution).

Carbethoxyaminoacetyl chloride and ethyl  $\beta$ -aminobutyrate yield *ethyl  $\beta$ -carbethoxyaminoacetamidobutyrate*,



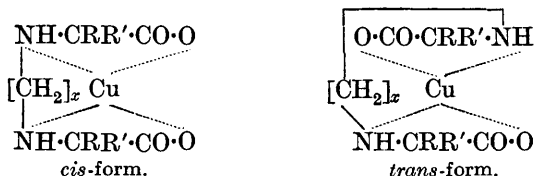
m. p. 58°, which is converted by ammonia into  $\beta$ -carbethoxyaminoacetamidobutyramide, m. p. 130—131°, and by mild hydrolysis into  $\beta$ -carbethoxyaminoacetamidobutyric acid (*ammonium* salt). More drastic hydrolysis leads to the production of the corresponding dibasic acid, which is converted by ethyl-alcoholic hydrogen chloride into the *diethyl* ester ( $\beta$ -series), m. p. 104°; the ester is transformed by methyl-alcoholic ammonia into the corresponding *diamide*, m. p. 172° (decomp.) after softening at 95—100°. H. W.

**Alkyl Esters of  $\alpha$ -Dialkylaminomethyl- $\alpha$ -alkylacetoacetic Acid.** SOC. OF CHEM. INDUSTRY IN BASLE (Swiss Pat. 107349, addn. to 107347, 107348, and 104344; from *Chem. Zentr.*, 1925, i, 2512—2513).—The following have been obtained by the condensation of alkyl esters of  $\alpha$ -alkyl- or  $\alpha$ -arylalkyl-acetoacetic acids with formaldehyde and secondary amines, or the methyloldialkylamines obtained by reaction of the latter: *ethyl  $\alpha$ -diethylaminomethyl- $\alpha$ -ethylacetoacetate*, b. p. 123°/8 mm.; *ethyl  $\alpha$ -diallylamino-methyl- $\alpha$ -ethylacetoacetate*, b. p. 93°/0.02 mm.; *ethyl  $\alpha$ -diethylaminomethyl- $\alpha$ -allylacetoacetate*, b. p. 95°/0.06 mm., and *ethyl  $\alpha$ -benzyl- $\alpha$ -diethylaminomethylacetoacetate*, b. p. 124°/0.01 mm. R. B.

**Stereochemistry of the Tetrahedral Carbon Atom. II. Configuration of the Diaminosuccinic Acids.** R. KUHN and F. ZUMSTEIN (*Ber.*, 1925, 58, [B], 1429—1432; cf. this vol., i, 781).—*dl*- $\alpha\beta$ -Dibenzamidosuccinic acid, m. p. 164°, is resolved into its optical antipodes by morphine in aqueous solution; *l*- $\alpha\beta$ -*dibenzamidosuccinic acid* has m. p. 163—164° (decomp.),  $[\alpha]_D^{20}$  —104.2° in 0.1*N*-ammonia, whereas the *d*-acid (*morphine* salt) has m. p. 163—164°,  $[\alpha]_D^{20}$  +106.5° in 0.1*N*-ammonia. The stereochemical configuration of the  $\alpha\beta$ -diaminosuccinic acids is thus established. *meso*- $\alpha\beta$ -*Dibenzamidosuccinic acid*, m. p. 212—213°, *meso*- $\alpha\beta$ -*diaminosuccinic acid dihydrochloride*, decomp. 186—187°, and *dl*- $\alpha\beta$ -*diaminosuccinic acid monohydrochloride*, decomp. 200°, are incidentally described. H. W.

**Spatial Relationships around the Copper Atom.** N. SCHLESINGER (*Ber.*, 1925, 58, [B], 1877—1889).—In the majority of its compounds copper has the co-ordination number 4, but it has not been hitherto possible to decide whether the groups around the copper atom lie in one plane or in the corners of a regular tetrahedron. The existence of reddish-violet forms of certain copper salts of bisimino-acids (which have the normal molecular weight in phenol) in addition to the dark blue varieties can scarcely

be explained except by the assumption of *cis-trans* isomerism and hence of the plane arrangement of the groups around the copper atom. The salts may be formulated.



When the value of  $x$  is small (2 or 3) the production of *cis*-salts may be expected, whereas when  $x$  is great (about 10) the formation of *trans*-salts appears to be favoured. When  $x$  has an intermediate value, both forms of salts can be obtained and their mutual transformation studied. The difference between the two series persists in solution, and the gradual interconversion can be followed by the change of colour; it cannot therefore be due to difference in formation of the crystal lattice.

Many of the compounds described have been recorded previously (Schlesinger, A., 1911, i, 427; 1912, i, 555; 1915, i, 506, 945), but the following are new.  $\alpha\alpha'$ -Trimethylenedi-iminodioctonitrile,  $\text{C}_3\text{H}_6[\text{NH}\cdot\text{CH}(\text{C}_6\text{H}_{13})\cdot\text{CN}]_2$ , is prepared as its *hydrochloride*, m. p. 215–230° after incipient decomp. 185°, by the action of trimethylenediamine hydrochloride and potassium cyanide on heptaldehyde in aqueous-alcoholic solution. It is hydrolysed by a mixture of sulphuric and hydrochloric acids to  $\alpha\alpha'$ -trimethylenedi-iminodioctoic acid; the corresponding *hydrochloride*, the pale blue, anhydrous copper salt, and the non-crystalline *methyl* ester are described. The copper salts of  $\alpha\alpha'$ -pentamethylenedi-iminodiiisobutyric acid are of particular interest, since the blue variety is unstable and is readily hydrolysed by water to the salt  $\text{C}_{13}\text{H}_{26}\text{O}_4\text{N}_2\cdot 3\text{C}_{13}\text{H}_{24}\text{O}_4\text{N}_2\text{Cu}$ , which is converted by copper hydroxide into the violet, insoluble salt  $\text{C}_{13}\text{H}_{24}\text{O}_4\text{N}_2\text{Cu}$ .

*Nickel*  $\alpha\alpha'$ -pentamethylenedi-iminodiphenyldiacetate is described.

Heptamethylenediamine hydrochloride is converted by potassium cyanide and acetaldehyde into  $\alpha\alpha'$ -heptamethylenedi-iminodipropionitrile hydrochloride, which is hydrolysed by fuming hydrochloric acid to  $\alpha\alpha'$ -heptamethylenedi-iminodipropionic acid,  $\text{C}_7\text{H}_{14}(\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{H})_2$ , decomp. above 270°; the corresponding *hydrochloride* and the pale blue, tetrahydrated copper salt are described.  $\alpha\alpha'$ -Heptamethylenedi-iminodiiisobutyronitrile [*hydrochloride*, m. p. about 129° (decomp.)] is hydrolysed to  $\alpha\alpha'$ -heptamethylenedi-iminodiiisobutyric acid, which softens but does not melt below 310°. The copper salt is obtained in the violet form by the addition of the equivalent quantity of an ammoniacal copper hydroxide solution to the acid; it is converted into the blue variety when its solution in phenol is mixed with alcohol and subsequently diluted with ether. The violet salt immediately gives a cherry-red solution in phenol, whereas the blue compound yields a blue solution which gradually becomes red.  $\alpha\alpha'$ -Heptamethylenedi-

*iminodiphenyldiacetonitrile*,  $C_7H_{14}(NH \cdot CHPh \cdot CN)_2$ , its *dihydrochloride*, m. p.  $144^\circ$  (decomp.) after softening at  $142^\circ$ , the corresponding *acid*, decomp. about  $231^\circ$ , its *hydrochloride*, *copper salt*, and *methyl ester*,  $d_4^{20}$  1.0854,  $n_D^{20}$  1.5293, are described.

$\alpha\alpha'$ -Decamethylenedi-*iminodisobutyronitrile*, prepared from decamethylenediamine hydrochloride, potassium cyanide, and acetone, is hydrolysed by fuming hydrochloric acid to  $\alpha\alpha'$ -*decamethylenediiminodisobutyric acid*, which appears to yield only a pinkish-violet *copper salt* insoluble in the usual solvents. H. W.

[Simple Cyano and Cyanuric Compounds. III. **Malononitrile and its Halogenation**]. E. OTT and H. FINKEN (*Ber.*, 1925, **58**, [B], 1703).—Dibromomalononitrile (Ott and Löpmann, A., 1922, i, 643) unites very readily with 1 mol. of water, giving dibromocyanoacetamide, m. p.  $123$ – $124^\circ$ , which is also obtained in small yield by the bromination of malononitrile in aqueous solution. Previously (*loc. cit.*) the compound has been considered erroneously to be dibromosuccinonitrile. Dichlorocyanoacetamide, m. p.  $91^\circ$ , is obtained similarly as a by-product of the chlorination of malononitrile. Dibromocyanoacetamide is converted by hydrobromic acid at  $100^\circ$  into dibromoacetanitrile. H. W.

**Action of Hydrazine on Halogen Derivatives of Malonamides and Acetoacetic Esters.** E. L. HIRST, A. K. MACBETH, and D. TRAILL (*Proc. Roy. Irish Acad.*, 1925, **37 B**, 47–52; cf. Ratz, A., 1904, i, 298, 857; Wolff, A., 1904, i, 722; 1905, i, 839; Thorpe, T., 1911, **99**, 2183; Whiteley, T., 1921, **119**, 359; Burton and Kenner, T., 1922, **121**, 489, 892, 903).—The following compounds react with hydrazine hydrate liberating nitrogen, the proportion of the theoretical amount set free being shown: chloromalonamide (99.3%), dichloromalonamide (99.2%), dibromomalonamide (90.5%; cf. Ruhemann and Orton, T., 1895, **67**, 1002), ethyl  $\alpha$ -chlorobenzoylacetate (66%), bromomalondimethylamide (no reaction in cold, vigorous on warming), dibromomalondimethylamide (slight liberation of nitrogen in cold, brisk on warming); the following compounds are not reduced by hydrazine hydrate at the laboratory temperature: bromo-, dichloro-, and dibromo-malondiethylamide, chloro- and dichloro-malondimethylamide. The low yields of nitrogen obtained on treating certain acetoacetic esters with hydrazine hydrate (T., 1923, **123**, 1122) are due to formation of cyclic compounds. By the action of hydrazine hydrate on the  $\alpha$ -chloro and  $\alpha$ -bromo derivatives of ethyl ethyl-, *n*-propyl-, and benzyl-acetoacetates, 3-methyl-4-ethyl-5-pyrazolone, m. p.  $220^\circ$  (cf. Locquin, A., 1904, i, 694, who gives m. p.  $195$ – $196^\circ$ ), 3-methyl-4-*n*-propyl-5-pyrazolone, m. p.  $206^\circ$ , and 4-benzyl-3-methyl-5-pyrazolone, m. p.  $213^\circ$  (decomp.), respectively, are obtained. Ethyl  $\alpha$ -chlorobenzoylacetate condenses with thiocarbamide giving ethyl 2-amino-4-phenyl-1-thiazole-5-carboxylate, m. p.  $173^\circ$ . Malonhydrazide, m. p.  $154^\circ$ , is readily prepared by treatment of ethyl malonate with excess of hydrazine.

L. F. H.



**Derivatives of Formaldehyde and Succinimide.** E. CHERBULIEZ and G. SULZER (*Helv. Chim. Acta*, 1925, **8**, 567—571).—*N-Hydroxymethylsuccinimide*, m. p. 66°, obtained by the action of aqueous formaldehyde on succinimide in presence of potassium carbonate, is readily condensed with piperidine to give *N-piperidino-methylsuccinimide*, m. p. 106—107°, and converted by phosphorus pentachloride into *N-chloromethylsuccinimide*, b. p. 158—160°/12 mm., m. p. 58° [*pyridinium chloride*, m. p. 65—105° (decomp.)]. The chloromethyl derivative reacts with benzene in carbon disulphide in presence of aluminium chloride to yield *N-benzylsuccinimide*, m. p. 101—103°, from which benzylamine is obtainable by alkaline hydrolysis—a method being thus available for the introduction of the aminomethyl group into the aromatic nucleus. Sodium ethoxide converts the chloromethyl derivative into *N-ethoxymethylsuccinimide*, b. p. 151—152°/14 mm., 262°/760 mm., m. p. 31—32°. *N-Acetoxyethylsuccinimide*, b. p. 170—175°/10 mm., 290°/760 mm., m. p. 51°, distilled with zinc dust gave small quantities of pyrrole derivatives not isolated in a state of purity, together with methylsuccinimide of m. p. 71°. G. M. B.

**Preparation of Thiocyanogen from Thiocyanic Acid.** H. P. KAUFMANN and F. KÖGLER (*Ber.*, 1925, **58**, [B], 1553—1556).—Solutions of thiocyanogen are obtained by shaking thiocyanic acid dissolved in anhydrous media, particularly carbon tetrachloride, with dry manganese dioxide or lead dioxide, but the yields are far below the theoretical even after allowance has been made for the part of the thiocyanogen hydrolysed by the water formed during the change. If, however, a solution of lead tetra-acetate in chloroform or glacial acetic acid is treated with a solution of thiocyanic acid in quantity rather greater than is required by the equation,  $\text{Pb}(\text{OAc})_4 + 4\text{HCNS} = \text{Pb}(\text{CNS})_2 + (\text{SCN})_2 + 4\text{CH}_3\cdot\text{CO}_2\text{H}$ , lead thiocyanate is precipitated and the filtered, lead-free solution contains thiocyanogen in almost theoretical amount. H. W.

**Etherates of the Magnesium Halides.** J. MEISENHEIMER, E. PIPER, and H. LANGE (*Z. anorg. Chem.*, 1925, **147**, 331—344; cf. A., 1921, i, 654).—The etherates of the magnesium halides may be formulated as  $[(\text{Et}_2\text{O})_2, \text{MgX}_2]$  or  $[(\text{Et}_2\text{O})_2, \text{Mg}]X_2$ . If the second formula is correct the halogen atoms should be loosely bound to the molecule, and it would be expected that attempts to prepare dietherates of mixed halides by the interaction of the etherate of a magnesium ethyl halide with an allyl halide,  $(\text{Et}_2\text{O})_2, \text{MgEtX}^1 + \text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{X}^2 = (\text{Et}_2\text{O})_2, \text{MgX}^1\text{X}^2 + \text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Et}$ , would lead only to a mixture of the etherates  $(\text{Et}_2\text{O})_2, \text{MgX}^1_2$  and  $(\text{Et}_2\text{O})_2, \text{MgX}^2_2$ . In order to distinguish mixed halides from mixtures of simple halides, the rate of loss of ether in a vacuum desiccator was measured. The results were not conclusive, but it is believed that mixed halides were obtained and that the first of the above formulæ is correct. A. G.

**Alkyl Compounds of Thallium.** E. KRAUSE and A. VON GROSSE (*Ber.*, 1925, **58**, [B], 1933—1939; cf. Meyer and Berthelm, A., 1904, i, 656; Goddard, T., 1921, **119**, 676; 1922, **121**, 36).—The

more highly alkylated derivatives of thallium can be obtained by addition of only a slight excess of the organo magnesium compound to the thallic salt so that the reducing action of the Grignard compound is avoided and if the Grignard reagent is prepared from the alkyl bromide or, preferably, chloride in place of the iodide. Crude thallic di-*n*-butyl bromide,  $\text{Tl}(\text{C}_4\text{H}_9)_2\text{Br}$ , is prepared from thallic chloride and magnesium *n*-butyl bromide in ethereal solution, treatment of the product with hydrobromic acid, and separation of thallic di-*n*-butyl bromide from thallium bromide (formed to the extent of 15% by reduction) by hot pyridine. The crude bromide is transformed by silver fluoride into *thallic di-n-butyl fluoride*, decomp.  $220\text{--}240^\circ$ , according to the rate of heating, from which the corresponding *chloride*, decomp.  $240\text{--}250^\circ$ ; *bromide*, decomp.  $240\text{--}250^\circ$ ; *iodide*, decomp.  $220\text{--}225^\circ$ ; *carbonate*, and *nitrate*, decomp.  $280\text{--}290^\circ$ , are prepared; *thallic di-n-butyl sulphate*, m. p.  $156\text{--}158^\circ$  when placed in a bath pre-heated at  $150^\circ$ , is obtained from the carbonate. *Thallic diisobutyl chloride* and the corresponding *nitrate* are described. *Thallic diisoamyl chloride*, decomp.  $253\text{--}257^\circ$  when rapidly heated, and the corresponding *fluoride*, m. p.  $216\text{--}218^\circ$  (decomp.), have been prepared. *Thallic diisopropyl chloride*, decomp.  $150^\circ$ , is much less stable than the higher alkyl derivatives; *thallic diisopropyl nitrate* is described. *Thallic disec.-butyl chloride*, decomp.  $150^\circ$ , and the corresponding *nitrate*, *thallic dicyclohexyl chloride*, decomp.  $210\text{--}230^\circ$ , and the *nitrate* have been prepared.

H. W.

**Chemistry of the Tin Trimethyl Group.** C. A. KRAUS and W. V. SESSIONS (*J. Amer. Chem. Soc.*, 1925, **47**, 2361—2368).—Tin tetramethyl on treatment with bromine yields tin trimethyl bromide, m. p.  $27^\circ$ , b. p.  $165^\circ$ , which gives a stable compound with ammonia,  $\text{SnMe}_3\text{Br}\cdot\text{NH}_3$  (cf. Kraus and Greer, A., 1924, i, 155). On treatment with sodium in liquid ammonia *tin trimethyl* is precipitated. Tin trimethyl, m. p.  $23^\circ$ , has b. p.  $85\text{--}88^\circ/45\text{ mm.}$ ,  $182^\circ/756\text{ mm.}$ ,  $d^{25}_{20} 1.570$ , but cannot be distilled in air as the vapours flash in the condenser. In boiling benzene, the molecular weight increases with the concentration, being 171.1 at low concentrations and 352 at high concentrations (cf. Rügheimer, A., 1909, ii, 134). With sodium in liquid ammonia, it yields sodium trimethylstannide. In the absence of oxidising agents, tin trimethyl is stable, but atmospheric oxygen converts it into an insoluble oxidation *product*, which yields tin trimethyl bromide with hydrobromic acid and the sulphate with sulphuric acid. Sulphur in benzene solution yields the analogous *tin trimethyl sulphide*, m. p.  $6^\circ$ , b. p.  $233.5\text{--}235.5^\circ/759\text{ mm.}$ ,  $d^{25}_{20} 1.649$ . Tin trimethyl combines with halogens at the ordinary temperature, in the proportion of one atom per atom of tin, yielding the tin trimethyl halide. Tin trimethyl chloride is also formed by reaction between tin trimethyl solutions and calcium chloride in dry air. Mercuric chloride in ether similarly yields tin trimethyl chloride and mercury is precipitated. Sodium trimethylstannide is also obtained by the reduction of tin trimethyl halides in liquid ammonia with sodium (cf. Kraus and Greer, A., 1923, i, 26). On evaporation of

its solution in liquid ammonia, a light yellow solid crystallises which readily decomposes at higher temperatures. With tin trimethyl halides, sodium trimethyl stannide reacts immediately, yielding tin trimethyl. With alkyl halides, union with the organic radical may take place. With *p*-dichlorobenzene in liquid ammonia containing a little ether a colourless substance,  $C_6H_4(SnMe_3)_2$ , m. p. 123—124°, is formed, which with iodine in benzene yields tin trimethyl iodide and *p*-di-iodobenzene. With *s*-dichloroethane, tin trimethyl and sodium chloride are formed, with evolution of a gaseous hydrocarbon. Tin triethyl iodide yields a compound,  $SnMe_3, SnEt_3$ ,  $d^{20}_{40}$  1.431, b. p. 235°/748 mm. Triphenylmethyl chloride yields a mixture of compounds, whilst attempts to condense sodium trimethyl stannide with lead triethyl chloride gave indefinite results. Sodium trimethyl stannide is also formed by the action of sodium on tin tetramethyl in liquid ammonia. The reaction supports Kraus and White's interpretation of the reduction of organic halides by alkali metals (A., 1923, i, 456). R. B.

**Compounds formed between Tin Trimethyl Hydroxide and Tin Trimethyl Halides.** C. A. KRAUS and T. HARADA (*J. Amer. Chem. Soc.*, 1925, 47, 2416—2419).—The crystalline substance, m. p. 143—153° (decomp.), produced by the action of sunlight on tin trimethyl iodide has the composition,  $(Me_3Sn \cdot OH)_2 Me_3SnI$ , and is identical with products obtained by oxidising tin trimethyl in moist benzene in the presence of tin trimethyl iodide, and by treating tin trimethyl iodide with 2 mols. of tin trimethyl hydroxide in benzene solution. Analogous compounds are obtained by similar methods from tin trimethyl bromide and tin trimethyl chloride. The bromine derivative has m. p. 113—115° (decomp.). Compounds of the type  $Me_3Sn \cdot OH, Me_3SnX, H_2O$  have been obtained by reaction of equimolecular proportions of tin trimethyl hydroxide and the corresponding halide in hot alcohol. The iodide has m. p. 221° (decomp.), the bromide, m. p. 210—211° (decomp.), the chloride, m. p. 90° (slow decomp.). R. B.

**Stereoisomeric Forms of Decahydronaphthalene.** W. HÜCKEL (*Ber.*, 1925, 58, [B], 1449—1452).—*trans*-Decahydronaphthalene, prepared by the action of sodium ethoxide on *trans*- $\beta$ -decahydronaphthalonesemicarbazone, and purified by successive distillation over sodium and treatment with concentrated sulphuric acid, has b. p. 185°,  $d^{20}_{40}$  0.8703,  $n^{20}_D$  1.46994. The constants of the hydrocarbon obtained from technical decahydronaphthalene from octahydronaphthalene, by Wolff's method and by Zelinski (this vol., i, 123), are in harmony and there appears to be no ground for the hypothesis of Eisenlohr and Polenske (A., 1924, i, 1292) that the product of the hydrogenation of naphthalene in the presence of nickel contains some component other than *trans*-decahydronaphthalene which tends to accumulate in the fractions of lowest b. p. The discrepancies between the results of Hückel (A., 1924, i, 32) and Eisenlohr and Polenske (*loc. cit.*) appear to be due to the reliance placed by the latter authors on Wolff's method, which,

however, does not invariably yield products which can be freed from oxygenated compounds by distillation over sodium. H. W.

**Structure of Benzene and *cyclo*Hexane and their Optical Anisotropy.** K. R. RAMANATHAN (*Nature*, 1925, **116**, 279—280).—Previous investigations on the anisotropy of gaseous molecules (this vol., ii, 478) have been extended to benzene and *cyclo*hexane. The depolarisation (*i.e.*, the ratio of the weak component to the strong) of the light scattered perpendicularly to the incident beam in benzene vapour is 0.067, and in *cyclo*hexane, 0.011. The results are in better agreement with the assumption for the benzene molecule of a puckered ring, as in diamond, than a plane ring, as in graphite, unless the polarisation of the carbon atoms is greater when the field is perpendicular than when parallel to the plane of the ring. In the case of *cyclo*hexane, the six extra hydrogen atoms are placed on opposite sides of the mean plane of the carbon atoms on either side alternately. A. A. E.

**Conception of Internal Molecular Strain and the Directing of Substituents in Benzene. II.** D. VORLÄNDER [with K. BÜCHNER, E. SPRECKELS, E. SCHROEDTER, O. MEISSNER, F. CAESAR, E. FISCHER, W. KÖNIG, and H. HOFFMANN] (*Ber.*, 1925, **58**, [B], 1893—1914; cf. Vorländer, A., 1919, i, 319).—The behaviour of positively and negatively substituted derivatives (*cf. loc. cit.*) of benzene has been examined further.

The iodinium salts are analogous to the ammonium compounds and hence in them the positive iodine influences two benzene nuclei; the iodo derivatives correspond with the nitro compounds. Iodoso- and iodoxy-benzene are reduced by concentrated nitric acid to iodobenzene, which is converted into *o*- and *p*-iodonitrobenzene. If the reducing action is avoided by addition of carbamide nitrate, iodoxybenzene is attacked with great difficulty by nitric acid; the iodine atom of the IO<sub>2</sub> group is therefore positive to the benzene nucleus. Diphenyliodinium nitrate is converted by nitric acid (*d* 1.52) and concentrated sulphuric acid into *di-m-nitrophenyliodinium nitrate*, m. p. 192—194° [corresponding *iodide*, m. p. 142—144° (decomp.); *perchlorate*, m. p. about 188°; *picrate*, m. p. about 194°]; the structure of the compound is established by comparison with a specimen of the nitrate obtained from *m*-iodosonitro- and *m*-iodoxynitrobenzene (*cf.* Willgerodt and Wikander, A., 1907, i, 1024) and by its fission by alkali hydroxide into *m*-iodonitrobenzene and *m*-nitrophenol (*p*-nitrophenol may be present in very small amount, but *o* nitrophenol is absent).

Lead tetraphenyl is not smoothly nitrated, the product giving much nitro- and some *m*-dinitrobenzene when poured into water. Lead diphenyl dinitrate is converted into *lead di-m-nitrophenyl dinitrate*, decomp. 210°, which is transformed almost quantitatively by bromine at 100° into lead bromide and *m*-bromonitrobenzene. Lead, like iodine, behaves positively towards both phenyl groups. The action of bismuth is shown to be similar, since *bismuth triphenyl dinitrate*, decomp. 130°, is transformed into *bismuth tri-m-nitrophenyl dinitrate*, decomp. about 145°, which is converted by bromine

into *m*-bromonitrobenzene. The similar behaviour of antimony and phosphorus has been observed by Morgan and Micklethwait (T., 1911, 99, 2286) and by Challenger and Wilkinson (this vol., i, 172). On the other hand, positive properties are not observed in tin and silicon, since their tetraphenyl derivatives yield mainly *tin tetra-p-nitrophenyl*, decomp. above 350°, and silicon *tetra-p-nitrophenyl*, from which *p*-bromonitrobenzene is obtained by the action of bromine.

The products of the nitration of triphenylcarbinol are amorphous and after drastic treatment have approximately the composition of a trinitrotriphenylcarbinol; it appears very doubtful, however, whether nitration follows a normal course. Triphenylacetoneitrile is converted by fuming nitric acid into *tri-p-nitrophenylacetoneitrile*, m. p. 210—220°, which is reduced by stannous chloride and concentrated hydrochloric acid to *tri-p-aminophenylacetoneitrile*, m. p. 280—290° after darkening at about 250°; the corresponding *acetyl* derivative and the condensation *product* with anisaldehyde are non-crystalline. The diazotised amine couples with phenol, giving the non-crystalline *derivative*, (?)  $(\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4)_3\text{CN}$ . The identity of *tri-p-aminophenylacetoneitrile* with the compound obtained from parafuchsin and potassium cyanide and its convertibility by concentrated hydrochloric acid into parafuchsin proves the original nitration to have occurred in the para position to the carbinol carbon atom, to which the cyanogen group therefore does not impart positive properties.

The experiments just described considered in conjunction with the literature show that an element which is united to two, three, or four benzene nuclei directs the entering substituent into these benzene nuclei either uniformly positively or uniformly negatively.

The pyridinium nitrogen atom of 1-phenylpyridinium directs the nitro group to the meta position in the benzene nucleus, the pyridine nucleus remaining unaffected. 1-Phenylpyridinium chloride (corresponding *picrate*, m. p. 121°; *perchlorate*, m. p. 221°) is converted by repeated evaporation with nitric acid (*d* 1.3) into 1-*phenylpyridinium nitrate*, m. p. 126°, which is transformed by fuming nitric acid (*d* 1.51) at 100° into 1-*m-nitrophenylpyridinium nitrate*, m. p. 204—208° after softening at 195° (corresponding *perbromide*, m. p. 117° after softening at 113°; additive *compound* of mercuric chloride with the chloride, m. p. 165—168° after softening at 163°; 1-*m-aminophenylpyridinium chlorostannate*; 1-*m-aminophenylpyridinium bromide perbromide*, m. p. 172—175°). The constitution of the nitrophenylpyridinium compound is established by comparison of its salts with those of the three synthetic nitrophenylpyridinium compounds. 1-*p-Nitrophenylpyridinium nitrate*, m. p. 174—177°, is prepared from pyridine, *p*-nitroaniline, and cyanogen bromide. The *chloride* and its additive *compound* with mercuric chloride, *perbromide*, m. p. about 165°, *picrate*, m. p. 147°, and *perchlorate*, m. p. about 176°, are described. 1-*p-Aminophenylpyridinium dinitrate*, decomp. above 210° after softening at 200°, the *dipicrate*, m. p. 158—161°, and the *dihydrochloride*, decomp. above 190°, have been prepared. 1-*p-Ethoxyphenylpyridinium*

*chloride*, m. p. 118° (and its additive compound with mercuric chloride), *perchlorate*, m. p. 134°, *picrate*, m. p. 139°, and *bromide* (+H<sub>2</sub>O) are described. 1-*m*-Nitrophenylpyridinium nitrate, m. p. 206—208° (decomp.) after softening at 196°, is prepared from pyridine, *m*-nitroaniline, and cyanogen bromide and is identical with the nitration product described above. 1-*o*-Nitrophenylpyridinium nitrate, m. p. 182—186° (decomp.), the corresponding *perbromide*, m. p. 90—93°, and the additive compound of the chloride with mercuric chloride, m. p. about 190°, have been prepared.

1-Phenyl-4-pyridone, in spite of the presence of an excess of concentrated nitric acid, does not appear to behave during nitration as an ammonium salt, but as a free pyridone, in which the nitrogen is negative towards phenyl. The salts of 1-phenyl-4-pyridone, m. p. 127°, are comparatively very stable; the *hydrochloride* (+H<sub>2</sub>O), m. p. about 192°, *nitrate* (+H<sub>2</sub>O), *perchlorate* (+H<sub>2</sub>O), m. p. (anhydrous) 164°, *picrate*, m. p. 193°, and additive compound of the hydrochloride with mercuric chloride, m. p. about 118°, are described. 1-Phenyl-4-pyridone is transformed by a large excess of hot, fuming nitric acid into 1-*p*-nitrophenyl-4-pyridone (+H<sub>2</sub>O), m. p. 202° [*nitrate* (+H<sub>2</sub>O), m. p. 146°; *perchlorate*, m. p. about 245°; *picrate*, m. p. about 190—192°]. It is reduced by stannous chloride in the presence of hydrochloric and glacial acetic acids to 1-*p*-aminophenyl-4-pyridone, m. p. 260—270° (decomp.), which after diazotisation and coupling with phenol yields a monotropic liquid-crystalline *acetate*, m. p. about 250° (decomp.), and an enantiotropic, liquid-crystalline *benzoate*, m. p. I about 263°, II about 250°, thus establishing the para position of the nitro group. This conception is confirmed by conversion of the aminophenylpyridone described above into 1-*p*-chlorophenyl-4-pyridone, m. p. 105°, which is identical with the synthetic product from *p*-chloroaniline and chelidonic acid. 1-*p*-Hydroxyphenyl-4-pyridone, decomp. above 200°, cannot readily be etherified, owing to the formation of resin. 1-*p*-Ethoxyphenyl-4-pyridone, m. p. 154—156°, obtained in very moderate yield from *p*-phenetidine and chelidonic acid at 130—170°, yields a *perchlorate*, m. p. 195°. *m*-Nitroaniline and chelidonic acid yield successively *chelidonic acid m*-nitrophenylamide, C<sub>13</sub>H<sub>8</sub>O<sub>7</sub>N<sub>2</sub>, and 1-*m*-nitrophenyl-4-pyridone, m. p. about 210° (*perchlorate*, m. p. about 176°; *picrate*, m. p. 175°). The synthesis of *o*- and *p*-nitrophenyl-4-pyridones along these lines is not easily effected. 1-Phenyl-4-pyridone is converted by thionyl chloride into 4-chloro-1-phenylpyridinium chloride (? +2H<sub>2</sub>O), m. p. 116° after softening at 83°; the additive compound with mercuric chloride, m. p. 180°; *perchlorate*, m. p. 210°; *picrate*, m. p. 155—158°, and *tribromide*, m. p. 137°, are described.

In diphenyl, each of the phenyl groups behaves towards the other as a negative substituent in the same manner as any other hydrocarbon residue. The action of a large excess of methyl sulphate and potassium carbonate on a hot, aqueous suspension of *p*-aminodiphenyl gives the corresponding trimethylammonium salts of which the *chloride*, *bromide*, m. p. 222° after softening at 210°, *tribromide*, m. p. about 188° (decomp.), *iodide*, m. p. 220° (decomp.)

after softening at 208°, *perchlorate*, decomp. above 300°, and *nitrate*, m. p. 255° (decomp.) after softening at 230°, are described. Nitration of the nitrate gives *p'*-nitrodiphenyl-*p*-trimethylammonium nitrate, m. p. 235° (decomp.) after darkening and softening at 212° [corresponding *bromide*, m. p. 243° (decomp.) after darkening and softening at 165°; *tribromide*, m. p. 198° (decomp.); *iodide*, m. p. 246° (decomp.); *picrate*, decomp. 200°]. The position of the nitro group is established by the conversion of the bromide at 240—260° into *p'*-nitro-*p*-dimethylaminodiphenyl, m. p. about 244°, and the identity of the latter with the product of the partial reduction and subsequent methylation of *p*:*p'*-dinitrodiphenyl. *p'*-Nitro-*p*-dimethylaminodiphenyl is slowly converted by nitrous acid into a dinitro derivative, m. p. 134°. *p'*-Amino-*p*-dimethylaminodiphenyl, m. p. about 146° (*hydrochloride*), is prepared in poor yield by reduction of the mononitro compound with stannous chloride; the *benzylidene* derivative, m. p. I 192°, II 183°, *p*-methylbenzylidene compound, m. p. I 248°, II 218°, and *anisylidene* derivative, m. p. I >270°, II 208°, are described. *pp'*-Tetramethyldiaminodiphenyl has m. p. about 315°. *p*-Nitrodiphenyl-*p'*-azobenzene, m. p. 180°, from nitrosobenzene and *p*-nitro-*p'*-aminodiphenyl in glacial acetic acid, is reduced by ammonium sulphide to *p*-aminodiphenyl-*p'*-azobenzene, m. p. about 178° (decomp.); the *hydrochloride*, *benzylidene* derivative, m. p. I 188°, II 171° (decomp.), and *anisylidene* compound, m. p. I >192°, II 173° (decomp.), are described. *p*-Dimethylaminobenzene-*p'*-azodiphenyl, prepared by coupling diazotised *p*-aminodiphenyl with dimethylaniline, has m. p. 208° after softening at 195°; the *hydrochloride* is described. *p*-Hydroxylaminodiphenyl, m. p. 132—134°, *p*-nitrosodiphenyl, m. p. 84°, and *p*-diazoaminodiphenyl, (C<sub>12</sub>H<sub>9</sub>)<sub>2</sub>N<sub>3</sub>H, m. p. 147°, are prepared by established methods.

H. W.

**Chemical Action of Light.** H. JOHN (*Ber.*, 1925, 58, [B], 1563—1565).—The photochemical oxidation of the side chains of aromatic hydrocarbons to the carboxyl group in the presence of anthraquinone by air or oxygen (cf. Eckert, this vol., i, 413) does not depend greatly on ultra-violet rays. Comparative experiments in Prague and Davos indicate that increasing altitude has an accelerating action on the change.

H. W.

**Polymerisation and Oxidation of Indene in the Vapour Phase.** R. L. BROWN (*Ind. Eng. Chem.*, 1925, 17, 920—924).—Indene, vaporised in nitrogen, is polymerised rapidly at 300—500°. If oxygen is present, oxidation occurs also, the proportion of indene removed from the gas by both processes increasing with the percentage of oxygen present, with the temperature, and with the reaction period. The chief products are resin, carbon dioxide, water, and a little carbon monoxide. [Cf. *B.*, 1925, 835.]

A. D.

**Action of Nitrogen Dioxide on Anthracene Derivatives.** E. DE B. BARNETT (*J. Chem. Soc.*, 1925, 127, 2040—2044).—9:10-Dinitro-9:10-dihydroanthracenes are prepared by passing

nitrogen dioxide into a cooled chloroform solution or suspension of the anthracene derivative. Substituents have no appreciable influence on the ease of addition to the "bridge"; *Bz*-substituents do not increase the stability of these additive compounds, whilst *ms*-substituents decrease it. In any compound



the bridge is re-established on treatment with pyridine and alcohol; thus 9 : 10-dinitro-9 : 10-dihydroanthracene gives 9-nitroanthracene. The additive compound from 9-nitroanthracene loses nitrous acid giving 9 : 10-dinitroanthracene, m. p. 310°, and that from 1-chloroanthracene loses hydrogen chloride giving 1-chloro-9(or 10)-nitroanthracene, m. p. 155°, which differs from the chloronitro compound prepared from 1-chloroanthracene and nitric acid (this vol., i, 18); the additive compound (an oil) from 2-chloroanthracene yields a mixture of isomeric chloronitro compounds; 1 : 5-dichloroanthracene yields 1 : 5-dichloro-9 : 10-dinitro-9 : 10-dihydroanthracene, m. p. 156° (decomp., with previous discoloration), which is converted into 1 : 5-dichloro-9-nitroanthracene; the 1 : 8-dichloroanthracene additive compound, m. p. 215° (decomp., with previous discoloration), which is not obtained free from solvent, is converted into the same 1 : 8-dichloro-9(or 10)-nitroanthracene as is obtained by the action of pyridine on the additive compound from 1 : 8-dichloroanthracene and nitric acid (*loc. cit.*); 9-bromoanthracene gives 9-bromo-9 : 10-dinitro-9 : 10-dihydroanthracene (sinters about 115°), converted into 9 : 10-dinitroanthracene, together with 9 : 10-dibromoanthracene.

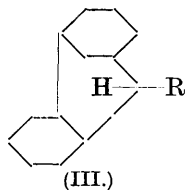
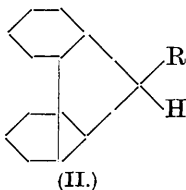
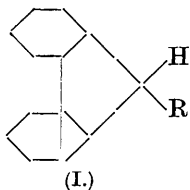
Compounds of the general formula  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CXNO}_2 \\ \text{CXNO}_2 \end{array} \text{C}_6\text{H}_4$ , where X is halogen, are very unstable, so that from 9 : 10-dibromoanthracene is obtained 9-bromo-9-nitroanthrone, m. p. 116° (which readily decomposes into anthraquinone), whilst 9 : 10-dichloroanthracene yields the very unstable 9 : 10-dichloro-9 : 10-dinitro-9 : 10-dihydroanthracene. Of the unsymmetrical halogen-nitro compounds, 1 : 5 : 9-trichloro-9 : 10-dinitro-9 : 10-dihydroanthracene, decomp. 156° (from 1 : 5 : 9-trichloroanthracene), yields 1 : 5-dichloro-9 : 10-dinitroanthracene, m. p. 277°. 2 : 3 : 9 : 10-Tetrabromoanthracene is converted by nitrogen dioxide into 2 : 3 : 9-tribromo-9-nitroanthrone, which on heating with toluene yields 2 : 3-dibromoanthraquinone. Nitrogen dioxide with anthranlyl methyl ether, 9-phenylanthracene, and 9-phenylanthranlyl methyl ether, respectively, gives 9-nitroanthrone, 9-nitro-10-phenylanthracene, and 9-phenyl-9-hydroxyanthrone, respectively. F. M. H.

**Composition of Rubicene,  $\text{C}_{26}\text{H}_{14}$ .** R. PUMMERER and H. M. ULRICH (*Ber.*, 1925, 58, [B], 1806—1808).—Analyses of rubicene obtained from fluorene (cf. Dziewoński and Suszko, A., 1922, i, 730) confirm the composition,  $\text{C}_{26}\text{H}_{14}$ , assigned to it by Pummerer (A., 1912, i, 182) in place of  $\text{C}_{26}\text{H}_{12}$  suggested by Dziewoński and Suszko (*loc. cit.*). H. W.



**Benzoyl Peroxide and Secondary Amines.** S. GAMBARJAN (*Ber.*, 1925, 58, [B], 1775—1778).—The conversion of diphenylamine by benzoyl peroxide into *N*-benzoyl-*o*-hydroxydiphenylamine has been presumed to involve the intermediate formation of *O*-benzoyldiphenylhydroxylamine (cf. Gambarjan, A., 1909, i, 910), and the reaction is closely analogous to that of benzoyl peroxide on isobutyl alcohol (Gelissen and Hermans, this vol., i, 813). The assumption is justified by the observation of the course of the reaction between benzoyl peroxides and secondary amines which are so chosen that isomerisation is excluded. Thus piperidine gives *N*-benzoyloxypiperidine, m. p. 62°, which is quantitatively reduced by zinc and acetic acid to benzoic acid and piperidine. Diethylamine affords *O*-benzoyldiethylhydroxylamine (*hydrogen sulphate*, m. p. 134°), which is reduced to benzoic acid and diethylamine, whereas diisobutylamine gives *O*-benzoyldiisobutylhydroxylamine (*hydrogen sulphate*, m. p. 123°). H. W.

**Stereochemistry of Aromatic Compounds. Isomerism of the 9-Aminofluorenes.** R. KUHN and P. JACOB (*Ber.*, 1925, 58, [B], 1432—1440).—Theoretical considerations lead to the prediction of the possible existence of five stereoisomeric forms of fluorenes substituted in position 9, two of which represent non-resolvable *cis* derivatives (I) and (II), whilst the remaining three comprise the *trans* compound (III) and its optical antipodes.



Reduction of fluorenoneoxime with zinc dust and glacial acetic acid gives 9-aminofluorene, m. p. 64°, which on account of its mode of preparation and m. p. of its acetyl derivative is considered to be identical with  $\alpha$ -9-aminofluorene, m. p. 53—55°, described by Schmidt and Stützel (A., 1908, i, 415). Schmidt's  $\beta$ -9-aminofluorene, m. p. 123° (*loc. cit.*), could not be obtained; the fraction of the crude basic mixture of m. p. 120—126° is found to contain the carbamate. Kerp's 9-aminofluorene, m. p. 161° (A., 1896, i, 239), is identified as  $\gamma$ -9-fluorylcarbamic acid. When treated with hydrochloric acid, it loses carbon dioxide and yields  $\gamma$ -9-aminofluorene hydrochloride, m. p. 216°, probably identical with the compound described by Wieland (A., 1911, i, 571). With pyridine and acetic anhydride, the carbamic acid yields  $\gamma$ -9-acetamidofluorene, m. p. 245.5—246°, whereas with concentrated ammonia it affords  $\gamma$ -9-aminofluorene, m. p. 60°, which absorbs carbon dioxide too readily to permit analysis. The active  $\gamma$ -base is much more readily acetylated than the corresponding  $\alpha$ -compound; hence, during the reduction of fluorenoneoxime as described above it is obtained in considerable amount as the acetyl derivative, whereas

the  $\alpha$ -amine remains as the acetate. Reduction of fluorenoneoxime by sodium amalgam does not lead to the production of the  $\gamma$ -base. It is, however, obtained by treatment of fluorenoneketazine with zinc and acetic acid, but could be isolated only as the acetyl derivative, which, like the acetylated  $\alpha$ -amine (Schmidt and Stützel, *loc. cit.*), is transformed by nitric acid (*d* 1.35) into 1 : 8-dinitrofluorenone, m. p. 196—197°.

$\alpha$ -9-Aminofluorene hydrochloride, m. p. 255°,  $\alpha$ -9-acetamidofluorene, m. p. 262° (corr.), and  $\alpha$ -9-fluoryldimethylcarbamide, m. p. 158—159°, are incidentally described. H. W.

**Phenylcarbamyl Derivatives of Nitrophenols.** O. L. BRADY and J. HARRIS (*J. Chem. Soc.*, 1925, 127, 2175—2176).—By boiling a toluene solution of a nitrophenol and phenylcarbimide, washing the crystalline product with sodium hydroxide, and recrystallising from chloroform, the pure nitrophenyl phenylcarbamate is obtained. *m*-Nitrophenyl phenylcarbamate has m. p. 129°. F. M. H.

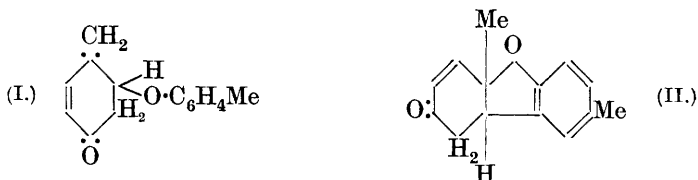
**Directive Influence of Substituents in the Benzene Ring.**  
**III. Active Agent in Aqueous Bromination.** A. W. FRANCIS (*J. Amer. Chem. Soc.*, 1925, 47, 2340—2348; cf. this vol., i, 1141).—A solution of hypobromous acid free from bromine is best obtained by saturating bromine water with solid silver sulphate and separating the silver bromide and excess of silver sulphate. The velocity of bromination of *m*-nitrophenol with free bromine is nearly a thousand times greater than that under similar conditions with the hypobromous acid solution. Since other sulphates have no negative catalytic effect on the bromination with bromine water, it is improbable that such effect is exercised by the silver or sulphate ions in the hypobromous acid, and accordingly it is improbable that hypobromous acid is the principal active brominating agent. Competition experiments between potassium iodide and organic compounds, such as dibromoresorcinol, *m*-aminophenol, and dibromophenol, for hypobromous acid and for free bromine in water gave ratios of rates which agreed closely and suggested that the same agent is effective in every case and that the observed ratios represent the actual relative reactivities of the competitors. Saturation of double bonds with bromine water gives chiefly bromohydrin derivatives, only 10—15% of dibromo derivative being formed with cinnamyl alcohol and cinnamic, maleic, or fumaric acid. Since, however, these compounds appear to be saturated more rapidly by bromine water than by hypobromous acid, and the relative amount of dibromide formed is as small with bromine water in 4*N*-sulphuric acid, it is improbable that bromohydrin formation involves the addition of hypobromous acid as a whole. It is suggested that the active agent consists of positively charged bromine atoms which add to one side of the double bond. The free positive radicals thus produced unite with negative bromine or hydroxyl ions according to their own characteristic properties. Support for this view is afforded by the formation of  $\alpha$ -chloro- $\beta$ -bromoethane from ethylene and bromine in neutral sodium chloride solution, of  $\alpha$ -chloro- $\beta$ -iodoethane similarly from ethylene, iodine, and sodium chloride.

and of  $\beta$ -bromoethyl nitrate from ethylene, bromine, and sodium nitrate. Further support for this view is afforded by the inactivity of hypobromous acid towards gold and by the greater tendency of this reagent, as compared with bromine water, to oxidise aniline and other amines.

R. B.

### Oxidation of Phenols. VIII. Dehydrogenation of *p*-Cresol.

R. PUMMERER, H. PUTTFARCKEN, and P. SCHOPFLOCHER (*Ber.*, 1925, **58**, [B], 1808—1820).—Re-examination of the ketone,  $C_{14}H_{14}O_2$ , obtained by the oxidation of *p*-cresol with potassium ferricyanide and considered to be 2-*p*-tolylloxy-2 : 3-dihydro-*p*-benzoquinonemethane (I) (cf. Pummerer, Melamed, and Puttfarcken, *A.*, 1922, i, 1161), has led the authors to assign to it the constitution (II). When hydrogenated in the presence of spongy



platinum, it absorbs 2 mols. of hydrogen (instead of 3 mols. as required by the previous formula), giving the *alcohol*,  $C_{14}H_{18}O_2$  m. p.  $74^\circ$ , which shows very characteristic colour changes with acids; the corresponding *phenylurethane*, m. p.  $131^\circ$ , is described. The ketone is converted by concentrated hydrochloric acid into a dihydric phenol,  $C_{14}H_{14}O_2$ , m. p.  $158^\circ$ , which is not identical with any of the three known dihydric phenols derivable from *p*-cresol (5 : 5'-dihydroxy-2 : 2'-dimethyldiphenyl, 2 : 5'-dihydroxy-2' : 5-dimethyldiphenyl, 2 : 4'-dihydroxy-5-methyldiphenylmethane). The remaining three possible dihydric phenols have now been synthesised and the product of the isomerisation has been found to be identical with 5 : 6'-dihydroxy-2' : 3-dimethyldiphenyl. Distillation of its dimethyl ether gives a substance, m. p.  $79-81^\circ$ , which has not been fully investigated. Oxidation of the ether with potassium permanganate yields 2 : 3'-dimethoxydiphenyl-5 : 6'-dicarboxylic acid, m. p.  $263-264^\circ$ , which could not be converted into the corresponding anhydride.

The synthesis of 5 : 5'-dihydroxy-2 : 2'-dimethyldiphenyl is accomplished in the following manner. *o*-Iodo-*p*-nitrotoluene is converted by copper powder at  $235-250^\circ$  into 5 : 5'-dinitro-2 : 2'-dimethyldiphenyl, m. p.  $177^\circ$ , which is reduced by stannous chloride and hydrochloric acid to 5 : 5'-diamino-2 : 2'-dimethyldiphenyl, b. p.  $225-228^\circ/13$  mm., m. p.  $96-98^\circ$  (*dihydrochloride*). The amine is converted in the usual manner into 5 : 5'-dihydroxy-2 : 2'-dimethyldiphenyl, m. p.  $229^\circ$ . *o*-Iodo-*p*-cresol, m. p.  $63-64^\circ$ , and its benzoate, m. p.  $53^\circ$ , are incidentally described.

*p*-Tolyl *p*-aminobenzyl ether (Pummerer and Melamed, *loc. cit.*) is converted by diazotisation in acetic and sulphuric acids and subsequent heating of the diazonium compound with acetic acid

into *p*-tolyl *p*-acetoxybenzyl ether, m. p.  $98^{\circ}$ , which, even under the mildest conditions of hydrolysis, is transformed into *p*-cresol and *p*-hydroxybenzyl alcohol.

6 : 4'-Dihydroxy-3-methyldiphenylmethane, m. p.  $135.5^{\circ}$  (diacetate, m. p.  $86^{\circ}$ ; dimethyl ether, m. p.  $74^{\circ}$ , is prepared by the action of sodium *p*-tolyl oxide on  $\omega$ -chlorotolyl carbonate, m. p.  $95^{\circ}$ . The methyl ether is also obtained by condensing anisyl chloride with *p*-tolyl methyl ether and reduction of the dimethoxymethylbenzophenone thus obtained by amalgamated zinc and hydrochloric acid; a substance, m. p.  $178-182^{\circ}$ , is simultaneously formed.

The by-products of the oxidation of *p*-cresol by potassium ferricyanide contain a dihydric phenol, m. p.  $194^{\circ}$ , to which the composition  $C_{14}H_{14}O_2$  has been assigned; since, however, it is not identical with any of the six dihydric phenols derivable from *p*-cresol, the correctness of this formula is in doubt, and the composition  $C_{14}H_{12}O_2$  is suggested. 6 : 6'-Dihydroxy-3 : 3'-dimethyldiphenyl, m. p.  $154^{\circ}$  (diacetate, m. p.  $88^{\circ}$ ; dimethyl ether, b. p.  $175^{\circ}/6$  mm., m. p.  $61^{\circ}$ ), is also present.

H. W.

### Catalytic Reduction by Means of Nickel and Hydrogen.

A. FELDMANN (*Giorn. Chim. Ind. Appl.*, 1925, **7**, 406—408).—A number of aromatic compounds were reduced by means of hydrogen at 8–10 atm. in presence of nickel. The reduction of sodium 1-nitroso- $\beta$ -naphthol-6-sulphonate to the corresponding amino compound ("Eikonogen") by this method is described, also the conversion of 2 : 4-dinitrophenol successively into 4-nitro-2-aminophenol and 2 : 4-diaminophenol, and of 2 : 4-dinitro-4'-hydroxydiphenylamine into the diamino compound. 1 : 5-Dinitronaphthalene-3 : 7-disulphonic acid yielded the diamino compound, but 1 : 8-dinitronaphthalene-3 : 6-disulphonic acid could not be reduced. Methylene-*p*-aminophenol, reduced by this method, regenerated *p*-aminophenol, hence it is probable that it is merely an additive compound of the latter with formaldehyde, and has not the constitution  $HO-C_6H_4-N:CH_2$  attributed to it. Benzoquinone was converted into quinol, and the sodium hydrogen sulphite compound of formaldehyde yielded sodium formaldehydesulphoxylate.

G. L. R.

### Bromophenols. VII. Bromine Substitution Products of

Quinol. M. KOHN and L. W. GUTTMANN (*Monatsh.*, 1925, **45**, 573—588; cf. this vol., i, 655).—Methylation of 2 : 5-dibromoquinol, m. p.  $184-186^{\circ}$  (cf. Benedikt, *Monatsh.*, 1880, **1**, 345; Sarauw, A., 1881, 1135), in alkaline solution with methyl sulphate affords 2 : 5-dibromo-1 : 4-dimethoxybenzene, m. p.  $142^{\circ}$ , identical with that obtained by the bromination of quinol dimethyl ether (cf. Habermann, A., 1878, 728). This is demethylated when boiled with hydrobromic acid in glacial acetic acid, whilst fuming nitric acid oxidises it to 2 : 5-dibromobenzoquinone, m. p.  $188-189^{\circ}$ , a nitro derivative not being produced (cf. Nölting and Werner, A., 1891, 209). Treatment of tribromoquinol in alkaline solution with methyl sulphate yields similarly the dimethyl ether, m. p.  $101-103^{\circ}$ , which on treatment with fuming nitric acid affords tetrabromo-

benzoquinone (bromanil) in small yield. Quinol monomethyl ether is obtained, together with some dimethyl ether, by treating quinol in alkaline solution with  $2/3$  mol. of methyl sulphate. When treated with 2 mols. of bromine in acetic acid, it affords a dark brown *solid*, which on methylation yields the above 2 : 5-dibromoquinol dimethyl ether. Treatment of 2 : 6-dibromoquinol dimethyl ether (cf. Ling, T., 1892, 61, 562) with fuming nitric acid affords 2 : 6-dibromo-3 : 5-dinitroquinol dimethyl ether, pale yellow, m. p. 150—151°. Detailed crystallographic data for several of the above products are included.

F. G. W.

**Bromophenols. VIII. Bromo- and Bromonitro-resorcinsols.** M. KOHN and G. LÖFF (*Monatsh.*, 1925, 45, 589—595).—4 : 6-Dibromoresorcinol, obtained when slightly less than 2 mols. of bromine are added to resorcinol suspended in carbon tetrachloride (cf. Zehenter, A., 1882, 193), affords the dimethyl ether, m. p. 138°, on treatment in alkaline solution with methyl sulphate. Treatment of the dimethyl ether with liquid bromine yields 2 : 3 : 6-tribromoresorcinol dimethyl ether (cf. Torrey and Hunter, A., 1911, i, 283) in a condition difficult to purify, which when boiled with hydrobromic acid in acetic acid yields 2 : 4 : 6-tribromoresorcinol, m. p. 111°, which is also obtained by methylating 2 : 4 : 6-tribromoresorcinol monomethyl ether (cf. Benedikt, *Monatsh.*, 1880, 1, 345). When the last is treated in acetic acid solution with potassium nitrite it yields 2 : 6-dibromo-4-nitro-3-hydroxyanisole, yellow, m. p. 122° (potassium and sodium salts, yellow; silver salt, red), which, on demethylation, affords 2 : 6-dibromo-4-nitroresorcinol (cf. Raiford and Heyl, A., 1910, i, 730).

F. G. W.

**Bromophenols. IX. Bromo- and Bromonitro-phenols.** M. KOHN and S. STRASSMANN (*Monatsh.*, 1925, 45, 597—603).—Treatment of 2 : 3 : 4 : 6-tetrabromoanisole with cold fuming nitric acid affords 2 : 3 : 4 : 6-tetrabromo-5-nitroanisole, m. p. 122°, which yields the corresponding tetrabromonitrophenol, m. p. 162°, on demethylation (cf. Blanksma, *Rec. trav. chim.*, 1908, 27, 31). Treatment of 2 : 3 : 4 : 6-tetrabromophenyl acetate with cold sulphuric and nitric acids affords 2 : 3 : 6-tribromo-5-nitrobenzoquinone, yellow, m. p. 285°. 2 : 4 : 6-Tribromoanisole affords similarly 2 : 4 : 6-tribromo-3 : 5-dinitroanisole, m. p. 148°, which yields the corresponding tribromodinitrophenol, m. p. 196°, on demethylation (cf. Jackson and Warren, A., 1894, i, 176). Addition of bromine (2 mols.) to a solution of *m*-bromophenol in glacial acetic acid affords 3 : 4 : 6- or 2 : 3 : 4-tribromophenol, m. p. 78°, the methyl ether of which, m. p. 67°, yields a mononitro derivative, m. p. 105°.

F. G. W.

**Bromophenols. X. Ethers of Chloronitro and Bromonitro Derivatives of Quinol and Toluquinol and the Mobility of the Halogen Atoms therein.** M. KOHN and R. MARBERGER (*Monatsh.*, 1925, 45, 649—662).—2 : 6-Dichloroquinol dimethyl ether reacts with cold, fuming nitric acid with formation of 2 : 6-dichloro-3 : 5-dinitroquinol dimethyl ether, pale yellow, m. p. 121—123°, monoclinic crystals,  $a : b : c = 0.98746 : 1 : 1.75961$ ,  $\beta = 90^\circ 42' 44''$ ;

there is also an orthorhombic form,  $a : b : c = 0.89446 : 1 : 1.61190$ . When boiled with pyridine, the dinitro derivative affords an *N-methylpyridinium* compound, which, when decomposed with aqueous potassium hydroxide, yields the *monomethyl ether*, 3 : 5-dichloro-2 : 6-dinitro-4-methoxyphenol, yellow, m. p.  $97^\circ$  (monoclinic,  $a : b : c = 1.12679 : 1 : 0.90567$ ,  $\beta = 93^\circ 59'$ ), as the red *potassium salt*. 3-Bromo-4 : 6-dinitro-2 : 5-dimethoxytoluene, m. p.  $124-126^\circ$ , obtained by nitrating the corresponding bromotoluquinol dimethyl ether, affords similarly 5-bromo-2 : 4-dinitro-6-methoxy-m-cresol, m. p.  $86^\circ$ , whilst 2 : 6-dibromo-3 : 5-dinitroquinol dimethyl ether yields in the same way 3 : 5-dibromo-2 : 6-dinitro-4-methoxyphenol, sulphur-yellow, m. p.  $135-137^\circ$  (*ammonium salt*, yellow; *silver salt*, orange), which affords the dimethyl ether when the silver salt is warmed with methyl-alcoholic methyl iodide. 2 : 6-Dinitro-3 : 5-dianilino-4-methoxyphenol, dark red, m. p.  $181^\circ$  (decomp.), is obtained when 2 : 6-dibromo- or 2 : 6-dichloro-3 : 5-dinitroquinol dimethyl ether is boiled with aniline. 2 : 4-Dinitro-5-anilino-6-methoxy-m-cresol, dark red, m. p.  $138-139^\circ$  (decomp.), is obtained similarly from bromodinitrotoluquinol dimethyl ether.

F. G. W.

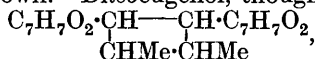
**Bromophenols. XI. Bromination of Quinol Monomethyl Ether and of Nitroquinol Dimethyl Ether.** M. KOHN and S. GRÜN (*Monatsh.*, 1925, 45, 603—607).—When quinol dimethyl ether is treated with excess of liquid bromine it yields 2 : 3 : 5-tribromo-4-hydroxyanisole, m. p.  $145^\circ$ , which affords the corresponding dimethyl ether on treatment in alkaline solution with methyl sulphate, and, when shaken with potassium nitrite in suspension in glacial acetic acid, yields either 2 : 5-dibromo-3-nitro-4-hydroxy- or 2 : 3-dibromo-5-nitro-4-hydroxy-anisole, m. p.  $170^\circ$  (decomp.). Nitroquinol dimethyl ether affords tetrabromoquinol dimethyl ether, m. p.  $191-192^\circ$ , when treated with liquid bromine (cf. Habermann, A., 1878, 728).

F. G. W.

**Monomethyl Styphnate and a New Trinitroguaiacol, 3 : 4 : 5-Trinitro-2-hydroxyanisole.** M. KOHN and G. LÖFF (*Monatsh.*, 1925, 45, 605—615).—Pyridine reacts immediately with trinitroresorcinol dimethyl ether (dimethyl styphnate) to form the *N-methylpyridinium* salt of *monomethyl styphnate*, yellow, m. p.  $131-132^\circ$  (cf. Kohn and Grauer, A., 1914, i, 83). The *N-methylquinolinium* salt, yellow, m. p.  $151^\circ$ , is obtained similarly. Both salts are decomposed by dilute hydrochloric acid with formation of monomethyl styphnate, m. p.  $80^\circ$  (cf. Blanksma, A., 1902, i, 442), of which the *pyridine* and *quinoline* salts, yellow, m. p.  $140-145^\circ$  (decomp.) and  $165-174^\circ$  (decomp.), respectively, depending on the rate of heating, are described. Whilst dimethyl styphnate affords styphnic acid when boiled with hydrobromic acid in acetic acid, 3 : 4 : 5-trinitroveratrole (cf. Klemenc, A., 1911, i, 779) loses only one methyl group under these conditions, with formation of a trinitroguaiacol, 3 : 4 : 5-trinitro-2-hydroxyanisole, m. p.  $143-149^\circ$  (decomp.) [*benzoate*, m. p.  $146^\circ$ ; *pyridine salt*, m. p.  $158^\circ$  (decomp.); *quinoline salt*, m. p.  $201^\circ$  (decomp.)]. The *N-methylpyridinium* salt, deep red, m. p.  $120^\circ$ , and the *N-methylquinolinium* salt, brilliant

red, m. p. 161—163°, of the above trinitroguaiacol are obtained by the action of pyridine and quinoline, respectively, on 3 : 4 : 5-trinitroveratrole. Both salts are decomposed by 20% sulphuric acid, with formation of trinitroguaiacol. F. G. W.

**Chlorination of Tetramethylene Polymerides.** E. PUXEDDU (*Gazzetta*, 1925, 55, 604—610; cf. A., 1920, i, 481)—These polymerides, derived from phenols, or their ethers, having propenylic side chains, no longer possess the propenylic double bond and hence give chlorination products only by substitution. The latter are yellow to red, amorphous powders, melting indefinitely, insoluble in water, but somewhat soluble in organic solvents and in hot alkali hydroxides. They are difficult to purify and their constitutions are unknown. Diisoeugenol, thought to be



is obtained by the action of concentrated hydrochloric acid on an ethyl-alcoholic solution of isoeugenol. On chlorination in chloroform at the ordinary temperature, in carbon tetrachloride at 76°, or in xylene at 140°, hexachlorodiisoeugenol,  $\text{C}_{20}\text{H}_{18}\text{O}_4\text{Cl}_6$ , decomp., without melting, at 105°, is obtained. Diisoeugenol dimethyl ether, produced by the action of methyl sulphate on an alkaline solution of diisoeugenol, gives, on chlorination, hexachlorodiisoeugenol dimethyl ether, contaminated by a higher chloro derivative. The product of chlorination of diisoeugenol diethyl ether is tetrachlorodiisoeugenol diethyl ether, decomp. 86°. Disosafrole chlorinates to hexachlorodisosafrole, decomp. 100—123° to a dense reddish-brown liquid. W. E. E.

**Triphenylmethyl. XXXIV. 2 : 5-, 2 : 4-, and 3 : 4-Dimethoxytriphenylmethylys.** M. GOMBERG and G. C. FORRESTER (*J. Amer. Chem. Soc.*, 1925, 47, 2373—2391).—In continuation of previous work (A., 1923, i, 211, 212) on the influence of methoxy groups on the dissociation of hexa-arylethanes, the behaviour of the 2 : 5-, 2 : 4-, and 3 : 4-dimethoxytriphenylmethylys has been examined. The free radicals are white when isolated, but slowly become yellow and yield red to orange-red solutions in organic solvents, the colour of these solutions deepening with the accumulation of methoxy groups in the molecule. These solutions are stable to heat and do not deteriorate on keeping. They are only slightly affected by exposure to strong diffused daylight or to the tungsten lamp, but decompose in direct sunlight. On saturation with hydrogen chloride, the triphenylmethane and triphenylmethyl chloride are produced,  $2\text{CR}_3 + \text{HCl} = \text{CHR}_3 + \text{CR}_3\text{Cl}$ . Although the dry radicals only absorb oxygen slowly, in solution practically quantitative oxidation to crystalline peroxides,  $(\text{CR}_3)_2\text{O}_2$ , is complete in about 5 mins. The dissociation of these free radicals in benzene, nitrobenzene, *p*-bromotoluene, and *p*-dichlorobenzene increases considerably with the temperature, but is unaffected by the concentration over the range (1—5%) examined. The degree of dissociation of the 2 : 5- and 2 : 4-dimethoxy compounds varies considerably with the solvent. The presence of two homonuclear

methoxy groups has, however, very little effect on the ratio of free radical to hexa-arylethane in solution, the percentage of dissociation in nitrobenzene, *p*-bromotoluene, and *p*-dichlorobenzene varying from 20% to 30% in the three compounds examined. The colour of these solutions varies considerably with the temperature and concentration, but the increase in colour with temperature and dilution is quite unrelated to the accompanying change in dissociation, an observation in harmony with the quinonoid theory of the colour of unimolecular triphenylmethylys.

The influence of the methoxy group on the synthesis of tetra-arylmethanes from magnesium phenyl bromide has been examined. Whilst triphenylmethyl chloride gives only 2—5% of tetraphenylethane, *o*-methoxytriphenylmethyl chloride gives a 38% yield of the tetra compound, the corresponding *p*-methoxy derivative giving only 4.3%. The 3 : 4-, 2 : 4-, and 2 : 5-dimethoxytriphenylmethyl chlorides give 30%, 25%, and 58% yields of the tetra-aryl compound, respectively. The 2 : 5-dimethoxy bromide similarly gives a 58% yield, whilst with magnesium phenyl iodide the 2 : 5-dimethoxytetraphenylmethane is obtained in 17% yield. In certain cases, the Grignard reagent acts as a reducing agent and the tri-arylmethane has been obtained in yields up to 53% of the theoretical. Attempts to prepare the dimethoxytetraphenylmethanes from triphenylmethyl chloride and the corresponding magnesium dimethoxyphenyl iodide were unsuccessful.

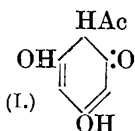
2 : 5-Dimethoxytriphenylcarbinol, m. p. 141°, was obtained in 92% yield from quinol dimethyl ether and benzophenone chloride in the presence of aluminium chloride. The *bromide*, m. p. 113°, *anilide*, m. p. 169.5°, and *p*-*toluidide*, m. p. 151°, are described. With molecular silver in bromobenzene, the bromide is converted into 2 : 5-dimethoxytriphenylmethyl (*peroxide*, m. p. 149°), which was obtained crystalline but not pure. 2 : 4-Dimethoxytriphenylcarbinol, similarly prepared from resorcinol dimethyl ether, yields an *anilide*, m. p. 143°, and a *chloride*, m. p. 97° (giving a red, additive compound with hydrogen chloride), which with molecular silver is similarly converted into 2 : 4-dimethoxytriphenylmethyl (*peroxide*, m. p. 146°). 3 : 4-Dimethoxytriphenylcarbinol and 3 : 4-dimethoxytriphenylmethyl (*peroxide*, m. p. 162.5°) were analogously obtained. 2 : 5-Dimethoxytetraphenylmethane from magnesium phenyl bromide or iodide and 2 : 5-dimethoxytriphenylmethyl chloride or bromide has m. p. 163°; 2 : 5-dimethoxytriphenyl- $\alpha$ -naphthylmethane, m. p. 175° (yield 41%); 3 : 4-dimethoxytetraphenylmethane, m. p. 170.5°; 2 : 4-dimethoxytetraphenylmethane, m. p. 180°; *o*-methoxytetraphenylmethane, m. p. 145°; and *p*-methoxytetraphenylmethane, m. p. 194°.

R. B.

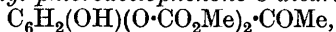
**Tautomerism of Derivatives of Phloroglucinol. Monomethyl Derivatives of Phloroacetophenone.** A. SONN and W. BÜLOW (*Ber.*, 1925, 58, [B], 1691—1698).—The action of acetonitrile and hydrogen chloride on an ethereal solution of phloroglucinol monomethyl ether in the presence of anhydrous zinc chloride yields a substance, m. p. 205—207°, which is regarded



provisionally as 4:6-dihydroxy-2-methoxyacetophenone, since it is transformed by anisaldehyde and potassium hydroxide into a chalkone, m. p. 169°, (?) 4:6-dihydroxy-2-methoxyphenyl 4-methoxystyryl ketone. If, however, phloracetophenone is treated with 1 mol. of diazomethane in ethereal solution, phloracetophenone dimethyl ether, unchanged phloracetophenone, and an isomeric phloracetophenone monomethyl ether, m. p. 136—137°, are obtained, to which, since it does not react with aldehydes, the constitution (I) is provisionally assigned, thus indicating the possibility of a dienolic-ketonic structure for phloracetophenone. The acylation of the latter substance is in harmony with this conception.



Thus whereas phloroglucinol is converted by methyl chloroformate in alkaline solution into tricarbomethoxyphloroglucinol, phloroglucinol-carboxylic acid under similar conditions yields only monocarbomethoxyphloroglucinolcarboxylic acid. Attempts to introduce similarly a single carbomethoxy group into phloracetophenone gave mainly dimethyl phloracetophenone-o-dicarboxylate,



m. p. 114—115°, together with a little methyl phloracetophenone-o-carboxylate, m. p. 152°, and unchanged phloracetophenone. Trimethyl phloracetophenonetricarboxylate, m. p. 65°, is readily prepared from methyl chloroformate and phloracetophenone in the presence of benzene and dimethylaniline. Hydrolysis of the tricarbomethoxy compound with 2 mols. of alkali hydroxide yields mainly a mixture of phloracetophenone and its dicarbomethoxy derivative. Benzoyl chloride (1 mol.) and sodium hydroxide (1 mol.) convert phloracetophenone into a mixture of much dibenzoylphloracetophenone, m. p. 109—110°, little monobenzoylphloracetophenone, m. p. 177—178°, and unchanged phloracetophenone. Triacetylphloracetophenone, from phloracetophenone and acetyl chloride in the presence of benzene and dimethylaniline, has m. p. 90°.

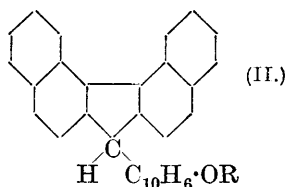
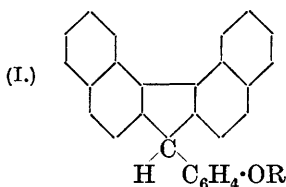
2:4:6-Trinitrobenzaldehyde is converted by ethereal diazomethane into 2:4:6-trinitroacetophenone, m. p. 90—92° (decomp.) (phenylhydrazone, m. p. 193—194°).

p-Methylcarbonatobenzaldehyde has m. p. 41—42° (Rosenmund, A., 1918, i, 300, gives m. p. 18.5°). H. W.

$\alpha\alpha$ - and  $\alpha\gamma$ -Isomerides of 2:4:6:3':4'-Pentamethoxydiphenylpropane. J. J. DRUMM, N. G. J. O'REILLY, and H. RYAN (Proc. Roy. Irish Acad., 1925, 37 B, 19—26; cf. T., 1902, 81, 1172; A., 1916, i, 722; 1923, i, 1221).—The observation of Freudenberg (A., 1920, i, 752) that the reduced methylation product of catechin (Kostanecki and Lampe, A., 1907, i, 73, 334; 1908, i, 86) is identical with 2:4:6:3':4'-pentamethoxy- $\alpha\gamma$ -diphenylpropane, m. p. 87—88°, in contradiction to Nierenstein's results (T., 1920, 117, 971, 1151), is confirmed. Maclurin pentamethyl ether on treatment with magnesium ethyl iodide in benzene solution yields 2:4:6:3':4'-pentamethoxy- $\alpha\alpha$ -diphenyl- $\Delta^a$ -propene, m. p. 95—96°, dibromide, m. p. 161—162°, which on reduction gives 2:4:6:3':4'-pentamethoxy- $\alpha\alpha$ -diphenylpropane, m. p. 80—81°. L. F. H.

**Triphenylcarbinol Hydrochloride.** B. HELFERICH and H. DEHE (*Ber.*, 1925, **58**, [B], 1605).—Triphenylcarbinol hydrochloride, m. p.  $174^{\circ}$ , obtained previously from triphenylmethyl chloride and water in the presence of pyridine (this vol., i, 790), is also prepared from triphenylcarbinol and hydrogen chloride in pyridine solution. H. W.

**Tautomerism of *o*-Hydroxytriarylcabinols which contain Naphthyl Groups.** M. GOMBERG and W. J. MCGILL (*J. Amer. Chem. Soc.*, 1925, **47**, 2392—2405).—The isomeric change of *o*-hydroxytriarylcabinols to the *o*-quinonoid form previously studied with *o*-hydroxytriphenylcarbinol (A., 1923, i, 212) and its *p*-methoxy derivative (A., 1918, i, 111) is now shown to be characteristic of *o*-hydroxytriarylcabinols containing one, two, or three naphthyl groups. Such isomeric change appears to be a necessary preliminary stage in the intramolecular condensation of the carbinols to the corresponding xanthenes, but the possibility of isolating any one of the successive stages, benzenoid or quinonoid carbinol, fuchsone or xanthen, depends on their relative stabilities. With successive replacement of the unsubstituted phenyl groups by naphthyl groups in *o*-hydroxytriphenylcarbinol, the quinonoid and fuchsone forms become more unstable and the *o*-hydroxyphenyldi- $\alpha$ -naphthylcarbinol undergoes dehydration to the xanthen even in neutral solvents. Similar influences are observed when the hydroxyl group is present in the naphthalene ring. With diphenyl-3-hydroxy- $\beta$ -naphthylcarbinol and di- $\alpha$ -naphthyl-3-hydroxy- $\beta$ -naphthylcarbinol there is little evidence of the existence of the quinonoid or fuchsone forms, the dehydration to xanthen taking place with little production of colour. 2-Hydroxy- $\alpha$ -naphthyl- and 1-hydroxy- $\beta$ -naphthyl-diphenylcarbinols, in agreement with the stability of the  $\alpha\beta$ -naphthaquinone structure (Marckwald, A., 1893, i, 603; 1894, i, 474), afford evidence of the existence of the fuchsone, and both the benzenoid and quinonoid forms of the former have been isolated. Both the methoxy and benzyloxy derivatives of this carbinol yield the fuchsone quantitatively when heated in acetic acid. The fuchsone is the stable form of the corresponding 1-hydroxy- $\beta$ -naphthyl compound and the xanthen could not be obtained. The methoxy and benzyloxy derivatives of *o*-hydroxyphenyldi- $\alpha$ -naphthylcarbinol and di- $\alpha$ -naphthyl-3-hydroxy- $\beta$ -naphthylcarbinol cannot easily form xanthenes and intramolecular condensation yields the corresponding phenyldi- $\alpha$ -naphthafluorene

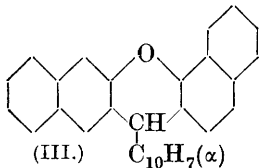


(I) or  $\beta$ -naphthyldi- $\alpha$ -naphthafluorene (II). Stable carbinols appear to yield stable chlorides and free radicals, whilst the tautomeric  
*yy*\*

diphenylhydroxynaphthylcarbinols give unstable chlorides, which pass at once into the fuchsone.

Colourless *o*-hydroxy-*p*-methoxytriphenylcarbinol on boiling with 70% acetic acid for 15 mins. yields an orange-yellow precipitate of the quinonoid carbinol. Both the coloured and colourless carbinols are transformed by heat into the fuchsone, m. p. 156°, but the coloured form is dehydrated more rapidly. Phenyl  $\alpha$ -naphthyl ketone and magnesium *o*-anisyl iodide give in 85% yield *o*-methoxydiphenyl- $\alpha$ -naphthylcarbinol, m. p. 156°, the *chloride*, m. p. 142°, of which, on treatment with silver in benzene, yields *o*-methoxydiphenyl- $\alpha$ -naphthylmethyl (peroxide, m. p. 111°). Attempts to demethylate the carbinol with aluminium chloride, antimony chloride, or hydrobromic acid yielded phenyl- $\alpha$ -naphthaxanthen. *o*-Methoxydiphenyl- $\alpha$ -naphthylmethane has m. p. 134°. *o*-Hydroxyphenyldi- $\alpha$ -naphthylcarbinol, m. p. 142°, with benzyl chloride and sodium hydroxide in acetone yields *o*-benzyloxyphenyldi- $\alpha$ -naphthylcarbinol, m. p. 149—150°, which on boiling with glacial acetic acid is converted into *o*-benzyloxyphenyldi- $\alpha$ -naphthylfluorene (I), m. p. 210°. *o*-Methoxyphenyldi- $\alpha$ -naphthylfluorene, m. p. 318°, is obtained similarly. Diphenyl-3-hydroxy- $\beta$ -naphthylcarbinol becomes coloured in acetic acid on warming, but on boiling is slowly converted into phenyl- $\beta$ -naphthaxanthen. Diphenyl-3-hydroxy- $\beta$ -naphthylmethyl (peroxide, m. p. 145°) is obtained by treating the carbinyl chloride with silver, but decomposes rapidly in solution, yielding diphenyl-3-hydroxy- $\beta$ -naphthylmethane and the phenyl- $\beta$ -naphthaxanthen, m. p. 171°. Methylation of the carbinol in acetone with methyl sulphate yields diphenyl-3-methoxy- $\beta$ -naphthylcarbinol, m. p. 175—176°. Calcium chloride and hydrogen chloride in benzene convert this into the *chloride*, m. p. 129—130°. The methane has m. p. 179—180°. Diphenyl-3-methoxy- $\beta$ -naphthylmethyl (peroxide, m. p. 169—170°) is a yellow solid. Diphenyl-3-benzyloxy- $\beta$ -naphthylcarbinol, m. p. 165°, the *chloride*, m. p. 115°, the methane, m. p. 141°, and diphenyl-3-benzyloxy- $\beta$ -naphthylmethyl were analogously obtained.

Di- $\alpha$ -naphthyl-3-hydroxy- $\beta$ -naphthylcarbinol on heating in acetone solution yields  $\alpha$ -naphthyl- $\alpha\beta$ -dinaphthaxanthen (III), m. p. 262°. The *methoxy* derivative of the carbinol, m. p. 252°, in boiling acetic acid, or with acetyl chloride in chloroform at 0°, yields 3-methoxy- $\beta$ -naphthyl-di- $\alpha$ -naphthylfluorene (II), m. p. 241—242°. Diphenyl-2-hydroxy- $\alpha$ -naphthylcarbinol, from methyl  $\alpha$ -hydroxy- $\beta$ -naphthoate and magnesium phenyl bromide, m. p. 195—198°, becomes red in boiling acetic acid solution and on cooling the solution deposits red crystals of the *o*-naphthafuchsone, m. p. 198°. The quinonoid carbinol, reddish-orange, m. p. 140—145°, is obtained by crystallisation from alcohol containing acetic acid, and is dehydrated more rapidly than the benzenoid form. The optical constants of both forms are given. Prolonged boiling with acetic acid converts the carbinol into phenyl- $\alpha$ -naphthaxanthen, m. p. 172—173°. Diphenyl-2-methoxy-



(III.)  $C_{10}H_7(\alpha)$

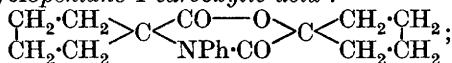
$\alpha$ -naphthylcarbinol, m. p. 148—150°, on heating in glacial acetic acid, yields *o*-naphthafuchstone, the same compound being formed in attempts to prepare the carbonyl chloride. Diphenyl-2-benzoyloxy- $\alpha$ -naphthylcarbinol, m. p. 142°, behaves similarly. Attempts to convert diphenyl-1-hydroxy- $\beta$ -naphthylcarbinol into a coloured form failed.

R. B.

### Naphthenic Acids derived from Nishiyama Petroleum.

Y. TANAKA and S. NAGAI (*J. Amer. Chem. Soc.*, 1925, **47**, 2369—2371).—The crude naphthenic acid from a neutral oil distillate, *d* 0.8578, from Echigo-Nishiyama petroleum was purified by conversion into the methyl ester, a pale yellow oil, *d*<sub>4</sub><sup>15</sup> 0.9446, *n*<sub>D</sub><sup>15</sup> 1.4651, 80% of which distils at 130—180°/8.9—9.0 mm. The pure naphthenic acid, a yellow, viscous oil, has *d*<sub>4</sub><sup>15</sup> 0.9741, *n*<sub>D</sub><sup>15</sup> 1.4762, neutralisation value 248, and 80% distils at 170—210°/8.9—9.0 mm. Fractionation of the methyl ester yielded mainly methyl dodecanaphthenate, b. p. 127—129°/8.9—9.0 mm., 265—266°/760 mm., *d*<sub>4</sub><sup>15</sup> 0.9412, *n*<sub>D</sub><sup>15</sup> 1.4579, methyl tridecanaphthenate, b. p. 136—138°/8.9—9.0 mm., 277—278°/760 mm., *d*<sub>4</sub><sup>15</sup> 0.9443, *n*<sub>D</sub><sup>15</sup> 1.4612, methyl tetradecanaphthenate, b. p. 145.5—147.5°/8.9—9.0 mm., 289—290°/760 mm., *d*<sub>4</sub><sup>15</sup> 0.9491, *n*<sub>D</sub><sup>15</sup> 1.4647, and methyl pentadecanaphthenate, b. p. 155—157°/8.9—9.0 mm., 300—301°/760 mm., *d*<sub>4</sub><sup>15</sup> 0.9501, *n*<sub>D</sub><sup>15</sup> 1.4672, from which dodecanaphthenic, C<sub>12</sub>H<sub>22</sub>O<sub>2</sub>, b. p. 168—170°/8.9—9.0 mm., *d*<sub>4</sub><sup>15</sup> 0.9712, *n*<sub>D</sub><sup>15</sup> 1.4697, tridecanaphthenic, C<sub>13</sub>H<sub>24</sub>O<sub>2</sub>, b. p. 177—179°/8.9—9.0 mm., *d*<sub>4</sub><sup>15</sup> 0.9736, *n*<sub>D</sub><sup>15</sup> 1.4727, tetradecanaphthenic, C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>, b. p. 186—188°/8.9—9.0 mm., *d*<sub>4</sub><sup>15</sup> 0.9762, *n*<sub>D</sub><sup>15</sup> 1.4759, and pentadecanaphthenic acids, C<sub>15</sub>H<sub>28</sub>O<sub>2</sub>, b. p. 194—196°/8.9—9.0 mm., *d*<sub>4</sub><sup>15</sup> 0.9776, *n*<sub>D</sub><sup>15</sup> 1.4784, were obtained as colourless, odourless liquids with no iodine value. The specific gravities of these naphthenic acids are much lower than those obtained from the corresponding acids occurring in Akita-Kurokawa and Echigo-Niitsu petroleum (A., 1923, i, 464; this vol., i, 252). R. B.

**Synthesis and Reactions of 1-Anilinocyclopentane-1-carboxylic Acid.** S. G. P. PLANT and J. E. FACER (*J. Chem. Soc.*, 1925, **127**, 2037—2040).—The original object of this investigation was to synthesise  $\psi$ -indoxylspirocyclopentane (T., 1921, **119**, 1825; 1923, **123**, 676) by a method analogous to that used for 2:2-dimethyl- $\psi$ -indoxyl (Bucherer and Grolée, A., 1906, i, 349). 1-Anilino-1-cyanocyclopentane, m. p. 58° (prepared by boiling a benzene solution of aniline with cyclopentanone cyanohydrin), is converted by cold sulphuric acid into 1-anilinocyclopentane-1-carboxylamide, m. p. 161° (nitrosoamine, m. p. 122°), which is hydrolysed to the acid, m. p. 162° [nitrosoamine, m. p. 124° (decomp.)]. On heating the acid at 230°, it is decomposed into aniline, water, and the lactone, m. p. 142°, of 1:1'-hydroxycyclopentane-1'-carboxylanilinocyclopentane-1-carboxylic acid:



the lactone is unchanged by aniline at 170° or by dry ammonia at 220° and is not basic. Fusion of 1-anilinocyclopentane-1-carboxylic acid with sodium ethoxide and potassium hydroxide at

270—320° gives carbazole, but no  $\psi$ -indoxylspirocyclopentane, nor has water been eliminated from the acid at a lower temperature. It has not been possible to convert the *acetyl* derivative, m. p. 195°, of the acid into 6-acetyl- $\psi$ -indoxylspirocyclopentane. F. M. H.

**Electrolytic Reduction of Benzoic Acid at the B. P.** V. DECANS and J. DUFOUR (*Bull. Soc. chim.*, 1925, [iv], **37**, 1167—1174).—By raising the temperature of the benzoic acid solution to the b. p. the use of alcohol as solvent (cf. Mettler, A., 1905, i, 436) is rendered unnecessary and greatly improved yields of benzyl alcohol on the current consumed are obtained. The electrolysis is conducted in 60% sulphuric acid and the cathode compartment consists of a porous cell to which a reflux condenser is attached. The annular space surrounding this forms the anode compartment and diffusion of hydrogen is prevented by coating the porous cell with a varnish which is not attacked by sulphuric acid. Lead electrodes are employed and the hydrogen escaping from the cathode is collected and measured, the volume being compared with that liberated in a voltmeter included in the circuit. The comparison serves as a guide to the addition of benzoic acid, which is added gradually in quantities of about 5 g. so as to keep the concentration approximately constant. The electrolysis is continuous, and when the addition of benzoic acid is stopped, the current is continued until 80% of the hydrogen is escaping. The ratio of cathodic surface to cathodic volume is very important and in the apparatus described should not exceed the limits 1 to 1.6. With a current density at the cathode of 12.2 amp./dm.<sup>2</sup>, yields of benzyl alcohol up to 75—80% of theory are obtained, the current efficiency being 90%. Benzyl ether (16—20%) and *isohydrobenzoin*, m. p. 119° (1—2%), are also formed, together with about 3% of tar. It is suggested that the benzyl ether results from the reduction of benzyl benzoate thus,  $\text{Ph}\cdot\text{CO}_2\text{CH}_2\text{Ph} + 2\text{H} \rightarrow \text{CHPh}(\text{OH})\cdot\text{OCH}_2\text{Ph} + 2\text{H} \rightarrow \text{H}_2\text{O} + (\text{CH}_2\text{Ph})_2\text{O}$ , the *isohydrobenzoin* resulting similarly from the intermediate formation of benzaldehyde:  $\text{Ph}\cdot\text{CO}_2\text{H} \rightarrow \text{CHPh}(\text{OH})_2 \rightarrow \text{H}_2\text{O} + \text{Ph}\cdot\text{CHO}$ ;  $2\text{Ph}\cdot\text{CHO} + 2\text{H} \rightarrow \text{CHPh}(\text{OH})\cdot\text{CHPh}\cdot\text{OH}$ . R. B.

**Reduction of the Group  $-\text{CH}(\text{OH})\cdot\text{CCl}_3$ .** I. A. N. MELDRUM and R. L. ALIMCHANDANI (*J. Indian Chem. Soc.*, 1925, **2**, 1—9).—Numerous examples of the reduction of the group  $\text{CH}(\text{OH})\cdot\text{CCl}_3$  to  $\text{CH}_2\cdot\text{CHCl}_2$  by the action of zinc dust and acetic acid (cf. Jocitsch, A., 1899, i, 748, 786; Alimchandani and Meldrum, T., 1921, **119**, 204) are given. By the condensation of 3-methoxy-*p*-toluic acid and chloral hydrate in the presence of sulphuric acid is obtained 3-methoxy-6- $\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethyl-*p*-toluic acid, m. p. 236—237° (decomp.) (calcium salt,  $+ 10\text{H}_2\text{O}$ , *acetyl* derivative, m. p. 203—204°), which on reduction yields 3-methoxy-6- $\beta\beta$ -dichloroethyl-*p*-toluic acid, m. p. 166—167°. The amorphous material obtained by the condensation of *m*-hydroxytoluic acid with chloral hydrate contains a crystalline substance,  $\text{C}_{14}\text{H}_{12}\text{O}_5\text{Cl}_9$ , m. p. 211—212°, of similar constitution to that derived from *p*-hydroxytoluic acid, yielding on reduction by zinc and acetic acid the compound

$C_{12}H_{12}O_3Cl_4$ , m. p. 164—165° (*calcium* salt described). Methyl  $\gamma\gamma$ -trichloro- $\beta$ -hydroxybutyrate, m. p. 65—66° (Auwers and Schmidt, A., 1913, i, 338, give 61—62°), on reduction yields the unstable methyl  $\gamma\gamma$ -dichlorobutyrate, b. p. 95—100°/36 mm., from which by the action of sodium hydroxide is obtained the acid, m. p. 103—104°, in which the  $CHCl_2$  group also suffers considerable hydrolysis. Dichloralcarbamide on reduction yields *s*-di- $\beta\beta$ -dichloroethylcarbamide, m. p. 222° (decomp.). The action of chloral on thiocarbamide yields dichloralthiocarbamide (*s*-di- $\beta\beta\beta$ -trichloro- $\alpha$ -hydroxyethylthiocarbamide), m. p. 150—151° (decomp.), which on reduction yields *s*-di- $\beta\beta$ -dichloroethylthiocarbamide, m. p. 162—163° (decomp.). Similarly, chloralurethane, m. p. 106—108° (Bischoff, A., 1874, 890, gives 103°), on reduction yields dichloroethylurethane,  $CHCl_2 \cdot CH_2 \cdot NH \cdot CO_2Et$ , b. p. 125—128°/13 mm., m. p. 13°, whilst chloralurethylane,  $CCl_3 \cdot CH(OH) \cdot NH \cdot CO_2Me$ , m. p. 125—128° (by the condensation of chloral and urethylane in the presence of concentrated hydrochloric acid), yields dichloroethylurethylane,  $CHCl_2 \cdot CH_2 \cdot NH \cdot CO_2Me$ , m. p. 90—93°, which on treatment with dry hydrogen chloride in ether yields the substance  $C_3H_4O_2NCl$ , m. p. 118—120°. J. W. B.

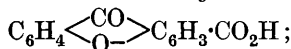
**Substituted Salicyclic Acids. V. Substituted Salicyclic Phthalidylidene Ether Esters.** H. P. KAUFMANN and E. ROSSBACH (*Ber.*, 1925, 58, [B], 1556—1560).—*s*-o-Phthaloyl chloride reacts with salicylic acid in the presence of dimethylaniline, giving salicylic phthalidylidene ether ester, m. p. 158.5° (cf. A., 1924, i, 176). Similarly, thiosalicylic acid yields thiosalicylic phthalidylidene ether ester,  $CO \langle \begin{smallmatrix} O \\ \text{C}_6\text{H}_4 \end{smallmatrix} \rangle C \langle \begin{smallmatrix} S-CO \\ O-C_6H_4 \end{smallmatrix} \rangle$ , m. p. 230°. The reaction does not

appear to be inhibited by the presence of a substituent in the salicylic acid molecule. Thus, 2-hydroxy-5-thiocyanobenzoic acid (cf. A., 1924, i, 210) gives 2-hydroxy-5-thiocyanobenzoic phthalidylidene ether ester, m. p. 199°, and 2-hydroxy-5-thiolbenzoic acid affords phthalidylidenedi-4-[salicylic phthalidylidene ether ester]-dithioether,  $CO \langle \begin{smallmatrix} O \\ \text{C}_6\text{H}_4 \end{smallmatrix} \rangle C \left[ S \cdot C_6H_3 \langle \begin{smallmatrix} CO-O \\ O \end{smallmatrix} \rangle C \langle \begin{smallmatrix} O \\ \text{C}_6H_4 \end{smallmatrix} \rangle CO \right]_2$ , decomp. above 200°.

The constitution of 2-hydroxy-5-thiocyanobenzoic acid is established by its production by diazotisation of 5-amino-2-hydroxybenzoic acid and treatment of the diazonium compound with potassium cuprothiocyanate. The acid is reduced by zinc dust to 2-hydroxy-5-thiolbenzoic acid, m. p. 148°, which is readily oxidised to the corresponding disulphide, m. p. 245°; the latter compound is also obtained by warming diazotised 5-amino-2-hydroxybenzoic acid with sodium sulphide or by treating 2-hydroxy-5-thiocyanobenzoic acid with alcoholic sodium hydroxide. H. W.

**Two Mixed Anhydromonohydroxybenzoic Acids and their Transformation into Xanthonecarboxylic Acids.** R. ANSCHÜTZ, W. STOLTENHOFF, and F. VOELLER (*Ber.*, 1925, 58, [B], 1736—1741; cf. Anschütz and Claasen, A., 1922, i, 456).—2-*p*-Tolyloxybenzoic acid,  $C_6H_4Me \cdot O \cdot C_6H_4 \cdot CO_2H$ , m. p. 126° (*silver*

salt), is oxidised by permanganate to *anhydro-o: p'-hydroxybenzoic acid (diphenyl ether 2:4'-dicarboxylic acid)*, m. p. 220°, which gives *silver, copper, and calcium* (monohydrate and anhydrous) salts: *methyl ester*, m. p. 72.5°; *ethyl ester*, b. p. 229°/19 mm.; *dichloride*, m. p. 165°; *diamide*, m. p. 238°; *dianilide*, m. p. 215°. The acid is converted by concentrated sulphuric acid, thionyl chloride, or acetyl chloride into *xanthone-2-carboxylic acid*,



the *silver, copper* (monohydrate and anhydrous), and *calcium* salts, *methyl ester*, m. p. 185°, *ethyl ester*, m. p. 152°, *chloride*, m. p. 173°, *amide*, m. p. about 324° (decomp.), and *anilide*, m. p. 271°, are described.

In a similar manner, *2-m-tolyloxybenzoic acid*, m. p. 95°, is oxidised to *anhydro-o:m'-hydroxybenzoic acid (diphenyl ether 2:3'-dicarboxylic acid)*, m. p. 215° (*silver and copper* salts; *methyl ester*, m. p. 92°; *ethyl ester*, b. p. 181°/15 mm., m. p. 44°; *dichloride*; *diamide*, m. p. 264°; *dianilide*, m. p. 232°). *Xanthone-1(?3)-carboxylic acid*, m. p. 312°, is prepared in 25% yield by the action of oxalic acid on a solution of the anhydro-acid in *s-tetrachloroethane* at 100–140°; the *copper salt* (anhydrous and monohydrate), *silver salt*, and the *methyl ester*, m. p. 212°, are described.

H. W.

**Mercury Compounds of *o*-Thiolbenzoic Acid.** G. SACHS and H. BLESSL (*Ber.*, 1925, **58**, [B], 1493–1499).—Cryoscopic measurements of the mol. wt. of ethylthiolmercuriacetate,  $\text{SEt}\cdot\text{Hg}\cdot\text{OAc}$ , in aqueous solution have led Smith and Semon (*A.*, 1924, ii, 763) to the conclusion that the compound probably has the structure  $\left[ \text{Hg} \begin{array}{c} \text{SEt} \\ \diagup \quad \diagdown \\ \text{SEt} \end{array} \text{Hg} \right] (\text{OAc})_2$ ; the conclusion does not seem entirely justified, since mol. wt. determinations are generally untrustworthy for substances of this class (cf. Steinkopf, Bielenberg, and Augestad-Jensen, *A.*, 1923, i, 125), and, in the present instance, the mol. wt. varies considerably with the concentration of the solution. The mercury derivatives of *o*-thiolbenzoic acid have therefore been examined in the hope of discriminating by chemical

means between the possible structures  $\text{C}_6\text{H}_4 \begin{array}{c} \text{S}^- \\ \diagup \quad \diagdown \\ \text{CO}_2 \end{array} \text{Hg}$  or  $\left[ \text{C}_6\text{H}_4 \begin{array}{c} \text{S}^- \\ \diagup \quad \diagdown \\ \text{CO}_2 \end{array} \text{Hg} \right]_n$  and  $\text{C}_6\text{H}_4 \begin{array}{c} \text{S}-\text{Hg}-\text{S} \\ \diagup \quad \diagdown \\ \text{CO}_2 \cdot \text{Hg} \cdot \text{CO}_2 \end{array} \text{C}_6\text{H}_4$ .

*Mercuribis-o-thiolbenzoic acid*,  $\text{Hg}(\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , m. p. 256°, is prepared by the action of mercuric cyanide on *o*-thiolbenzoic acid in aqueous or alcoholic solution; the *potassium, ammonium, and copper* salts are described. *o*-Thiolbenzoic acid or potassium mercuribis-*o*-thiolbenzoate is converted by mercuric acetate into the *anhydride*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{S}^- \\ \diagup \quad \diagdown \\ \text{CO}_2 \end{array} \text{Hg}$ , which, under definite conditions, may be obtained in the crystalline state. It is converted by boiling sodium chloride solution into *o*-chloromercurithiolbenzoic acid.

The latter compound is converted by concentrated ammonia into the substance  $C_{14}H_{16}O_6N_2S_2Hg_2$ , decomp.  $206^\circ$ . H. W.

**Steric Series. VI. Configuration of Mandelic Acid.** K. FREUDENBERG and L. MARKERT (*Ber.*, 1925, **58**, [B], 1753—1760).—If conditions are so chosen that the influence of the solvent is excluded as far as possible (cf. Freudenberg and Rhino, A., 1924, i, 1173), it is found that the hypothesis of the similar effect of like changes on the rotation of analogous compounds of similar configuration is confirmed. Measurements on optically active mandelic acid and its derivatives under these conditions confirm the position of *l*-mandelic acid among the  $\alpha$ -hydroxy-acids of the *d*-series (cf. Freudenberg, Brauns, and Siegel, A., 1923, i, 215). Additional confirmation is deduced from the results of Wood and Comley (this vol., ii, 264) and Wood, Such, and Scarf (T., 1923, **123**, 600). The following substances do not appear to have been described previously: *methyl l*-acetylmandelate, from methyl *l*-mandelate, acetic anhydride, and pyridine, b. p.  $100^\circ/1$  mm.; *methyl dl*-acetylmandelate, b. p.  $100^\circ/1$  mm.; *methyl dl*-benzoylmandelate, m. p.  $76^\circ$ ; *methyl l*-benzoylmandelate, b. p.  $165^\circ/2$  mm.; *ethyl dl*-benzoylmandelate, b. p.  $166^\circ/2$  mm.; *ethyl l*-benzoylmandelate, b. p.  $166^\circ/2$  mm.; *methyl dl*-cinnamoylmandelate, m. p.  $81^\circ$ ; methyl *l*-cinnamoylmandelate is a liquid which becomes completely racemised during distillation (b. p.  $208^\circ/2$  mm.); *ethyl dl*-cinnamoylmandelate, m. p.  $59^\circ$ ; *methyl dl*- $\beta$ -phenylpropionylmandelate, m. p.  $65^\circ$ ; *methyl l*- $\beta$ -phenylpropionylmandelate, m. p.  $34^\circ$ ; *ethyl dl*- $\beta$ -phenylpropionylmandelate, b. p.  $182^\circ/2$  mm.; *ethyl l*- $\beta$ -phenylpropionylmandelate, b. p.  $172^\circ/1$  mm.; *d*(-)-hexahydromandelic acid, m. p.  $129^\circ$ ; *methyl d*(-)-acetylhexahydromandelate, b. p.  $87$ — $88^\circ/0.5$  mm.; *methyl d*(-)-benzoylhexahydromandelate, b. p.  $127$ — $128^\circ/0.5$  mm.; *methyl d*(-)- $\beta$ -phenylpropionylhexahydromandelate, b. p.  $161$ — $162^\circ/0.5$  mm.; *methyl d*(-)-*p*-toluenesulphonylhexahydromandelate, b. p.  $187^\circ/0.5$  mm. The mandelic acid derivatives are prepared from the laevorotatory acid from amygdalin. The rotations of the optically active compounds for the wave-lengths 637, 578, 546, and 434 are recorded, the materials being superfused or dissolved in a variety of solvents. H. W.

**Structure of  $\alpha$ -Campholytic Acid. Correction.** J. P. C. CHANDRASENA, C. K. INGOLD, and J. F. THORPE (*J. Chem. Soc.*, 1925, **127**, 1677—1678).—The structure  $CMe_2 \begin{matrix} < CHMe & \text{---} & CO \\ & & & CH(CO_2H) \cdot O \end{matrix}$ , assigned by the authors (T., 1922, **121**, 1542) to the lactonic acid derived by the oxidation of campholytic acid was based on its identity with that prepared by Pandya and Thorpe (T., 1923, **123**, 2865), who assigned this structure to it through a misstatement by Balbiano, now corrected (this vol., i, 884). The lactonic acid has actually the structure  $CMe_2 \begin{matrix} < CMe(CO_2H) \cdot O \\ & & & CH_2 & \text{---} & CO \end{matrix}$ , the evidence for the formula for campholytic acid being thus still ambiguous.

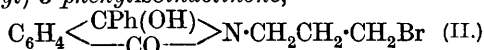
F. G. W.



**Carboxycamphoranic Acids.** M. SINGH and R. SINGH (*J. Chem. Soc.*, 1925, **127**, 1966—1968).—By heating anthranilic acid, camphoric anhydride, and sodium acetate at 125—130°, there is produced 2'-carboxycamphoranic acid (+3H<sub>2</sub>O and anhydrous), m. p. 75—80°, followed by solidification and remelting at 199—200°,  $[M]_D -584^\circ$  in methyl alcohol. Similarly, from *m*-aminobenzoic acid at 160° is formed 3'-carboxycamphoranic acid, m. p. 249°,  $[M]_D +466^\circ$  in methyl alcohol (yield quantitative), whilst *p*-aminobenzoic acid at 140—145° gives 4'-carboxycamphoranic acid (+H<sub>2</sub>O and anhydrous), m. p. 149—150°, followed by solidification and remelting at 212°,  $[M]_D +860^\circ$  in methyl alcohol (yield 95%). The carboxycamphoranic acids are stable, and attempts to convert them into camphorimides have been unsuccessful. In each of four solvents examined, the optical rotations of the acids are in the order  $p > m > o$ , whilst for a given acid the rotation diminishes with decrease in the dielectric constant of the solvent.

F. M. H.

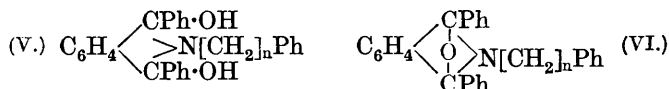
**Compounds obtained by the Action of Magnesium Phenyl Bromide on  $\beta$ -Bromoethylphthalimide and  $\gamma$ -Bromopropylphthalimide.** M. KOHN and R. LAKNER (*Monatsh.*, 1925, **45**, 617—630).—Magnesium phenyl bromide reacts with  $\beta$ -bromoethylphthalimide in ethereal suspension (cf. Sachs and Ludwig, A., 1904, i, 266) with formation of 3-hydroxy-2-( $\beta$ -bromoethyl)-3-phenylisoindolinone,  $C_6H_4 \langle \begin{smallmatrix} \text{CPh(OH)} \\ \text{CO} \end{smallmatrix} \rangle N \cdot CH_2 \cdot CH_2Br$  (I), m. p. 189—191°. This yields, on treatment with pyridine, a *pyridinium bromide*, from which the corresponding *picrate* and *chloroaurate* were prepared.  $\gamma$ -Bromopropylphthalimide affords similarly 3-hydroxy-2-( $\gamma$ -bromopropyl)-3-phenylisoindolinone,



m. p. 169—171°, from which the corresponding *pyridinium bromide* and *chloroaurate* were obtained. Methyl-alcoholic sodium methoxide and ethyl-alcoholic sodium ethoxide convert (I) and (II) into the *anhydrides* (III), m. p. 148°, and (IV), m. p. 126—128°, respectively. Boiling aqueous 20% potassium hydroxide also



converts (II) into the anhydride, but dissolves (I) with formation of *o*-benzoylbenzoic acid. Each of the above anhydrides reacts with 2 mols. of magnesium phenyl bromide, one of which adds on to the carbonyl group, whilst the other opens the anhydride ring. The primary dihydroxy products (V) ( $n=2$  or 3) then lose water



with formation of the inner *anhydrides* (VI), m. p. 172° and 194°, respectively.

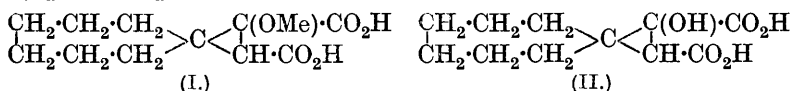
F. G. W.

**3-Nitrophthalic Anhydride as a Reagent for Alcohols.**

B. H. NICOLET and J. SACKS (*J. Amer. Chem. Soc.*, 1925, **47**, 2348—2350).—3-Nitrophthalic anhydride on warming with half its weight of an alcohol readily yields a 2-monoalkyl ester. These esters crystallise well from water and can be used for the identification of the lower monohydric alcohols. All the monoalkyl nitrophthalates with m. p. close to one another yield mixtures with much lower m. p. When dilute alcoholic solutions are to be tested, the alcohol should be salted out with potassium carbonate as the reagent reacts rapidly with water. The following solubilities are given for 3-nitrophthalates at 20° (g. per 100 g. water): 2-methyl ester, 0.185 (monohydrate, 0.200); 2-ethyl ester, 0.290; 2-*n*-propyl, m. p. 141—142° (cf. Cohen, T., 1916, **109**, 233), 0.114; 2-isopropyl, m. p. 152—153°, 0.082; 2-*n*-butyl, m. p. 146—147°, 0.051; 2-iso-butyl, m. p. 182—183° (cf. Cohen, *loc. cit.*), 0.024; and 2-isoamyl, 0.024.  
R. B.

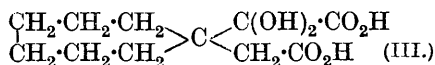
**Monoimide of Perylenetetracarboxylic Acid and its Derivatives.** KALLE UND Co. A.-G. (D.R.-P. 411217, addn. to D.R.-P. 394794; from *Chem. Zentr.*, 1925, i, 2514).—The *monoimide* of tetrachloroperylene-tetracarboxylic acid, from the corresponding di-imide, is a scarlet powder which with sulphuric acid at high temperatures yields tetrachloroperylene-tetracarboxylic anhydride.  
R. B.

**Formation and Stability of *spiro*-Compounds. XII. Further Evidence for the Multiplanar Configuration of the *cyclo*Heptane Ring.** J. W. BAKER (*J. Chem. Soc.*, 1925, **127**, 1678—1682).—Hydrolysis of ethyl  $\alpha\alpha'$ -dibromocycloheptane-1:1-diacetate (cf. Baker and Ingold, T., 1923, **123**, 122) with boiling methyl-alcoholic potassium hydroxide affords cycloheptanespiro-1-methoxycyclopropane-1:2-dicarboxylic acid (I), m. p. 165°, whilst hydrolysis with boiling 64% aqueous potassium hydroxide yields about 1% of the corresponding hydroxy-acid (II), a large proportion of the *hydrated keto-acid* (III), liquid, and a liquid lactonic by-product, probably identical with that obtained by hydrolysing



(I.)

(II.)



(III.)

the bromolactone with concentrated potassium hydroxide solution (cf. Baker and Ingold, *loc. cit.*). Hydrolysis of (I) with hydrobromic acid affords a small proportion of *cycloheptanespirocyclopropane*-1:2-dicarboxylic acid, together with (III), of which the *silver* salt is described, and yields, when treated with semicarbazide acetate in presence of sodium acetate, the *monosodium* salt, decomp. at 235°, or the *disodium* salt, decomp. at 240°, of a *semicarbazido-acid*. The strongly acid character of the latter probably explains the failure to prepare semicarbazones of the ketoglutaric acids, the

semicarbazido-acids of which may form sodium salts too soluble to separate from the reaction mixtures. It appears, therefore, that in presence of hot, concentrated alkalis a tautomeric equilibrium exists between the hydroxy-ring acid and the keto-acid, in which the open-chain form is greatly favoured, and the results are taken to indicate that the *cycloheptane* ring is nearly strainless, as previously suggested (*loc. cit.*).

The acid given as 2-carboxy*dicyclo*-[3, 1, 0]heptane-1-acetic acid, m. p. 186° (see this vol., i, 917), has now been found to be a lactonic acid derived by hydrolytic fission of the 3-membered ring.

F. G. W.

[Behaviour of] Aldehydes and Ethylene Oxide in the Friedel-Crafts Synthesis. A. SCHAARSCHMIDT, L. HERMANN, and B. SZEMZÖ (*Ber.*, 1925, 58, [B], 1914—1916).—The action of aluminium chloride on a mixture of benzaldehyde and benzene yields anthracene (30%) and triphenylmethane (21%), whereas in the presence of anhydrous ferric chloride the yields of anthracene and triphenylmethane are 6% and 30%, respectively. *iso*Valeraldehyde and benzene in the presence of aluminium chloride afford  $\delta\delta$ -diphenyl- $\beta$ -methyl- $\Delta\gamma$ -butene together with saturated products. The action of gaseous ethylene oxide and hydrogen chloride on a suspension of aluminium chloride in benzene gives dibenzyl (40%) and  $\beta$ -phenylethyl alcohol (1%).

H. W.

Beckmann's Rearrangement. XIII. Catalytic Action of Reduced Copper on Benzaldoximes. S. YAMAGUCHI (*Mem. Coll. Sci. Kyōtō*, 1925, 9, [A], 33—36).—Aldoximes, as well as ketoximes, undergo the Beckmann rearrangement, forming acid amides when treated with a suitable reagent. Thus  $\alpha$ -benzaldoxime, passed with hydrogen over reduced copper at 200°, yielded principally benzamide, with benzoic acid, benzonitrile, benzaldehyde, benzylamine, and ammonia in smaller amounts.  $\beta$ -Benzaldoxime behaves similarly, probably being first transformed into the  $\alpha$ -isomeride.

B. W. A.

Supposed Formation of Carbon from Piperonyl Derivatives. P. PASCAL (*Bull. Soc. chim.*, 1925, [iv], 37, 1043—1045).—The black carbonaceous deposit formed by heating piperonal or piperonylic acid with dilute hydrochloric acid at 200° (Fittig and Remoen, *Annalen*, 1871, 159, 129; 1873, 168, 96) is not pure carbon as Fittig and Remsen supposed, but a carbonaceous resin, representing a yield of 30—35%, produced as a result of a "bakelite" process of condensation from the formaldehyde and diphenol first formed.

R. B.

Substitution in Derivatives of Quinol Ethers. L. RUBENSTEIN (*J. Chem. Soc.*, 1925, 127, 1998—2004; cf. T., 1923, 123, 2830; 1924, 125, 2355).—The nitration and bromination of substances having the formula,  $C_6H_3(OR)_2 \cdot CHO[CHO:OR:OR=1:2:5]$ , in which only *ortho* substitution with respect to the alkyloxy groups can take place, have been examined. When 2-hydroxy-5-methoxybenzaldehyde, b. p. 124°/12 mm. (prepared by the action of aqueous

sodium hydroxide and chloroform on quinol monomethyl ether, and purified through the hydrogen sulphite compound), is nitrated, the product is regarded as 3-nitro-2-hydroxy-5-methoxybenzaldehyde (I), m. p. 132° (p-nitrophenylhydrazone, decomp. 250°), because the product of methylation by means of methyl iodide and silver oxide in presence of chloroform, 3-nitro-2:5-dimethoxybenzaldehyde, m. p. 113°, is reconverted by hydrolysis into (I). Bromination of 2-hydroxy-5-methoxybenzaldehyde yields 3-bromo-2-hydroxy-5-methoxybenzaldehyde (II), m. p. 107° (p-nitrophenylhydrazone, decomp. above 250°); treatment of an alcoholic solution with methyl p-toluenesulphonate and sodium hydroxide gives 3-bromo-2:5-dimethoxybenzaldehyde (III), m. p. 63°. The identity of (II) is established because 3-nitro-2:5-dimethoxybenzaldehyde is oxidised by potassium permanganate to 3-nitro-2:5-dimethoxybenzoic acid, m. p. 182—183°, which is reduced with hydrochloric acid and tin to 3-amino-2:5-dimethoxybenzoic acid (blackens at 170°, decomp. 210—215°; the hydrochloride darkens at 170°, decomp. 215°), and this yields 3-bromo-2:5-dimethoxybenzoic acid, m. p. 132°, which is also obtained by oxidation of (III). Nitration of 2:5-dimethoxybenzaldehyde gives 3-nitro-2:5-dimethoxybenzaldehyde (20%) and 6-nitro-2:5-dimethoxybenzaldehyde, m. p. 159° (80%) [p-nitrophenylhydrazone, m. p. 245—250° (decomp.)], in which the nitro group is shown to be in the *ortho* position to the aldehyde group, since with acetone and alkali 4:4':7:7'-tetramethoxyindigotin (sublimes at 350°) is formed; oxidation of 6-nitro-2:5-dimethoxybenzaldehyde gives 6-nitro-2:5-dimethoxybenzoic acid, m. p. 192°. Bromination of 2:5-dimethoxybenzaldehyde gives 6-bromo-2:5-dimethoxybenzaldehyde, m. p. 125—126° (p-nitrophenylhydrazone, m. p. 204—206°), which may be oxidised to 6-bromo-2:5-dimethoxybenzoic acid, m. p. 164—165°.

Nitration of 2:5-dimethoxyacetanilide yields 4-nitro-2:5-dimethoxyacetanilide, m. p. 165°, the identity of which is established, since on hydrolysis it forms 4-nitro-2:5-dimethoxyaniline, m. p. 153° [hydrochloride, m. p. 160° (decomp.)], of which the hydrobromide on diazotisation and treatment with cuprous bromide yields 2-bromo-5-nitroquinol dimethyl ether (also prepared by bromination of nitroquinol dimethyl ether). Bromination of 2:5-dimethoxyacetanilide yields 4-bromo-2:5-dimethoxyacetanilide, m. p. 122°, which on hydrolysis forms 4-bromo-2:5-dimethoxyaniline, m. p. 106° (hydrochloride becomes blue at 160°, decomp. above 300°, hydrobromide discolours at 160°), which is converted by diazotisation and treatment with cuprous bromide into 2:5-dibromoquinol dimethyl ether (also prepared by bromination of quinol dimethyl ether).

F. M. H.

**Substitution in the Benzene Nucleus. Varying Influence of certain Alkoxy Groups on the Synthesis of Aldehydes by Means of Hydrocyanic Acid.** A. SONN and E. PATSCHKE (*Ber.*, 1925, 58, [B], 1698—1703).—The orienting influence of the ethoxy, propoxy, allyloxy, and benzyloxy groups in comparison with that of the methoxy radical on the introduction of the aldehyde group

into the benzene nucleus has been examined by submitting various alkylated resorcinol methyl ethers to the Gattermann process and determining the solidifying point of the product. The orienting power of the groups is found to diminish in the order allyloxy, ethoxy, *n*-propoxy, methoxy, from which it appears that maximum action is shown by those ethereal groups in which the alkyl radical makes the smallest valency demand on the oxygen. The effect of the benzyl group cannot be observed, since partial hydrolysis occurs during the treatment of the aldimine hydrochloride with hot water.

The following compounds have not been described previously: 3-benzyloxyanisole, b. p. 186°/14 mm., m. p. 31—32°; 2-methoxy-4-ethoxybenzaldehyde, m. p. 58—59°, from 4-hydroxy-2-methoxybenzaldehyde, ethyl bromide, and sodium ethoxide; 4-methoxy-2-ethoxybenzaldehyde, m. p. 64—65°; 2-methoxy-4-*n*-propoxybenzaldehyde, m. p. 45°; 4-methoxy-2-*n*-propoxybenzaldehyde, m. p. 37°; 2-methoxy-4-allyloxybenzaldehyde, m. p. 47—48°; 4-methoxy-2-allyloxybenzaldehyde, m. p. 38°; 2-methoxy-4-benzyloxybenzaldehyde, m. p. 95°; 4-methoxy-2-benzyloxybenzaldehyde, m. p. 67°. H. W.

**Derivatives of cycloHexanone.** C. E. GARLAND and E. E. REID (*J. Amer. Chem. Soc.*, 1925, 47, 2333—2340).—Unsaturated 2 : 6-disubstituted cyclohexanones have been obtained in 60—70% yield by the condensation of cyclohexanone with 2 mols. of *p*-tolualdehyde, 2 : 4-dimethyl-, and *p*-bromo-benzaldehyde in alcoholic sodium hydroxide. Mono-substitution products are also formed, but are very difficult to isolate, as the second substitution appears to have a higher reaction velocity than the first. The new 2 : 6-cyclohexanone derivatives resemble the compounds obtained by condensing aromatic aldehydes with aliphatic ketones, but are less soluble in cold organic solvents. Their orange-yellow colour is probably due to the chromophoric effect of the double bonds on the carbonyl group. The unsaturated ketones show halochromism, but this property disappears on reduction to the corresponding saturated ketones, which are colourless. Neither the unsaturated nor the saturated ketones react with semicarbazide, possibly owing to the presence of heavy groups on both sides of the carbonyl (cf. Haller, A., 1923, i, 92). Attempts to condense propaldehyde, butaldehyde, and heptaldehyde with cyclohexanone were unsuccessful, the aldehydes condensing only with themselves. A further series of derivatives was obtained by the action of methyl and ethyl Grignard reagents on cyclohexylidenecyclohexanone, and dehydration of both the unsaturated tertiary alcohols and the saturated derivatives. The unsaturated hydrocarbons were finally reduced to the cyclohexylcyclohexane.

cycloHexylidenecyclohexanone, b. p. 273—275°/760, 150—152°/20 mm.,  $d^{18}_4$  1.005,  $n^{18}_D$  1.5082, was obtained by Wallach's method; the crystalline intermediate additive compound has m. p. 41—43°. 2 : 6-Di-*p*-methylbenzylidenecyclohexanone has m. p. 170.1°; 2 : 6-di-2' : 4'-dimethylbenzylidenecyclohexanone, m. p. 115.5°; 2 : 6-di-*p*-bromobenzylidenecyclohexanone, m. p. 155.7°. 2-Furfurylidene-

6-cyclohexylidenecyclohexanone, m. p.  $80^{\circ}$ , was similarly obtained from cyclohexylidenecyclohexanone and furfuraldehyde. The *tetra-bromo* derivative of 2:6-dibenzylidenecyclohexanone has m. p.  $184^{\circ}$  (decomp.). On reduction with platinum oxide catalyst in 95% alcohol (Adams and Voorhees, A., 1922, ii, 558), 2:6-dibenzylidenecyclohexanone yields 2:6-dibenzylcyclohexanone, m. p.  $121^{\circ}$  (cf. Borsche, A., 1912, i, 194). 2:6-Di-*p*-methylbenzylcyclohexanone, m. p.  $111.8^{\circ}$ ; 2:6-di-2':4'-dimethylbenzylcyclohexanone, m. p.  $105^{\circ}$ ; 2:6-di-*p*-chlorobenzylcyclohexanone, m. p.  $143^{\circ}$ ; 2:6-dianisylcyclohexanone, m. p.  $157^{\circ}$ ; and 2:6-dipiperonylcyclohexanone, m. p.  $146^{\circ}$ , were similarly obtained.

cycloHexylidenecyclohexanone on treatment with methyl Grignard reagent for 3 days gives on decomposition in the usual way 1-methyl-2-cyclohexylidenecyclohexanol, b. p.  $146\text{--}148^{\circ}/20\text{ mm.}$ ,  $d_4^{20}$  0.9841. 1-Ethyl-2-cyclohexylidenecyclohexanol, b. p.  $155\text{--}157^{\circ}/20\text{ mm.}$ ,  $d_4^{20}$  0.9863, is similarly obtained. Both tertiary alcohols yield acetates which are readily dehydrated, and with diphenylcarbamide chloride in pyridine are themselves dehydrated. Reduction by Adams and Voorhees' method yields 1-methyl-2-cyclohexylcyclohexanol, b. p.  $148.5\text{--}150^{\circ}/20\text{ mm.}$ ,  $d_4^{20}$  0.9719, and 1-ethyl-2-cyclohexylcyclohexanol, b. p.  $154\text{--}156^{\circ}/20\text{ mm.}$ ,  $d_4^{20}$  0.9778, respectively, whilst on dehydration with phthalic anhydride at  $165\text{--}170^{\circ}$  they yield 1-methyl-6-cyclohexylidene- $\Delta^1$ -cyclohexene, b. p.  $130\text{--}132^{\circ}/20\text{ mm.}$ ,  $d_4^{20}$  0.9282, and 1-ethyl-6-cyclohexylidene- $\Delta^1$ -cyclohexene, b. p.  $139\text{--}141^{\circ}/20\text{ mm.}$ ,  $d_4^{20}$  0.9308. 1-Ethyl-6-cyclohexyl- $\Delta^1$ -cyclohexene, b. p.  $141\text{--}143^{\circ}$ ,  $d_4^{20}$  0.9274, is similarly obtained from the corresponding cyclohexylcyclohexanol. On hydrogenation by Adams and Voorhees' method, these unsaturated hydrocarbons yield 1-methyl-2-cyclohexylcyclohexane, b. p.  $131\text{--}133.5^{\circ}/20\text{ mm.}$ ,  $d_4^{20}$  0.9058, and 1-ethyl-2-cyclohexylcyclohexane, b. p.  $141\text{--}142.5^{\circ}$ ,  $d_4^{20}$  0.9126. R. B.

**Reaction of 2-Benzylhydrindonephenylhydrazine with Phenylhydrazine.** H. LEUCHS and K. WINZER (*Ber.*, 1925, 58, [B], 1520—1527).—The compound  $C_{28}H_{25}N_3$ , obtained by the action of an excess of phenylhydrazine on 2-benzyl-1-hydrindone at  $130^{\circ}$  (cf. A., 1913, i, 855), is converted by boiling acetic anhydride into a diacetyl derivative,  $C_{26}H_{23}O_3N$ , m. p.  $155\text{--}157^{\circ}$ , with loss of a phenylhydrazine residue. When boiled with the requisite alcohol, it loses an acetyl group with formation of the acetylmethoxy compound,  $C_{25}H_{23}O_2N$ , m. p.  $164\text{--}166^{\circ}$ , and the acetyloxy derivative,  $C_{26}H_{25}O_2N$ , m. p.  $125\text{--}127^{\circ}$ . The diacetyl or acetylmethoxy compound is converted by acetic acid, hydrochloric acid, or phenylhydrazine into the monoacetylhydroxy derivative,  $C_{24}H_{21}O_2N$ , m. p.  $196\text{--}198^{\circ}$ . The mono- or di-acetyl or the acetylmethoxy compounds are readily halogenated, yielding the compounds  $C_{24}H_{20}O_2NBr$ , m. p.  $251\text{--}253^{\circ}$  after softening at  $246^{\circ}$ ,  $C_{24}H_{20}O_2NCl$ , m. p.  $238^{\circ}$ , and  $C_{24}H_{19}O_2NCl_2$ , m. p.  $265^{\circ}$ , in which the halogen is attached to an aromatic nucleus. Similarly, benzoylation of the compound  $C_{28}H_{25}N_3$  gives dibenzoylphenylhydrazine and the dibenzoyl compound,  $C_{36}H_{27}O_3N$ , m. p.  $191\text{--}193^{\circ}$ , which

is converted into the *benzoylmethoxy* derivative,  $C_{30}H_{25}O_2N$ , m. p. 163—164°, and a *monobenzoylhydroxy* compound,  $C_{29}H_{23}O_2N$ , m. p. 160—161°, and a *bromide*,  $C_{29}H_{22}O_2NBr$ , m. p. 208—209°. On the other hand, phthalic anhydride gives a *monophthaloyl* derivative,  $C_{30}H_{21}O_3N$ , m. p. 256—258°.

The compound  $C_{28}H_{25}N_3$  is converted by concentrated hydrochloric acid into phenylhydrazine and a *base*,  $C_{22}H_{17}N$ , m. p. (anhydrous) 123—124°, m. p. (+H<sub>2</sub>O) 110—115° [*hydrochloride*, m. p. 206—208° (decomp.)]. The base contains a double linking; it is converted by acetic anhydride or phthalic anhydride into the diacetyl or phthaloyl compound described above and by phenylhydrazine into the substance  $C_{28}H_{25}N_3$ . It is also obtained by the action of concentrated hydrochloric acid on 2-benzylhydrindone-phenylhydrazone. It therefore appears that the base  $C_{22}H_{17}N$  is formed primarily from the phenylhydrazone by a type of indole

synthesis and the constitution  $\begin{array}{c} \text{CH}_2-\text{CH}\cdot\text{CHPh} \\ | \quad \quad | \\ \text{C}_6\text{H}_4\cdot\text{C}=\text{N} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array}$  is assigned to it, since the benzyl group appears to be involved. Subsequent addition of phenylhydrazine yields the compound  $C_{28}H_{25}N_3$ .  
H. W.

### Condensation of Aldehydes with Methyl Ethyl Ketone.

H. RYAN and J. J. LENNON (*Proc. Roy. Irish Acad.*, 1925, **37** B, 27—36; cf. Harries and Müller, A., 1902, i, 295; Ryan and Dunlea, A., 1915, i, 416).— $\alpha$ -Phenyl- $\beta$ -methyl- $\Delta^a$ -buten- $\gamma$ -one condenses with benzaldehyde in alkaline media yielding 3 : 4-diphenyl-5-methyl- $\Delta^2$ -cyclopenten-1-one, m. p. 57—58.5°, *dibromide*, m. p. 136—137°, which on treatment with acid yields 3 : 4-diphenyl-5-methyl- $\Delta^3$ -cyclopenten-1-one (Japp and Meldrum, T., 1901, **79**, 1033). Both these compounds on further condensation with benzaldehyde yield 2-benzylidene-3 : 4-diphenyl-5-methyl- $\Delta^3$ -cyclopenten-1-one (Ryan and Devine, A., 1916, i, 654). Anisaldehyde condenses with  $\alpha$ -phenyl- $\beta$ -methyl- $\Delta^a$ -buten- $\gamma$ -one, giving 4-phenyl-3-anisyl-5-methyl- $\Delta^2$ -cyclopenten-1-one, m. p. 120—121°, which in turn condenses with anisaldehyde, giving 4-phenyl-3-anisyl-2-anisylidene-5-methyl- $\Delta^3$ -cyclopenten-1-one, m. p. 97.5—98.5°.  $\alpha$ -Phenyl- $\beta$ -methyl- $\Delta^a$ -buten- $\gamma$ -one condenses with piperonal, yielding 3-piperonyl-4-phenyl-5-methyl- $\Delta^2$ -cyclopenten-1-one, m. p. 113—114°, which gives 2-piperonylidene-4-phenyl-3-anisyl-5-methyl- $\Delta^3$ -cyclopenten-1-one, m. p. 225—226°.  
L. F. H.

### Photodimerides of Derivatives of $\gamma$ -Ketopentadienes.

H. STOBBE, E. FÄRBER, and F. RAU (*Ber.*, 1925, **58**, [B], 1548—1553).—Bisdistyryl ketone (Praetorius and Korn, A., 1910, i, 859) is readily depolymerised to distyryl ketone when heated somewhat above 248°, treated with concentrated sulphuric acid at the atmospheric temperature, with moistened trichloroacetic acid at 25°, or exposed to the light of the mercury vapour lamp. Di-*p*-methoxystyryl ketone is also polymerised, whereas its additive compound with uranyl chloride (Praetorius and Korn, *loc. cit.*) or with stannic

*chloride*, m. p.  $173^{\circ}$ , does not appear to yield a dimeride when exposed to light. Towards chemical reagents, the methoxy compound appears also to be more stable than distyryl ketone.

Methyl  $\gamma$ -ketopentadienedicarboxylate (cf. Straus, A., 1904, i, 851) is readily converted by light into a *dimeride*, m. p.  $239$ – $240^{\circ}$ , which is not oxidised by permanganate and does not absorb bromine and to which the constitution

$$\begin{array}{c} \text{CO}_2\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me} \\ \text{CO}_2\text{Me}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me} \end{array}$$

is therefore assigned. Under analogous conditions, ethyl  $\gamma$ -ketopentadienedicarboxylate appears to suffer profound oxidative fission.

H. W.

### Polymerisation of Cinnamylideneacetophenone Derivatives.

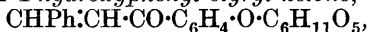
M. GIUA (*Gazzetta*, 1925, 55, 567–576; cf. A., 1921, i, 730).—In aqueous-alcoholic solution, under the influence of sodium hydroxide, cinnamaldehyde condenses with *m*-nitroacetophenone to give *cinnamylidene-m-nitroacetophenone*, m. p.  $135$ – $136^{\circ}$ ; its *tetrabromide*, m. p.  $203$ – $204^{\circ}$  (decomp.), is also described. Similarly, *p-methoxycinnamylidene-m-nitroacetophenone*, m. p.  $157$ – $158^{\circ}$ , is prepared. When a 10% chloroform solution of the last compound was exposed for 15 days to sunlight or to ultra-violet rays from a mercury vapour lamp for 12 hrs., a semi-solid substance was obtained which slowly became a resin with a fracture like that of colophony; it melted at  $65$ – $70^{\circ}$ , swelling up. In this resinification *cinnamylidene-m-nitroacetophenone* resembles *cinnamylidene-p-aminoacetophenone*, but is in contrast with *cinnamylideneacetophenone*, which, under the action of light, polymerises (Stobbe and Rücker, A., 1911, i, 385). Although at present no general hypothesis is advanced, it is suggested that the groups  $-\text{NO}_2$  and  $-\text{NH}\cdot\text{CO}\cdot\text{Me}$  act as resinophores.

[With G. GUASTALLA.]—The binary systems of *cinnamylideneacetophenone* with the following substances are described: *o*- and *p*-chloronitrobenzene, *p*-bromonitrobenzene, *m*-dinitrobenzene, 1 : 2 : 4-bromodinitrobenzene, *p*-aminoacetophenone, and thymoquinone. From their study it is concluded that *cinnamylideneacetophenone* forms additive compounds only with polynitro aromatic derivatives (cf. Giua, A., 1916, i, 205). W. E. E.

### Glucosides of Chalkones [Phenyl Styryl Ketones].

G. BARGELLINI and P. LEONE (*Atti R. Accad. Lincei*, 1925, [vi], 2, 35–39; cf. A., 1915, i, 19, 62).—By the condensation of various aromatic aldehydes with *p*-hydroxyacetophenone glucoside (piceol) (cf. Tanret, A., 1894, i, 616), the following chalkone glucosides with the glucose residue in the place of the hydroxylic hydrogen of the hydroxyacetophenone have been obtained.

The glucoside of 4-hydroxyphenyl styryl ketone,



prepared from benzaldehyde and tetra-acetyl piceol, m. p.  $195^{\circ}$ ; glucoside of 4-hydroxyphenyl 4-methoxystyryl ketone, from anisaldehyde, m. p.  $183^{\circ}$ ; glucoside of 4-hydroxyphenyl 4-hydroxy-3-methoxystyryl ketone,  $\text{C}_{22}\text{H}_{24}\text{O}_9$ , from vanillin, m. p.  $193^{\circ}$ ; glucoside



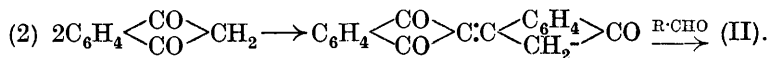
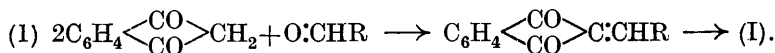
of 4-hydroxyphenyl 3:4-dioxymethylenestyryl ketone,  $C_{22}H_{22}O_9 + H_2O$ , from piperonaldehyde, m. p.  $181^\circ$ ; glucoside of 4-hydroxyphenyl furfurylidenemethyl ketone ( $+H_2O$ ) (all the preceding are yellow); glucoside of p-hydroxyphenyl cinnamylidenemethyl ketone, from cinnamaldehyde, m. p.  $185^\circ$ . T. H. P.

**Interaction of Ethyl Acetoacetate and o-Hydroxydistyryl Ketones.** II. I. M. HEILBRON, T. A. FORSTER, and A. B. WHITWORTH (*J. Chem. Soc.*, 1925, **127**, 2159—2167; cf. A., 1924, i, 1323). —In the condensations examined, cyclohexenones alone are formed. The action of potassium hydroxide on an alcoholic solution of 4'-dimethylamino-2-hydroxydistyryl ketone and ethyl acetoacetate gives ethyl 3-p-dimethylaminophenyl-5-o-hydroxystyryl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate,  $CO_2Et \cdot CH \cdot CO \cdot CH$  (I), m. p.  $196^\circ$  ( $+C_2H_5 \cdot OH$ ,  $+C_6H_6$ , and anhydrous). By oxidation it yields salicylic acid. The acid, m. p.  $225^\circ$ , obtained by alkaline hydrolysis, on boiling with acetic acid and dilute sulphuric acid is converted into 3-p-dimethylaminophenyl-5-o-hydroxystyryl- $\Delta^5$ -cyclohexen-1-one, m. p.  $232^\circ$ . Methylation of (I) in acetone solution (T., 1921, **119**, 1500) gives ethyl 3-p-dimethylaminophenyl-5-o-methoxystyryl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate (II), m. p.  $164^\circ$ . 4:4'-Tetramethyldiaminodistyryl ketone and ethyl acetoacetate condense similarly, giving ethyl 3-p-dimethylaminophenyl-5-p-dimethylaminostyryl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate, m. p.  $174$ — $175^\circ$  (phenylhydrazone, m. p.  $239^\circ$ ), whilst from p-dimethylaminostyryl methyl ketone is obtained ethyl 3-p-dimethylaminophenyl-5-methylcyclohexan-5-ol-1-one-2-carboxylate, m. p.  $149^\circ$  (phenylhydrazone, m. p.  $179^\circ$ ), which when heated with alcoholic sodium hydroxide loses water, forming ethyl 3-p-dimethylaminophenyl-5-methyl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate, m. p.  $66^\circ$ . Thus although the p-dimethylamino group is normally a retarding factor, it does not necessarily rule out the structure (I). The anomalous behaviour is connected with the peculiar activity of the ketone: with 4'-dimethylamino-2-hydroxy-4-methoxydistyryl ketone, in which the "active" properties are suppressed, ethyl acetoacetate yields 3-(2'-hydroxy-4'-methoxy)phenyl-5-p-dimethylaminostyryl- $\Delta^5$ -cyclohexen-1-one, m. p.  $218^\circ$ , in which the carbethoxyl group is eliminated, but the "active" compound 4'-dimethylamino-2-hydroxy-3-methoxydistyryl ketone gives ethyl 3-p-dimethylaminophenyl-5-(2'-hydroxy-3'-methoxy)styryl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate, m. p.  $197$ — $198^\circ$ , and similarly 4'-dimethylamino-2-hydroxy-5-methoxydistyryl ketone gives ethyl 3-p-dimethylaminophenyl-5-(2'-hydroxy-5'-methoxy)styryl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate, m. p.  $196$ — $197^\circ$  ( $+C_6H_6$ ), which is converted by aqueous pyridine into 3-(2'-hydroxy-5'-methoxy)phenyl-5-p-dimethylaminostyryl- $\Delta^5$ -cyclohexen-1-one, m. p.  $250^\circ$ . With 4'-dimethylamino-2-methoxydistyryl ketone two isomerides have been isolated, of which one is (II), and the other is ethyl 3-o-methoxyphenyl-5-p-dimethylaminostyryl- $\Delta^5$ -cyclohexen-1-one-2-carboxylate, m. p.  $114^\circ$ , which is formed by the normal reaction; it is converted by the action of sodium ethoxide and methyl iodide

into *ethyl 1-methoxy-3-o-methoxyphenyl-5-p-dimethylaminostyryl-Δ<sup>1:5</sup>-cyclohexadiene-2-carboxylate*, m. p. 148°.

The point at which ethyl acetoacetate enters the molecule must depend largely on the polar character of the substituent groups and their effect on the doubly-conjugated system. Steric influences may play a part in determining the position taken by the entering group. Thus ethyl acetoacetate may cause the co-ordinated *cis*-form of 4'-dimethylamino-2-hydroxydistyryl ketone to undergo transformation into a *trans*-isomeride. On the other hand, this ketone with ethyl cyanoacetate gives *γ-p-dimethylaminocinnamoyl-β-o-hydroxyphenylpropane-αα'-dicarboxylic acid*, m. p. 220°; treatment of the acid with potassium hydroxide gives *p*-dimethylamino-benzaldehyde but no trace of salicylaldehyde. F. M. H.

**Derivatives of Indandione and Di-indone. I. Mechanism of the Condensation of Indandione with Aldehydes.** D. RADULESCU and V. GEORGESCU (*Bull. Soc. chim.*, 1925, [iv], **37**, 1069—1078).—The course of the condensation of indandione with aldehydes varies both with the nature of the aldehyde and with the condensing agent employed. Aliphatic aldehydes in the presence of potassium hydroxide yield the di-indandionylmethane (I),  $R\cdot CH\left(\text{CH}\left\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\right\rangle C_6H_4\right)_2$ , and the condensation product of the di-indone with the aldehyde (II),  $C_6H_4\left\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\right\rangle C:C\left\langle\begin{smallmatrix} C_6H_4 \\ C(CHR) \end{smallmatrix}\right\rangle CO$ . The mechanism of the reaction in these cases is represented:



The rate of formation of the di-indone is normally very great and hence, except when the rate of formation of the indogenide,  $C_6H_4\left\langle\begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix}\right\rangle C:CHR$ , is also high, the main reaction products will be the condensation products of the di-indone with the aldehyde or with the indogenide, *e.g.*,  $\begin{array}{c} C_6H_4\cdot CO \\ | \\ CO-CH\cdot CHR\cdot CH\cdot C \\ | \quad \quad \quad | \\ CO\cdot C_6H_4 \quad CO\cdot C_6H_4 \end{array}$ . With aromatic aldehydes, the indogenide can add a molecule of water at the double linkage, yielding a carbinol



and in the presence of potassium hydroxide this reaction preponderates. In the presence of piperidine, this addition does not take place and the main product is the indogenide. More complex condensation products of the type  $\begin{array}{c} CO-C \\ | \quad \quad \quad | \\ C_6H_4\cdot C:CR\cdot CH:C\cdot CO \end{array}$  have also been isolated. Benzaldehyde and indandione in nitrobenzene at 110—120° yield a fraction insoluble in alcohol consisting of

benzylidenedi-indone,  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}:\text{C}\langle\text{C}(\text{CHPh})\rangle\text{CO}$ , m. p.  $235^\circ$ ,

a *truxenequinone*,  $\text{C}_6\text{H}_4\cdot\text{C}(\text{CO})=\text{C}(\text{CO})\cdot\text{C}_6\text{H}_4$ , m. p. above  $300^\circ$ , and a

soluble fraction containing benzylideneindandione, m. p.  $151\text{--}152^\circ$  (Wislicenus, A., 1889, 1067; 1894, i, 133), together with (yield 45—50%) the carbinol, *phenylindandionylmethyl alcohol*,  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{CH}\cdot\text{CHPh}\cdot\text{OH}$ , m. p.  $158^\circ$  (potassium salt, red, *phenylurethane*, m. p.  $154\text{--}155^\circ$ ). The benzylideneindandione is obtained in 70—75% yield by condensation in glacial acetic acid, whilst in alcoholic potassium hydroxide the yield of carbinol is almost quantitative. On heating in benzene or toluene, the carbinol is converted into the indogenide, whilst concentrated sulphuric acid converts it quantitatively into benzylideneindandione. The corresponding carbinols obtained from the nitro-, hydroxy-, alkoxy-, and amino-benzaldehydes are unstable and can only be isolated as their salts. The potassium salt of *m*-nitrobenzylideneindandione is described.

Formaldehyde and indandione in the presence of potassium hydroxide yield *di-indandionylmethane*,  $\text{CH}_2(\text{CH}\langle\text{CO}\rangle\text{C}_6\text{H}_4)_2$ , m. p.  $201\text{--}202^\circ$ . The disodium salt,  $\text{C}_{19}\text{H}_{10}\text{O}_4\text{Na}_2$ , and the barium salt,  $\text{C}_{19}\text{H}_{10}\text{O}_4\text{Ba}$ , are described. Similarly, acetaldehyde and indandione in pyridine yield  $\alpha\alpha$ -*di-indandionylethane*,  $(\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{CH})_2\text{CHMe}$ , m. p.  $226\text{--}227^\circ$  (*tetraoxime*, m. p.  $243\text{--}245^\circ$ ), but acetone is the only ketone which condenses with indandione, yielding in the presence of alcoholic potassium hydroxide  $\beta\beta$ -*di-indandionylpropane*,  $\text{CMe}_2(\text{CH}\langle\text{CO}\rangle\text{C}_6\text{H}_4)_2$ , yellow, m. p.  $118\text{--}119^\circ$ , giving green solutions in aqueous alkalis.

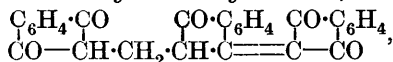
Disubstituted indandiones of the type  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{CR}_2$  do not react with phenylhydrazine, whilst monosubstituted indandiones give coloured hydrazines with reducing properties. Thus di-indandionylmethane yields the *phenylhydrazine*.

$\text{CH}_2(\text{C}\langle\text{CO}\rangle\text{C}(\text{NH}\cdot\text{NHPh})\rangle\text{C}_6\text{H}_4)_2$ ,  
m. p.  $215\text{--}216^\circ$ , whilst with hydrazine hydrate it yields the yellow *hydrazonium* salt,  $\text{CH}_2(\text{C}\langle\text{CO}\rangle\text{C}(\text{ON}_2\text{H}_5)\rangle\text{C}_6\text{H}_4)_2$ , m. p.  $181\text{--}182^\circ$ . Hydroxylamine yields a mixture of insoluble tri- and tetra-oximes, m. p.  $235^\circ$ , exploding at temperatures a little above the m. p.

R. B.

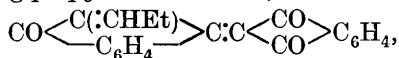
**Derivatives of Indandione and Di-indone. II. Condensation Products of Aldehydes with Di-indone.** D. RADULESCU and V. GEORGESCU (*Bull. Soc. chim.*, 1925, [iv], **37**, 1187—1194).—Indandione and di-indone yield the same condensation products

with aliphatic aldehydes, the rate of condensation of the aldehyde with indandione being negligible in comparison with the rate of auto-condensation of the latter. With formaldehyde in the presence of alkali the product in both cases is *bisdi-indonylmethane*,  $\left( \begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{CO} \quad \text{C}_6\text{H}_4 \cdot \text{CO} \\ \text{CO} - \text{C} = \text{C} - \text{CH} \end{array} \right)_2 \text{CH}_2$ , an olive powder, m. p.  $239^\circ$ , whilst with excess of alkali *indandionyl-di-indonylmethane*,

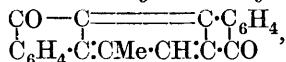


greenish-yellow needles, m. p.  $210-212^\circ$ , is also produced, through the action of alkali on the bisdi-indonylmethane. With phenylhydrazine in methyl alcohol the latter yields the *dihydrazino* derivative of di-indandionylmethane, m. p.  $217-219^\circ$ , and the hydrazone of indandione. In the presence of tertiary or secondary bases, the aromatic alcohols yield the corresponding di-indogenides, whilst with alkalis the aryldi-indonylmethanols are formed. With excess of diketone in the presence of pyridine, the condensation yields products of the type of methenylbisindandione (Errera, A., 1903, i, 265, 854),  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \\ \text{CO} \end{array} > \text{C} : \text{CH} \cdot \text{CH} < \begin{array}{c} \text{CO} \\ \text{CO} \end{array} > \text{C}_6\text{H}_4$ . Indandi-

one or di-indone condenses with propaldehyde in the presence of pyridine, yielding *propylidenedi-indone*,



m. p.  $256-257^\circ$ , which gives a green colour with alkalis and on warming is converted into 5-methyl-o-trans-fluoracenedione

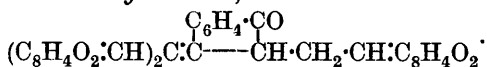


m. p.  $290-291^\circ$ , also obtained directly from propaldehyde and di-indone or indandione by subsequent warming of the condensation product. Similarly, benzaldehyde with di-indone in the presence of pyridine yields *benzylidenedi-indone*, greenish-violet needles, m. p.  $235^\circ$ , and in the presence of potassium hydroxide *phenyldi-indonyl-carbinol*,  $\begin{array}{c} \text{CO} - \text{CH} \cdot \text{CHPh} \cdot \text{OH} \\ \text{C}_6\text{H}_4 \cdot \text{C} : \text{C} \cdot \text{C}_8\text{H}_4\text{O}_2 \end{array}$ , yellow powder, m. p.  $238^\circ$  with

decomp. to benzylidenedi-indone. With 4 mols. of indandione in the presence of pyridine *phenylindandionyl-di-indonylmethane*,

$\begin{array}{c} \text{CO} \cdot \text{C}_6\text{H}_4 \\ \text{C}_8\text{H}_4\text{O}_2 \cdot \text{CH} \cdot \text{CHPh} \cdot \text{CH} \cdot \text{C} : \text{C} : \text{C}_8\text{H}_4\text{O}_2 \end{array}$ , yellow powder, m. p.  $303^\circ$ , is formed. The same compound is obtained by the action of indandione on benzylideneindandione in boiling alcohol in the presence of piperidine. Di-indandionylmethane is not attacked by boiling acetic anhydride and does not undergo the typical tetraketone dehydration to pyrone derivatives. On boiling with nitrobenzene or on atmospheric oxidation in alkaline solution, it is converted almost quantitatively into methenylbisindandione, whilst with sulphuric acid in glacial acetic acid it yields a substance,  $\text{C}_{38}\text{H}_{22}\text{O}_7$ , canary-yellow, m. p.  $180-181^\circ$ ,  $+1\text{C}_2\text{H}_4\text{O}_2$ , lemon-

yellow needles, m. p. 234°, which is provisionally regarded as *anhydrobisdi-indandronylmethane*,



Di-indone and indandione combine slowly in pyridine to give the truxenequinone, m. p. above 300°, mentioned in the preceding abstract.

R. B.

**Simplest *O*-Alkyl Ethers of Benzoylacetone and Phenylmethylisooxazole.** C. WEYGAND [with L. FRIELING] (*Ber.* 1925, 58, [B], 1473—1482).—The product of the action of ferric chloride on benzoylacetone and ethyl orthoformate is converted by hydroxylamine into the phenylmethylisooxazole, m. p. 68°, together with products of lower m. p.; the phenylmethylisooxazole, m. p. 42°, described by Claisen (*A.*, 1907, i, 940) could not be isolated. Since this *isooxazole* is also obtained from the undoubted *O*-ether, CPh(OEt):CHAc (Ruhemann and Watson, *T.*, 1904, 85, 464, 1180), this constitution must be ascribed also to Claisen's condensation product instead of the formula, CHBz:CMe·OEt, adopted by Claisen. The ether, CPh(OMe):CHAc, b. p. 148—149°/13 mm., is obtained by the interaction of styryl methyl ketone dibromide and sodium methoxide, phenylacetylacetylene and methyl alcohol, benzoylacetone and diazomethane, benzoylacetone and methyl orthoformate, and the sodium salt of benzoylacetone and methyl sulphate; its constitution is established by its conversion by ozone into methyl benzoate. The known *O*-alkyl ethers of benzoylacetone are therefore derived from the enolic form of benzoylacetone established by Scheiber and Herold (*A.*, 1914, i, 927).

The course of the action of hydroxylamine on benzoylacetone *O*-alkyl ethers depends somewhat on the nature of the medium; in neutral or faintly alkaline solution a product, m. p. 81—82°, is occasionally obtained instead of phenylmethylisooxazole, m. p. 68°. Claisen's phenylmethylisooxazole, m. p. 42°, b. p. 234°, appears to be formed by the action of hydroxylamine on phenylacetylacetylene in faintly alkaline solution; its constitution has not been elucidated.

H. W.

**2-Chloro-3 : 5-dinitrobenzamide.** E. DE B. BARNETT (*Ber.*, 1925, 58, [B], 1610—1611).—2-Chloro-3 : 5-dinitrobenzoic acid is converted by thionyl chloride into the corresponding *chloride*, from which the *amide*, m. p. 180°, and the *anilide*, m. p. 177°, are obtained. 1 : 2'-*Chloro-3' : 5'-dinitrobenzamidoanthraquinone*, m. p. 278°, and 2 : 2'-*chloro-3' : 5'-dinitrobenzamidoanthraquinone*, m. p. 302°, are obtained from the respective bases and the acid chloride in the presence of tetrachloroethane and quinoline.

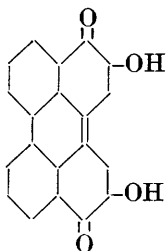
H. W.

**Preparation and Properties of 1-Benzamido-2-methylantraquinone.** W. H. BEISLER and J. L. BRAY (*J. Amer. Chem. Soc.*, 1925, 47, 2371—2373).—1-Benzamido-2-methylantraquinone, yellow, m. p. 200—202°, is obtained in 30% yield by benzoylation of 1-amino-2-methylantraquinone in toluene in the presence of sodium carbonate. It is readily hydrolysed by concen-

trated sulphuric acid, but not by hydrochloric acid. From a hyposulphite vat it dyes lemon-yellow shades on cotton and artificial silk, but possesses less affinity for textile fibres than 1-benzamidoanthraquinone. Nitrogen in the substance cannot be determined by the Dumas method. R. B.

**Substituted *o*-Benzoylbenzoic Acids and the Corresponding Anthraquinones.** O. R. QUAYLE and E. E. REID (*J. Amer. Chem. Soc.*, 1925, **47**, 2357—2361; cf. A., 1924, i, 965).—The condensation of phthalic anhydride with *m*-fluorotoluene, *o*- and *p*-fluoro- and *o*-chloro-ethylbenzene, *m*-diethyl-, *m*-di-*isopropyl*-, and *cyclohexyl*-benzene has been investigated. *m*-Fluorotoluene yields a mixture of isomerides the predominating one of which is readily obtained pure. Since the *para*-orienting influence of the methyl group is greater than that of fluorine (Swarts, *Rec. trav. chim.*, 1915, **34**, 131), this is regarded as 2-*fluoro-4-methylbenzoyl-o-benzoic acid*. The corresponding chloro- and bromo-toluenes yield similar mixtures, but the acids could not be obtained in a state of purity. With *o*-fluoroethylbenzene and *o*-chloroethylbenzene, the chief product is the 3-*fluoro-* or 3-*chloro-4-ethylbenzoyl-o-benzoic acid*. The fluorine derivative yields an anthraquinone on dehydration, but the chlorine derivative does not. These constitutions are deduced from the behaviour of *o*-chlorotoluene (A., 1908, i, 994; 1914, i, 413) and *o*-fluorotoluene (Hahn and Reid, *loc. cit.*). Whilst *p*-fluoroethylbenzene readily yields 5-*fluoro-2-ethylbenzoyl-o-benzoic acid*, *p*-iodotoluene yields an acid containing only a trace of iodine. A sample of diethylbenzene in which the *m*-isomeride probably predominates yielded a diethylbenzoyl-*o*-benzoic acid which was probably a mixture of isomerides, but gave on dehydration a *diethylantraquinone*, m. p. 83—85°, probably the 1:3-isomeride. Diisopropylbenzene behaves similarly, both the acid and anthraquinone being apparently mixtures of isomerides. *cyclohexyl*benzene yields *p-cyclohexylbenzoyl-o-benzoic acid*, m. p. 166—167°, which was purified with difficulty and could not be converted into an anthraquinone. Attempts to obtain 4-nitrobenzoyl-*o*-benzoic acid by nitration and subsequent oxidation of benzyl-*o*-benzoic acid yielded a mixture of mono- and di-nitro-acids from which the dinitro-acid (probably 2':6-dinitrobenzyl-*o*-benzoic acid), m. p. 163—164°, was isolated and oxidised to 2':6-dinitrobenzoyl-*o*-benzoic acid, m. p. 201°, with chromic and acetic acids. Heating with 23% fuming sulphuric acid and boric acid at 150° converts this into 1:8-dinitroanthraquinone, m. p. 310°. Attempts to condense naphthalic anhydride with benzene were unsuccessful. 2-Fluoro-4-methylbenzoyl-*o*-benzoic acid, m. p. 129°, with 10 parts of concentrated sulphuric acid yields 4-*fluoro-2-methylantraquinone*, m. p. 135.5—137°. *o*-Fluoroethylbenzene, b. p. 136—137°,  $d_4^{20}$  1.002, obtained by Holleman's method (A., 1904, i, 232, 486), yields 3-*fluoro-4-ethylbenzoyl-o-benzoic acid*, m. p. 120°, from which 3-*fluoro-2-ethylantraquinone*, m. p. 110°, is similarly obtained. *p*-Fluoroethylbenzene, b. p. 141°,  $d_4^{20}$  0.994; 5-*fluoro-2-ethylbenzoyl-o-benzoic acid*, m. p. 210—220°, and 4-*fluoro-*

1-ethylanthraquinone, m. p. 80—82°, are analogously obtained.  
3-Chloro-4-ethylbenzoyl-o-benzoic acid has m. p. 105°. R. B.



**Perylene Dyes.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 412120; from *Chem. Zentr.*, 1925, i, 2664).—1 : 1'-Dinaphthyl-3 : 4 : 3' : 4'-diquinone, 3 : 3' : 4 : 4'-tetrahydroxy-1 : 1'-dinaphthyl, or dinaphthyldiquinhydrone on heating with aluminium chloride at 130—150° yields a vat dye (annexed formula) dyeing bluish-black shades on cotton.

R. B.

**Camphor Series.** V. S. KOMATSU and M. KURATA (*Mem. Coll. Sci. Kyōtō*, 1925, 9 [A], 23—28).—When *l*-menthone is passed slowly through a glass or silica tube at 300°, up to 7% inversion to the *d*-form takes place, whereas in presence of reduced copper at 200°, more than 50% of the *d*-form is produced. With the same catalyst at 300°, *l*-menthone yields 70% of thymol, 22% of cymene, and 3% of menthene. Reduced copper apparently catalyses the keto-enolic change in *l*-menthone, especially at high temperatures.

B. W. A.

**Action of Potassium Cyanide on Pernitroso Derivatives.** M. PASSERINI (*Gazzetta*, 1925, **55**, 559—567).—In hot aqueous alcoholic solution, potassium cyanide quickly combines with pernitrosocamphor, giving the *potassium* compound of 6-cyano-camphane-6-nitrosohydroxylamine,  $C_{10}H_{16}(CN)\cdot N_2O_2H$ ; the latter is itself obtained, by the action of mineral acid on the potassium compound, as an unstable, strongly acidic substance, giving *copper* and *silver* salts. It does not respond to the Liebermann test or to that of Thiele and Lachmann. At  $85^\circ$ , it loses nitrous oxide, giving a neutral substance, possibly *camphor cyanohydrin*, m. p.  $209\text{--}210^\circ$ . Heated for a short time with a little strong hydrochloric acid, this compound is transformed into the corresponding *amide*, m. p.  $198^\circ$ , which, after 80 hrs.' boiling with strong hydrochloric acid, gives two *acids* of the formula,  $C_{11}H_{16}O_2$ , m. p.  $90\text{--}92^\circ$  and  $157\text{--}158^\circ$ , respectively. The action of 40% sulphuric acid on the cyanohydrin produces another pair of *acids*, isomeric with the former, m. p.  $108\text{--}110^\circ$  and  $137\text{--}138^\circ$ , respectively. Although the empirical formula of these four acids suggests that they are bornylenecarboxylic acids, their stability towards potassium permanganate militates against this conclusion. As described above, 6-cyanofenchane-6-nitrosohydroxylamine and its *potassium* and *silver* compounds were also obtained. The first decomposes at  $83\text{--}84^\circ$  with evolution of nitrous oxide, giving as chief product a substance, m. p.  $166\text{--}168^\circ$ , having  $[\alpha]_D^{10} +15\text{--}12^\circ$  (in alcohol), which is thought to be *fenchone cyanohydrin*, and a small quantity of an *isomeride*, m. p.  $100\text{--}102^\circ$ , having  $[\alpha]_D^{10} +50\text{--}49^\circ$  (in alcohol). From these compounds ethereal hydrogen chloride produces the corresponding *amides*, m. p.  $170\text{--}172^\circ$  and  $116\text{--}117^\circ$ , respectively.

The action of hot potassium hydroxide on these substances causes evolution of ammonia with the formation of acidic substances as yet uninvestigated.

W. E. E.

### Stereochemical Studies. X. *l*-O-Menthylthiourethanes.

B. HOLMBERG and W. ROSÉN (*Ber.*, 1925, **58**, [B], 1834—1842).—*l*-Menthol is treated with sodium in the presence of xylene at 140—145° and subsequently with carbon disulphide at 30°, whereby sodium *l*-menthyl dithiocarbonate is precipitated. The salt is converted by chloroacetamide in warm, alcoholic solution into the substance  $C_{10}H_{19}O \cdot CS \cdot S \cdot CH_2 \cdot CO \cdot NH_2$ , m. p. 98—99°,  $[\alpha]_D -64.0^\circ$  in alcohol. The action of aqueous ammonia on the crude product of the successive action of carbon disulphide and chloroacetamide on *l*-menthol leads to the formation of *l*-O-menthylthiourethane,  $C_{10}H_{19}O \cdot CS \cdot NH_2$ , m. p. 147.5—148.5°,  $[\alpha]_D -112.5^\circ$  in alcohol,  $-120.1^\circ$  in benzene. The thiourethane is converted by hydrogen peroxide in part into *l*-menthylurethane, m. p. 165—166°,  $[\alpha]_D -81.4^\circ$  in alcohol,  $-85.2^\circ$  in chloroform, but mainly into a substance,  $C_{22}H_{38}O_2N_2S$ , m. p. 105—106°,  $[\alpha]_D -134.4^\circ$  in benzene. *l*-O-Menthyl-N-methylthiourethane, m. p. 91—92°,  $[\alpha]_D -106.0^\circ$  in alcohol,  $-114.1^\circ$  in benzene, *l*-O-menthyl-N-dimethylthiourethane, m. p. 26.5—27°,  $[\alpha]_D -107.7^\circ$  in alcohol,  $-106.2^\circ$  in benzene, and the corresponding non-crystalline *ethyl* and *diethyl* derivatives have also been prepared. The action of bromoacetic acid on the *l*-O-menthylthiourethanes leads to the formation of dextrorotatory menthyl bromides, whereas previous attempts to convert *l*-menthol into the corresponding bromide have given inactive or levorotatory products, a very feebly dextrorotatory bromide being obtained only by the action of phosphorus pentabromide on *l*-menthol. The steric uniformity of the authors' products is not established, but it is considered probable that the *d*-bromide is configurationally related to *l*-menthol, and that any admixture with a diastereoisomeric *l*-bromide is due to subsequent processes in the change, which does not proceed very smoothly.

H. W.

**Relations between Organic Ring Systems and Unsaturation Properties. II.** B. K. MEREJKOVSKI (*Bull. Soc. chim.*, 1925, [iv], **37**, 1174—1187).—On treatment of the pyrazoline base obtained from carvenone with potassium hydroxide and platinum-black at 210—220°, according to Kishner's method (A., 1913, i, 1163),  $\Delta^3$ -menthene (*nitrosochloride*, m. p. 118.5°) is obtained in place of the thujane expected. Similarly, carvone yields mainly *isolimone* with some *dipentene*, whereas Kishner (A., 1913, i, 187) only observed the formation of *l*-limonene. *cyclopentenone* on analogous decomposition yields only *cyclopentene* and not *dicyclopentene*. In all these cases the formation of a dicyclic compound would involve the formation of a second ring without the addition of fresh carbon atoms to the molecule, an addition which is characteristic of the usual methods of synthesising dicyclic compounds. The author accordingly formulates the rule that the existence of a ring system in a molecule opposes the formation of a second ring system, unless external energy is supplied to the



system in the form of additional carbon atoms. The dicyclic compound is, however, probably formed in all cases, at least as an intermediate stage in Kishner's reaction. In the cases covered by the rule, it is unstable and undergoes rearrangement to the monocyclic compound. Accordingly, it is suggested that the compound obtained by Zelinski and Uspenski by the action of zinc on 2:6-dibromo-4:4-dimethylcyclohexane (A., 1913, i, 607) is not 3:3-dimethyl-0:1:3-dicyclohexane as supposed, the latter being unstable and isomerising to a dimethylcyclohexene, which with its reduction products, a dimethylcyclohexane or a trimethylcyclopentane, were probably the compounds actually obtained.

R. B.

### Terpenes. III. Synthetic Diterpenes and Polyterpenes.

I. KONDAKOV and S. SAPRIKIN (*Bull. Soc. chim.*, 1925, [iv], **37**, 1045—1069; cf. this vol., i, 1163).—Pinene obtained from different sources, when polymerised by treatment with acetic and sulphuric acids, with zinc chloride, benzenesulphonic acid, antimony trichloride, aluminium iodide or chloride, ferric chloride, or boron trifluoride, yields diterpenes apparently identical with those obtained from pinene and  $\alpha$ -terpineol derivatives by the Kondakov method. Approximately 50% of the pinene polymerises in the Bertram-Walbaum process (acetic and sulphuric acids), 35—40% being converted into dipentene and 10% into ethers of terpineol, borneol, etc. In the presence of camphene, the reaction is slower. The diterpenes have b. p. varying slightly within the range 170—180°/11 mm.,  $d$  0.920—0.937, and  $n_D$  1.515—1.521, these differences being probably due to varying proportions of isomerides or to impurities difficult to remove. Diterpenes obtained from monocyclic terpenes containing two double bonds closely resemble in physical properties the diterpenes obtained from pinene, but differ from the diterpenes obtained from such monocyclic terpenes as the phellandrenes. The mechanism of formation is similar in both cases and these synthetic diterpenes contain the fundamental structures of the original monoterpenes. They are accordingly represented by structures in which one terpene molecule is substituted through a single carbon linking in a second molecule. The natural diterpenes, however, are hydrogenated naphthalene or phenanthrene derivatives. The synthetic diterpenes are colourless, almost odourless liquids which when kept gradually become yellow through oxidation. They are insoluble in cold hydroxylic solvents, but dissolve on warming and are readily soluble in hydrocarbons. They possess valuable solvent properties for resins etc. At low temperatures they combine with bromine, but the products rapidly decompose, losing hydrogen bromide. They yield no definite crystalline derivatives with the hydrogen halides, but the diterpenes regenerated from such derivatives are not identical with the original diterpenes. At high temperatures, they are decomposed into monoterpenes. On oxidation, they do not yield resin acids, the latter substances containing either a naphthalene or a phenanthrene ring. It is possible that the synthetic diterpenes contain trimethyl-

ene or cyclobutane rings. Besides the diterpenes, small amounts of triterpenes and tetraterpenes are formed. Thus the action of antimony trichloride on *l*-pinene yields also a *triterpene*, b. p. 250—255°/11 mm.,  $\alpha_D -1.3^\circ$ ,  $d_{25}^{25.5}$  0.890, whilst in the polymerisation of pinene with aluminium chloride, boron trifluoride, and antimony trichloride, small quantities of tetraterpenes, m. p. 75—90° (mainly 75—80°), have been obtained. These tetraterpenes, which are stable and do not oxidise in the air, give no crystalline compounds and only indefinite nitro compounds with nitric acid. They can be used in place of colophony in the preparation of varnishes, sealing-wax, etc. No higher polymerides than tetraterpenes were obtained, and it would appear that chemical polymerisation gives less complex products than electro-synthesis. The diterpenes themselves do not undergo further polymerisation, and it is only in appearance that the polyterpenes resemble colophony. R. B.

**Action of Formic Acid on certain Sesquiterpenes.** J. M. ROBERTSON, C. A. KERR, and G. G. HENDERSON (*J. Chem. Soc.*, 1925, **127**, 1944—1946).— $\beta$ -Caryophyllene, b. p. 118—119°/9.7 mm.,  $n_D^{17}$  1.5009,  $d_4^{17}$  0.9052 (dihydrochloride, m. p. 69°,  $[\alpha]_D^{15} +67.2^\circ$  in 2.5% ethyl-alcoholic solution), when heated with formic acid gives the *formic ester*, b. p. 141—145°/10 mm.,  $d_4^{17}$  1.22,  $n_D^{20}$  1.4967,  $[\alpha]_{461}^{17} -10.46^\circ$ , of caryophyllene alcohol (yield 35%), together with hydrocarbons, including clovene, showing that ring closure has been effected by the action of formic acid. Cadinene, b. p. 134—136°/11 mm.,  $d_4^{20}$  0.9189,  $n_D^{20}$  1.5079,  $[\alpha]_{3461}^{18} -125^\circ$ , when heated with formic acid at 100°, is partly converted into an unsaturated hydrocarbon,  $C_{15}H_{24}$ , b. p. 118—124°/9 mm.,  $d_4^{17}$  0.9086,  $n_D^{14}$  1.5010. Cedrene, b. p. 122—124°/9 mm.,  $d_4^{20}$  0.9361,  $n_D^{21}$  1.5005, on similar treatment is transformed into an isomeric unsaturated hydrocarbon, b. p. 114—118°/9 mm.,  $d_4^{20}$  0.9333,  $n_D^{21}$  1.4988 (yield 50%), which is probably tricyclic. F. M. H.

**Apparently New Component of Oil of Lemon.** G. ROMEO (*Annali Chim. Appl.*, 1925, **15**, 305—309).—Pure oil of lemon, largely freed from terpenes by concentration in a vacuum and subsequent distillation in a current of steam, deposits a crystalline compound,  $C_{10}H_{18}O_2 \cdot 3H_2O$ , m. p. 58° (hydrated) or 69—71° (anhydrous), b. p. 260° (slight alteration),  $[\alpha]_D +39.26^\circ$ . The compound decolorises permanganate and bromine water, and gives a bright red coloration with concentrated sulphuric acid. It gives no coloration with ferric chloride and is not hydrolysed by alcoholic potassium hydroxide, but reduces ammoniacal silver nitrate solution slightly. When heated in aqueous solution with hydrochloric acid, it is converted into a liquid *isomeride*. T. H. P.

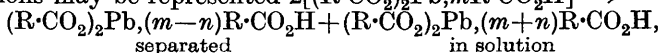
**Travancore Essential Oils. VI. Oil from *Cymbopogon Cæsius*, Stapf. (Inchi Grass).** K. L. MOUDGILL (*J. Indian Chem. Soc.*, 1925, **2**, 23—37).—The flowers and leaves of the grass *Cymbopogon Cæsius* from the Western Ghats of South Travancore on steam distillation yield a sweet-smelling oil different in character from oils obtained from similar grasses. More oil is obtained from

the leaves than from the flowers, but that obtained from the latter is richer in sesquiterpene constituents and has a lower acetyl value. The oil does not undergo any change on storage. Repeated fractionation shows that the chief constituents of the oil are *l*-limonene, *l*-camphene, *l*-borneol, *l*-terpineol, a dicyclic *sesquiterpene*,  $d_4^{30}$  0.9064,  $n_D^{30}$  1.5005,  $\alpha_D^{30}$   $-12^\circ$  (a liquid *dibromide* and a *monohydrobromide* are described), an optically inactive *sesquiterpene alcohol*, b. p. 147—149°/16 mm., which was not obtained in the pure state, an *aldehyde*, b. p. 92—94°/4—5 mm.,  $\alpha_D^{30}$   $-6.5^\circ$ ,  $d_4^{30}$  0.9694,  $n_D^{30}$  1.4980 (two *semicarbazones*, m. p. 181° and 164°, were obtained), which gives a sodium salt of a sulphonic acid on treatment with sodium hydrogen sulphite, together with esters of acetic and butyric acids and of an unsaturated *acid*,  $C_{16}H_{20}O_2$ . J. W. B.

**Oleo-resin of Indian Valerian Root.** K. BULLOCK (*Pharm. J.*, 1925, 115, 122—125).—Indian valerian root (probably old) yielded, on moistening, powdering, and extracting with light petroleum, 1.64% of extract, containing 47.4% of oleo-resin (*i.e.*, material soluble in 70% alcohol). The oleo-resin contained a large proportion of free acids, including valeric (of slight positive optical rotation, probably containing  $\alpha$ -methylbutyric acid), oleic, linolenic, linoleic, and various saturated acids; and 8.8% of esters (calculated as bornyl valerate). The part of the original extract insoluble in 70% alcohol contains a liquid hydrocarbon, and a semi-solid alcohol of high b. p.; from the unsaponified matter an acetyl derivative, m. p. 65.5—66.5°, was isolated. B. F

**Solutions of Lead Resinates.** I. C. COFFIGNIER (*Bull. Soc. chim.*, 1925, [iv], 37, 1078—1085).—Solutions of lead resinates in benzene, turpentine, and "white spirit" ( $d$  0.780) have been examined for stability for periods up to 2 months. The resinates examined were obtained by fusing colophony with 5% and 10% of lead oxide. The resinate obtained with 5% of lead oxide gives stable solutions in benzene and in turpentine, but in the latter case slight deposits are observed in 10%, 15%, and 20% solutions, whilst in 15%, 20%, and 25% solutions a tendency to assume the colloidal form is indicated by an increase in the viscosity, varying directly with the time and concentration of the solution. The solutions in "white spirit" show no alteration of viscosity, but become almost colourless and give rise to varying deposits, the production of which persists during 6 months, and it appears probable that in this solvent the resinate would ultimately separate completely. In dilute solutions, the resinate separating is less acid than that remaining in solution, but its acidity decreases further when separating from more concentrated solutions. The separation is less marked in more concentrated solutions and a 25% solution is stable. In the final stages of the separation, the more acid resinate is that precipitated. Similar results were obtained with resinate from 10% of lead oxide, but in this case turpentine gives the most stable solution, although the increase in viscosity is much more marked than with the 5% resinate, and in 25% solution there is a pronounced increase in the size of the granules. Benzene and

"white spirit" solutions show variable deposits accompanied by slight changes in viscosity. The general reaction in all these solutions may be represented  $2[(R \cdot CO_2)_2Pb, mR \cdot CO_2H] \rightarrow$



and the deposited resinate will be more or less acid than that remaining in solution according as  $m$  is greater or less than  $n$ .

R. B.

**Lead Resinates.** R. UZAC (*Bull. Soc. chim.*, 1925, [iv], 37, 1194—1196).—Solutions in "white spirit" of neutral lead resinate obtained by double decomposition of alkali resinate and lead salts, deposit on cooling a basic lead resinate of similar composition to that deposited from solutions of acid lead resinates obtained by the action of lead oxide or carbonate on resin. A similar basic resinate, approximate composition  $Pb(OH)_2, 2(C_{20}H_{29}O_2)_2Pb$ , is obtained by precipitation from sodium resinate with lead subacetate in the presence of excess of alkali. This resinate is soluble in turpentine, but only slightly soluble in light petroleum, chloroform, "white spirit," and linseed oil, and is probably the cause of the thickening of paints. In general, the basic resinate is mixed with more or less free resin. [Cf. B., Nov 27th.]

R. B.

**d-Mannitol from *Gardenia turgida*.** M. O. FORSTER and K. A. N. RAO (*J. Chem. Soc.*, 1925, 127, 2176).—The exudation from *Gardenia turgida* is free from nitrogen, aldehydes, and ketones, and does not give furfuraldehyde on boiling with hydrochloric acid. By treating an aqueous solution of the powdered substance with tri-basic lead acetate and decomposing the filtrate with hydrogen sulphide, there is obtained a 40% yield of *d*-mannitol. F. M. H.

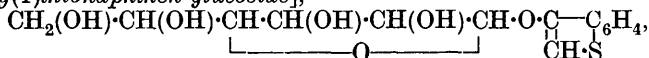
**Gitoxin, a Glucoside Insoluble in Chloroform from *Digitalis Leaves*.** A. WINDAUS and G. SCHWARTE (*Ber.*, 1925, 58, [B], 1515—1519).—Treatment of Merck's by-products of the preparation of digitoxin with a boiling mixture of chloroform and methyl alcohol leads to the isolation of gitoxin,  $C_{42}H_{66}O_{14} \cdot H_2O$ , decomp. 266—269°, which appears to be identical with the anhydrogitalin of Kraft (A., 1912, i, 373) and with the glucoside described by Kiliani (A., 1915, i, 281). It is hydrolysed by boiling, aqueous-alcoholic hydrochloric acid to digitoxose and *gitoxigenin*,  $C_{24}H_{36}O_5$ , m. p. 224—225° (decomp.), which affords a *dibenzoyl* compound, m. p. 262°, and a *dihydro* derivative, m. p. 226°; it contains a lactone group, three hydroxyl groups, and a double linkage. The genin is converted by cold, concentrated hydrochloric acid into "*dianhydrogitoxigenin*," identical with digitaligenin from "*Digitalinum verum*." The latter substance is not present as such in "*D. verum*," but is formed by loss of water from an aglykon,  $C_{24}H_{36}O_5$ , which has the same composition as gitoxigenin. Since, however, the aglykon cannot be isolated as such under the drastic conditions required for the decomposition of "*D. verum*," the identity of the two products cannot be placed beyond doubt. The two glucosides, gitoxin and "*D. verum*," are certainly very closely related to one another, probably differing only in the sugar component.

H. W.

zz\*

**Glucosides. III. Synthesis of "Thioindican."** J. CRAIK and A. K. MACBETH (*J. Chem. Soc.*, 1925, **127**, 1637—1640).—Tetra-acetylbromoglucose was heated with excess of 3-oxy(1)thionaphthen and quinoline for 2 hrs. at 105—110°, the product poured into ice-water, and extracted with ether. After extraction of the quinoline with acid, excess of oxythionaphthen was removed by steam distillation, water being then distilled off under reduced pressure. Treatment of the residual syrup with acetic anhydride and pyridine afforded tetra-acetyl-3-oxy(1)thionaphthen glucoside,  $\text{CH}_2(\text{OAc})\cdot\text{CH}(\text{OAc})\cdot\text{CH}\cdot\text{CH}(\text{OAc})\cdot\text{CH}(\text{OAc})\cdot\text{CH}\cdot\text{O}\cdot\text{C}_8\text{H}_5\text{S}$ , m. p. 106°.

De-acetylation of the last with the calculated amount of barium hydroxide, or with alcoholic ammonia, yielded "thioindican" [3-oxy(1)thionaphthen glucoside],



m. p. 73·5°. Determination of the oxythionaphthen content of the thioindican by simultaneous hydrolysis and condensation with isatin (cf. Orchardson, Wood, and Bloxam, A., 1907, ii, 203) gives satisfactory results only when carried out in alcoholic solution.

F. G. W.

**Constitution of Indian Kamala. I.** S. DUTT (*J. Chem. Soc.*, 1925, **127**, 2044—2052).—Rottlerin,  $\text{C}_{33}\text{H}_{30}\text{O}_8$ , m. p. 206—207°, from kamala, possibly contains one alcoholic and six phenolic hydroxyl groups; treatment with acetic anhydride and a little pyridine yields *hepta-acetylrottlerin*, m. p. 165°, whilst methyl sulphate in presence of sodium hydroxide gives *hexamethylrottlerin*, m. p. 135—137° (*acetylhexamethylrottlerin*, m. p. 215—217°), and benzoyl chloride with sodium hydroxide gives *hexabenzoylrottlerin* (unmelted below 300°). The presence of a double linkage is indicated by the formation of *hepta-acetylrottlerin dibromide*, m. p. 145°, and of *acetylhexamethylrottlerin dibromide* (decomp. on heating), and also because the action of fuming nitric acid below 0° gives *p*-nitrocinnamic acid.

Since fusion of rottlerin with potassium hydroxide yields phloroglucinol (together with acetic and benzoic acids), oxidation of hepta-acetylrottlerin with potassium permanganate yields (together with benzoic, oxalic, acetic, and phthalic acids) triacetylphloroglucinoldicarboxylic acid, and since, similarly, oxidation of hexamethylrottlerin yields (together with benzoic, acetic, phthalic, and terephthalic acids) trimethylphloroglucinoldicarboxylic acid, it is concluded that rottlerin contains two phloroglucinol residues joined to the parent structure by one or two side chains, and, if by one, an alkyl substituent is present in the phloroglucinol nucleus. The oxidation of rottlerin with nitric acid (*d* 1·5 and 1·2), alkaline permanganate, alkaline hydrogen peroxide, alkaline potassium ferricyanide, and potassium persulphate is investigated, and it is found that phthalic and terephthalic acids are nearly always formed (acetic, benzoic, *p*-nitrobenzoic, succinic, oxalic, and cinnamic acids have also been isolated, as have benzaldehyde and *p*-nitrobenz-

aldehyde, a dibasic *acid*,  $C_{18}H_{20}O_4$ , m. p.  $192^\circ$ , and an *acid*, m. p.  $216^\circ$ , which is probably tribasic); they are probably produced by selective elimination of a side chain from a benzene nucleus containing three side chains in the 1:2:4-positions. Besides this nucleus and the two phloroglucinol residues, there is probably a residue,  $Ph\cdot CH:CH\cdot C$ . Examination for methoxyl by Zeisel's method gives a negative result. Since cinnamic acid is readily formed on oxidation of rottlerin, and dihydrocinnamic acid on its reduction, it is concluded that the molecule contains the residue  $Ph\cdot CH:CH\cdot CO\cdot$  or  $Ph\cdot CH:CH\cdot C(OH):$ ; the action of zinc dust and sodium hydroxide, tin and hydrochloric acid, sodium hyposulphite, and hydriodic acid and phosphorus has been examined, and besides dihydrocinnamic acid there have been isolated succinic and acetic acids and a liquid, b. p.  $152-159^\circ$  (probably *n*-propylbenzene), and sometimes a residue which yields phloroglucinol on fusion with potassium hydroxide. Distillation with zinc dust in a current of hydrogen gives 2-methylanthracene, gaseous hydrocarbons, and a liquid, b. p.  $230-240^\circ$ .

F. M. H.

**Complex Metallic Derivatives of Chlorophyll. I. R. KUNZ and K. SEHRBUNDT** (*Ber.*, 1925, **58**, [B], 1868—1876).—Chlorophyll resembles indigotin (Kunz, A., 1923, i, 155, 1134) in its ability to form complex compounds, yielding metallic derivatives and additive compounds of analogous composition. The reaction is accompanied by darkening in colour and, in the majority of cases, the compounds formed contain an atom of the metal or a molecule of another compound for four pyrrole nuclei the nitrogen atoms of which produce the anion. The compounds from chlorophyll and indigotin are very sensitive to acids, but comparatively stable towards alkalis. The order of activity is the same in each series, the copper compounds being most, the potassium compounds least stable. The most important method for preparing the compounds of the chlorophyllins with the heavy metals consists in the use of the metallic acetates. Additive *compounds* of erythroporphyrin with copper, phylloporphyrin ester with copper and zinc, pyrroporphyrin ester with copper and zinc, and rhodoporphyrin with copper and zinc have been prepared in this manner. In all of these one atom of metal is present for every four pyrrole nuclei except in the rhodoporphyrin-copper compound, which contains only one atom of copper for every eight pyrrole nuclei (compare the analogous case of copper and *NN'*-diphenylindigotin). The metallic compounds of copper and the chlorophyll derivatives can also be obtained by use of the metal in xylene solution; as in the case of the indigotin derivatives, hydrogen is not displaced. Qualitative observations indicate that zinc and magnesium derivatives can be obtained directly by use of zinc or magnesium amalgam.

The product obtained by Willstätter (A., 1910, i, 129) from rhodoporphyrin and ferric chloride in pyridine-acetic acid appears to be initial material contaminated with the iron salt. On the other hand, the compound  $C_{35}H_{40}O_4N_4\cdot FeCl_3$  is obtained in acetonitrile solution; its chemical behaviour is exactly analogous

to that of the additive compounds of ferric chloride and the indigotins.

As in the case of indigotin derivatives, the action of potassium on chlorophyll derivatives in anhydrous solvents occurs without evolution of hydrogen and the compounds formed are therefore to be regarded as additive; the action of potassium on aetioporphyrin (Willstätter and Fischer, A., 1913, i, 1218) is described in detail.

The parallelism between the metallic compounds of indigotin and chlorophyll extends to the process of salt formation with mineral acids, which in each case is accompanied by darkening in colour. The analogous behaviour of 2-methylindyl-2'-methylindolidene-methane shows that the carbonyl groups of indigotin do not take any essential part in the action.

H. W.

[**Tetrahydrofurfuraldehyde.**] H. SCHEIBLER, F. SOTSCHKE, and H. FRIESE (*Ber.*, 1925, 58, [B], 1961; cf. A., 1924, i, 1218).—Tetrahydrofurfuraldehyde has  $d_{20}^{20}$  1.0749,  $d_4^{20}$  1.0727,  $n_D^{20}$  1.43415,  $n_D^{20}$  1.43658,  $n_B^{20}$  1.44173.

H. W.

**Carbylamines. XII. Reactions between Phenylcarbylamine and  $\alpha$ -Naphthol.** M. PASSERINI (*Gazzetta*, 1925, 55, 555—559; cf. A., 1924, i, 57, 751, 1319, 1320).—After about 4 days' heating on the water-bath, a benzene solution of phenylcarbylamine mixed with  $\alpha$ -naphthol yields 1:1-dianilinodihydro- $\alpha$ -naphthafurandione-2-anil, m. p. 220° (decomp.), together with small quantities of diphenylcarbamide and a colourless, insoluble substance of high m. p., not further studied. Hydrolysed with concentrated hydrochloric acid, the main product gives  $\alpha$ -naphthol-2-glyoxylic acid, m. p. 147—149° (decomp.); yellow barium salt (believed to be identical with dihydro- $\alpha$ -naphthafuran-1:2-dione, Giua, A., 1924, i, 1093). The corresponding ethyl ester, m. p. 69—70°, is similarly obtained by the action of ethyl-alcoholic hydrogen chloride. In acetic acid, hydrogen peroxide oxidises  $\alpha$ -naphthol-2-glyoxylic acid to  $\alpha$ -naphthol-2-carboxylic acid.

W. E. E.

**Heterocyclic Ring Systems. II.** R. SEKA (*Ber.*, 1925, 58, [B], 1783—1787; cf. this vol., i, 57).—Further attempts are described to obtain substances containing the ring system,

$X \begin{array}{c} \text{C} \cdot \text{C} \cdot \text{C} \\ \diagup \quad \diagdown \\ \text{C} \cdot \text{C} \cdot \text{C} \end{array} X$ , in which X is an atom other than carbon. 2:5-Diphenylfuran-3:4-dicarboxylic anhydride is converted by carb-

amide at 190—230° into 2:5-diphenylfuran-3:4-dicarboxylimide,

$O \begin{array}{c} \text{CPh} \cdot \text{C} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CPh} \cdot \text{C} \cdot \text{CO} \end{array} NH$ , m. p. 304—304.5°, and by thiocarbonyl

into 2:5-diphenylfuran-3:4-dicarboxanil, m. p. 279—280°. Ethyl 2:5-diphenylpyrrole-3:4-dicarboxylate is hydrolysed by alcoholic potassium hydroxide to 2:5-diphenylpyrrole-3:4-dicarboxylic acid, m. p. 98° (ammonium, silver, and copper salts), which is accompanied by 2:5-diphenylpyrrole; cautious treatment of the acid with acetic anhydride affords 2:5-diphenylpyrrole-3:4-dicarboxylic anhydride. m. p. 268° (decomp.). Ethyl thiodiglycollate is converted

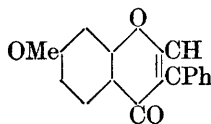
by diacetyl in the presence of sodium ethoxide into 3 : 4-dimethylthiophen-2 : 5-dicarboxylic acid, m. p. 327—328° (decomp.) (ammonium, silver, copper, and barium salts), in which, however, the carboxyl groups are so firmly retained that the possibility of converting it successively into 3 : 4-dimethylthiophen and thiophen-3 : 4-dicarboxylic acid is excluded. Oxidation of the acid with potassium permanganate in alkaline solution affords much unchanged material and 4-methylthiophen-2 : 3 : 5-tricarboxylic acid, m. p. 258° (decomp.). H. W.

**Two Mixed Anhydromonohydroxybenzoic Acids and their Transformation into Xanthonecarboxylic Acids.** R. ANSCHÜTZ, W. STOLTENHOFF, and F. VOELLER.—(See i, 1273.)

**$\beta$ -Phenylcoumarins.** G. BARGELLINI (*Atti R. Accad. Lincei*, 1925, [vi], 2, 32—35; cf. A., 1911, i, 901, 902).—5 : 7-Dihydroxy-4-p-hydroxyphenylcoumarin, prepared by heating 5 : 7-dihydroxy-4-p-methoxyphenylcoumarin (cf. Sonn, A., 1918, i, 401) with either concentrated hydriodic acid or hydrobromic and glacial acetic acids, has m. p. 285—288°, the corresponding triacetoxy compound, m. p. 185—187°, and 5 : 7-dimethoxy-4-p-methoxyphenylcoumarin, m. p. 249—251°, are described. T. H. P.

**Synthetical Experiments in the isoFlavone Group.** I. W. BAKER and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 1981—1986).—

In view of the possible identity of prunetol and genistein, the iso-flavones are being studied, and 7-methoxyiso-flavone (annexed formula) has been synthesised. isoFlavones unsubstituted in position 2 are not easy to prepare. The method used for anhydro-brazilic acid (T., 1908, 93, 503) is inapplicable. Interaction of 2 : 4-dihydroxyphenyl benzyl



ketone, cinnamic anhydride, and sodium cinnamate at 170—215° gives 7-cinnamoyloxy-2-styryliso-flavone, m. p. 213—214°; hydrolysis with potassium hydroxide, followed by methylation at 60° with methyl sulphate and aqueous potassium hydroxide, forms 7-methoxy-2-styryliso-flavone, m. p. 204—205°, which on oxidation of its pyridine solution at 0° by means of potassium permanganate, followed by thermal decomposition of the resulting 7-methoxyiso-flavone-2-carboxylic acid, yields 7-methoxyiso-flavone, m. p. 155°.

2-Substituted iso-flavones are readily obtained. Interaction of 2 : 4-dihydroxyphenyl benzyl ketone, acetic anhydride, and sodium acetate at 170—180°, followed by hydrolysis of the resulting acetyl derivative, gives 7-hydroxy-2-methyliso-flavone (I), m. p. 240° (yield 90%), which may be similarly prepared from 2 : 4-diacetoxyphenyl benzyl ketone; its methyl ether, obtained by action of methyl sulphate and potassium hydroxide at 60°, has m. p. 135.5°, and its acetyl derivative, m. p. 162°. Similarly, 2 : 4-dihydroxyphenyl benzyl ketone, benzoic anhydride, and sodium benzoate give rise to 7-hydroxy-3-phenylflavone (II), m. p. 270—271°, the alkali-metal salts of which exhibit colloidal properties; acetyl derivative, m. p. 208—209°. 2 : 4 : 6-Trihydroxyphenyl benzyl ketone, acetic



anhydride, and sodium acetate give 5 : 7-dihydroxy-2-methylisoflavone (III), m. p. 228°; diacetyl derivative, m. p. 169°; 7-monomethyl ether, m. p. 186—187°.

Ghosh (T., 1916, 109, 105) and Jacobson and Ghosh (T., 1915, 107, 1051) claim to have prepared substances (I), (II), and (III), but they are different from the specimens now described. In the case of the present synthesis, no alternative is possible with regard to (II). As regards (I), the only possible alternative is the production of 7-hydroxy-4-benzylcoumarin, and that is disproved by preparation of this substance, m. p. 225—226°, by condensation of ethyl  $\beta$ -keto- $\gamma$ -phenylbutyrate and resorcinol in presence of concentrated sulphuric acid. Hence the compound obtained by Ghosh from acetylphenylacetone and resorcinol must be 7-hydroxy-3-phenyl-4-methylcoumarin and perhaps all the compounds described as  $\gamma$ -pyrones are  $\alpha$ -pyrones (*loc. cit.* and T., 1915, 107, 424, 959). 2 : 4-Diacetoxypheyl benzyl ketone is stable to acetic anhydride, but suffers ring closure by this agent in presence of sodium acetate.

F. M. H.

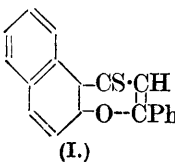
### Organic Compounds of Sulphur. III. Thioketones. A.

SCHÖNBERG [with A. ROSENBAACH, H. KRÜLL, and U. OSTWALD] (*Ber.*, 1925, 58, [B], 1793—1801).—Attempts to prepare thioketones by the action of sulphur on tetra-arylethylenes are generally unsuccessful, but dixanthylene is transformed by sulphur in an atmosphere of carbon dioxide at 270° into xanthione,  $O < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > CS$ , in

80% yield; the process appears applicable to derivatives of dixanthylene, but not to the production of selenoketones. 2 : 7-Dimethylxanthione, m. p. 188°, is described. The product obtained by the action of thiocarbonyl chloride on *o*-tolyl ethyl ether is identified as 4 : 4'-diethoxy-3 : 3'-dimethylthiobenzophenone, since it is transformed by sodamide in toluene and subsequent hydrolysis of the amide so produced into 4-ethoxy-*m*-toluic acid, m. p. 199°.  $\beta$ -Naphthaflavone, m. p. 164° (cf. Ruhemann, A., 1914, i, 316), is prepared by the action of phosphoric oxide on a mixture of benzoyl-acetic acid and  $\beta$ -naphthol and is transformed by phosphorus pentasulphide into  $\beta$ -naphthathioflavone (I), m. p. 149°.

Additive compounds are described of mercuric chloride with 4 : 4'-dimethoxythiobenzophenone, 4 : 4'-diethoxy-3 : 3'-dimethylbenzophenone, xanthione; of mercuric bromide with 4 : 4'-dimethoxythiobenzophenone, 4 : 4'-diethoxy-3 : 3'-dimethylthiobenzophenone, dimethylxanthione, 2 : 6-dimethyl-4-thiopyrone, 2 : 3-dimethyl-4-thiochromone, and  $\beta$ -naphthathioflavone. Tin tetrachloride affords additive compounds with 4 : 4'-dimethylbenzil and 4 : 4'-dimethoxybenzil.

Dianisyl thioketone and fluorene at 270° yield hydrogen sulphide and diphenylenedianisylethylene,  $\begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > C:C(C_6H_4.OMe)_2$ , m. p. (indef.) 148°, whereas di-*p*-ethoxyphenyl thioketone affords di-



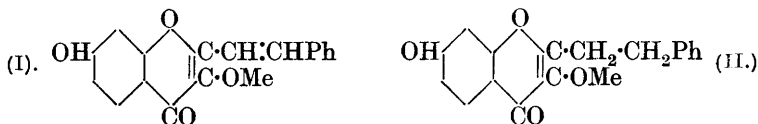
(I.)

*phenylenedi-p-ethoxyphenylethylene*. Xanthione is reduced by zinc and hydrochloric acid in glacial acetic acid solution to dixanthyl.

The action of magnesium phenyl bromide or magnesium  $\alpha$ -naphthyl bromide on dianisyl thioketone appears to yield *tetra-anisylethylene sulphide*,  $\begin{matrix} \text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2 \\ \text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2 \end{matrix} > \text{S}$ , m. p. (indef.)  $215^\circ$ , which is reduced by zinc and hydrochloric acid to tetra-anisylethylene.

H. W.

**Synthesis of 2-Styrylchromonol Derivatives.** R. ROBINSON and J. SHINODA (*J. Chem. Soc.*, 1925, **127**, 1973—1980).—In the belief that representatives of the styrylchromones occur in nature, some styrylchromone derivatives, which are related to flavonols, have been synthesised by a method previously employed (this vol., i, 148, 1302). It is found that the styryl compounds are more intensely coloured than the corresponding flavones, and possess greater tinctorial power as mordant dyes.  $\omega$ -Methoxyresacetophenone, cinnamic anhydride, and sodium cinnamate are heated at  $180$ — $185^\circ$  and the product is hydrolysed by potassium hydroxide, when treatment of its aqueous solution with carbon dioxide precipitates *7-hydroxy-3-methoxy-2-styrylchromone* (I), m. p.  $250^\circ$ ; reduction with hydrogen in presence of palladium yields



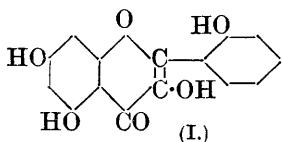
*7-hydroxy-3-methoxy-2- $\beta$ -phenylethylchromone* (II), m. p.  $186$ — $187^\circ$ , which is also prepared by heating  $\omega$ -methoxyresacetophenone, sodium  $\beta$ -phenylpropionate, and  $\beta$ -phenylpropionic anhydride, b. p.  $216$ — $217^\circ/14$  mm. [prepared by boiling  $\beta$ -phenylpropionic acid with acetic anhydride (cf. Liebermann, A., 1889, 283)], at  $180^\circ$ . Demethylation of (I) by means of hydriodic acid gives *3:7-dihydroxy-2-styrylchromone*, m. p.  $257^\circ$ , which on various mordants produces different tones and intensities from those produced by *3:7-dihydroxyflavone* ( $+\text{H}_2\text{O}$ ), m. p.  $258^\circ$  (prepared by demethylation of *7-hydroxy-3-methoxyflavone*). Demethylation of (II) gives *3:7-dihydroxy-2- $\beta$ -phenylethylchromone*, m. p.  $169^\circ$ . A synthesis similar to that of (I) yields *5:7-dihydroxy-3-methoxy-2-styrylchromone*, m. p.  $241^\circ$ , which by demethylation is converted into *3:5:7-trihydroxy-2-styrylchromone*, m. p.  $249^\circ$  (*triacetyl* derivative, m. p.  $215$ — $216^\circ$ ), and this is the styryl analogue of galangin.

*4-Methoxycinnamic acid*, m. p.  $173^\circ$  (prepared by interaction of anisaldehyde, malonic acid, pyridine, and piperidine), is converted by acetic anhydride into *4-methoxycinnamic anhydride*, m. p.  $119$ — $120^\circ$ ; replacement of hydrogen by methoxyl in the *p*-position in benzoic and cinnamic acids appears to increase the difficulty of anhydride formation, whilst in the *m*-position it may have the opposite effect. *4-Methoxycinnamic anhydride* is also prepared by addition of pyridine to a chloroform solution of *4-methoxycinnamic acid* and

the corresponding chloride. Hydrolysis of the product obtained by heating  $\omega$ -methoxyphloroacetophenone, 4-methoxycinnamic anhydride, and sodium 4-methoxycinnamate gives 5:7-dihydroxy-3:4'-dimethoxy-2-styrylchromone, m. p. 228° (yield 90%). Demethylation does not give a crystalline product, so that the styryl analogue of kaempferol has not been obtained; treatment with aqueous sodium hydroxide and methyl sulphate yields 5-hydroxy-3:7:4'-trimethoxy-2-styrylchromone, m. p. 156°. Before the difficulty of demethylation was known, kaempferol was synthesised for comparison: thus anisic anhydride, m. p. 98—99°,  $\omega$ -methoxyphloroacetophenone, and sodium anisate condense to give 5:7-dihydroxy-3:4'-dimethoxyflavone, m. p. 234°, which on demethylation yields kaempferol, m. p. 276—277°, identical with the natural product (tetra-acetyl derivative, m. p. 181—182°, sometimes with sintering at 116—120°).

3:4-Dimethoxycinnamic acid is obtained by condensation of veratraldehyde and malonic acid in pyridine-piperidine solution, or by the action of methyl sulphate and aqueous alkali on ferulic acid, m. p. 171° (prepared from vanillin and malonic acid in presence of pyridine and piperidine). The action of acetic anhydride on 3:4-dimethoxycinnamic acid gives 3:4-dimethoxycinnamic anhydride, m. p. 174—175°. From  $\omega$ -methoxyphloroacetophenone, 3:4-dimethoxycinnamic anhydride, and sodium 3:4-dimethoxycinnamate is obtained 5:7-dihydroxy-3:3':4'-trimethoxy-2-styrylchromone (+H<sub>2</sub>O), m. p. 233—234°. Demethylation does not yield a crystalline product, so that the styryl analogue of quercetin was not obtained, but the action of aqueous potassium hydroxide and methyl sulphate gives 5-hydroxy-3:7:3':4'-tetramethoxy-2-styrylchromone, m. p. 203—204°. F. M. H.

**Synthesis of Datiscetin.** J. KALFF and R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 1968—1973).—The datiscetin of Schunck and Marchlewski (A., 1894, i, 142) is found to be mixed with galangin, and their datiscin may have been a mixture of galangin rhamnoside and datiscetin glucoside. Datiscetin (I) has now

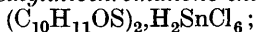


been synthesised (cf. this vol., i, 148, 423). *o*-Methoxybenzoic anhydride (prepared in 85% yield by reaction of *o*-methoxybenzoic acid, pyridine, and carbonyl chloride in benzene solution),  $\omega$ -methoxyphloroacetophenone, and sodium *o*-methoxybenzoate are heated at 180° and the product is hydrolysed with aqueous or alcoholic potassium hydroxide; the phenol is precipitated with carbon dioxide, and, on again treating with potassium hydroxide and reprecipitating, is obtained in 75% yield; diacetyl derivative, m. p. 141.5—142.5° (corr.), reconverted by hydrolysis into datiscetin 3:2'-dimethyl ether, m. p. 218—219° (corr.). By boiling 5:7-diacetoxy-3:2'-dimethoxyflavone with hydriodic acid and treatment of the hydriodide with dilute sulphurous acid, datiscetin (3:5:7:2'-tetrahydroxyflavone) is obtained, m. p. 276° (corr.) [tetra-acetyl derivative, m. p. 141° (corr.), benzoyl derivative, m. p.



Quinol monomethyl ether and  $\beta$ -chloropropionic acid in the presence of potassium hydroxide yield  $\beta$ -anisoxypropionic acid,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $110.5^\circ$ , which is converted by the successive action of phosphorus pentachloride and aluminium chloride into 6-methoxychromanone, m. p.  $49^\circ$  (oxime, m. p.  $119^\circ$ ; semicarbazone, m. p.  $229.5^\circ$ ). 3-Oximino-6-methoxychromanone, m. p.  $145^\circ$ , is hydrolysed by dilute sulphuric acid to 3-hydroxy-6-methoxychromone, m. p.  $170^\circ$ . Similarly, guaiacol and  $\beta$ -chloropropionic acid yield  $\beta$ -o-methoxyphenoxypropionic acid, m. p.  $135$ — $136^\circ$ , which is transformed successively into 8-methoxychromanone, m. p.  $89.5^\circ$  (oxime, m. p.  $145$ — $146^\circ$ ; semicarbazone, m. p.  $232^\circ$ ), 3-oximino-8-methoxychromanone, m. p.  $163^\circ$  (decomp.), and 3-hydroxy-8-methoxychromone, m. p.  $182$ — $183^\circ$ . Pyrogallol dimethyl ether and  $\beta$ -chloropropionic acid afford  $\beta$ -2 : 3-dimethoxyphenoxypropionic acid, from which 7 : 8-dimethoxychromanone, m. p.  $101^\circ$  (cf. Pfeiffer and Emmer, A., 1920, i, 561), 3-oximino-7 : 8-dimethoxychromanone, decomp.  $170^\circ$ , and 3-hydroxy-7 : 8-dimethoxychromone, m. p.  $174$ — $175^\circ$ , are derived. H. W.

**Halochromism of Hydrogenated Pyrone and Thiopyrone Systems.** F. ARNDT and J. PUSCH (*Ber.*, 1925, 58, [B], 1648—1654).—1-Thiobenzopyrone derivatives containing a hydrogenated hetero ring give intensely coloured solutions in concentrated sulphuric acid, whereas solutions of the corresponding sulphones are colourless. Conversely, among the dehydrogenated systems only the sulphones give coloured solutions. Halochromism is established definitely by the isolation of a series of coloured salts which, since the corresponding ability is lacking in the sulphones, are regarded as sulphonium compounds (oxonium compounds in the chromanone series). In the simple pyranone series, it has not been found possible to establish the ability of these compounds to form the organic components of coloured salts, and there is considerable evidence to the contrary. It appears, therefore, that halochromism is conditioned by a factor which is immediately present in the benzo series, but is introduced by some transformation in the simpler series. The following salts are described : 6-methylthiochromanone perchlorate, which is immediately decomposed by water to 6-methylthiochromanone; 6-methylthiochromanone chlorostannate,



the additive compounds of stannic chloride with 6-methylthiochromanone and chromanone; chromanone chlorostannate.

[With R. SCHWARZ.]—Benzylidenemesityl oxide is converted by hydrogen sulphide and sodium acetate in boiling alcoholic solution into 2-phenyl-6 : 6-dimethylthiopyranone,  $\text{S} \begin{smallmatrix} \text{CMe}_2-\text{CH}_2 \\ \text{CHPh}-\text{CH}_2 \end{smallmatrix} \text{CO}$ , m. p.  $42^\circ$ , b. p.  $175$ — $176^\circ/10$  mm., the colourless solution of which in concentrated sulphuric acid becomes carmine-red in 1—2 mins. 4-Methylchroman-4-ol, m. p.  $107^\circ$ , from chromanone and magnesium methyl iodide, and 4 : 6-dimethylthioflavan-4-ol, m. p.  $115$ — $116^\circ$  (perchlorate), are described. H. W.

**Thiochromanones and their Transformation Products.**

II. F. KROLLPFEIFFER [with H. SCHULTZE, H. SCHLUMBOHM, and E. SOMMERMEYER] (*Ber.*, 1925, **58**, [B], 1654—1676; cf. Krollpfeiffer and Schultze, *A.*, 1924, i, 411; Arndt, this vol., i, 1309). —The following acids are prepared by the method described previously (*A.*, 1923, i, 1114):  $\beta$ -*p*-chlorophenylthiolpropionic acid, m. p. 90—91°;  $\beta$ -*p*-methoxyphenylthiolpropionic acid, m. p. 81—82°;  $\beta$ -1-tetrahydronaphthylthiolpropionic acid, m. p. 95°;  $\beta$ -phenylthiol-*n*-butyric acid, b. p. 185°/10 mm.;  $\beta$ -*p*-tolylthiol-*n*-butyric acid, m. p. 44—45°, b. p. 193°/10 mm. Ring closure of these acids by concentrated sulphuric acid or phosphoric oxide yields the following thiochromanones: 6-chlorothiochromanone, m. p. 67—69° after softening; 6-methoxythiochromanone, b. p. 185—186°/12 mm., m. p. 29—30° [semicarbazone, m. p. 212° (decomp.) when slowly heated, m. p. 221° when rapidly heated]; 2-methylthiochromanone, b. p. 152°/13 mm., m. p. 18—19° (semicarbazone, m. p. 167—168°); 2 : 6-dimethylthiochromanone, b. p. 179°/20 mm., m. p. 64—65° (semicarbazone, m. p. 205—206°); the product obtained from  $\beta$ -2-tetrahydronaphthylthiolpropionic acid gives a tetrahydrobenzothiochromanone, m. p. 60—61° [the semicarbazone, m. p. 224°, described previously (*A.*, 1923, i, 1114) is a mixture of the semicarbazone, m. p. 255°, and a second semicarbazone, m. p. 238—240°, which yields an isomeric tetrahydrobenzothiochromanone, b. p. 223°/14 mm.]; 7 : 8-tetrahydrobenzothiochromanone, m. p. 60—61°.

6-Methylthiochromanone is converted by 1 mol. of bromine into 6-methylthiochromanone *perbromide*, which when exposed to air gives 3-bromo-6-methylthiochromanone; it is converted by diethylaniline into 6-methylthiochromanone and by cold water into 6-methylthiochromanone sulphoxide, m. p. 110° (also obtained from 6-methylthiochromanone and hydrogen peroxide). The sulphoxide is converted by hydrobromic acid into 3-bromo-6-methylthiochromanone and reduced by zinc and sulphuric acid to 6-methylthiochromanone. 2 : 6-Dimethylthiochromanone sulphoxide has m. p. 97—98°.

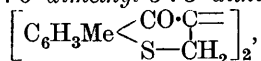
Bromination of the thiochromanones is effected in the presence of carbon disulphide or, occasionally, glacial acetic acid. 3-Bromothiochromanone, m. p. 76—77°, 3-bromo-6-methylthiochromanone, m. p. 60—61°, 3 : 3-dibromo-6-methylthiochromanone, m. p. 156° (decomp.), 3-bromo-2 : 6-dimethylthiochromanone, m. p. 101—102°, 3 : 3-dibromo-2 : 6-dimethylthiochromanone, m. p. 111—112°, 6-chloro-3-bromothiochromanone, m. p. 111—112° after softening, 3-bromo-6-methoxythiochromanone, and 3 : 3-dibromo-5 : 6-benzothiochromanone, m. p. 115—116°, are described. Removal of hydrogen bromide from these compounds by boiling dimethylaniline leads to the formation of the following thiochromones: 6-methylthiochromone, m. p. 69—70°, b. p. 194°/12 mm.; 3-bromo-6-methylthiochromone, m. p. 117°; 6-chlorothiochromone, b. p. 205—210°/12 mm., m. p. 143—144°; 6-methoxythiochromone, m. p. 110—111° (prepared also from  $\beta$ -*p*-methoxyphenylthiolpropionic acid and phosphoryl chloride); 2 : 6-dimethylthiochromone, m. p. 120—121°; 3-bromo-

2 : 6-dimethylthiochromone, m. p. 134—135°; 3-bromo-5 : 6-benzothiochromone, m. p. 168—169°.

3-Bromo-6-methylthiochromanone is converted by aqueous-alcoholic ammonia into 6-methylthiochromone, but by absolute-alcoholic ammonia into 3-amino-6-methylthiochromanone, m. p. 67—68° (decomp.) after softening, which readily loses ammonia under the influence of acids.

3-Bromo-6-methylthiochromanone is converted by boiling, aqueous-alcoholic sodium hydroxide solution into o-aceto-p-thiocresol, b. p. 144—146°/12 mm. (semicarbazone, m. p. 199—200°; corresponding disulphide, m. p. 173—174°), without apparent formation of 6-thiol-m-toluic acid. 3-Bromo-2 : 6-dimethylthiochromanone under similar conditions yields 6-thiol-m-toluic acid, m. p. 155—157° after softening [corresponding disulphide, m. p. 291° after softening; 6-methylthiol-m-toluic acid, m. p. 140—141° (?); cf. this vol., i, 1311]. 3-Bromo-6-methylthiochromone is transformed by cold, alcoholic sodium ethoxide into 3-hydroxy-5-methylthionaphthen-2-aldehyde,  $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{S} \end{smallmatrix} > C \cdot CHO$ , m. p. 126—127° (sodium salt; phenylhydrazone, m. p. 143°). Since the oxythionaphthaldehydes are readily accessible by other methods, the process affords a convenient method of determining the constitution of thiochromones and thiochromanones. Thus 3-bromo-4 : 6-benzothiochromone is transformed into 3-hydroxy-4 : 5-benzothionaphthen-2-aldehyde, m. p. 147°, identical with the product obtained from 3-hydroxy-4 : 5-benzothionaphthen by Gattermann's method, using hydrocyanic acid.

3-Bromo-6-methylthiochromanone is converted by crystalline sodium acetate in alcoholic solution into 6-methylthiochromone, whereas glacial acetic acid and anhydrous sodium acetate transform it mainly into 6 : 6'-dimethyl-3 : 3'-dithiochromanol,

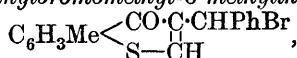


m. p. 151—152°. Attempts to prepare the latter compound by the condensation of 6-methylthiochromanone with the p-dimethyl-aminoanil of 6-methylthiochromonol in the presence of acetic anhydride gave 3-N-acetyl-N-dimethylaminophenylamino-6-methylthiochromone,  $C_6H_3Me \begin{smallmatrix} \text{CO} \cdot C \cdot NAc \cdot C_6H_4 \cdot NMe_2 \\ \diagup \quad \diagdown \\ \text{S} - CH \end{smallmatrix}$ , m. p. 193°, which is

hydrolysed by sulphuric acid to 6-methylthiochromonol and p-aminodimethylaniline (picrate, m. p. 139°). 3-N-Propionyl-N-dimethylaminophenylamino-6-methylthiochromone has m. p. 157—158°. Under analogous conditions, 6-chloro-3-bromothiochromanone is converted mainly into 6-chlorothiochromone, whereas 3-bromo-6-methoxythiochromanone yields 6 : 6'-dimethoxy-3 : 3'-dithiochromanol, m. p. 168—169°; a bimolecular product could not be obtained from 3-bromo-6-methylthiochromanone and β-bromo-1-ketotetrahydronaphthalene, m. p. 40—41°. The dithiochromanols are converted by bromine in acetic acid solution into the corresponding dibromides (6 : 6'-dimethyl-3 : 3'-dithiochromanol dibromide,

decomp. 290—295° after darkening at 130°), which are transformed by boiling pyridine or quinoline into the corresponding dithiochromones; 3 : 3'-dithiochromone,  $\left[ \text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{C} \\ \text{S} - \text{CH} \end{smallmatrix} \right]_2$ , and 6 : 6'-dimethyl-3 : 3'-dithiochromone are described.

3-Benzylidene-6-methylthiochromanone is converted by bromine in carbon disulphide into the corresponding dibromide, m. p. 167° (decomp.), which when heated above its m. p. loses hydrogen bromide and passes into 3-phenylbromomethyl-6-methylthiochromone,



m. p. 115—116° (pyridinium salt,  $\text{C}_{22}\text{H}_{18}\text{ONBrS}$ , m. p. 137—138°). The monobromo compound is converted into 3-phenylmethoxymethyl-6-methylthiochromone, m. p. 118—119° after softening, 3-phenylethoxymethyl-6-methylthiochromone, m. p. 124—125°, 3-phenylacetoxymethyl-6-methylthiochromone, m. p. 120—121°, and 3-phenylphenylthiomethyl-6-methylthiochromone, m. p. 129—130°.

Reduction of thiochromanones by Clemmensen's method leads to the corresponding thiochromans; thiochroman, b. p. 124—125°/10 mm. (sulphone, m. p. 87—88°), 6-methylthiochroman, b. p. 137°/12 mm. (sulphone, m. p. 81° after softening), and 6 : 8-dimethylthiochroman, b. p. 146—147°/12 mm. (sulphone, m. p. 101—102°), are described.

The action of Grignard's reagents on thiochromanones yields the corresponding thiochromanols, from which the  $\Delta^3$ -thiochromenes are derived by distillation over phosphoric oxide. The following individuals are described: 4-methylthiochroman-4-ol, m. p. 109—111°; 4-methyl- $\Delta^3$ -thiochromene, b. p. 138°/12 mm.; 4 : 6-dimethylthiochroman-4-ol, m. p. 119—120°; 4 : 6-dimethyl- $\Delta^3$ -thiochromene, b. p. 145—146°/16 mm.; 4 : 6 : 8-trimethylthiochroman-4-ol, m. p. (indef.) 46—49°; 4 : 6 : 8-trimethyl- $\Delta^3$ -thiochromene, b. p. 155—157°/12 mm.; 6-methyl-4-ethylthiochroman-4-ol, m. p. 52—53°, b. p. 159—160°/12 mm.; 6-methyl-4-ethyl- $\Delta^3$ -thiochromene, b. p. 158—160°/12 mm.; 4-phenyl-6-methylthiochroman-4-ol, m. p. 112—113°; 4-phenyl-6-methyl- $\Delta^3$ -thiochromene, b. p. 211°/12 mm., m. p. 47—48°.

H. W.

### Pyrone Problem. 1-Thiopyrones and 1-Thiopyranones.

F. ARNDT, P. NACHTWEY, and J. PUSCH (*Ber.*, 1925, 58, [B], 1633—1644).—Diacetylacetone is converted by phosphorus pentasulphide in the presence of benzene into (?) trithiodiacetylacetonecyclo-disulphide,  $\begin{smallmatrix} \text{S} \cdot \text{CMe} \cdot \text{CH} \\ \text{S} \cdot \text{CMe} \cdot \text{CH} \end{smallmatrix} > \text{CS}$ , m. p. 183—184°. The action of hydrogen sulphide on distyryl ketone in boiling alcoholic solution in the presence of sodium acetate leads to the formation of 2 : 6-diphenylthiopyranone (A form),  $\text{S} \begin{smallmatrix} \text{CHPh} \cdot \text{CH}_2 \\ \text{CHPh} \cdot \text{CH}_2 \end{smallmatrix} > \text{CO}$ , m. p. 113—114° [*phenylhydrazone*, m. p. 155—156°, decomp. 190°; *semicarbazone*, m. p. 206—207° (decomp.)]. If the proportion of sodium acetate is increased, 2 : 6-diphenylthiopyranone (B form), m. p. 87—88°, is



obtained [the corresponding *phenylhydrazone*, m. p. 142—145° (decomp.), and *semicarbazone* are described]. The isomerism of these substances persists in all their derivatives which contain the hydrogenated ring, but disappears when the ring is ruptured or dihydrogenated; the compounds therefore stand probably in a *cis-trans* relationship to one another. 2:6-Diphenylthiopyranone *A* is converted by hydrogen peroxide in glacial acetic acid into 2:6-diphenylthiopyranonesulphone *A*, m. p. 235°, an additive compound,  $C_{27}H_{16}O_3S, H_2O_2$ , m. p. 134—135° (decomp.), being immediately produced, whereas it is oxidised by bromine in the presence of water and ether or pyridine to 2:6-diphenylthiopyranone sulfoxide *A*, m. p. 196—198°. 2:6-Diphenylthiopyranonesulphone *B*, m. p. 196°, its additive compound, m. p. 123°, with hydrogen peroxide, and 2:6-diphenylthiopyranone sulfoxide *B*, m. p. 136—137°, are similarly prepared. The sulfoxides and sulphones are very sensitive to alkali hydroxide, whereby they are smoothly decomposed into distyryl ketone, sodium sulphide and sulphate. Introduction of bromine into the sulfoxides could not be effected, whereas the sulphones yield respectively 3:5-dibromo-2:6-diphenylthiopyranonesulphone *B*, m. p. 234—235°, and 3:5-dibromo-2:6-diphenylthiopyranonesulphone *A*, m. p. 247°; introduction of a single bromine atom could not be effected. Bromination of the 2:6-diphenylthiopyranones is exceedingly difficult to control, since the halogen tends to cause opening of the ring and also the introduction of substituents in position 3 appears invariably to lead to more or less resinous products; either form of 2:6-diphenylthiopyranone gives with bromine in chloroform solution a small proportion of a substance,  $C_{17}H_{14}OS$ , m. p. 142°, together with distyryl ketone tetrabromide. The action of phosphorus pentachloride in the presence of benzene on 2:6-diphenylthiopyranone *A* or *B* results in the production of 2:6-diphenyl-1-thiopyrone,  $S < \begin{smallmatrix} CPh:CH \\ CPh:CH \end{smallmatrix} > CO$ , m. p. 132—133° (hydrochloride), and 3-chloro-2:6-diphenylthiopyrone, m. p. 119—120° (hydrochloride); 2:6-diphenylthiopyrone dibromide has m. p. 171°. 2:6-Diphenylthiopyronesulphone, m. p. 144—145°, obtained by oxidation of 2:6-diphenylthiopyrone with hydrogen peroxide or, more conveniently, by treating 3:5-dibromo-2:6-diphenylthiopyranonesulphone with boiling pyridine, is immediately decomposed into distyryl ketone by treatment with alkali hydroxide. 3-Chloro-2:6-diphenyl-1-thiopyronesulphone, m. p. 163°, is obtained by oxidation of 3-chloro-2:6-diphenylthiopyrone or by the action of chlorine in carbon tetrachloride on 2:6-diphenylthiopyronesulphone. The oximes of 2:6-diphenylthiopyronesulphone and 3-chloro-2:6-diphenylthiopyrone have m. p. 186—187° (incipient decomp. 165°) and 211° (incipient decomp. 180°), respectively.

2:6-Diphenylpyranone, prepared from acetonedicarboxylic acid and benzaldehyde followed by heating of the initial product in alkaline solution, appears to exist in two isomeric (? *cis-trans*) forms, m. p. 130° and 74—75°. 2:6-Diphenylpyrone dibromide, m. p. 165—166°, is described.

In analogy with the nomenclature of the benzopyrone series, it is proposed to apply the term pyranone to tetrahydropyrone.

H. W.

**Chromone and 1-Thiochromone Series.** F. ARNDT [with W. FLEMMING, E. SCHOLZ, V. LÖWENSOHN, S. KÄLLNER, and B. EISTERT] (*Ber.*, 1925, **58**, [B], 1612—1632; cf. A., 1923, i, 826).—Bromination of thiochromanones occurs stepwise, so that the desired degree of bromination can be secured by regulating the quantity of bromine used, but the further bromination of a bromo derivative is more difficult than the formation of the more highly brominated compound from non-halogenated material. 6-Methylthiochromanone is converted successively into 3-bromo-6-methylthiochromanone,  $C_6H_3Me \begin{smallmatrix} \diagup CO \cdot CHBr \\ | \\ S-CH_2 \end{smallmatrix}$ , m. p. 60—61°, and 3:3-di-

bromo-6-methylthiochromanone, m. p. 155° (decomp.); further bromination does not occur. Thiochromanone, on the other hand, is converted successively into 3-bromothiochromanone, m. p. 76°, 3:3-dibromothiochromanone, m. p. 97°, and 3:3:6-tribromothiochromanone, m. p. 171°. The position of the halogen atoms in these compounds is established by the observation that the dibromo compound described above differs from the 3:6-dibromothiochromanone, m. p. 109—110°, obtained by bromination of 6-bromothiochromanone, m. p. 70° (prepared from  $\beta$ -p-bromophenylthiolpropionic acid, m. p. 119°), whereas identical (3:3:6-) tribromo derivatives are derived from thiochromanone and its 6-bromo compound. The thioflavanones behave similarly. The following compounds are described: 3-bromo-6-methylthioflavanone, m. p. 120°; 3:3-dibromo-6-methylthioflavanone, m. p. 138°; 3-bromothioflavanone, m. p. 135°; 3:3-dibromothioflavanone; 3:3:6-tribromothioflavanone, m. p. 157°. The 3-bromo-thiochromanones and -thioflavones lose hydrogen bromide under the influence of alcoholic alkali hydroxide or, preferably, pyridine, giving thiochromones or thioflavones; the latter substances may also be obtained by the action of phosphorus pentachloride on thiochromanones if they do not contain a bromine atom in the pyrone ring. The following individuals are described: 6-methylthiochromone,  $C_6H_3Me \begin{smallmatrix} \diagup CO \cdot CH \\ | \\ S-CH \end{smallmatrix}$ ,

m. p. 61—62°; 1-thiochromone, m. p. 78°; 3-bromo-6-methylthiochromone, m. p. 117—118°; 3-bromothiochromone, m. p. 142—143°; 6-bromothiochromone, m. p. 157°; 3:6-dibromothiochromone, m. p. 178°; 1-thioflavone, m. p. 125°; 6-methylthioflavone, m. p. 149—150°; 3-bromo-6-methyl-1-thioflavone, m. p. 117—118°; 3-bromo-1-thioflavone, m. p. 136°; 3:6-dibromothioflavone, m. p. 195—196°. (The action of phosphorus pentachloride on chromanone affords a ready method of preparing chromone.)

The action of bromine on thiochromones and thioflavones is primarily additive, yielding dibromides which are more or less intensely coloured. Chromone itself yields colourless *chromone dibromide* [2:3-dibromochromanone], m. p. 104—105° (which is converted by boiling alcohol into 3-bromochromone, m. p. 65—66°),

together with *dichromone hydrotribromide*,  $(C_9H_6O_2)_2 \cdot HBr \cdot Br_2$ , m. p. 127°, but it remains uncertain whether the thio derivatives are constituted analogously. The following compounds are described: *6-methylthiochromone dibromide*, a yellow and a red modification, m. p. 142—143°, which yields 3-bromo-6-methylthiochromone when heated with alcohol; *1-thiochromone*, yellow form, m. p. 141°, red variety, m. p. (indef.) 130—135°; (?) *3-bromo-6-methylthiochromone dibromide*; *6-methyl-1-thioflavone dibromide*, m. p. 121—123° (decomp.), and hence 3-bromo-6-methylthioflavone (labile form), m. p. 98—99°; *1-thioflavone dibromide*, m. p. 111—112°, and hence 3-bromothioflavone; *3-bromo-6-methylthioflavone dibromide*, m. p. (indef.) 97—99°; *3 : 3-dibromo-6-methylthioflavanone tetrabromide*, m. p. 127—129° (decomp. 137—140°) after softening at 120°, and hence 3-bromo-6-methylthioflavone dibromide and 3-bromo-6-methylthioflavone.

The oxidation of thiochromanones and thioflavanones to the corresponding sulphones is readily effected by the prolonged action of cold hydrogen peroxide. They are readily decomposed by alkali hydroxide, yielding strongly acidic non-homogeneous thio compounds, probably mixtures of sulphonic and sulphinic acids; the thioflavanonesulphones also give benzaldehyde in quantity much less than corresponds with the phenyl group present in them. The thiochromones and thioflavones are much less readily oxidised and their sulphones are far more stable towards alkali hydroxide. The following compounds are described in this connexion:  *$\beta$ -p-tolylsulphoxylpropionic acid*,  $C_{10}H_{12}O_3S$ , m. p. 147—148°;  *$\beta$ -p-tolylsulphonylpropionic acid*, m. p. 112—113°; *p-tolylsulphonyl- $\beta$ -phenylpropionic acid*, m. p. 200—201°; *6-methylthiochromanonesulphone*, m. p. 163°; *thiochromanonesulphone*, m. p. 131—132°; *6-methylthioflavanone sulphoxide*, m. p. 177—178°; *6-methylthioflavanonesulphone*, m. p. 177—178° when rapidly heated, m. p. 191—192° after softening at 177° when slowly heated; *3-bromo-6-methylthiochromanonesulphone*, m. p. 165°; *3-bromo-6-methylthiochromanone sulphoxide*, m. p. 158°; *3-bromothiochromanonesulphone*, m. p. 199—200°; *3 : 3-dibromo-6-methylthiochromanonesulphone*, m. p. 198°; *3 : 3-dibromo-6-methylthiochromanone sulphoxide*, m. p. 166°; *3-bromo-6-methylthioflavanonesulphone*, decomp. 238—239°; *3-bromothiochromanonesulphone*, m. p. 175—176°; *3 : 3-dibromo-6-methylthioflavanonesulphone*, decomp. 232—239°; *3-benzylidene-6-methylthiochromanonesulphone*, m. p. 204—205°, from 3-benzylidene-6-methylthiochromanone and hydrogen peroxide or from 6-methylthiochromanonesulphone and benzaldehyde; *6-methylthiochromonesulphone*, m. p. 145°, from 6-methylthiochromone and hydrogen peroxide in boiling glacial acetic acid or from 3-bromo-6-methylthiochromanonesulphone and boiling pyridine [6-methylthiochromone and hydrogen peroxide give an additive compound, m. p. 125° (decomp.) in cold acetic acid solution]; *thiochromonesulphone*, m. p. 144°; *2 : 3-dibromo-6-methylthiochromanonesulphone*, m. p. 192° (decomp.), from the methylthiochromonesulphone and bromine in acetic acid solution; *3-bromo-6-methylthiochromonesulphone*, m. p. 216—217°, from 3 : 3-dibromo-

6-methylthiochromanonesulphone or 2:3-dibromo-6-methylthiochromanonesulphone by loss of hydrogen bromide or by oxidation of 3-bromo-6-methylthiochromone; 6-methylthioflavonesulphone, m. p. 156—157°; thioflavonesulphone, m. p. 132—133°; 2:3-dibromo-6-methylthioflavonesulphone, m. p. 221°; 3-bromo-6-methylthioflavonesulphone, labile form, m. p. 175—176°, stable variety, m. p. 206—207°.

Only one bromine atom can be introduced into the thiochromonols; the 2-bromothiochromonols yield intensely yellow alkali salts. 2-Bromothiochromonol,  $C_9H_5O_2BrS$ , m. p. 195°, and 2-bromo-6-methylthiochromonol, m. p. 179°, are described. With chlorine, on the other hand, 2-chloro-6-methylthiochromonol, m. p. 175—176°, or 2:2-dichloro-6-methylthiochromonol, m. p. 138—139°, can be obtained. The latter substance is decomposed by boiling water into 5-methylthionaphthenquinone, m. p. 145°, and 6-thiol-m-toluic acid, m. p. 224° (?) [6-methylthiol-m-toluic acid, m. p. 134° (?); cf. this vol., i, 1306]. 6-Methylthiochromonol is converted by methyl sulphate into the corresponding O-methyl ether, m. p. 108—109°, and by benzoyl chloride into O-benzoyl-6-methylthiochromonol, m. p. 181°.

H. W.

[Non-catalytic] Reduction of Thionaphthen. R. FRICKE and G. SPILKER (*Ber.*, 1925, **58**, [B], 1589—1601).—*o*-Ethylthiophenol, obtained by the reduction of thionaphthen by sodium and ethyl alcohol (cf. Fricke and Spilker, this vol., i, 249), has b. p. 210.1—210.9°/768 mm.,  $d_4^{20}$  1.0349, whereas its methyl derivative has b. p. 228.2—228.6°/773 mm.,  $d_4^{20}$  1.0253. The residue left after removal of *o*-ethylthiophenol contains unchanged thionaphthen and 2:3-dihydrothionaphthen, b. p. 233.5—234.5° (corr.)/768 mm.,  $d_4^{20}$  1.1125, which are separated from one another by taking advantage of the ability of the former and inability of the latter to yield a picrate or, more conveniently, by converting the latter into its additive compound, m. p. 128—129°, with mercuric chloride. 2:3-Dihydrothionaphthensulphone, m. p. 91.5—92°, is prepared by oxidising 2:3-dihydrothionaphthen dissolved in glacial acetic acid with hydrogen peroxide.

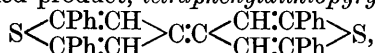
The constitution of *o*-ethylthiophenol is established by converting it by chlorine in glacial acetic acid solution into *o*-ethylbenzenesulphonyl chloride and thence into *o*-ethylbenzenesulphonamide, m. p. 126—126.5°. [The product described as *o*-ethylbenzenesulphonamide in the literature (m. p. 99—100° or 97°), prepared by the sulphonation of ethylbenzene, is shown to be a mixture of *o*- and *p*-ethylbenzenesulphonamide, m. p. 109°]. Further, authentic *o*-ethylbenzenesulphonamide is reduced to *o*-ethylthiophenol identical with that derived from thionaphthen. Reduction of thionaphthen by sodium and ethyl alcohol causes mainly fission of the heterocyclic ring; very similar results are obtained when methyl or amyl alcohol is used. Hydrogenation of thionaphthen by hydrogen at elevated temperatures and under high pressure in the absence of a catalyst leads to the formation of benzene, toluene, ethylbenzene, *o*-ethylthiophenol, thionaphthen, 2:3-di-

hydrothionaphthen, anthracene, hydrogen sulphide, methane, and its homologues; the yield of 2:3-dihydrothionaphthen is very small.

H. W.

**Conversion of 4-Thiopyrones into Dipyrlylene. Dithiopyrlylene.** F. ARNDT, P. NACHTWEY, and J. PUSCH (*Ber.*, 1925, 58, [B], 1644—1646; cf. this vol., i, 57).—In part, a reply to Schönberg (this vol., i, 149).

*Dithioflavone*, m. p. 112—113°, prepared by the action of phosphorus pentasulphide on 1-thioflavone in the presence of benzene, remains unchanged when heated alone and does not give a definite product when heated with copper. 2:6-Diphenyldithiopyrlylene,  $S \begin{smallmatrix} \text{CPh:CH} \\ \text{CPh:CH} \end{smallmatrix} CS$ , m. p. 129—130°, and 3-chloro-2:6-diphenyldithiopyrlylene, m. p. 155°, are affected by heat, but only the former gives a well-defined product, *tetraphenyldithiopyrlylene*,



m. p. 312—313°; the "dipyrlylene reaction" appears to lead to isolable products only when the initial material is symmetrically substituted with respect to the thio keto group.

2:6-Diphenyl-1-thiopyroneoxime, m. p. 197—198°, is prepared by prolonged treatment of diphenyldithiopyrlylene with hydroxylamine; under similar treatment diphenyl-1-thiopyrone remains unchanged.

H. W.

**Anthraquinone- and Anthracene-oxythionaphthens.** Soc. OF CHEM. IND. IN BASLE (Swiss Pat. 107333, addn. to 106422 and 103648; from *Chem. Zentr.*, 1925, i, 2514).—Anthraquinone-2-thioglycol-3-carboxylic acid when heated with acetic anhydride or anhydrous sodium acetate until evolution of carbon dioxide ceases, yields the yellow *acetyl* derivative of 2:3-anthraquinoneoxythionaphthen, from which the latter substance, deep blue, changed to orange by acids, is obtained on alkaline hydrolysis. 2:3-Anthracene-oxythionaphthen, brown (*acetyl* derivative, brown), is analogously obtained. Ring-closure of the anthracene-2-thioglycol-3-carboxylic acid also takes place in the presence of condensing agents at high temperatures.

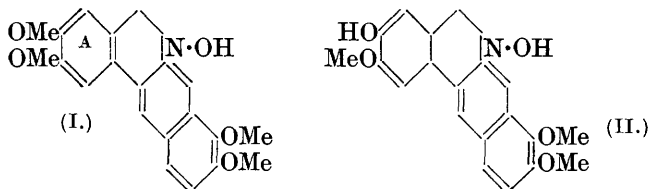
R. B.

**Possible Existence of Indigoid Dyes with a Hydrogenated Six-membered Ring.** F. ARNDT and J. PUSCH (*Ber.*, 1925, 58, [B], 1646—1647).—The following experiments indicate the improbability of the existence of the dyes named in the title. 6-Methylthiochromonol and potassium ferricyanide do not react in cold solution, whereas, in hot solution, 5:5'-dimethylthioindigotin is produced in poor yield by contraction of the ring. Molar quantities of 6-methylthiochromanone or 6-methylthiochromonol and thionaphthenquinoneanil do not yield a dye when boiled with acetic anhydride. 6-Methylthiochromanone or 6-bromothiochromanone when boiled with 2:2-dibromo-oxythionaphthen in glacial acetic acid solution yield thioindigotin, in the formation of which the chromanone does not participate. The isolation of 3-bromo-6-methylthiochromonol in addition to thioindigotin from 6-methyl-

thiochromonol and 2:2-dibromo-oxythionaphthen shows that the first step in the change consists in the redistribution of a hydrogen and a bromine atom between the components. The inverse change occurs when 2:2-dichloro-6-methylthiochromonol is boiled with oxythionaphthen in glacial acetic acid solution, whereby thio-indigotin and 2-chloro-6-methylthiochromonol are produced.

H. W.

**Alkaloids of the Calumba Root. III. Constitution of Columbamine and Jatrorrhizine.** E. SPÄTH and R. DUSCHINSKY (*Ber.*, 1925, 58, [B], 1939—1946; cf. Günzel, A., 1906, i, 976; Feist, A., 1908, i, 100; Späth and Lang, A., 1922, i, 166; Späth and Böhm, A., 1922, i, 1174).—The identity of tetrahydrocolumbamine with tetrahydropalmatine is confirmed by comparison of the bases, their chloraurates and chloroplatinates. Feist's columbamine consists mainly of palmatine (I) and it is therefore proposed



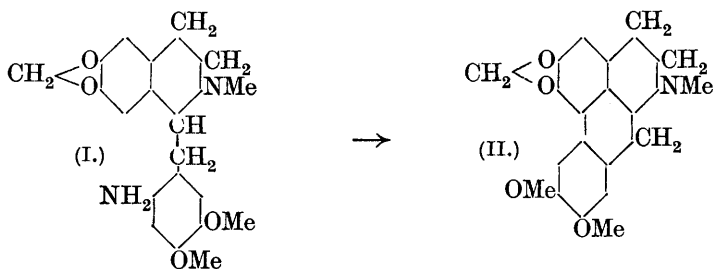
to discard the name columbamine provisionally and to apply it subsequently to another alkaloid of the Calumba root.

Jatrorrhizine is readily reduced by zinc and dilute sulphuric acid to tetrahydrojatrorrhizine, m. p. 217—218° (Feist records m. p. 206°), which is characterised by its sparingly soluble hydrochloride. Tetrahydrojatrorrhizine is converted by diazomethane into tetrahydropalmatine and by methyl iodide and alcoholic alkali hydroxide into tetrahydropalmatine methiodide; since it contains three methoxyl groups it differs from tetrahydropalmatine in that one methoxyl group of the latter is replaced by hydroxyl. To elucidate its constitution *tetrahydrojatrorrhizine ethyl ether methiodide*, m. p. 248—249° (prepared by ethylation of *tetrahydrojatrorrhizine methiodide*), is degraded by Emde's method to the substance,  $C_{22}H_{30}O_4$ , m. p. 80—83°, which, however, could not be prepared synthetically. More successful results were obtained by ethylating tetrahydrojatrorrhizine with ethyl iodide and alcoholic sodium ethoxide, conversion of the ethiodide into the ethochloride, and oxidation of the latter by potassium permanganate in alkaline solution, whereby 3-methoxy-4-ethoxyphthalic acid (identified as the ethylimide, m. p. 205—206°) and hemipinic acid are obtained, thus establishing the presence of the hydroxyl group in the nucleus A of palmatine (I). The exact position of this hydroxyl group is proved by the mild oxidation of tetrahydrojatrorrhizine ethyl ether to 7-methoxy-6-ethoxy-1-keto-1:2:3:4-tetrahydroisoquinoline, thus establishing the constitution (II) for jatrorrhizine.

*m*-Hemipinic acid is converted by partial demethylation into 4-hydroxy-3-methoxy-o-phthalic acid, m. p. about 205° with con-

version into the *anhydride*, m. p. 217.5—219.5°. The acid is converted by ethyl iodide and sodium ethoxide into 3-methoxy-4-ethoxy-*o*-phthalic acid, m. p. 184° (anhydride, m. p. 197°; ethylimide, m. p. 203°).  
H. W.

**Synthesis of *dl*-Dicentrine.** R. D. HAWORTH, W. H. PERKIN, jun., and J. RANKIN (*J. Chem. Soc.*, 1925, **127**, 2018—2023).—The preparation of the *methiodide*, m. p. 239—240°, of 1-veratryl-6:7-methylenedioxydihydroisoquinoline (A., 1924, i, 1099) is accompanied by that of the *methiodide*, m. p. 232—233° (decomp.), of 6:7-methylenedioxy-3':4'-dimethoxy-1-benzoyl-3:4-dihydroisoquinoline (A., 1924, i, 1336), which arises by spontaneous oxidation of the veratryl compound. The *methiodide* mixture, after conversion into the more soluble methochlorides, is completely reduced, first by zinc dust and sulphuric acid and then electrolytically, to 1-veratrylhydrohydrastinine, an uncrystallisable syrup [*hydrochloride*, m. p. 215—216°; *hydriodide*, m. p. 180—182°; *picrate*, m. p. 188—189° (decomp.)]. Nitration in acetic acid solution gives 6'-nitroveratrylhydrohydrastinine, m. p. 118° (*hydriodide*, m. p. 213°; *picrate*, m. p. 192°), reduced by stannous chloride and hydrochloric acid to 6'-aminoveratrylhydrohydrastinine (I), an uncrystallisable



oil [*dihydrochloride*, m. p. 250° (decomp.)]. Treatment with copper powder after diazotisation gives a 15% yield of *dl*-dicentrine (II), m. p. 178—179° [*methiodide*, m. p. 228—229°, *hydrochloride*, m. p. 263—265° (decomp.), *picrate*, m. p. 188—189°]. The authors hope to obtain, by resolution, an optically active base identical with the naturally occurring dicentrine.  
M. J.

**Strychnos Alkaloids. LXV. Oxidation of Hanssen's Acid.** H. LEUCHS [and, in part, K. TAUBE] (*Ber.*, 1925, **58**, [B], 1729—1732).—Hanssen's acid (cf. A., 1887, 505; Leuchs, Mildbrand, and Leuchs, A., 1922, i, 1052) is converted by hydrogen peroxide into the corresponding amine oxide,  $C_{19}H_{22}O_7N_2$ , isolated as the *hydrobromide*. Attempted ozonisation of the acid yielded mainly the *nitrate* of the acid  $C_{19}H_{22}O_6N_2 \cdot HNO_3$ , owing to the presence of nitrogen in the oxygen employed. Bromine in the presence of hydrobromic acid converts Hanssen's acid into the *hydrobromide*,  $C_{19}H_{22}O_8N_2 \cdot HBr \cdot 3H_2O$  [the corresponding *nitrate* and the free *amino-acid* (+ $H_2O$ ) are described]; it appears most probable that the group  $C_2:C:C_2$  of the acid is oxidised to a diketone,  $C_2:CO/$

$\text{CO}\cdot\text{C}_2$ , and this probability is strengthened by the isolation of the *monoxime hydrochloride*,  $\text{C}_{19}\text{H}_{22}\text{O}_8\text{N}_3\cdot\text{HCl}$ . H. W.

**Preparation of Oxycodoinones.** E. MERCK, CHEMISCHE FABRIK (D.R.-P. 411530; from *Chem. Zentr.*, 1925, ii, 94—95).—Codeinones or codeines are oxidised with chromic acid in acetic acid solution. Oxycodoinone, m. p. about  $273^\circ$  (decomp.), has therapeutic uses. A. C.

**Condensation Reactions of Oxindole and 3-Oxythionaphthen.** A. K. MACBETH and J. CRAIK (*Proc. Roy. Irish Acad.*, 1925, 37, B, 53—57; cf. Orchardson, Wood, and Bloxam, A., 1907, ii, 203; Friedländer and others, A., 1907, i, 334; 1914, i, 876; Perkin and Thomas, T., 1909, 95, 796).—Oxindole and 3-oxythionaphthen may be determined by means of their sparingly soluble condensation products with aldehydes, which are formed in quantitative yields. Oxindole condenses quantitatively with anthraquinone-2-aldehyde and 5-nitroanthraquinone-2-aldehyde, forming *anthraquinone-2-aldehydeindogenide*, red, m. p.  $327^\circ$ , and *5-nitroanthraquinone-2-aldehydeindogenide*, brown, decomp. about  $315^\circ$ , respectively. 3-Oxythionaphthen condenses with anthraquinone-2-aldehyde, 5-nitroanthraquinone-2-aldehyde, 1-chloroanthraquinone-2-aldehyde, and isatin forming condensation products of the general formula,  $\text{R}\cdot\text{CH}\cdot\text{C}\begin{smallmatrix} \text{---S---} \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$ , the four products being, respectively, yellow, m. p.  $320^\circ$ ; yellow, m. p.  $270^\circ$ ; yellow, decomp.  $264^\circ$ ; red, not melting below  $330^\circ$ .

L. F. H.

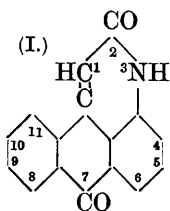
**4- and 6-Methylisatin.** F. MAYER and R. SCHULZE (*Ber.*, 1925, 58, [B], 1465—1469).—The action of concentrated sulphuric acid on *isonitrosoaceto-m-toluidide* at  $65^\circ$  yields a mixture of 4- and 6-methylisatin which can be separated roughly into its components by taking advantage of the varying rates at which they separate from aqueous acidic solution. 4-Methylisatin, m. p.  $189^\circ$  after softening at  $175^\circ$ , is converted by hydrogen peroxide in alkaline solution entirely into 6-amino-*o*-toluic acid; it appears to be the chief component of the mixture described by Bauer (A., 1907, i, 603; 1909, i, 466) as 6-methylisatin. 6-Methylisatin could not be isolated in the homogeneous form, the product on treatment with alkali hydroxide and hydrogen peroxide giving a small proportion of 6-amino-*o*-toluic acid in addition to 2-amino-*p*-toluic acid. (The two acids are readily separated from one another, since the latter is completely precipitated from alkaline solution by addition of hydrochloric acid and sodium acetate, whereas the former is only precipitated as the *copper* salt). Homogeneous 6-methylisatin appears to have been obtained by Findeklee (A., 1906, i, 21).

2-Amino-*p*-toluic acid is converted by methyl alcohol and hydrogen chloride into the *methyl* ester, m. p.  $44^\circ$ , whereas 6-amino-*o*-toluic acid is not esterified under these conditions.

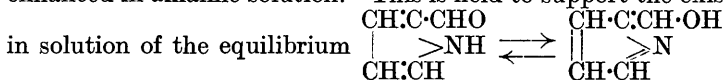
H. W.



**Pyridanthrone Synthesis.** R. SEKA and G. SCHRECKENTAL (*Ber.*, 1925, **58**, [B], 1778—1783).—*m*-Cinnamoylamino benzoic acid, m. p. 242° (acetyl derivative), prepared by the action of cinnamoyl chloride on *m*-aminobenzoic acid in boiling benzene or from the acid and excess of ethyl cinnamate at 120°, is converted by concentrated sulphuric acid at 80—90° into pyridanthrone (I), m. p. 406—408° after darkening, identical with one of the components of technical pyridanthrone. Similarly *m*-cinnamoylaminoanisic acid, m. p. 267—268°, yields 4-methoxypyridanthrone in poor yield, probably owing to the possibility of the condensation proceeding in two directions. *m*-Cinnamoylamino-*p*-toluic acid, m. p. 279°, with which this possibility is excluded, gives much better yields of 4-methylpyridanthrone, decomp. 356—359° after darkening at 330°. H. W.



**Constitution of Pyrrolealdehyde.** G. RASTELLI and A. MINGOZZI (*Gazzetta*, 1925, **55**, 549—551).—The absorption spectrum of the so-called pyrrolealdehyde has been studied. Since pyrrole itself exhibits continuous absorption (Hartley and Dobbie, T., 1902, **81**, 929) or, at high concentration, a slight band at  $\nu=3800$  (Korschun and Roll, A., 1923, ii, 107), and since also the absorption of the group  $\text{-CHO}$  is general (Stewart and Baly, T., 1899, **75**, 489), true pyrrolealdehyde should give a continuous absorption. In opposition to the formula suggested by Fischer (Angeli, A., 1923, i, 135), pronounced absorption bands exist, that at  $\nu=3100$  being enhanced in alkaline solution. This is held to support the existence



W. E. E.

**Pyridine Derivatives.** A. PIERONI [with B. HAUPT] (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 125—127).—A preliminary notice of the following preparations: 2-chloro-5-iodopyridine  $\rightarrow$  2-chloro-5-pyridyl iodochloride (m. p. 115°, decomp.)  $\rightarrow$  2-chloro-5-iodoxypyridine (explodes at 205°); 3-nitro-2-aminopyridine  $\rightarrow$  3-bromo-5-nitro-6-aminopyridine  $\rightarrow$  2-chloro-5-bromo-3-nitropyridine; 3-nitro-2-aminopyridine  $\rightarrow$  3-nitro-2-acetamidopyridine  $\rightarrow$  3-amino-2-acetamidopyridine; 2-chloro-5-aminopyridine  $\rightarrow$  2-chloro-5-pyridylazo- $\beta$ -naphthol (m. p. 185°); 2-chloro-5-pyridyldiazonium chloride  $\rightarrow$  2-chloro-5-pyridylhydrazine (m. p. 127°)  $\rightarrow$  benzaldehyde-2-chloro-5-pyridylhydrazine (m. p. 208°). W. E. E.

**Products of the Nitration of 2- and 4-Benzylpyridine.** A. E. TSCHITSCHIBABIN, B. M. KUINDSHI, and S. W. BENEWOLEN-SKAJA (*Ber.*, 1925, **58**, [B], 1580—1587).—The main product of the action of a cold mixture of sulphuric ( $d$  1.84) and nitric ( $d$  1.4) acids on 2-benzylpyridine is 2-*p*-nitrobenzylpyridine, m. p. 81° (cf. Königs and others, this vol., i, 833), the constitution of which is established by oxidation to 2-*p*-nitrobenzoylpyridine, m. p. 100°,

and *p*-nitrobenzoic acid. 2-*p*-Nitrobenzylpyridine methiodide, decomp. above 240°, is described. The nitro compound or 2-*p*-nitrobenzylpyridine is converted by more drastic nitration into 2-*o*:*p*-dinitrobenzylpyridine, m. p. 93° [*picrate*, m. p. 164—165°; *chloroplatinate*, m. p. 209—211° (decomp.)], the pale yellow crystals of which rapidly become violet and then blue when exposed to direct sunlight, probably owing to conversion into the corresponding pyridone methide, since 2-*o*:*p*-dinitrobenzylpyridine methiodide, m. p. (indef.) 197—198°, gives dark blue 2-dinitrobenzylidene-1-methyl-dihydropyridine, m. p. 201° (decomp.), when treated with alkali. 2-*o*:*p*-Dinitrobenzoylpyridine has m. p. 148°. 2-*p*-Aminobenzylpyridine, m. p. 60° (*hydrochloride*, m. p. 60°), and 2-*p*-hydroxybenzylpyridine, m. p. 130°, are described.

4-Benzylpyridine is converted by cold nitric and sulphuric acids mainly into 4-*p*-nitrobenzylpyridine, m. p. 74° (*picrate*, m. p. 167—168°; *methiodide*, m. p. 106—108°); in addition 4-*o*:*p*-dinitrobenzylpyridine and a compound yielding a *picrate*, m. p. 156—157°, apparently isomeric with 4-*p*-nitrobenzylpyridine *picrate*. Oxidation of 4-*p*-nitrobenzylpyridine affords 4-*p*-nitrobenzoylpyridine, m. p. 123—124°, and *p*-nitrobenzoic acid. 4-*o*:*p*-Dinitrobenzylpyridine, m. p. 80—81°, conveniently prepared by nitration of the mononitro compound at 70—80°, yields a *picrate*, m. p. 150—151°. 4-*p*-Aminobenzylpyridine, m. p. 152—153°, and 4-*p*-hydroxybenzylpyridine, m. p. 180—181°, are described.

H. W.

**Quinoline Derivatives. I. Synthesis of 2-Phenyl-4-aminomethylquinoline.** H. JOHN (*Ber.*, 1925, **58**, [B], 1489—1491).—*o*-Amino- $\omega$ -phthalimidoacetophenone is converted by acetophenone in boiling aqueous-alcoholic sodium ethoxide solution into 2-phenyl-4-phthalimidomethylquinoline, m. p. 261° (a *hydrate* is also described), which is hydrolysed to 2-phenyl-4-aminomethylquinoline; the *dihydrochloride*, m. p. 232—235° (decomp.), *mono-hydrochloride*, *chloroplatinate*, which decomposes without melting below 287°, and additive *compound* with mercuric chloride are described.

H. W.

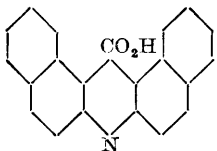
**Preparation of Quinolinic Acid and certain of its Derivatives.** E. SUCHARDA (*Ber.*, 1925, **58**, [B], 1727—1729).—Quinolinic acid is readily prepared by cautious treatment of 8-hydroxyquinoline with nitric acid. Oxidation of the imide of quinolinic acid with sodium hypochlorite affords aminonicotinic acid (yield 23%) and aminopicolinic acid (yield 67%). Quinolinimide is conveniently prepared by heating quinolinic acid with acetic anhydride, and removal of a part of the acetic acid and acetic anhydride by distillation followed by treatment of the residue with acetic anhydride and acetamide; the latter reaction appears to be generally applicable for the conversion of acid anhydrides into imides.

H. W.

**3-Methoxy-2-phenylquinoline-4-carboxylic Acid.** [3-Methoxyatophan.] W. DILTHEY and C. THELEN (*Ber.*, 1925, **58**, [B], 1588—1589).—3-Methoxy-2-phenylquinoline-4-carboxylic acid,

m. p. 225—226°, is prepared by the action of isatin on  $\omega$ -methoxy-acetophenone in boiling, aqueous or alcoholic, alkaline solution. When treated with aluminium chloride in the presence of boiling benzene, it yields 3-hydroxy-2-phenylquinoline-4-carboxylic acid, m. p. 204—205° (cf. Berlingozzi and Marzella, A., 1924, i, 314), which passes in boiling nitrobenzene solution into 3-hydroxy-2-phenylquinoline (hydrochloride, m. p. 261° after softening at 160°; Berlingozzi and Marzella record m. p. 243—245°). H. W.

**Acridine Syntheses from 4:5-Benzocoumarandione and Aniline.** K. SAFTIEN (*Ber.*, 1925, 58, [B], 1958—1960; cf. Fries and Pusch, this vol., i, 569).—4:5-Benzocoumarandione is converted by boiling aniline into 2-hydroxy-1-naphthoylformanilide-anil,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{C}(\text{NPh})\cdot\text{CO}\cdot\text{NHPh}$ , m. p. about 175° (decomp.), which is transformed by restricted treatment with boiling glacial acetic acid into 4:5-benzocoumarandione-3-anil, m. p. 182°, and by boiling glacial acetic acid and aniline into  $\beta$ -naphthacridine-12-carboxylic acid, m. p. 284°. Similarly, 4:5-benzocoumarandione and  $\beta$ -naphthylamine in boiling glacial acetic acid solution afford 3:4:6:7-dibenzacridine-5-carboxylic acid (dinaphthacridine-14-carboxylic acid; annexed formula), m. p. 260° with formation of 3:4:6:7-dibenzoacridine (dinaphthacridine), m. p. 216°. Under similar conditions, *p*-anisidine yields 10-methoxy- $\beta$ -naphthacridine-12-carboxylic acid, decomp. 286°, and thence 10-methoxy- $\beta$ -naphthacridine, m. p. 157°, whereas aceto-*p*-phenylenediamine yields 10-acetamido- $\beta$ -naphthacridine-12-carboxylic acid, m. p. 292°, and thence 10-acetamido- $\beta$ -naphthacridine, m. p. 275°. H. W.

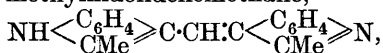


**Compound of Veronal and Pyramidone.** P. PFEIFFER (*Z. physiol. Chem.*, 1925, 146, 98—102).—By evaporation of an aqueous solution containing veronal and pyramidone, a molecular compound (1:1) is obtained as needles, melting at 113—115° to a cloudy liquid which clears at 140°. The m. p. curve has been studied. [Cf. B., 1925, 781.] P. W. C.

**Complex Metallic Compounds of Indigotin.** III. R. KUNZ and W. STÜHLINGER (*Ber.*, 1925, 58, [B], 1860—1868; cf. A., 1923, i, 155, 1134).—The complex metallic compounds of indigotin with copper and zinc, obtained previously with aid of the metals, can also be prepared from indigotin and copper or zinc acetates in the presence of pyridine; although a hydrogen atom in indigotin does not suffer replacement, acetic acid is produced in almost quantitative amount, probably owing to a type of decomposition,  $2(\text{CH}_3\cdot\text{CO}_2)_2\text{Cu} = 2\text{Cu} + 3\text{CH}_3\cdot\text{CO}_2\text{H} + \text{CO}_2 + \text{C}$ , observed by Krönig in the case of the acetates of the heavy metals, but not of magnesium, which does not give a complex derivative under these conditions. *NN'*-Diphenylindigotin and copper acetate in the presence of pyridine give the compound  $(\text{C}_{28}\text{H}_{18}\text{O}_2\text{N}_2)_4\text{Cu}$ , which is very sensitive to moisture and acetic acid. In contrast to the acetates of the heavy metals, ferric chloride gives dark-coloured, additive compounds

with indigoid dyes; acetonitrile is particularly suitable as solvent, whereas addition of pyridine causes dissociation. 7 : 7'-Dimethyl-indigotin yields the compound  $(C_{18}H_{14}O_2N_2)_2 \cdot FeCl_3$ , from the components in acetonitrile, whereas in toluene solution the substance  $C_{18}H_{14}O_2N_2 \cdot FeCl_3$  is produced.  $N : N'$ -Diphenylindigotin and ferric chloride give the compound  $C_{28}H_{18}O_2N_2 \cdot FeCl_3$ .  $NN'$ -Diphenyl-7 : 7'-dimethylindigotin appears also to be able to give complex compounds; thus with potassium the substance  $C_{30}H_{22}O_2N_2 \cdot K$  is produced.

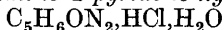
The possibility that the carbonyl oxygen atoms of indigotin and its derivatives are involved in the production of the complex compounds with metals is excluded by the observation that oxygen-free analogues of indigotin afford similar derivatives. Thus 2-methylindolyl-2'-methylindolidenemethane,



gives the compounds  $C_{19}H_{16}N_2Cu$  and  $C_{19}H_{16}N_2Ag$  with copper acetate and silver acetate in pyridine, whereas with ferric chloride in acetonitrile the substance  $C_{19}H_{16}N_2 \cdot FeCl_3$  is produced; these substances are closely similar in chemical behaviour to the corresponding indigoid products. On the other hand, the indole derivative forms with potassium in the presence of xylene at  $140^\circ$  a substituted compound in which the metal replaces the hydrogen atom of the imino group.

H. W.

**Amino-4-pyridones.** W. H. CROWE (*J. Chem. Soc.*, 1925, 127, 2028—2029).—The action of a mixture of fuming nitric and concentrated sulphuric acids on 4-pyridone at  $100^\circ$  yields 3-nitro-4-pyridone, m. p.  $279^\circ$  [cf. Koenigs and others, A., 1924, i, 989, 990, m. p.  $269$ — $270^\circ$  (decomp.),  $284^\circ$  (decomp.)], reduced by tin and hydrochloric acid to 3-amino-4-pyridone hydrochloride,

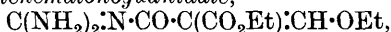


[chloroplatinate,  $(C_5H_6ON_2)_2 \cdot H_2PtCl_6 \cdot H_2O$ ]. Similar nitration at  $140^\circ$  yields 3 : 5-dinitro-4-pyridone (cf. Koenigs, *loc. cit.*, monohydrate, m. p.  $325^\circ$ ), reduced by alcoholic ammonium sulphide to 3-nitro-5-amino-4-pyridone, isolated as the hydrochloride. The sodium salts of the nitro compounds are described.

M. J.

**Condensations of Amidines with Ethoxymethylene Derivatives of  $\beta$ -Ketonic Esters,  $\beta$ -Diketones, and Cyanoacetic Ester.** II. P. C. MITTER and N. PALIT (*J. Indian Chem. Soc.*, 1925, 2, 61—70).—In extension of earlier work (cf. Mitter and Bardhan, T., 1923, 123, 2179), various aliphatic and complex amidines have been condensed with ethyl ethoxymethylenemalonate, ethyl ethoxymethyleneacetoacetate, and ethyl ethoxymethylene-cyanoacetate to yield pyrimidine derivatives. Employing sodium ethoxide as the condensing agent, the following products have been obtained: ethyl ethoxymethylenecyanoacetate condenses with benzamidine to yield 5-cyano-4-keto-2-phenyl-1 : 4-dihydropyrimidine, m. p.  $295^\circ$  [which on hydrolysis of the cyanogen group yields the corresponding acid, m. p.  $271^\circ$  (decomp.)], together with two substances, m. p.  $145$ — $152^\circ$  and  $130^\circ$ , respectively; with *p*-toluamidine,

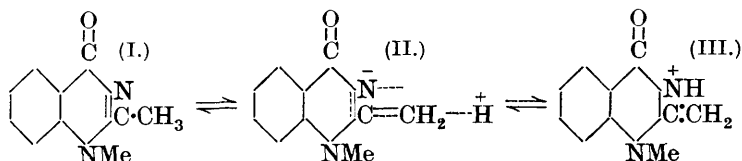
it yields 5-cyano-4-keto-2-tolyl-1:4-dihydropyrimidine, m. p. 303—304°, which on hydrolysis yields the acid, m. p. 282°; with *p*-anisamidine is obtained 5-cyano-4-keto-2-anisyl-1:4-dihydropyrimidine, m. p. 286° [acid, m. p. 271° (decomp.)]; with  $\beta$ -naphthamidine it yields 5-cyano-4-keto-2- $\beta$ -naphthyl-1:4-dihydropyrimidine, m. p. 305—306° [acid, m. p. 291° (decomp.)], together with a substance, m. p. 147—148°. Ethyl ethoxymethyleneacetoacetate condenses with guanidine to yield ethyl 2-amino-4-methylpyrimidine-5-carboxylate, m. p. 222° [acid, m. p. 256—258° (decomp.)]; with anisamidine is obtained ethyl 2-anisyl-4-methylpyrimidine-5-carboxylate, m. p. 80° (?) (acid, m. p. 232—233°); with naphthamidine is obtained ethyl 2- $\beta$ -naphthyl-4-methylpyrimidine-5-carboxylate, m. p. 118° (acid, m. p. 245—246°). Ethoxymethyleneacetylacetone condenses with anisamidine to yield 5-acetyl-2-anisyl-4-methylpyrimidine, m. p. 113—115°; and with naphthamidine to yield 5-acetyl-2- $\beta$ -naphthyl-4-methylpyrimidine, m. p. 151—153°. Ethyl ethoxymethylene malonate condenses with guanidine to yield ethyl 2-amino-4-keto-1:4-dihydropyrimidine-5-carboxylate, m. p. 285° (acid, m. p. 238°), and in this case the intermediate compound, ethyl ethoxymethylenemalonoguanidate,



m. p. 295° [readily hydrolysed by 50% hydrochloric acid to yield malonoguanidic acid,  $\text{C}(\text{NH}_2)_2\text{:N}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 254° (decomp.)], was isolated. With anisamidine is obtained ethyl 4-keto-2-anisyl-1:4-dihydropyrimidine-5-carboxylate, m. p. 222—224°; whilst with  $\beta$ -naphthamidine is obtained ethyl 4-keto-2-naphthyl-1:4-dihydropyrimidine-5-carboxylate, m. p. 213—215°.

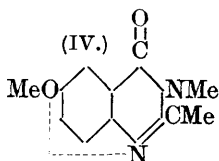
J. W. B.

**Chemical Reactivity and Conjugation. II. Reactivity of the 2-Methyl Group in the 4-Quinazolone Series.** I. M. HEILBRON, F. N. KITCHEN, E. B. PARKES, and G. D. SUTTON (*J. Chem. Soc.*, 1925, **127**, 2167—2175).—1:2-Dimethyl-4-quinazolone, like the 2:3-dimethyl isomeride (Bogert, Beal, and Amend, A., 1911, i, 162, 580), contains a reactive methyl group in the 2-position. This reactivity must be ascribed to the tendency of the unsaturated nitrogen atom, like that of the carbonyl oxygen atom of 2:3-dimethylchromone (T., 1923, **123**, 2559), to acquire a slight negative charge, thus producing an activated phase of the molecule which, in its final state, may be represented as completed isomeric change into the methylene form. Thus:



The 1:2-dimethyl-4-quinazolones, owing their reactivity to the nitrogen in the 3-position, are, in general, more reactive than the 2:3-dimethyl isomerides, owing their reactivity to the nitrogen in the 1-position, probably because they contain a conjugated system

$O=C-N=CMe$ , analogous to that contained in 2:3-dimethylchromone. Substitution of methoxyl in the 7-position of 1:2-dimethyl-4-quinazolone causes a certain retardation of activity, due to neutralisation of partial valency forces between the carbonyl group and the methoxy group. 6-Methoxy-1:2-dimethyl-4-quinazolone and 7-methoxy-2:3-dimethyl-4-quinazolone, which are incapable of forming closed valency circuits, have unimpaired



reactivity, whereas 6-methoxy-2:3-dimethyl-4-quinazolone (IV) gives no styryl derivatives, owing to complete neutralisation of valency forces. Direct methylation of anthranilamide (Weddige, A., 1887, 1043) gives a poor yield of methyl derivative. Distillation of the ammonium salt of methylanthranilic acid (*carbethoxy*-derivative, m. p. 108°) fails to yield the amide. The acid, successively treated with ethyl chloroformate and acetyl chloride, gives *methylisatoic anhydride*, m. p. 180°, converted by concentrated ammonia into methyl anthranilamide (cf. Niementowski, *Ber.*, 1889, 22, 1672). Acetylation and loss of water give 1:2-dimethyl-4-quinazolone (Weddige, *loc. cit.*). Condensation with aromatic aldehydes at the ordinary temperature in presence of alcoholic sodium ethoxide gives: 2-styryl-1-methyl-4-quinazolone, m. p. 245°, 4'-methoxy-2-styryl- (+2H<sub>2</sub>O), m. p. 94°, anhyd., m. p. 156°, 3':4'-methylenedioxy-2-styryl-, m. p. 264°, and 4'-dimethylamino-2-styryl-1-methyl-4-quinazolone, m. p. 274°.

2:3-Dimethyl-4-quinazolone gives: 4'-methoxy-2-styryl-, m. p. 146°, 3':4'-dimethoxy-2-styryl-, m. p. 208°, 3':4'-methylenedioxy-2-styryl-, m. p. 185°, and 4'-dimethylamino-2-styryl-3-methyl-4-quinazolone, m. p. 175°.

6-Nitro-3-methoxybenzoic acid (+1H<sub>2</sub>O), m. p. 97°, gives 5-methoxyanthranilic acid, 5-methoxymethylanthranilic acid, m. p. 163°, 6-methoxymethylisatoic anhydride, m. p. 233°, 5-methoxymethylanthranilamide, m. p. 145°, 6-methoxy-1:2-dimethyl-4-quinazolone, m. p. 220°, and thence 6-methoxy-3':4'-methylenedioxy-2-styryl-1-methyl-4-quinazolone, m. p. 284°.

5-Methoxyacetylthranil, m. p. 124°, from 5-methoxyanthranilic acid, gives 6-methoxy-2-methyl-4-quinazolone, m. p. 270°, and 6-methoxy-2:3-dimethyl-4-quinazolone (+1H<sub>2</sub>O), m. p. 87°, anhyd., m. p. 133°.

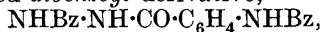
4-Methoxyanthranilic acid gives 4-methoxymethylanthranilic acid, m. p. 165°, 7-methoxymethylisatoic anhydride, m. p. 200°, 4-methoxymethylanthranilamide, m. p. 138°, 7-methoxy-1:2-dimethyl-4-quinazolone (+1H<sub>2</sub>O), indef. m. p., anhyd., m. p. 193°, and thence 7-methoxy-3':4'-methylenedioxy-2-styryl-, m. p. 280°, and 7-methoxy-4'-dimethylamino-2-styryl-1-methyl-4-quinazolone, m. p. 266°.

4-Methoxyacetylthranil, m. p. 128°, from 4-methoxyanthranilic acid, gives 7-methoxy-2-methyl-4-quinazolone, m. p. 272°, 7-methoxy-2:3-dimethyl-4-quinazolone (+1H<sub>2</sub>O), m. p. 80°, anhyd., m. p. 149°, and thence 7-methoxy-3':4'-methylenedioxy-2-styryl-3-methyl-4-quinazolone, m. p. 193°.

5-Chloro-2-amino-4-methoxytoluene, m. p.  $116^{\circ}$  (*acetyl* derivative, m. p.  $183\text{--}184^{\circ}$ ), was obtained instead of the simple amino compound by reduction of *o*-nitro-*p*-cresol methyl ether with tin and hydrochloric acid during the preparation of 4-methoxyanthranilic acid. M. J.

**Quinazolones from Acylated *o*-Aminobenzhydrazides.** G. HELLER, with E. GÖRING, J. KLOSS, and W. KÖHLER (*J. pr. Chem.*, 1925, [ii], **111**, 36—53).—The action of alcoholic hydrazine hydrate on ethyl *o*-acetamidobenzoate affords 3-amino-2-methyl-4-quinazolone (cf. Bogert, A., 1909, i, 679) instead of the expected *o*-acetamidobenzhydrazide. 3-Acetamido-2-methyl-4-quinazolone (cf. Bogert, *loc. cit.*) is obtained by treating *o*-aminobenzhydrazide with acetic anhydride, the mixture being evaporated to dryness. When *o*-aminobenzhydrazide is treated with acetic anhydride in ethyl acetate solution at  $50^{\circ}$ , *acetyl-o-aminobenzhydrazide*,  $\text{NHAc}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , m. p.  $181^{\circ}$ , is obtained, which is converted into the above aminomethylquinazolone when heated at  $220^{\circ}$  or when boiled with alcoholic hydrochloric acid, a conversion necessitating a wandering of the *acetyl* group. Treatment of the *acetylhydrazide* with sodium nitrite in presence of dilute hydrochloric acid affords 3-acetamidobenzazimide, m. p.  $206^{\circ}$  (decomp.) (cf. Bamberger, A., 1901, i, 391), whilst the action of benzoyl chloride in pyridine yields *acetyl-o-benzamidobenzhydrazide*, m. p.  $236^{\circ}$  (decomp.), which is converted by hot, dilute hydrochloric acid into 3-amino-2-phenylquinazolone (cf. Heller, A., 1915, i, 844) and yields, when heated at  $250^{\circ}$ , 3-acetamido-2-phenyl-4-quinazolone, m. p.  $122^{\circ}$ . *Benzoyl-o-aminobenzhydrazide*,  $\text{NHBz}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , m. p.  $178^{\circ}$ , is obtained, together with a *dibenzoyl* derivative, by the action of benzoyl chloride on *o*-aminobenzhydrazide in warm ethyl acetate. It yields anthranilic acid when warmed with 85% sulphuric acid, and 3-amino-2-phenyl-4-quinazolone when heated at  $210\text{--}220^{\circ}$ , the acyl group again migrating to the other nitrogen atom.

3-Benzamidobenzazimide, m. p.  $205\text{--}206^{\circ}$  (decomp.), obtained by the action of nitrous acid on the above benzoyl-*o*-aminobenzhydrazide, yields *o*-azoimidobenzoic acid when warmed with alkalis. When benzoyl-*o*-aminobenzhydrazide is treated in aqueous solution with acetic anhydride, the corresponding *acetamido* derivative ( $+\text{H}_2\text{O}$ ), sintering at  $108^{\circ}$  and losing water at  $115^{\circ}$ , is obtained, which is converted by the action of warm dilute hydrochloric acid, or when heated alone at  $180^{\circ}$ , into 3-benzamido-2-methyl-4-quinazolone. Benzoylation of *o*-aminobenzhydrazide in pyridine affords the above-mentioned *dibenzoyl* derivative,



m. p.  $239^{\circ}$  (decomp.), together with a *substance*, m. p.  $205^{\circ}$ . When the former product is heated at  $250^{\circ}$ , it yields 3-benzamido-2-phenyl-4-quinazolone, m. p.  $202^{\circ}$ . The following compounds, prepared analogously to those above, are described: *acetyl-o:m-nitrobenzamidobenzhydrazide*, m. p.  $205^{\circ}$  (decomp.); 3-acetamido-2-m-nitrophenyl-4-quinazolone ( $+\text{H}_2\text{O}$ ), m. p.  $183^{\circ}$  (anhydrous); 3-amino-

2-m-nitrophenyl-4-quinazolone, m. p. 222°; m-nitrobenzoyl-o-amino-benzhydrazide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , m. p. 192°; m-nitrobenzoyl-o:m-nitrobenzamidobenzhydrazide, pale yellow, m. p. 217°; 3-m-nitrobenzamidobenzazimide, m. p. 185° (decomp.); m-nitrobenzoyl-o-acetamidobenzhydrazide, m. p. 167° (decomp.), with formation of 3-m-nitrobenzamido-2-methyl-4-quinazolone, m. p. 231°; 2-m-nitrobenzamidobenzoylbenzhydrazide, m. p. 217° (decomp.); 3-benzamido-2-m-nitrophenyl-4-quinazolone, m. p. 221°; m-nitrobenzoyl-o-benzamidobenzhydrazide, m. p. 236° (decomp.); 3-m-nitrobenzamido-2-phenyl-4-quinazolone, m. p. 198°; acetyl-o-propionamidobenzhydrazide, m. p. 160° (decomp.); 3-acetamido-2-ethyl-4-quinazolone, m. p. 135°; 3-amino-2-ethyl-4-quinazolone, m. p. 123°; propionyl-o-amino-benzhydrazide, m. p. 137°; 3-propionylaminobenzazimide, m. p. 181°; propionyl-o-acetamidobenzhydrazide, m. p. 167° (decomp.); and 3-propionamido-2-methyl-4-quinazolone, m. p. 170°.

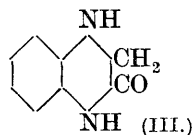
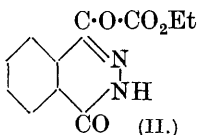
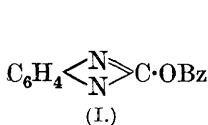
The action of hydrazine hydrate on methyl methylantranilate affords *methylanthranilic hydrazide* (o-methylaminobenzhydrazide), m. p. 141—142°, from which benzoyl-o-methylaminobenzhydrazide, m. p. 192°, is obtained by the action of benzoyl chloride in pyridine, together with the *dibenzoyl* derivative, m. p. 179—180°. The former product is changed when heated at 250°, probably by wandering of the benzoyl group, to a crystalline product. *Acetyl-o-methylaminobenzhydrazide*, m. p. 152°, yields an oily *nitrosoamine*. *Methyl-acetyl-anthranilic hydrazide* (o-acetomethylaminobenzhydrazide), m. p. 234—235° (*nitrosoamine*, decomp. 250—260°), is described. 3-Acetophenoneaminobenzazimide (*methylbenzylidene-3-aminobenzazimide*), pale yellow, m. p. 168.5°, is obtained by the action of sodium nitrite and acetic acid on acetophenone-o-aminobenzhydrazide, which has m. p. 174—175° (cf. Thode, A., 1904, i, 347). The latter yields, on treatment with acetic anhydride, o-acetamidobenzhydrazideacetophenone (*methylbenzylidene-o-acetamidobenzhydrazide*), m. p. 202—203° (decomp.), which, when heated at 200°, yields 3-p-acetylphenylamino-2-methyl-4-quinazolone, m. p. 195°. 3-Aminobenzazimide, m. p. 152—153°, is obtained by the action of cold, 18% hydrochloric acid on the above 3-acetophenoneaminobenzazimide. The use of hot, dilute hydrochloric acid leads to the production of o-phenylenecarbamide. When 3-aminobenzazimide is treated with zinc dust and acetic acid, benzazimide is obtained. F. G. W.

### Tautomerisation Phenomena in Heterocyclic Compounds.

G. HELLER [with A. BUCHWALDT, R. FUCHS, W. KLEINICKE, and J. KLOSS] (*J. pr. Chem.*, 1925, [ii], 111, 1—22).—The conversion of isatin into isatol by the action of benzoyl chloride on the silver salt, and into 2:3-dihydroxyquinoline by the action of diazomethane, led to the following examination of similarly constituted substances, but in no case were analogous transformations observed. The action of acetyl chloride in benzene on the silver salt of phthalimidine yields acetylphthalimidine. When silver phthalimidine is allowed to stand in the dark in contact with a solution of benzoyl chloride in dry ether, a mixture of two isomeric benzoyl derivatives, one colourless, the other light red, is obtained, but the



individual isomerides cannot be separated by means of solvents. Phthalimidine is not attacked by ethereal diazomethane. When the silver salt of saccharin is treated at  $100^{\circ}$  with methyl iodide in dry ether, a mixture of the *N*- and *O*-methyl derivatives is obtained. Ethyl iodide affords similarly the two ethylsaccharins. The action of cold, ethereal acetyl chloride on silver saccharin yields acetylsaccharin, m. p.  $193^{\circ}$ , whilst benzoyl chloride affords similarly *N*-benzoylsaccharin, m. p.  $163$ — $165^{\circ}$ , together with a small proportion of a crystalline compound, m. p.  $255$ — $257^{\circ}$ , probably the *O*-benzoyl derivative. Saccharin reacts vigorously with ethereal diazomethane, the *O*- and *N*-methyl derivatives being formed in the proportion of 1 : 4. Disodium *o*-phenylenecarbamide is precipitated in crystalline form when 25% sodium hydroxide is added to a solution of *o*-phenylenecarbamide in the dilute alkali. The monosodium salt is obtained by the addition of alcoholic sodium hydroxide to a solution of the carbamide in alcohol. The silver salt is obtained by mixing hot, aqueous *o*-phenylenecarbamide with an equivalent of aqueous silver nitrate, and adding gradually dilute aqueous ammonia as long as the precipitate increases. When the disodium salt is shaken with benzoyl chloride in benzene, the NN'-dibenzoyl derivative, m. p.  $212$ — $213^{\circ}$ , is obtained in 85% yield. The action of benzoyl chloride in ether or benzene on the monosodium salt also affords this dibenzoyl derivative, together with the free carbamide, the former being also obtained on benzoylation of the carbamide in pyridine. *O*-Benzoyl-*o*-phenylenecarbamide (I), m. p.  $205^{\circ}$ , is obtained when the silver salt is shaken with benzoyl chloride in benzene, the *O*-acetyl derivative, m. p.  $205^{\circ}$ , being obtained similarly. The NN'-diacetyl derivative, m. p.  $149^{\circ}$ , is obtained analogously to the dibenzoyl derivative. Alkyl derivatives could not be obtained from the sodium or silver salts, on which ethyl chloroformate is also without action. Diazomethane does not react with the free carbamide. When potassium *o*-phthalhydrazide is shaken with benzoyl chloride in benzene, *O*-benzoyl-



*phthalhydrazide*, m. p.  $221$ — $222^{\circ}$ , is obtained in 90% yield, and is also produced by the action of benzoyl chloride on the silver salt in pyridine. The *O*-acetyl derivative, m. p.  $164.5^{\circ}$ , is obtained similarly, whilst the *O*-methyl ether, m. p.  $187^{\circ}$ , is obtained by treating the silver salt with ethereal methyl iodide at  $100^{\circ}$ . The action of ethyl chloroformate on the silver salt in benzene affords a mixture of the *O*-carbethoxy derivative (II), m. p.  $145^{\circ}$  with subsequent resolidification and m. p.  $180^{\circ}$  (decomp.), and the NN'-dicarbethoxy derivative, m. p.  $136^{\circ}$ . When phenyleneoxamide is treated with benzoyl chloride in pyridine, *O*-benzoylphenyleneoxamide, m. p.  $176^{\circ}$ , is produced. Reduction of phenyleneoxamide with zinc and hydrochloric acid affords *hydroxydihydroquinoxaline*

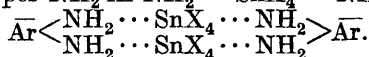
(III), m. p. 93—94°, with resolidification and m. p. 132—133°, again resolidifying and becoming gradually yellow to brown and melting partly at 153—155°, and completely at about 180°. The *disilver* and *monopotassium* salts of phenyleneoxamide are described, as well as the *sodium* and *silver* salts of benzoylenecarbamide. When benzoylenecarbamide is treated with benzoyl chloride in pyridine, a mixture of *dibenzoylbenzoylenecarbamide*, m. p. 153—154°, and *monobenzoylbenzoylenecarbamide*, m. p. 206° (decomp.) (*sodium* salt), is obtained. The latter is also produced when either sodium or silver benzoylenecarbamide is heated with benzoyl chloride in benzene. When benzoylanthranilic acid is heated with an equivalent of carbamide at 140—150°, 4-hydroxy-2-phenylquinazoline is produced (cf. Körner, A., 1887, 1044), together with benzoylenecarbamide and a red, amorphous *substance*. When benzoylcarbamide is heated with anthranilic acid at 100°, an isomeric *benzoylbenzoylenecarbamide*, m. p. 216—217° (decomp.), is produced, which is much more readily hydrolysed to benzoylenecarbamide than the above monobenzoyl derivative. Attempts to acetylate benzoylenecarbamide produced a brown, amorphous *substance*, whilst treatment of the sodium or silver salt with acetyl chloride afforded only the original benzoylenecarbamide. When sodium or *silver* benzazimide is heated with benzoyl chloride in toluene or benzene, *benzoylbenzazimide*, m. p. 132—133°, is obtained. *Acetylbenzazimide*, m. p. 165°, is produced similarly, whilst the action of methyl iodide on the silver or sodium salt yields the known methyl derivative. *Ethyl benzazimidcarboxylate*, m. p. 65—66°, obtained from either the silver or sodium salt and ethyl chloroformate, is converted into carbonylsalicylamide and salicylic acid when warmed with dilute hydrochloric acid. Reduction of benzazimide proceeds irregularly, but the action of zinc dust and ammonia afforded, in one experiment, *o*-hydrazinobenzoic anhydride.

F. G. W.

**Ring Formation in Additive Compounds. II.** W. HIEBER (*Annalen*, 1925, 444, 249—265; cf. A., 1924, i, 1249). **Constitution of Compounds of Stannic Chloride with Polycarboxylic Esters** [with R. BECKER].—The bimolecular structures for the additive compounds of stannic chloride with dicarboxylic esters indicated by molecular weight determinations (*loc. cit.*) receive confirmation in the formation, from ethyl ethylenetetracarboxylate, of *compounds* of the type  $2\text{SnCl}_4\cdot 2\text{ester}$ , m. p. 94—95° (from equimolecular mixture in carbon tetrachloride);  $3\text{SnCl}_4\cdot 2\text{ester}$ , m. p. 94—95° (from  $1\frac{1}{2}$  or 2 mols. of stannic chloride and 1 mol. of ester in carbon tetrachloride);  $4\text{SnCl}_4\cdot 2\text{ester}$ , m. p. 94—95° (obtained pure only by melting together the components with large excess of stannic chloride, which is removed afterwards by suction).

Ethyl ethanetetracarboxylate yields a similar series of three *products*, but as those richest in stannic chloride are very easily formed, excess of this salt must be avoided. The m. p. of all three are the same, viz., 124°. With ethyl tricarballylate, *compounds*  $2\text{SnCl}_4\cdot 2\text{ester}$ , m. p. 118°, and  $3\text{SnCl}_4\cdot 2\text{ester}$  are obtained.

**Compounds of Stannic Halides with Isomeric Diamines** [with R. WAGNER].—*o*-, *m*-, and *p*-Phenylenediamines and benzidine, like the simple amines, form compounds with stannic chloride and bromide in which one molecule of the inorganic salt is linked by subsidiary valency bonds to two nitrogen atoms. Dianiline-stannic chloride (Werner and Pfeiffer, A., 1898, i, 464) decomposes at 200°; *dianiline-stannic bromide* at 150°. *o*-Phenylenediamine-stannic chloride, decomp. 230°, and *bromide*, decomp. 180°, have apparently unimolecular structures containing a 5-membered ring. On the other hand, *m*- and *p*-phenylenediamines and benzidine give compounds of the types  $\text{NH}_2 \cdot \text{Ar} \cdot \text{NH}_2 \cdots \text{SnX}_4 \cdots \text{NH}_2 \cdot \text{Ar} \cdot \text{NH}_2$  and



*Di-m-phenylenediamine-stannic chloride*, *m-phenylenediamine-stannic chloride*, the corresponding *para chlorides* and *bromides*, *benzidine-stannic chloride*, and *dibenzidine-stannic chloride*, are described. In the case of ethyl *o*- and *p*-aminobenzoates, the subsidiary valency of the nitrogen alone takes part in the additive reaction, i.e., there is no ring formation. The compounds  $\text{SnCl}_4 \cdot 2\text{ester}$  and  $\text{SnBr}_4 \cdot 2\text{ester}$  are obtained from ethyl anthranilate, and the compound  $\text{SnCl}_4 \cdot 2\text{ester}$  from ethyl *p*-aminobenzoate. All the amine and diamine compounds with stannic halides decompose without melting at 150–230°. C. H.

**2-Amino-4 : 5-dimethylglyoxaline.** R. BURTLES and F. L. PYMAN (*J. Chem. Soc.*, 1925, 127, 2012–2018).—The normal behaviour of 8-aminopurine towards nitrous acid (A., 1909, i, 434), together with the formation of an oximino derivative from creatinine (A., 1912, i, 719), suggests that the abnormality of 2-aminoglyoxaline (Fargher and Pyman, T., 1919, 115, 217; A., 1922, i, 1197) may be conditioned by the possibility of substitution at the 4- and 5-positions. This supposition is negatived by the failure of 2-amino-4 : 5-dimethylglyoxaline to react smoothly with nitrous acid. Neither the original amine nor any definite reaction product could be isolated.

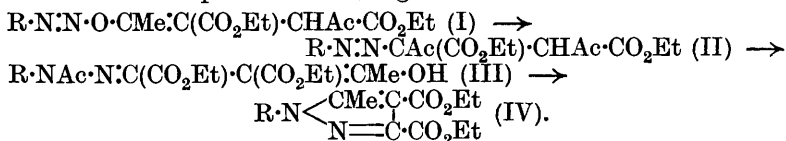
*2-Amino-4 : 5-dimethylglyoxaline* [hydrochloride, m. p. 289°, carbonate ( $\text{1H}_2\text{O}$ ), m. p. 144°, picrate, m. p. 245°, acetyl derivative, m. p. 270°] is obtained by reduction of 2-*p*-bromobenzeneazo-4 : 5-dimethylglyoxaline, m. p. 213–214° (hydrochloride, decomp. 135°). This substance, prepared by coupling diazotised *p*-bromoaniline with 4 : 5-dimethylglyoxaline, causes irritation of the eyelids. An attempt to prepare the amine by condensation of  $\alpha$ -bromoethyl methyl ketone with guanidine was unsuccessful. Treatment of 4(5)-methylglyoxaline with diazotised *p*-bromoaniline gives, besides the bisazo compound, crude m. p. 100–102°, 5(4)-*p*-bromobenzeneazo-4(5)-methylglyoxaline, m. p. 238° [hydrochloride, m. p. 188° (decomp.)], and 2-*p*-bromobenzeneazo-4(5)-methylglyoxaline, m. p. 225–226°. The last-named, on reduction with hot stannous chloride, gives *p*-bromoaniline, alacreatinine, and 2-amino-4(5)-methylglyoxaline isolated as picrate, m. p. 186–187°. An aqueous solution of the non-crystalline hydrochloride resembles that of 2-aminoglyoxaline hydrochloride in its behaviour towards nitrous acid. M. J.

**Dissociation Constants of Glyoxaline-4:5-dicarboxylic Acid.**

H. PAULY (*Ber.*, 1925, **58**, [B], 1791—1792; cf. Pauly and Ludwig, *A.*, 1922, i, 953).—A reply to Lehmstedt (this vol., i, 1103).

H. W.

**Azo Compounds with Ethyl Diacetylsuccinate and Bülow's Synthesis of Substituted Pyrazoles.** C. BÜLOW and K. BAUR (*Ber.*, 1925, **58**, [B], 1926—1932).—Diazonium compounds of monoacetylated diamines have been coupled with ethyl diacetylsuccinate and the products converted into pyrazoles. The reaction is considered to proceed according to the scheme:



*Ethyl p*-acetamidophenylazodiacetylsuccinate (II,  $\text{R}=\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot$ ), m. p.  $134^\circ$ , is prepared by the action of diazotised acet-*p*-phenylenediamide on ethyl diacetylsuccinate in aqueous-alcoholic solution in the presence of sodium acetate and is readily converted into *ethyl 1-p*-acetamidophenyl-5-methylpyrazole-3:4-dicarboxylate (IV,  $\text{R}=\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot$ ), m. p.  $158^\circ$ . *1-p*-Acetamidophenyl-5-methylpyrazole-3:4-dicarboxylic acid, m. p.  $264^\circ$  (decomp.), *1-p*-acetamidophenyl-5-methylpyrazole, and *1-p*-aminophenyl-5-methylpyrazole-3:4-dicarboxylic acid, m. p.  $276^\circ$  (decomp.), are described. The diazotised solution of the amino-acid couples with ethyl acetoacetate, yielding *ethyl 3:4-dicarboxy-5-methylpyrazole-1-benzeneazoacetoacetate*,  $\begin{array}{c} \text{C}(\text{CO}_2\text{H})=\text{N} \\ \text{C}(\text{CO}_2\text{H})\cdot\text{CMe} \end{array} > \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CHAc}\cdot\text{CO}_2\text{Et}$ , m. p.  $215\text{—}216^\circ$  (decomp.), according to the rate of heating, with acetoacetanilide to give the corresponding *anilide*, decomp. about  $266^\circ$ , and with ethyl acetonedicarboxylate to give the compound,  $\text{C}_{21}\text{H}_{22}\text{O}_9\text{N}_4$ , decomp.  $265^\circ$ .

*N*-Monoacetylbenzidine, m. p.  $195\text{—}196^\circ$ , is conveniently prepared from benzidine and acetic anhydride in chloroform solution at  $+5^\circ$ . It is diazotised and coupled with ethyl diacetylsuccinate to *ethyl p*-acetamidodiphenylazodiacetylsuccinate (II,  $\text{R}=\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot$ ), m. p.  $163^\circ$ , which passes when melted or boiled with alcohol into *ethyl 1-p*-acetamidodiphenyl-5-methylpyrazole-3:4-dicarboxylate (IV,  $\text{R}=\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot$ ), m. p.  $168^\circ$ ; the corresponding dicarboxylic acid, m. p.  $285^\circ$  (decomp.), and its normal *potassium* and *potassium hydrogen* (decomp.  $325^\circ$ ) salts are described. *1-p*-Aminodiphenyl-5-methylpyrazole-3:4-dicarboxylic acid has m. p.  $287^\circ$  (decomp.).

Tetrazotised benzidine and ethyl diacetylsuccinate yield *ethyl diphenylbisazobisdicetylsuccinate*, m. p.  $152^\circ$  (decomp.), which readily loses acetic acid and passes into *ethyl 1-p*-diphenylbis-(5-methylpyrazole-3:4-dicarboxylate)



m. p. 141°; the corresponding tetracarboxylic acid, m. p. 302° (decomp.), and its *tetrapotassium* and *dipotassium dihydrogen* salts are described.

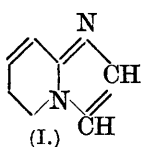
H. W.

**Tautomerism of 4-Aminopyridine. II. Methylated Derivatives of 4-Aminopyridine.** A. E. TSCHITSCHIBABIN and E. D. OSSETROWA (*Ber.*, 1925, 58, [B], 1708—1712; cf. A., 1921, i, 450).—The action of methyl iodide on 4-aminopyridine gives 1-methyl-4-pyridoneimine hydriodide, m. p. 187—188°, from which the free base,  $\text{MeN} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{NH}$ , m. p. 150—151°, b. p. 180—181°/10 mm., is obtained by means of silver oxide [*picrate*, m. p. 188—189°; *chloroplatinate*, m. p. 226—227° (decomp.)]. The base is also the main product of the action of methyl iodide on the sodium derivative of 4-aminopyridine. It is hydrolysed by concentrated potassium hydroxide solution to ammonia and 1-methyl-4-pyridone.

4-Methylaminopyridine, m. p. 115—118° (*chloroplatinate*, m. p. 214—215°; *picrate*, m. p. 168.5—169°), is prepared by cautiously heating 4-methylaminopyridine-2 : 6-dicarboxylic acid in a vacuum.

H. W.

**Tautomerism of 2-Aminopyridine. IV. Method for the Preparation of Pyriminazole and its Homologues.** A. E. TSCHITSCHIBABIN (*Ber.*, 1925, 58, [B], 1704—1706; cf. this vol., i, 158).—*Pyriminazole* (I), b. p. 153—155°/27 mm. [*chloroplatinate*



(+2H<sub>2</sub>O)], is obtained by heating 2-aminopyridine with bromoacetaldehyde or its acetals at 150—200°; if the acetals are used, the alkyl bromides formed during the action cause the product to be mixed with much alkylpyridine. Chloroacetone appears to yield only one of the two possible *methylpyriminazoles*, the *chloroplatinate* of which is described.

H. W.

**2-Amino-3-methylpyridine and Dinitro-2-aminopyridine.** A. E. TSCHITSCHIBABIN (*Ber.*, 1925, 58, [B], 1707—1708).—In reply to Rāth (this vol., i, 432), the author maintains the identity of Seide's 2-amino-3-methylpyridine; the method used by Rāth appears likely to lead to a mixture of methylated aminopyridines.

Re-examination of the compound obtained by Tschitschibabin and Razorenov (A., 1915, i, 992) establishes its identity as 3 : 5-dinitro-2-aminopyridine, and not 5-nitro-2-hydroxypyridine as stated by Rāth (*loc. cit.*).

H. W.

**2-Amino-3-methylpyridine.** O. SEIDE (*Ber.*, 1925, 58, [B], 1733—1734).—The author has failed to obtain Rāth's results on repeating his experiments with synthetic 3-methylpyridine (cf. Rāth, this vol., i, 437), and maintains the identity of the compound described as 2-amino-3-methylpyridine (Seide, this vol., i, 72). Rāth's compound is probably 2-amino-4-methylpyridine. H. W.

**Nitro Derivatives of Methylated Forms of 2-Aminopyridine.** A. E. TSCHITSCHIBABIN and R. A. KONOVALOVA (*Ber.*, 1925, 58, [B], 1712—1717).—1-Methyl-2-pyridimine is converted by an

ice-cold mixture of sulphuric acid ( $d$  1.84) and nitric acid ( $d$  1.4) into 1-methyl-2-pyridylnitroimine,  $C_5H_5NMe \cdot N \cdot NO_2$ , m. p.  $161^\circ$  [identical with the product obtained by Tschitschibabin and Menschikov (this vol., i, 437) by methylation of pyridyl-2-nitroamine], and 5-nitro-1-methyl-2-pyridimine, m. p.  $181^\circ$  (*hydriodide*, m. p.  $205-207^\circ$ ; *picrate*, m. p.  $200-201^\circ$ ); the latter substance is also obtained by the isomerisation of 1-methyl-2-pyridylnitroimine by sulphuric acid and by the action of methyl iodide on 5-nitro-2-aminopyridine. Nitration of 5-nitro-2-aminopyridine gives 5-nitro-2-nitroaminopyridine, which, when treated with methyl sulphate in the absence of excess of alkali hydroxide, gives 5-nitro-1-methyl-2-pyridylnitroimine, m. p.  $182^\circ$  [this substance is unusually sensitive to hydroxyl ions, by which it is converted into 5-nitro-1-methyl-2-pyridone, m. p.  $172^\circ$ , identical with the product described by Fischer and Chur (A., 1916, i, 741)]; in addition to the compound of m. p.  $182^\circ$ , a substance, m. p.  $60^\circ$ , apparently an isomeric 5-nitro-1-methyl-2-pyridylnitroimine, is obtained which is also formed by the nitration of 5-nitro-1-methyl-2-pyridimine. The cause of the isomerism has not been elucidated. 3-Nitro-2-aminopyridine is nitrated in cold sulphuric acid solution to 3-nitro-2-nitroaminopyridine, m. p.  $137^\circ$  (decomp.), which is transformed by methyl iodide into 3-nitro-1-methyl-2-pyridylnitroimine, m. p.  $209^\circ$ ; like the compound of m. p.  $182^\circ$ , this substance is readily decomposed by hydroxyl ions into nitrous oxide and 3-nitro-1-methyl-2-pyridone, m. p.  $175-176^\circ$ .  
H. W.

**Preparation of N-2-Pyridylpyrroles.** CHEM. FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 412168; from *Chem. Zentr.*, 1925, ii, 94).—A mixture of 2-aminopyridine and dried mucic acid, when subjected to dry distillation, gives N-2-pyridylpyrrole, b. p.  $130-140^\circ/12$  mm. Similarly, N-6-methyl-2 : 3-ethylpyridylpyrrole, m. p.  $129-130^\circ$ , b. p.  $150-170^\circ/15$  mm., is obtained from 2-amino-6-methyl-3-ethylpyridine and saccharic acid. A. C.

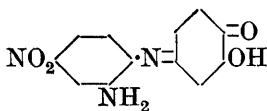
**Homologues of 2 : 2'-Diquinolyl.** E. J. V. CONOLLY (*J. Chem. Soc.*, 1925, 127, 2083—2085).—6 : 6'-Dimethyl-2 : 2'-diquinolyl, m. p.  $202.5-203^\circ$  [*hydrochloride*, colourless needles, *picrate*, m. p.  $282-283^\circ$  (decomp.), *ethiodide*, darkening at  $275^\circ$ , m. p.  $277-278^\circ$  (decomp.)]; 7 : 7'-dimethyl-2 : 2'-diquinolyl, m. p.  $208-209^\circ$  [*picrate*, darkening at  $284^\circ$ , m. p.  $285-286^\circ$  (decomp.), *ethiodide*, m. p.  $274-275^\circ$  (decomp.)]; and 8 : 8'-dimethyl-2 : 2'-diquinolyl, m. p.  $147-147.5^\circ$  (*picrate*, darkening at  $258^\circ$ , m. p.  $264-265^\circ$ ), are obtained by the action of sodium on 6-, 7-, and 8-methylquinolines (cf. Weidel, A., 1886, 950). The small yield of the 8 : 8'-compound and failure to obtain its ethiodide are ascribed to steric hindrance. Attempts to synthesise 6 : 6'-dimethyl-2 : 2'-diquinolyl from 2-bromo-6-methylquinoline, m. p.  $117-118^\circ$  (cf. Fischer and Guthmann, A., 1916, i, 743, m. p.  $126^\circ$ ), obtained from 2-hydroxy-6-methylquinoline, m. p.  $232-233^\circ$  (cf. Einhorn and Lauch, *Annalen*, 1888, 243, 359, m. p.  $228^\circ$ ), were unsuccessful.  
M. J.

**Dyes.** AKT.-GES. F. ANILIN-FABRIK. (F.P. 584401; from *Chem. Zentr.*, 1925, i, 2665).—When the product obtained by heating 1:2-naphthaphenazine-8-sulphonic acid with alkali is treated with sulphuryl chloride in nitrobenzene there results a yellow *trichloro* derivative, decomp. above 250°, dyeing bright golden-yellow shades on cotton which are very fast to light. The *tribromo* derivative, yellow, m. p. above 300°, is used as a pigment colour. 1:1':2:2'-Dinaphthazine-8:8'-disulphonic acid similarly yields a red *chloro* derivative, and a *bromo* derivative with bromine. R. B.

**Dyes Derived from Oxalyldibenzyl Ketone. I. Azine and Azonium Derivatives.** G. C. CHAKRAVARTI (*J. Indian Chem. Soc.*, 1925, 2, 71—76).—*Azines* have been prepared by condensing oxalyldibenzylketone (cf. Claisen and Ewan, A., 1895, i, 373) with the following diamines: *o*-phenylenediamine, m. p. 251°; 1:3:4:5-bromotolylenediamine, m. p. 230°; 1:6:3:4-chlorotolylenediamine, m. p. above 300°; 1:2-naphthylenediamine, m. p. 285°; *o*-phenylenediamine-3-sulphonic acid (*calcium* salt described); 1:2-naphthylenediamine-4-sulphonic acid, amorphous; 1-amino-2-anilinonaphthalene (*hydrochloride*, m. p. 195°, nitrate, m. p. above 300°). These products resemble closely the phenanthrazines and acenaphthazines in colour and tinctorial properties. J. W. B.

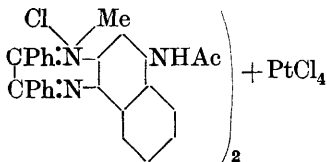
**Syntheses in the Group of the Quinoneimine Dyes. XI. Derivatives of Phenazine.** F. KEHRMANN and E. HAENNY (*Helv. Chim. Acta*, 1925, 8, 676—685).—The condensation of 4-nitro-*o*-phenylenediamine and hydroxybenzoquinone in acetic acid solution has been studied and various derivatives of the resulting products have been prepared. The precipitated product on acetylation yields 3-nitro-7-acetoxyphenazine, m. p. 210°, which on hydrolysis yields 3-nitro-7-hydroxyphenazine, and on reduction with zinc and acetic acid yields first 3-nitro-7-acetoxylhydroxyphenazine and finally 3-amino-7-acetoxyphenazine, m. p. 203°, which on treatment with concentrated ammonia solution yields 3-amino-7-hydroxyphenazine (cf. Nietzki and Almenrader, A., 1896, i, 164), which separates with water of crystallisation in a reddish-brown form, changing to orange on becoming anhydrous (*hydrochloride* and *chloroplatinate* described). On heating in a sealed tube at 210—220° with 10% sulphuric acid, it is converted into 3:7-dihydroxyphenazine (*diacetyl* derivative, m. p. 224°). 3-Amino-7-hydroxyphenazine yields a *diacetyl* derivative, m. p. 258°, which on treatment with sulphuric acid or 10% sodium hydroxide yields 3-acetamido-7-hydroxyphenazine; this exists in two forms, being obtained on precipitation by alkalis in the cold from its solution in dilute acetic acid as a yellow crystalline powder, which becomes brick-red on heating at 110°. Addition of water to the acetic acid mother-liquor of the original condensation yields, after acetylation of the product, 3-nitro-8-acetoxyphenazine, m. p. 224—227°, which on hydrolysis forms 3-nitro-8-hydroxyphenazine. The latter on reduction with zinc and acetic acid yields first 3-nitro-8-hydroxydihydro-

phenazine and finally 3-amino-8-hydroxyphenazine, which forms a diacetyl derivative, m. p. 249°, and this on warming with dilute sodium hydroxide yields 3-acetamido-8-hydroxyphenazine. The final mother-liquor from the original condensation contains an anilide (annexed formula), m. p. 206°, which, when heated in acetic acid solution with *o*-phenylenediamine, yields an azine.



J. W. B.

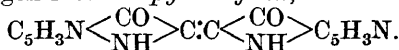
**Syntheses in the Group of Quinoneimine Dyes. X. Aminoazines derived from Naphthalene.** F. KEHRMANN and I. SAFAR (*Helv. Chim. Acta*, 1925, 8, 668—676).—The authors have condensed 4-acetamido-1:2-naphthylenediamine with a large number of *o*-diketones to produce a series of aminoazines. Except in the case of *s*-dihydroxyquinone, two isomeric azines should be produced and were actually isolated in each case. Azines are derived by the condensation of 4-acetamido-1:2-naphthylenediamine with phenanthraquinone (hydrolyses to the corresponding aminoazine, m. p. 309—316°); benzil (aminoazine, m. p. 245°); 4-acetamido-1:2-naphthaquinone (the same products being obtained by the autoxidation of the original diamine); 3-acetamido-1:2-naphthaquinone (aminoazines described); *s*-dihydroxyquinone; hydroxy- $\alpha$ -naphthaquinone (aminoazine and its dihydrochloride described). Several of the azines are converted by the action of methyl sulphate into salts of the azonium



bases, that obtained from the benzil derivative being isolated in the form of its chloroplatinate (annexed formula).

J. W. B.

**Synthesis of “ $\delta$ -Pyrindigotin.”** E. SUCHARDA (*Ber.*, 1925, 58, [B], 1724—1727).—3-Aminopyridine-2-carboxylic acid is converted by chloroacetic acid and aqueous potassium carbonate solution into 3-pyridylglycine-2-carboxylic acid, which is transformed by successive treatment with molten potassium hydroxide and atmospheric oxygen into “ $\delta$ -pyrindigotin,”



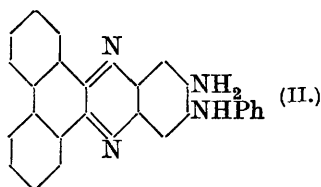
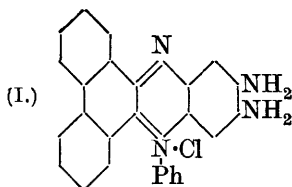
It is converted by hydrochloric acid into “leuco- $\delta$ -pyrindigotin hydrochloride,” which does not melt below 360°, and thence into “leuco- $\delta$ -pyrindigotin.” Tetra-acetyl-leuco- $\delta$ -pyrindigotin is described.

H. W.

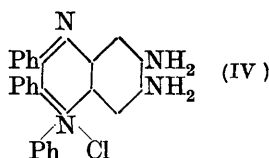
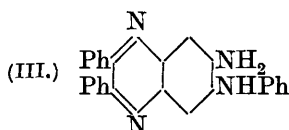
**Monophenyltetra-aminobenzene and some of its Derivatives.** F. KEHRMANN and L. STANOYÉVITCH (*Helv. Chim. Acta*, 1925, 8, 663—668).—Nitration of *m*-chloroacetanilide with a mixture of concentrated nitric and sulphuric acids yields 2:4-dinitro-5-chloroacetanilide, m. p. 136°; when boiled with excess of aniline, this yields 2:4-dinitro-5-acetamidodiphenylamine, m. p. 233·5°, which on hydrolysis yields 2:4-dinitro-5-aminodiphenylamine,



m. p. 20.5°. This on reduction with stannous chloride yields mono-phenyltetra-aminobenzene (*trihydrochloride* described), which condenses with phenanthraquinone to yield a mixture of 11 : 12-*diamino*-

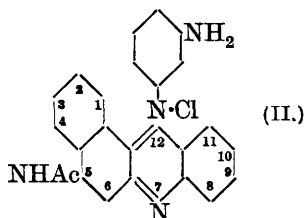
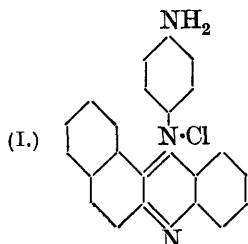


9-phenylphenanthraphenazonium chloride (I) (*chloroplatinate* and *perchlorate* described) and 12-amino-11-anilinophenanthraphenazine



(II) (main product). With benzil, it yields the corresponding *amino-anilindiphenylquinoxaline* (III) and the *azonium compound* (IV) (*chloroplatinate* and *perchlorate* described). J. W. B.

**Syntheses in the Group of Quinoneimine Dyes. VIII. The Eighteenth Isomeride of Rosinduline.** F. KEHRMANN and L. LISTWA (*Helv. Chim. Acta*, 1925, 9, 655—661).—The condensation of 2 : 4'-diaminodiphenylamine with  $\beta$ -naphthaquinone yields a mixture of *isosindulines*, one of which has previously been obtained (cf. Kehrman and Ott, A., 1901, i, 767), the other (I) being the



eighteenth isomeride, which has not been previously prepared (*perchlorate* and *chloroplatinate* described). Separation is effected by converting the mixture into the perchlorates, acetylating the amino group, and fractional crystallisation of the product from alcohol, the new isomeride being the more soluble. The condensation of 4-acetamido- $\beta$ -naphthaquinone with 2 : 3'-diaminodiphenylamine yields a small quantity of 6 : 12-diaminophenyl-naphthaphenazonium chloride (cf. Kehrman and Nuesch, A., 1901, i, 767), together with 5-acetamido-12-m-aminophenyl- $\alpha$ -naphthaphenazon-

*ium chloride* (II) (*perchlorate* and *chloroplatinate* described). This on hydrolysis yields the corresponding 5-amino-12-m-aminophenyl- $\alpha\beta$ -naphthaphenazonium chloride (*sulphate* and *perchlorate* described), which with acetic anhydride at the ordinary temperature yields 5-amino-12-m-acetamidophenyl- $\alpha\beta$ -naphthaphenazonium chloride (*perchlorate* described). It was not found possible to replace the amino group in this compound by hydrogen to produce the acetyl derivative of the nineteenth isomeride of isorosinduline. On treatment with acetic anhydride and sodium acetate at 100°, either of the isomeric monoacetyl derivatives is converted into 5-acetamido-12-m-acetamidophenyl- $\alpha\beta$ -naphthaphenazonium chloride. [Most of the formulæ in the paper contain obvious misprints of Ac for Cl.—Abstr.] J. W. B.

**Synthesis of a Tetrapyrrolethylene and of Some 2 : 3-Dimethylpyrrole Derivatives.** H. FISCHER and H. BELLER (*Annalen*, 1925, 444, 238—248).—The tetrapyrrolethanes hitherto described (Fischer and Eismayer, A., 1914, i, 993; Fischer and Schubert, A., 1923, i, 707), unlike *ætioporphyrin*, readily decompose into dipyrrolymethenes. Since this might be due to the position of the methyl groups (2 : 4- instead of 2 : 3- in the products from blood pigments), derivatives of 2 : 3-dimethylpyrrole have now been prepared. The conclusion is reached that *ætioporphyrin* is not a simple linking of four pyrrole nuclei by the group C.C, but contains also two methine linkings.

4-Carbethoxy-2 : 3-dimethylpyrrole-5-carboxylic acid, prepared in 30% yield by Piloty's method (A., 1912, i, 899; 1913, i, 292) from aminobutanone and ethyl oxalacetate, gives ethyl 2 : 3-dimethyl-4-carboxylate by dry distillation. This condenses readily with glyoxal in alcohol containing a little hydrogen chloride, giving an 80% yield of *tetra*-(4-carbethoxy-2 : 3-dimethylpyrrol)ethane, m. p. 238·5°, which is oxidised by alcoholic ferric chloride to *bis*-(4-carbethoxy-2 : 3-dimethylpyrrol)methene hydrochloride, m. p. 161°, showing no m. p. depression when mixed with the synthetic methene hydrochloride of m. p. 163° (below). The tetrapyrrolethane is converted by treatment with aluminium chloride in boiling carbon disulphide into *tetra*-(4-carbethoxy-2 : 3-dimethylpyrrol)ethylene, m. p. 229°, which regenerates the tetrapyrrolethane in impure form when reduced with sodium amalgam. The tetrapyrrolethylene solution in chloroform is pure yellow (absorption in the violet at  $\lambda$  462·9), becoming intensely red (absorption at  $\lambda$  557·1—524·1) on addition of hydrochloric or nitric acid.

Ethyl 2 : 3-dimethyl-5-aldehydopyrrole-4-carboxylate, m. p. 129° (*oxime*, m. p. 140°; *semicarbazone*, m. p. 212°; condensation product with rhodanin, m. p. 242°), prepared from ethyl dimethylpyrrole-carboxylate and hydrocyanic acid (cf. Fischer and Zerweck, A., 1922, i, 758), is hydrolysed by sodium hydroxide to the free *aldehyde-acid*, darkening at 250° and decomposing at 259°, which, when heated in nitrogen at 280°/140 mm., gives a small yield of 2 : 3-dimethylpyrrole-5-aldehyde, m. p. 126°. Ethyl 5-acetyl-2 : 3-dimethylpyrrole-4-carboxylate (Piloty, Wilke, and Blömer, A., 1915, i, 175),

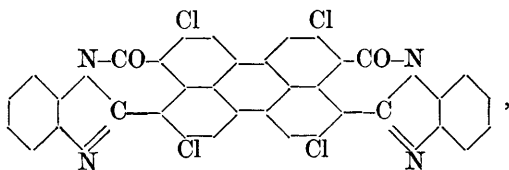
m. p. 129—130°, prepared from ethyl dimethylpyrrolecarboxylate and acetonitrile, is similarly converted into 5-acetyl-2 : 3-dimethylpyrrole, m. p. 112·5°.

Ethyl 2 : 3-dimethylpyrrole-4-carboxylate condenses with formaldehyde in the presence of a little hydrochloric acid to give 5 : 5'-bis-(4-carbethoxy-2 : 3-dimethylpyrryl)methane, m. p. 180°.

An equimolecular mixture of ethyl 2 : 3-dimethyl-5-aldehydopyrrole-4-carboxylate and ethyl 2 : 3-dimethylpyrrole-4-carboxylate, boiled for a short time in concentrated hydrochloric acid, yields bis-(4-carbethoxy-2 : 3-dimethylpyrryl)methene hydrochloride, m. p. 163°. The free methene base, m. p. 156° (*copper salt* described), is obtained from this hydrochloride or by shaking with sodium hydroxide an ether solution of the product of the oxidation of bis-(carbethoxydimethylpyrryl)methane by ferric chloride.

Ethyl 2 : 3-dimethylpyrrole-5-carboxylate, m. p. 114°, obtained from magnesyl 2 : 3-dimethylpyrrole and ethyl chloroformate, is a suitable starting-material for the preparation of hæmopyrrole-carboxylic acid and hæmopyrrole. It condenses readily with formaldehyde in hydrochloric acid solution to give a crystalline bis-(5-carbethoxy-2 : 3-dimethylpyrryl)methane, m. p. 207—208°. These compounds will be more fully reported on later. C. H.

**Vat Dyes.** KALLE & CO. AKT.-GES. (D.R.-P. 412122; from *Chem. Zentr.*, 1925, i, 2666).—Dichloroperylenetetracarboxylic di-imide is converted by phenol and sodium hydroxide into a chlorine-free vat dye, which gives bluish-violet shades on cotton, fast to chlorine. *p*-Toluidine similarly yields a dye, Bordeaux-red shades on cotton, fast to washing and chlorine. A similar dye is obtained by treating the chlorination product of perylenetetracarboxylic acid diphenyldi-imide with phenol and potassium hydroxide. The bluish-violet vat dye,

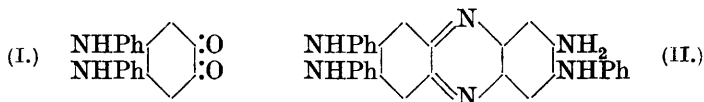


obtained by chlorinating the condensation product of perylene-tetracarboxylic acid and *o*-phenylenediamine, or through chlorination of perylenetetracarboxylic acid anhydride and condensation of the tetrachloro compound with *o*-phenylenediamine, is similarly converted by phenol and potassium hydroxide into a blue vat dye. A bluish-violet dye is similarly obtained from the nitration product of perylenetetracarboxylic acid di-imide and phenol.

R. B.

**Syntheses in the Group of Quinoneimine Dyes. IX. Total Synthesis of Induline-6B.** F. KEHRMANN and L. STANOYÉVITCH (*Helv. Chim. Acta*, 1925, 8, 661—663).—By the condensation of

dianilino-*o*-benzoquinone (I) with *s*-dianilino-*m*-phenylenediamine is obtained 2-amino-8-anilino-3 : 7-diphenylphenosafranine (II), which



on heating with aniline and aniline hydrochloride is converted quantitatively into induline-6B and ammonium chloride, thus confirming by direct synthesis the constitution previously given (cf. Kehrmann and Klopfenstein, A., 1924, i, 213). J. W. B.

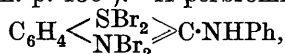
**Constitutional Formulæ of Anthranil and Anthroxanic Acid.** H. LEUCHS (*Ber.*, 1925, 58, [B], 1452—1454).—In the hope of deciding between the constitutional formulæ,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}^- \\ \diagup \quad \diagdown \\ \text{CH} \end{array} \text{O}$

and  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}^- \\ \diagdown \quad \diagup \\ \text{CH} \end{array} \text{O}$ , for anthranil (cf. Bamberger, A., 1909, i, 509), the behaviour of anthroxanic (2-anthranilcarboxylic) acid towards optically active bases has been examined, since if it is derived from the first formula it contains an asymmetric carbon atom. The acid cannot be resolved into its optical antipodes by means of its *brucine* salt, m. p. 210—212° (decomp.) after softening at 200°, *quinine* salt, m. p. 198—202° (decomp.) after softening at 190°, or *strychnine* salt, m. p. 210—212° (decomp.) after softening at 200°. Preference is therefore accorded to the second formula for anthranil. H. W.

**Fission of Ring Systems.** J. MEISENHEIMER (*Ber.*, 1925, 58, [B], 1491—1492).—The recent criticisms of Kuhn and Ebel (this vol., i, 781) have no bearing on the fission of the *isooxazole* ring with production of substituted benziloximes, since, under these conditions, the groups which are responsible for the stereochemical configuration are not affected by the change. H. W.

**Simplest *O*-Alkyl Ethers of Benzoylacetone and Phenyl-methylisooxazole.** C. WEYGAND and L. FRIELING.—(See i, 1288.)

**Aminobenzthiazoles. I. 1-Anilinobenzthiazole and its Tolyl Homologues.** R. F. HUNTER (*J. Chem. Soc.*, 1925, 127, 2023—2028; cf. Hugershoff, A., 1903, i, 865).—Bromination of *s*-diphenylthiocarbamide in chloroform suspension yields the tetrabromide of 1-anilinobenzthiazole, m. p. 117° (decomp.) (cf. Hugershoff, *loc. cit.*, m. p. 136°). A perbromide formula,



is ascribed to this compound, since it is reduced by sulphurous acid to the free base (*acetyl* derivative, m. p. 158°), is converted on treatment with alkalis into dibromoanilinobenzthiazole, and, on exposure to air, passes spontaneously into a stable *tribromide*, yellow prisms, sintering at 120°, m. p. 125°. The last-named shows similar reactions with sulphurous acid and alkalis. Bromination of di-*o*-

tolylthiocarbamide gives the unstable 1-o-toluidino-3-methylbenzthiazole hexabromide,  $C_6H_3Me\langle\begin{smallmatrix} SBr_4 \\ NBr_2 \end{smallmatrix}\rangle C\cdot NH\cdot C_7H_7$ , red needles, losing bromine at  $60^\circ$ , m. p.  $76-78^\circ$ , from which the free base, the tribromide, yellow prisms, m. p.  $250^\circ$  (decomp.), and dibromo-1-o-toluidino-3-methylbenzthiazole,  $C_6H_2MeBr\langle\begin{smallmatrix} S \\ N \end{smallmatrix}\rangle C\cdot NH\cdot C_7H_6Br$ , colourless needles, m. p.  $205^\circ$  [hydrobromide, m. p.  $280^\circ$  (decomp.)], are obtained. Di-*p*-tolylthiocarbamide gives 1-*p*-toluidino-5-methylbenzthiazole tetrabromide, red needles, sintering at  $130^\circ$ , m. p.  $145^\circ$ , from which the free base (acetyl derivative, m. p.  $158^\circ$ ), the tribromide, orange needles, m. p.  $148^\circ$  (decomp.), and dibromo-1-*p*-toluidino-5-methylbenzthiazole, m. p.  $159-160^\circ$  (hydrobromide, m. p.  $256-258^\circ$ ), are obtained. Di-*m*-tolylthiocarbamide gives 1-*m*-toluidino-4(6)-methylbenzthiazole hexabromide hydrobromide, red tablets, m. p. above  $200^\circ$ , from which the free base, m. p.  $184-186^\circ$ , and the tribromide hydrobromide, yellow crystals, sintering at  $190^\circ$ , are obtained.

It is suggested that the bromides, in view of their stability, may be hexabromides of condensation products, 1-anilinobenzthiazole tribromide, for example, being written



M. J.

### Relations between Constitution and Tinctorial Properties.

H. JOHN (*Z. angew. Chem.*, 1925, **38**, 903—904).—A comparison of corresponding derivatives of 6-hydroxy-2-phenyl-4-methylquinoline,  $\beta$ -naphthol, and "naphthol AS." The azo dyes, obtained by coupling with a variety of diazotised amines, possess almost identical fastness. The derivatives of the hydroxyquinoline are more fast towards soaps and alkalis, but are less vivid and more yellow in shade than those obtained from  $\beta$ -naphthol and "naphthol AS." The new azo dyes also show very poor fastness to light.

W. T. K. B.

**Mechanism of Reduction of Azobenzene by Magnesium Organo-halides.** H. GILMAN and R. M. PICKENS (*J. Amer. Chem. Soc.*, 1925, **47**, 2406—2416).—The interaction of azobenzene in boiling ether solution and magnesium methyl, *n*-butyl, cyclohexyl, phenyl, and *p*-tolyl halides gives hydrazobenzene and the dialkyl or diaryl hydrocarbon in approximately corresponding yield, whilst no olefines are formed. These facts support the view of the mechanism of the reaction advanced by Franzen and Deibel (*A.*, 1905, i, 843). The presence of an  $\cdot MgX$  group on each nitrogen atom is further established by the formation of diacetyl- and dibenzoyl-hydrazobenzene when acetyl chloride or benzoyl chloride is added to the mixture of azobenzene and Grignard reagent after the customary period of heating. With magnesium ethyl and phenyl bromides significant quantities of monoacetyl-hydrazobenzene were also formed when acetyl chloride or acetic anhydride was added, an observation harmonising better with

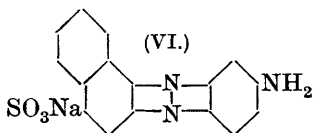
Hess and Rheinboldt's theory of reduction by the hypothetical magnesium hydrogen halide (cf. A., 1921, i, 777). Further support for the latter theory is possibly afforded by the absence of apparent reduction with magnesium phenylacetylene bromide, magnesium dibromoacetylene, and magnesium triphenylmethyl chloride, types which should be incapable of yielding magnesium hydrogen halides. It is possible, however, that the failure of the magnesium acetylene halides to reduce is at least partly due to their lesser reactivity, but it is unlikely that the behaviour of the triphenylmethyl compound is due to steric hindrance. Reduction takes place, however, with magnesium methyl iodide, magnesium benzyl chloride, and magnesium aryl halides, in which cases also formation of the magnesium hydrogen halide is highly improbable. The absence of reducing action with magnesium ethyl bromide at low temperatures, a substance, m. p. 232—235°, being obtained in the presence of benzoyl chloride, would also agree with the Hess-Rheinboldt theory. The evidence here points to the existence of an intermediate molecular additive compound which only dissociates on heating, and this failure to reduce at low temperatures may only be an example of the general inertness of the azobenzene group. The addition of ethyl sulphate to the reaction product of azobenzene and magnesium phenyl bromide gives some evidence of the formation of *s*-diphenyldiethylhydrazine, a further indication of the presence of two  $\cdot\text{MgX}$  groups. Further reduction to aniline was observed in several experiments, probably either by decomposition of hydrazobenzene during the vacuum distillation into aniline and azobenzene, or by reduction of the hydrazobenzene by Grignard reagent (cf. Wieland and Roseau, A., 1915, i, 797). The reduction of azobenzene to hydrazobenzene only takes place at the b. p. of ether, and the formation of azo compounds in the reactions between aromatic nitro compounds and Grignard reagents (Hepworth, T., 1920, 117, 1004; Busch and Hobein, A., 1907, i, 552) is due to the external cooling employed. Other reductions by means of the Grignard reagent possibly involve a similar mechanism (cf. Meisenheimer, this vol., i, 527). Magnesium styryl bromide gives a 77.7% yield of  $\alpha\gamma$ -diphenylbutadiene, and the reaction possibly affords a convenient method of synthesising such compounds or the acyl derivatives of unstable hydrazines. With *pp'*-azotoluene and magnesium phenyl bromide no *pp'*-hydrazotoluene could be isolated, but evidence of reduction was afforded by a 74% yield of diphenyl and 26% of *p*-toluidine. Magnesium benzyl chloride and *p*-dimethylaminoazobenzene in the presence of benzoyl chloride afford *s*-diphenylethane (66%), a little benzanilide, and the mono- and di-benzoyl derivatives of *p*-dimethylaminohydrazobenzene. Magnesium ethyl bromide and diazoaminobenzene with benzoyl chloride yield *s*-diphenyltribenzoyltriazan (31.3%), benzanilide, and benzamide. Reaction of magnesium ethyl bromide with either azobenzene or hydrazobenzene and phenylcarbimide gives no definite results owing to the formation of by-products (probably cyclic). Similar indefinite results were obtained with magnesium phenyl bromide.

R. B

**Action of Sulphites on Aromatic Hydroxy and Amino Compounds. XI. Action of Phenylhydrazine Sodium Hydrogen Sulphite Mixture on Azo Dyes.** H. T. BUCHERER

and F. STICKEL (*J. pr. Chem.*, 1925, [ii], **110**, 309—353; cf. A., 1922, i, 465).—Orange-II ( $\beta$ -naphtholazobenzene-*p*-sulphonic acid) dissolves unchanged in cold sodium hydrogen sulphite solution, but is converted by the latter at water-bath temperatures into the additive *product*  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}(\text{SO}_3\text{Na})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$  (I), orange-yellow, which separates on cooling, whilst the solution contains 1-amino-2-naphthol-4-sulphonic acid. The latter is obtained, together with sulphanilic acid, when the sodium hydrogen sulphite solution of orange-II is boiled for 12 hrs. When orange-II is dissolved in warm, 33% sodium hydrogen sulphite solution, and the mixture treated with phenylhydrazine, the yellow *compound*  $\text{NHPh}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}(\text{SO}_3\text{Na})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$  (II), is produced, which, when boiled with aqueous alkali or potassium cyanide, loses sodium hydrogen sulphite with formation of the bluish-red *dye*  $\text{NHPh}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$  (III). The latter affords, on treatment with sodium nitrite in presence of excess of hydrochloric acid, sodium  $\psi$ -azoimidophenylsulphonate,  $\text{C}_{10}\text{H}_6\cdot\left<\text{N}\right>\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$  (IV), (cf. Witt, A., 1894, i, 608), whilst

in presence of acetic acid, the action of sodium nitrite leads to the formation of the corresponding phenyl- $\psi$ -azoimide, m. p.  $107^\circ$  (cf. A., 1886, 244; 1894, i, 608; 1895, i, 669). When boiled with alkali in presence of air (III) is oxidised to the *disazo* compound,  $\text{NPh}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$  (V), pale brown, the reverse reaction taking place when the latter is warmed with dextrose in dilute alkaline solution. The production of the disazo derivative from orange-II can be carried out in one operation, and a similar process applied to orange-I [cf. D.R.-P. 59173 19 14]. When (III) is treated with cold, concentrated hydrochloric acid, it yields 9-amino-phenonaphthazine (cf. A., 1905, i, 553), together with a *compound*, soluble in alkali, which is not identifiable as the product of a semidine transformation, and yields sulphanilic acid when boiled with concentrated hydrochloric acid. Condensation of orange-II with sodium hydrogen sulphite and *p*-phenylenediamine in boiling aqueous solution, followed by basification with cold sodium hydroxide solution and subsequent boiling with concentrated hydrochloric acid, affords sulphanilic acid and a violet *precipitate*, possibly (VI), which behaves as a vat dye.



couples with diazotised sulphanilic acid with formation of a violet *dye*, the colour of which is changed to yellowish-brown with alkali, without the dye undergoing decomposition.

When (II) is warmed with sodium hydrogen sulphite solution,

when  $\beta$ -naphthol, *p*-phenylenediamine, and sodium hydrogen sulphite solution are boiled together for 12 hrs. This yields, when warmed with acetic anhydride, an acetyl derivative, which

it is decomposed, with formation of aniline, sulphanilic acid, a yellow *product* resembling (II), and a colourless *sulphonic acid*, unidentified; (V) yields similarly sulphanilic acid and a *compound*,  $C_{16}H_9O_3N_3SNa$ , probably a  $\psi$ -azoimido derivative. Treatment of (II) with warm hydrochloric acid affords sulphanilic acid and a *product*, unidentified, insoluble in aqueous ammonia.

F. G. W.

**Bromination of Acyl Derivatives of Phenylhydrazine.**  
**Preparation of 2:4-Dibromophenylhydrazine.** J. E. HUMPHRIES and R. EVANS (*J. Chem. Soc.*, 1925, 127, 1676—1677).—*Acetyl-p-bromophenylhydrazine hydrobromide*, m. p.  $132^\circ$  (decomp.), is precipitated when bromine (1 mol.) is added to a solution of acetylphenylhydrazine in chloroform below  $0^\circ$ . *Acetyl-2:4-dibromophenylhydrazine*, m. p.  $146^\circ$  (decomp.), is obtained similarly by the action of 2 mols. of bromine at  $0^\circ$ , whilst benzoylphenylhydrazine affords, in the same way, 2:4-dibromophenylhydrazine hydrobromide. Formation of diazonium salts was not observed (cf. Michaelis, A., 1893, i, 705; Vaubel, A., 1894, i, 453), nor was evidence obtained of the existence of *N*-bromo compounds (cf. Chattaway, T., 1908, 93, 852).

F. G. W.

**Organic Compounds of Arsenic. II. Reaction between the Grignard Reagent and Arsenic Trioxide.** K. MATSUMIYA and M. NAKAL (*Mem. Coll. Sci. Kyōtō*, 1925, 8, 307—317; cf. Matsumiya, A., 1920, i, 777).—From a repetition of the work of Sachs and Kantorowicz (A., 1908, i, 1031) and from a study of the action of magnesium  $\alpha$ -naphthyl bromide on arsenious oxide, the authors conclude that the views of Sachs and Kantorowicz are incorrect and that the reaction must be represented thus:  $As_2O_3 + 4RMgBr = (R_2As)_2O + 2MgO + 2MgBr_2$ ;  $(R_2As)_2O + 2RMgBr = 2R_3As + MgO + MgBr_2$ . The following compounds are described: *di- $\alpha$ -naphthylarsine oxide*, m. p.  $240$ — $241^\circ$ ; *di- $\alpha$ -naphthylarsine trichloride*; *di- $\alpha$ -naphthylarsinic acid*, m. p.  $228$ — $229^\circ$ ; *di- $\alpha$ -naphthylmethylarsine*, m. p.  $145$ — $146^\circ$ , and a *substance*,  $[(C_{10}H_7)_2AsCl_2]_2O$ .

R. W. W.

**Organic Compounds of Arsenic. III. Reaction between Arsenic Trichloride and  $\alpha$ -Naphthyl Compounds of Mercury.** K. MATSUMIYA (*Mem. Coll. Sci. Kyōtō*, 1925, 8, 391—396).—The action of mercury  $\alpha$ -naphthyl chloride on arsenious chloride is similar to that of magnesium  $\alpha$ -naphthyl bromide (A., 1920, i, 777), but is not so vigorous. Mercury  $\alpha$ -naphthyl chloride and mercury di- $\alpha$ -naphthyl are conveniently prepared by adding mercuric chloride to an ethereal solution of the Grignard reagent.

R. W. W.

**Relative Rates of Conversion of Phenoxyphenyldichloroarsine and its Chloro Derivatives into Chlorophenoxarsines.** E. ROBERTS and E. E. TURNER (*J. Chem. Soc.*, 1925, 127, 2004—2012).—The main determining factor affecting ring-closure of phenoxyphenyldichloroarsines to chlorophenoxarsines appears to



be a steric one, modified by polar effects. In order to compare their rates of ring-closure, *o*-phenoxyphenyldichloroarsine (this vol., i, 706) and its *o*-, *m*-, and *p*-chloro derivatives were heated at 200° in a current of carbon dioxide, and the hydrogen chloride liberated was determined at intervals. The parent substance underwent ring-closure much more readily than the *meta* derivative, where the steric effect of the chlorine atom outweighs the polar effect. The *ortho* and *para* derivatives, where the steric effect of the chlorine atom enhances the polar effect, underwent ring-closure at approximately equal and very much slower rates. 4-Chloro-2-phenoxyphenyldichloroarsine is, according to expectation, more readily converted into a phenoxarsine than *o*-phenoxyphenyldichloroarsine itself.

Similar considerations affect the conversion of the *o*-phenoxyphenylarsinic acids into phenoxarsinic acids on heating with concentrated sulphuric acid. The parent substance undergoes sulphonation and ring-closure. The *o*-chloro derivative, owing to combined polar and steric effects of the chlorine atom, undergoes sulphonation more rapidly than ring-closure. The *meta* derivative, owing to the steric effect of the chlorine atom on sulphonation, and the *para* derivative, owing to blocking of sulphonation by the chlorine atom, give phenoxarsinic acids.

2-Chloro-, m. p. 48°, b. p. 209°/9 mm., 3-chloro-, b. p. 204°/8 mm., and 4-chloro-2'-nitrodiphenyl ether, m. p. 44—45°, b. p. 208°/11 mm., 220°/20 mm., give 2-chloro-, m. p. 44—45°, b. p. 185°/9 mm. (hydrochloride, m. p. 171—173°), 3-chloro-, b. p. 195°/13 mm. (hydrochloride, m. p. 149—151°; benzoyl derivative, m. p. 106°), and 4-chloro-2'-aminodiphenyl ether, b. p. 202°/15 mm. (hydrochloride, m. p. 190—191°; benzoyl derivative, m. p. 108—109°). These are converted, after diazotisation, into 2-*o*-chloro-, m. p. 195—195·5°, 2-*m*-chloro-, m. p. 177—179°, and 2-*p*-chloro-phenoxyphenylarsinic acid, m. p. 187—188°, giving, on reduction in warm concentrated hydrochloric acid suspension with sulphur dioxide in presence of a little potassium iodide, 2-*o*-chloro-, b. p. 217°/8 mm. (partial decomp.), 2-*m*-chloro-, b. p. 220°/10 mm. (decomp.), and 2-*p*-chloro-phenoxyphenyldichloroarsine, m. p. 67—68°, b. p. 220°/10 mm. (partial decomp.). Ring-closure of these compounds gives 5:9-dichlorophenoxarsine, m. p. 99°, 5:8-dichlorophenoxarsine, m. p. 125° [alternatively prepared by hydrochloric-hydriodic-sulphurous acid reduction of 8-chlorophenoxarsinic acid, m. p. 250—252° (sodium salt, sparingly soluble in alkali), obtained by the action of sulphuric acid on 2-*m*-chlorophenoxyphenylarsinic acid], and 5:7-dichlorophenoxarsine, m. p. 144—145° (alternatively obtained, together with an arsenic-free substance, m. p. 119—120°, by reduction of 7-chlorophenoxarsinic acid, m. p. 240—242°, from 2-*p*-chlorophenoxyphenylarsinic acid). The constitution of 5:8-dichlorophenoxarsine was established by a synthesis, excluding the 5:6 alternative, from 2:4-dichloronitrobenzene through 5-chloro-2-nitrodiphenyl ether, m. p. 85°, the amino-ether, 4-chloro-2-phenoxyphenylarsinic acid, m. p. 182°, and 4-chloro-2-phenoxyphenyldichloroarsine, m. p. 91—92°.

*o*-Aminodiphenyl ether (*acetyl* derivative, colourless prisms) gives *o*-phenoxyphenylarsinic acid, m. p. 167—168°. M. J.

**Preparation of Symmetrical Organic Compounds of Mercury.** F. HEIN and K. WAGLER (*Ber.*, 1925, **58**, [B], 1499—1509).—Mercury diaryls do not appear to react with copper in the presence of pyridine if they are completely free from mercury aryl halides. The latter compounds, however, become quantitatively transformed into mercury diaryls thus:  $2\text{PhHgBr} + 2\text{Cu} \rightarrow \text{HgPh}_2 + \text{Cu}_2\text{Br}_2 + \text{Hg}$ . The change appears to depend on the initial liberation of the group  $\text{RHg}^\cdot$ , which becomes dimerised to  $\text{R}_2\text{Hg}_2$  and subsequently decomposes into  $\text{R}_2\text{Hg}$  and  $\text{Hg}$ . The method appears to be superior to any described hitherto for the preparation of mercury diphenyl, dimethyl, diethyl, dibenzyl, di- $\alpha$ -naphthyl, or di-*p*-dimethylaminodiphenyl.

[With W. RETTER.]—The following new compounds have been prepared: *mercury di-o-nitrophenyl*, m. p. 206—207°; *mercury di-p-chlorophenyl*, m. p. 242—243°; *mercury di-p-bromophenyl*, m. p. 244—245°. H. W.

**Constitution of Proteins.** E. ABDERHALDEN (*Z. physiol. Chem.*, 1925, **146**, 147—150).—Polemical. P. W. C.

**Horn-dissolving Action of Alkali Sulphides.** P. PULEVKA (*Z. physiol. Chem.*, 1925, **146**, 130—142).—The increase in weight of horn on soaking for a known time in various strengths of sodium hydroxide and in saturated calcium, strontium, and barium sulphide solutions has been measured. The hydrosulphide ion assists much more powerfully than the hydroxyl ion in the solution of horn, but it must be present in alkaline solution. P. W. C.

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### Biochemistry.

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Muscular Exercise, Lactic Acid, and the Supply and Utilisation of Oxygen. XI. Pulse Rate and Oxygen Intake during the Early Stages of Recovery from Severe Exercise. R. J. LYTHGOE and J. R. PEREIRA (*Proc. Roy. Soc.*, 1925, B, 98, 468—479). XII. Technique of Determining the Resting Oxygen Intake while Breathing Oxygen Mixtures. J. R. PEREIRA (*ibid.*, 480—484).—XI. In the case of severe exercise (standing running) the oxygen consumption and heart rate fall off at the end of the exercise. The rate of fall, which is greater for the oxygen intake, is roughly inversely proportional to the time. This may be due, in part, to the greater coefficient of utilisation of the oxygen in the blood during the exercise. It is more probable, however, that it is due to an immediate decrease in the output of the heart per beat when exercise ends.

XII. The oxygen intake at rest is practically the same while breathing air and while breathing nearly pure oxygen mixtures. The difference already described (A., 1924, i, 1363) is shown to be due to the incorrect assumption that in the Douglas bag technique the total amount of nitrogen is the same in the inspired as in the expired air. O. O.

[Iron the Oxygen-carrying Component of the Respiratory Enzyme.] P. ELLINGER (*Ber.*, 1925, 58, [B], 1547).—A reply to Warburg (this vol., i, 471). H. W.

**Maintenance of Carbonic Acid Equilibrium in the Body.** C. D. MURRAY and A. B. HASTINGS (*J. Biol. Chem.*, 1925, 65, 265—278).—A theoretical discussion of the part played by respiration and kidney function in the maintenance of a constant carbonate concentration of the blood during the arterio-venous cycle, and of the evidence in favour of the hypothesis of the control of respiration by the tension of carbon dioxide in the plasma. C. R. H.

**$p_H$  Limits of Normal Blood. Regulation of  $p_H$  in Normal and Pathological Conditions.** E. J. BIGWOOD (*Bull. Soc. Chim. biol.*, 1925, 7, 868—883, 884—892).—A critical discussion of the errors involved in the various methods of determining the  $p_H$  of the blood. Using proper precautions, the colorimetric method of Cullen or the modified method of Hastings and Sendroy will give results agreeing within  $\pm p_H$  0.02 with the electrometric method carried out at 38°. This should be a very close approximation to the actual  $p_H$  *in vivo*. The  $p_H$  of the blood of normal individuals varies between the limits 7.30 and 7.40.

In most pathological conditions, the blood  $p_H$  is maintained within the normal limits by variations in the concentrations of free and bound hydrogen carbonate. In certain epileptic conditions, however, this regulatory mechanism may break down, with the consequent occurrence of abnormal values for the  $p_H$ . The ingestion of acid or alkali may also displace the  $p_H$  temporarily beyond the normal limits. H. P. M.

**Naphthol Reaction of Red Blood-corpuscles.** W. LOELE (*Virchow's Archiv*, 1924, 251, 156—159; from *Chem. Zentr.*, 1925, i, 2704—2705).—Acids dissolve naphthol blood-corpuscles only within certain ranges of concentration, depending on their dissociation constants. Solution by pepsin also depends on hydrogen-ion concentration. Red corpuscles which are comparatively stable to hydroxyl ions, become sensitised by treatment with naphthol. Naphthol also renders trypsin capable of dissolving blood-corpuscles. G. W. R.

**Deposition, Separation, and Reabsorption of Haemoglobin in the Organism and their Relation to the Deposition of Iron Pigment.** K. SHIMURA (*Virchow's Archiv*, 1924, 24, 464—493; from *Chem. Zentr.*, 1925, ii, 54).—Haemoglobin, given to dogs intravenously, was rapidly excreted. The separation is brought about by the kidneys, liver, gall-ducts, and suprarenals;

in the remaining organs the hæmoglobin is stored up and decomposed into iron pigment. A. C.

**Development of Blood Plasma. I. Genesis of Coagulable Materials in Embryo Chicks.** J. W. PICKERING and R. J. GLADSTONE (*Proc. Roy. Soc.*, 1925, B, 98, 516—522).—Fibrinogen and prothrombin, which appear to develop simultaneously in the blood of chick embryos, are absent in the early stages, and their absence is responsible for the incoagulability of the blood. Globulin does not appear until after the 12th day. Serum-globulin is not essential to the coagulation of the blood. An excess of material which is not antithrombic, but which is protective against the inception of clotting, exists in the plasma of early embryos. Hydrogen ions appear to catalyse the clotting of the embryonic plasma. Antithrombins were prepared from embryonic blood and other tissues at the stage where the mother substance of thrombin had not appeared in the plasma. This is opposed to the current view that antithrombins are produced by a reaction of the organism in response to the presence of thrombin. Calcium ions are deficient in the plasma of embryos aged 12 to 19 days. This shortage disappears about the 20th day after incubation. It appears that the impact of a definite number of calcium ions in a definite time interval is an essential factor in the inauguration of blood coagulation.

O. O.

**Folin and Wu's Method of Blood Analysis.** O. LATHAM (*Med. J. Australia*, 1924, Suppl., 412—417).—Colorimetric methods are examined, and a simple colorimeter is described. Departures from the normal values of non-protein nitrogen, urea nitrogen, creatinine, uric acid, dextrose, and carbon dioxide coefficient follow physical rather than mental disabilities.

#### CHEMICAL ABSTRACTS.

**Nature of the Sugar in Blood.** M. B. VISSCHER (*Amer. J. Physiol.*, 1924, 68, 135—136).—Winter and Smith's observation, that if an extract containing the sugar of normal blood is kept for several days the optical rotatory power increases, whilst the copper reduction value is constant, whereas the opposite is the case for diabetic blood, was confirmed for normal blood. The previously observed difference between normal and diabetic blood could, however, be obtained by varying the hydrogen-ion concentration of the filtrate concentrate of normal blood. It is not believed that the change in rotation is due to the sugar being converted into a more stable form. A. A. E.

**Sugar of the Blood.** D. A. SCOTT and C. H. BEST (*Amer. J. Physiol.*, 1924, 68, 144).—The fact that an extract of blood from a hypoglycæmic rabbit may reduce the blood-sugar of a normal rabbit to a very low level, and the consistent rapid fall in blood-sugar during the first  $\frac{1}{2}$  hr. after the administration of insulin suggest that the mechanism of the rapid disappearance of sugar from the blood is to be found in the blood itself. The reducing power of the blood of starved normal rabbits or dogs is only slightly

increased by hydrolysis with dilute sulphuric acid or trypsin. If the starved animals have been rendered hypoglycæmic with insulin, hydrolysis of the blood causes a pronounced rise in reducing power.

A. A. E.

**Glycolysis *in Vitro*.** S. MORGULIS and O. BARKUS (*J. Biol. Chem.*, 1925, 65, 1—5).—The disappearance of dextrose from blood kept under aseptic conditions *in vitro* is accompanied by an accumulation of lactic acid, and differs in this respect from the hypoglycæmia induced by insulin. The inorganic phosphorus of the blood remains unchanged during glycolysis unless hæmolysis occurs, when it increases in amount.

C. R. H.

**Glycolysis.** H. J. JOHN (*Ann. Clin. Med.*, 1925, 3, 667—696).—Uniform glycolysis takes place in blood *in vitro*; it is less in diabetic than in normal blood, and is also less at 0° than at the ordinary temperature.

CHEMICAL ABSTRACTS.

**Determination of Uric Acid in Blood.** M. DELAVILLE and C. M. JONES (*Bull. Soc. Chim. biol.*, 1925, 7, 785—796).—The total uric acid is determined after hydrolysis with dilute sulphuric acid, and ultra-filtration, the uric acid being determined colorimetrically in the ultra-filtrate. It is thus shown that the usual method of determination on the protein-free filtrate gives low results, some of the uric acid being carried down by the precipitated proteins. A critical study of the colorimetric method of Folin and Denis reveals the fact that the theoretical direct proportionality between dilution and depth of liquid required to give a certain colour does not hold when the solutions are only slightly alkaline (sodium carbonate). Under these conditions, the observed points fall on a straight line which does not pass through the origin. An equation is given, applicable to solutions containing 30—200 mg. of uric acid per litre.

H. P. M.

**Presence of Isoagglutinins in the Blood of Dogs.** E. I. McENERY, A. C. IVY, and C. E. PECHOUS (*Amer. J. Physiol.*, 1924, 68, 133—134).—Isoagglutinins are present in the blood of dogs. The results of a large number of experiments were such that blood groups could not be formed.

A. A. E.

**Artificial Production of Autohæmolysin.** M. NANBA (*Deut. med. Woch.*, 1925, 51, 594—595; from *Chem. Zentr.*, 1925, i, 2705).—After injection of Fossmann's antigen, an emulsion of guinea-pig's kidneys, into syphilitic rabbits a marked formation of autohæmolysin occurs. It is found that the same effect can be obtained with healthy animals. The autohæmolysin appears generally 5 to 6 days after injection and disappears after 1 to 3 weeks. Autohæmolysin thus produced is inactivated by warming for 30 mins. at 50°, and is not reactivated by addition of normal rabbit or guinea-pig serum. It consists probably of amboceptor and complement, and, as is the case with the autohæmolysin of hæmoglobinuria, requires a low temperature for its combination with red corpuscles. Hæmolysis takes place *in vivo* if the temperature is lowered.

G. W. R.

**Nature of the Specific Hæmolysins.** F. KLOPSTOCK (*Deut. med. Woch.*, 1925, **51**, 592—593; from *Chem. Zentr.*, 1925, ii, 55).—Hæmolysins may be adsorbed and elutriated by the methods which are applicable to enzymes. Hæmolysins therefore are either dissolved colloidal particles with an amphoteric charge or they are deposited on the accompanying material with amphoteric charge. The adsorption of hæmolysin is not a simple protein adsorption.

A. C.

**Hæmolytic Action of Ammonium Salts.** M. H. JACOBS (*Amer. J. Physiol.*, 1924, **68**, 134—135).—Neither the osmotic theory nor the theory that the effect is due to free ammonia is adequate to explain the hæmolytic action of ammonium salts. It is assumed that the corpuscles are relatively impermeable to ammonium ions as well as to the other cations, but are freely permeable to anions and to ammonium hydroxide or ammonia molecules.

A. A. E.

**Precipitin Reaction of Thyroglobulin.** L. HEKTOEN and K. SCHULHOF (*Proc. Nat. Acad. Sci.*, 1925, **11**, 481—484).—Thyroglobulin precipitins are specific for thyroglobulin, but not consistently species-specific. Thyroglobulin may occur in the lymph, blood, and the colloid material of the thyroid. Rabbits produce precipitin for rabbit thyroglobulin. Exophthalmic goitrous glands appear to yield the same thyroglobulin as normal glands.

H. J. C.

**Pathological Increase in Globulin (in Blood). Relationship between Decomposition of Hæmoglobin and Increase in Globulin.** G. C. REYMANN (*Z. Immunit.*, 1924, i, **41**, 209—301; from *Chem. Zentr.*, 1925, i, 2705—2706).—During immunisation against diphtheria in horses, decrease in the hæmoglobin content and the number of red corpuscles in the blood sets in, together with the formation of antitoxin in most cases. This is followed first by an increase in fibrinogen and then in globulin. The connexion between decomposition of red corpuscles and increase in globulin appears to exist even in normal horses. The loss of red corpuscles during immunisation must be compensated by increased formation, since in the later stages the decrease becomes less. The formation of globulin is greatest in the later stages, but as a rule finally decreases. There is often a decrease in fibrinogen accompanied by increase in hæmoglobin and red corpuscles during this stage, a circumstance which may be due to the weakening of the function of the liver. Similar results were obtained with goats, using staphylolysin and pyrocin. From theoretical considerations, it is supposed that globin is one of the sources of globulin. In the hæmolysis of total blood, spontaneously or by dilution, there is the same displacement of the protein fractions as in immunisation, *i.e.*, increase in the fraction precipitable with the globulins and fibrinogen and decrease in the albumin.

G. W. R.

**Blood of the Seal.** M. SUZUKI (*Jap. J. Med. Sci.*, 1925, **1**, 71—72).—The nitrogen partition of two specimens of blood is given.

H. D. K.

**Removal of Proteins from Body Fluids with Colloidal Ferric Hydroxide. Indirect Determination of Proteins in Cerebro-spinal Fluid etc.** H. WUNSCHENDORFF (*Bull. Soc. Chim. biol.*, 1925, 7, 768—777, 778—784).—A modification of the Michaelis method of precipitating proteins with colloidal ferric hydroxide is described which is stated to give filtrates entirely free from protein: To 2 c.c. of the clear, centrifuged serum or other organic fluid, diluted with 20 c.c. of water, are added drop by drop, with continual shaking, 15 c.c. of a specially prepared colloidal ferric hydroxide. If the fluid contains hæmoglobin, 0.1 g. of powdered potassium sulphate should also be added. After keeping for 15 mins., the liquid is filtered, the first portion of the filtrate being returned to the filter. The filtrate is slightly acid,  $p_H$  6—6.5.

The nitrogen content of the original fluid, and of the protein-free filtrate as obtained above, is determined, and the difference calculated as protein. The nitrogen is determined as follows: 1 c.c. of the fluid is digested with 0.5 c.c. of concentrated sulphuric acid and 0.5 c.c. of 0.5% copper sulphate solution until all organic matter has been destroyed. After cooling, the ammonia is determined by means of Nessler's reagent.

H. P. M.

**Purification of Heparin and its Presence in Blood.** W. H. HOWELL (*Amer. J. Physiol.*, 1925, 71, 553—562).—Heparin gives no reactions for protein, sulphur, or phosphorus; it is not precipitated by acids, phosphotungstic acid, or salts of most of the heavy metals. It contains 2.7% of nitrogen and gives a positive Molisch carbohydrate reaction. It is not an antithrombin, but when added to blood it causes the formation of antithrombin by reaction with a thermolabile constituent of the plasma. Heparin is present in normal blood-plasma; injection of peptone into dogs greatly increases the amount. Heparin apparently constitutes the inhibitory factor which preserves the fluidity of circulating blood.

A. A. E.

**Biochemistry of the Fats.** W. R. BLOOR (*Chem. Reviews*, 1925, 2, 243—300).

**Cholesterol Content of the Testicles and Suprarenals.** C. J. PARHON and V. MARZA (*Compt. rend. Soc. Biol.*, 1925, 92, 727—729; from *Chem Zentr.*, 1925, ii, 54).—Chiefly birds were investigated. The cholesterol content of the suprarenals ranged from 12 to 14 g. per kg., that of the testicles from 2 to 5.5 g. The amount appears to be influenced by the time of the year. A. C.

**New Cerebroside.** E. KLENK (*Z. physiol. Chem.*, 1925, 145, 244—260).—A new cerebroside, similar to kersin, for which the name "nervone" is suggested, has been obtained from the light petroleum extract of human and ox brain. The kephalin is first removed by addition of alcohol and decantation, and the "nervone" precipitated by lead acetate in alcohol, after removal of the light petroleum. The precipitate is suspended in boiling alcohol, the lead removed by hydrogen sulphide, and the precipitate obtained after



cooling the filtrate to  $0^{\circ}$  is freed from phosphatides by extracting with acid acetone and dissolving the residue in warm chloroform-methyl alcohol. On cooling, a precipitate is obtained, from which the last traces of phosphorus are removed with cadmium acetate in hot methyl alcohol. After removal of the cadmium, a white precipitate separates on cooling. This is further separated from traces of cerebrone and kersin by fractional precipitation from warm methyl alcohol, and then from 1 : 2 chloroform-methyl alcohol, by which process the iodine value is raised from 52 to 60.

The purified substance crystallises in rosettes, probable formula  $C_{47}H_{89}O_8N$ , m. p.  $180^{\circ}$ ,  $[\alpha]_D^{25} -4.33^{\circ}$ . It is decomposed by boiling with sulphuric acid in methyl alcohol into sphingosine, galactose, and a new unsaturated *acid*, probable formula  $C_{24}H_{46}O_2$ , m. p.  $41^{\circ}$ , iodine value 66.3.  
H. P. M.

**Chemistry of the Oviduct of the Hen.** G. D. BUCKNER, J. H. MARTIN, and A. M. PETER (*Amer. J. Physiol.*, 1925, **71**, 349—354).—The calcium deposited as egg shell appears not to be associated with the phosphorus of the oviduct, but comes to the uterus in the blood-stream in another form.  
A. A. E.

**Conversion Products of the Pigments of Flesh and Blood.**  
**IV. Production of Porphyrins in Flesh. V. Hæmochromogens and Hæmatins Derived from Putrefied Flesh and Blood, and the Related Porphyrins.** O. SCHUMM (*Z. physiol. Chem.*, 1925, **147**, 184—220; 221—247).—IV. From fresh ox-flesh and ox-heart a chloroform-soluble porphyrin may be separated in very small quantities; this appears to be identical with the chloroform-soluble  $\alpha$ -porphyroidin previously described. (Coproporphyrin has not been detected.) The yield of this substance in these circumstances is markedly increased if the tissue is allowed to undergo spontaneous putrefaction at  $15^{\circ}$ . Two porphyrins were present in certain of the experiments in which meat was allowed to putrefy at  $37^{\circ}$ , viz., the first-mentioned, chloroform-soluble pigment, and a second allied to, if not identical with, coproporphyrin. The latter pigment is also similar to mesoporphyrin and hæmoporphyrin. When putrefied meat is treated with excess of fuming hydrochloric acid, a mixture of various porphyrins is produced. Together with the two pigments just mentioned is a third, a chloroform-soluble porphyrin, different from Nencki's hæmatoporphyrin and neither mesoporphyrin nor coproporphyrin. The identification of small quantities of coproporphyrin in tissues is rendered more difficult by the fact that a closely related blood pigment which is very similar to coproporphyrin in its reactions, but which has a slightly different absorption spectrum, is usually present also.

V. The following hæmatins are obtained by putrefaction of flesh or blood: (1)  $\alpha$ -hæmatin, (2) a hæmatin which resembles the iron derivative of Nencki's hæmatoporphyrin, (3) a hæmatin which corresponds spectroscopically with the iron derivative of mesoporphyrin or coproporphyrin, (4) a hitherto unknown *pigment*

allied to hæmatin which, on removal of the iron, gives a spectrum closely allied to that of hæmoporphyrin or ætioporphyrin.

H. D. K.

**Nitrogen Distribution and Percentages of Some Amino-acids in the Muscle of the Shrimp, *Peneus setiferus* (L.).** D. B. JONES, O. MOELLER, and C. E. F. GERSDORFF (*J. Biol. Chem.*, 1925, 65, 59—66).—The air-dried fat-free muscle of the shrimp has amide nitrogen 8.13, humin nitrogen 1.29% of the total nitrogen; it contains cystine 1.75, arginine 10.24, lysine 7.60, histidine 3.78, tryptophan 1.21, tyrosine 4.88, aspartic acid 6.98, and glutamic acid 15.0%. The figures show a general similarity to those obtained similarly for the muscle of the scallop.

C. R. H.

**Cetacea. IX. Serological Investigation of the Biological Relationship of Various Types of Whale.** N. FUSE (*Jap. J. Med. Sci.*, 1925, 1, 1—4).—Both precipitin and fixation of complement reactions indicate that the three types of whale investigated [sperm whale, fin-back whale, and rorqual (*Balaenoptera borealis*)] are closely related to one another.

H. D. K.

**Cetacea. X. Synovial Fluid of Whales.** N. FUSE (*Jap. J. Med. Sci.*, 1925, 1, 5—9).—Some physical and chemical properties of whale's synovial fluid are recorded. It is less dense than that of mammals, has  $p_H$  about 7.75, and contains mucin.

H. D. K.

**Cetacea. XI. Physiological Significance of the Compartments in the Stomach of the Whale.** M. TAKATA (*Jap. J. Med. Sci.*, 1925, 1, 11—13).—The chemical composition and enzyme content of the gastric mucosa in the various stomachs of the rorqual leads to the following conclusions. The first stomach is an organ for temporary storage, analogous to the crop of the bird. The second stomach has similar functions to those of the fundus region in the stomachs of other mammals, producing a secretion rich in pepsin. The third stomach probably behaves like the pyloric region in other animals, secreting hydrochloric acid but little pepsin. The third stomach is well developed, and appears to play an important part in digestion, possibly in the digestion of fat.

H. D. K.

**Cetacea. XII. Physico-chemical Properties of the Urine of the Rorqual.** S. MORIMURA (*Jap. J. Med. Sci.*, 1925, 1, 25—27).—The specific gravity, electrical conductivity,  $p_H$ , and surface tension of the urine of three male and four female whales have been determined. The values are similar to those found for human urine.

H. D. K.

**Cetacea. XIII. Contents of Genital Cysts. Composition of Fluid Found in the Uterus.** K. OKAZAKI (*Jap. J. Med. Sci.*, 1925, 1, 29—30).—Preliminary experiments.

H. D. K.

**Cetacea. XIV. Nature and Constitution of Ambergris.** M. SUZUKI (*Jap. J. Med. Sci.*, 1925, 1, 31—42).—A red pigment, allied to the porphyrins, is present in a specimen of ambergris found in the intestine of a whale. The salt content of ambergris is

small, being mainly calcium and phosphate. The portion of the ethereal solution of ambergris which is insoluble in methyl alcohol appears to be a single substance, *ambrain*,  $C_{26}H_{44}O$ , m. p.  $83^{\circ}$ ; solution in 99% alcohol dextrorotatory. Ambrain may be reduced, taking up four atoms of hydrogen per mol.

Ambraïn gives colour reactions with certain of the reagents used for cholesterol, but does not combine with digitonin. It appears to be either a sterol or a sterol derivative. Twenty-five % of the original ambergris is ambrain. Ambraïn is not found in the normal intestinal contents of the whale.

H. D. K.

**Cetacea. XV. Composition of the Blood of the Fin-back Whale.** Y. OKAHARA (*Jap. J. Med. Sci.*, 1925, 1, 43—47).—The nitrogenous constituents, fat, sterol, and phosphatide, sugar and salts of the blood have been determined quantitatively. The blood has a high sodium chloride content, but is otherwise similar to the blood of other mammals.

H. D. K.

**Cetacea. XVI. Whale's Flesh.** M. SUZUKI (*Jap. J. Med. Sci.*, 1925, 1, 49—50).—Preliminary observations.

H. D. K.

**Cetacea. XVII. Peritoneal Fluid.** N. FUSE (*Jap. J. Med. Sci.*, 1925, 1, 51—53).—The chemical composition of a specimen of whale's peritoneal fluid has been determined.

H. D. K.

**Cetacea. XVIII. Sugar Content of the Blood.** Y. MASUMIZU (*Jap. J. Med. Sci.*, 1925, 1, 55—60).—The sugar content of whale's blood (taken an average of 9—12 hrs. after the death of the animal killed by the usual painful process), determined by several methods, is found to be higher than that of land animals.

H. D. K.

**Cetacea. XIX. Composition of Tendon and Sclera. Separation of  $d$ - $\alpha$ -Aminobutyric Acid from Sclera Protein.** S. OIKAWA (*Jap. J. Med. Sci.*, 1925, 1, 61—67).—The protein of the sclera contains a larger amount of monoamino-acids than tendon protein, and a smaller amount of diamino-acids.  $d$ - $\alpha$ -Aminobutyric acid is present in the sclera protein in fairly large quantities.

H. D. K.

**Cetacea. XX. Composition of the Urine in the *Delphinidae*.** M. SUZUKI (*Jap. J. Med. Sci.*, 1925, 1, 69—70).—The specific gravity, cryoscopic constant, nitrogen partition, and chloride have been determined in three cases.

H. D. K.

**Cetacea. XXI. Enzymes of the Pancreas.** M. TAKATA (*Jap. J. Med. Sci.*, 1925, 1, 73—89).—Although various methods of extraction of the whale's pancreas have been tried, none has yielded an active amylase. The gland contains trypsinogen and lipase.

H. D. K.

**Cetacea. XXII. Cartilage.** S. OIKAWA (*Jap. J. Med. Sci.*, 1925, 1, 91—95).—Determination of preformed chondroitin-sulphuric acid, analysis of chondromucoid (nitrogen distribution in seven groups), and analysis of gelatin from whale's cartilage all

indicate that this tissue is similar in composition to cartilage of land mammals.

H. D. K.

**Cetacea. XXIII. Amniotic Fluid of the Sperm Whale.** M. SUZUKI (*Jap. J. Med. Sci.*, 1925, **1**, 97—101).—The cryoscopic constant, nitrogen partition, sugar, lactic acid, fat, and ash have been determined in this fluid, of  $d^{26}_4$  1.013. The sugar appears to be exclusively l  vulose.

H. D. K.

**Direct Precipitation of Calcium in Cow's Milk.** C. S. ROTHWELL (*J. Biol. Chem.*, 1925, **65**, 129—133).—Calcium may be directly precipitated from diluted cow's milk by the addition of ammonium oxalate and then determined by the method of Kramer and Tisdall (A., 1921, ii, 595). This procedure is not applicable to human milk.

C. R. H.

**Comparative Biochemistry of Urine.** N. FUSE (*Jap. J. Med. Sci.*, 1925, **1**, 103—110).—The urines of the following wild mammals have been analysed: weasel, marten, tiger, leopard, hyena, bat, and also the liquid portion of the excrement of the python. The urine of the weasel, although sugar-free, is always definitely dextrorotatory. Bats' urine contains less urea nitrogen and more creatinine nitrogen than that of carnivorous animals. The liquid excreted by the python, although acid in reaction, contains 40% of its nitrogen as ammonia. Detailed protocols are given.

H. D. K.

**Urine Analysis.** D. RAQUET and M. PAGET (*Ann. Chim. analyt.*, 1925, [ii], **7**, 258).—A sample of urine, normal in chlorides, phosphates, and urea, was found to contain 1.84 g. of purine bases per litre, or three times the normal quantity, using the Haycraft-Denig  s method of determination. The abnormality was found to be due to the presence of iodide in the urine, and after preliminary precipitation of this salt a normal result was obtained. Iodides, bromides, sulphides, theobromine, and probably homogentisic acid will all react with the ammoniacal silver magnesium mixture used in this method, and increase the apparent total of uric acid.

D. G. H.

**Loss of Bases in Diuresis and its Effect on the Alkali Reserve of the Blood.** B. M. HENDRIX and D. B. CALVIN (*J. Biol. Chem.*, 1925, **65**, 197—214).—Diuresis induced in dogs by intravenous injections of hypertonic salt solutions caused a loss from the body of bases which were excreted in the form of phosphates and the salts of organic acids; as a result of this loss of base there was a fall in the alkali reserve of the blood.

C. R. H.

**Organic Bases in Urine.** J. HEFTER (*Z. physiol. Chem.*, 1925, **145**, 290—294).—Treatment of 40 litres of urine by the mercury method failed to reveal the presence of any carnosine, but a small quantity of a crystalline, l  vorotatory substance, which appeared to be histidine, was obtained.

H. P. M.

**Melanin and its Detection in Urine.** AUFRECHT (*Pharm. Ztg.*, 1925, **70**, 1161—1162).—Melanin occurs in urine, sometimes

free, and sometimes in the form of melanogen, which gives melanin on oxidation. The method of detection is given as follows: the urine is filtered and diluted, and first examined spectroscopically for blood pigments. Excessive amounts of urobilinogen are removed by extraction with ethyl acetate after acidifying with acetic acid. On subsequent addition of chlorine water or hydrogen peroxide, a dark brown coloration or precipitate is produced, soluble in chloroform, giving a blue or violet solution. A brown coloration insoluble in chloroform is given by other substances (unknown) in certain abnormal urines. An alkaptonuric urine can be distinguished by its power to reduce Fehling's solution, although not optically active.

P. E.

**Determination of Urobilin in Urine and Fæces. Rôle of the Liver in Excretion of Urobilin.** J. G. F. VAN SPENGLER (*Dissert.*, Leyden, 1924; from *Chem. Zentr.*, 1925, i, 2716).—Since the portal blood of young calves and rabbits contains more urobilin than the blood in other parts of the circulation, the formation of urobilin by the intestine is indicated. It can, however, be formed in other organs. Pathological urobilinuria indicates derangement of the liver. The normal amount of urobilin excreted daily in the urine is 3 mg.; in the fæces, 100–150 mg. (maximum 200 mg.). The ratio of partition of the urobilin between the urine and the fæces is not greater than 1:50. This ratio is changed in pathological conditions.

G. W. R.

**Determination of Urobilin and Urobilinogen in Urine and Fæces.** A. J. L. TERWEN (*Dissert.*, Amsterdam, 1924; from *Chem. Zentr.*, 1925, i, 2716).—Pure urobilin has not hitherto been isolated. The bacterial reduction of urobilin to urobilinogen is untrustworthy, since urobilin cannot be again obtained from the product of reduction. Nascent ferrous hydroxide, or magnesium powder activated with 0.1% of mercuric chloride may be used for this reduction. The medium should be slightly alkaline. Urobilinogen may be extracted from the fæces by light petroleum, which does not dissolve any pigment. For quantitative purposes, ether is a better solvent. By reduction of the filtrate from urine or fæces rich in urobilin and subsequent extraction with light petroleum, urobilin was obtained as a non-hygroscopic, amorphous substance, m. p. 99°. At 45°, the colour changes from orange-red to black with decrease in volume. The empirical formula is  $C_8H_{12}ON_2$ , and the mol. wt. 758(?).

G. W. R.

**Characterisation of Hæmatoporphyrin and Urobilin in Urine by Means of Wood's Light.** A. POLICARD and A. LEULIER (*Compt. rend. Soc. Biol.*, 1924, 91, 1422–1423; from *Chem. Zentr.*, 1925, ii, 78).—Fluoroscopy by means of Wood's light (light from the mercury arc filtered through a nickel screen) is more sensitive than ordinary spectroscopy. The hæmatoporphyrin must be extracted from the urine, since the latter gives a weak blue fluorescence.

A. C.

**Dehydration following Pyloric Obstruction.** J. L. GAMBLE and S. G. ROSS (*J. Clin. Invest.*, 1925, 1, 403—423).—The chief factor in dehydration is loss of sodium ions. Repair is effected by introduction of sodium ions, as sodium chloride, and water, the excess of sodium ions being excreted as hydrogen carbonate, whereby chloride ions are saved for the body fluids. Water alone or ammonium chloride is ineffective.

CHEMICAL ABSTRACTS.

**Concentrations of Inorganic Substances in Blood-serum and Spinal Fluid.** B. HAMILTON (*J. Biol. Chem.*, 1925, 65, 101—115).—The concentrations of the inorganic constituents of the blood-serum and cerebro-spinal fluid were normal in cases of epilepsy. A comparison of the ratios of individual ions in the two fluids in these and other cases indicated a constant relationship except in the case of bicarbonate. Differences in the ratios of individual ions were found, however, which were outside the limits of experimental error, so that the distribution of these ions between the two fluids could not be explained on the basis of Donnan's theory of membrane equilibria.

C. R. H.

**Glycolysis *in Vivo* with Normal and Depancreatized Dogs. Action of Insulin.** I. I. NITZESCU and I. CADARIU (*Compt. rend. Soc. Biol.*, 1925, 92, 298—300; from *Chem. Zentr.*, 1925, ii, 52).—Whilst Thomas found the behaviour of the blood of a diabetic animal unaltered with regard to glycolysis by the addition of insulin *in vitro*, the power of glycolysis which is almost entirely lost by living depancreatized animals is restored by insulin.

A. C.

**Rate of Excretion of Ingested Sugars in Phloridzin Diabetes.** H. J. DEUEL, jun., and W. H. CHAMBERS (*J. Biol. Chem.*, 1925, 65, 7—20).—After administration of various sugars to fasting phloridzinised dogs, the extra dextrose excreted in the urine was equivalent to 100% of the ingested sugar in the case of lævulose and to 88% in the case of galactose, the greater part of the excretion taking place in the first 5 hrs.; in the case of lactose, the extra dextrose excreted amounted to only 50% in 12 hrs.

C. R. H.

**Animal Calorimetry. XXX. Metabolism of Glycerol in Phloridzin Diabetes.** W. H. CHAMBERS and H. J. DEUEL, jun. (*J. Biol. Chem.*, 1925, 65, 21—29).—After administration of glycerol to phloridzinised dogs amounts of extra dextrose were excreted in the urine which were equivalent to from 55% to 98% of the glycerol taken; the respiratory quotient showed a slight fall, which could be accounted for by the conversion of glycerol into dextrose and did not indicate the general oxidation of either of these two substances.

C. R. H.

**Blood-sugar Time Curves following Ingestion of Dihydroxyacetone.** I. M. RABINOWITCH (*J. Biol. Chem.*, 1925, 65, 55—58).—The administration to a diabetic individual of dihydroxyacetone in amount equivalent to the individual's tolerance to carbohydrate is followed by a diminution of the blood-sugar;

dihydroxyacetone, therefore, is not only more easily tolerated by the diabetic than dextrose, but has an actual insulin-like action on the general carbohydrate metabolism.

C. R. H.

**Physiological Ontogeny. A. Chicken Embryos. II. Catabolism. Chemical Changes in Fertile Eggs during Incubation.** H. A. MURRAY (*J. Gen. Physiol.*, 1925, 9, 1—37).—The loss of water by eggs during incubation is chiefly a function of the humidity of the surrounding atmosphere and depends to a much smaller extent on the thickness and area of the shell, atmospheric temperature, and heat produced by the embryo. The loss of weight by the shell is greatest during the later stages of incubation. There is close agreement between the amount of expired carbon dioxide and that which would arise from the amount of fat oxidised during incubation; the disappearance of the fat accounts for 98% of the weight of solids lost by the egg.

H. J. C.

**Excretion of Carbon Dioxide by Frog Nerve.** G. H. PARKER (*J. Gen. Physiol.*, 1925, 8, 21—31; cf. this vol., i, 849).—Quiescent sciatic nerve of the frog, *Rana grylio*, Stejneger, discharges carbon dioxide at the average rate of 0.00876 mg. per g. of nerve per min. If allowance is made for the connective-tissue present in the nerve, which itself discharges carbon dioxide at the rate of 0.0097 mg. per g. of tissue per min., the output of carbon dioxide from the strictly nervous components is 0.008 mg. per g. of nerve per min. Stimulation of the nerve results in an increase of approximately 14% in the carbon dioxide output, or, when allowance is made for the connective-tissue present, of approximately 16%. Stimulation of boiled, blocked, or degenerated nerve or of connective-tissue results in no such increase.

W. O. K.

**Metabolism of Ammonium Salts and of Urea in Man.** E. F. ADOLPH (*Amer. J. Physiol.*, 1925, 71, 355—361).—The author gives curves indicating the rate of elimination of various dissolved substances at various times after their ingestion. The form in which ingested ammonia-nitrogen is eliminated does not depend on whether it was ingested as ammonia or as urea, but on the acid-base equilibrium in the body.

A. A. E.

**Relationship of Arachidonic Acid to Saturated Fatty Acids in Metabolism.** L. G. WESSON (*J. Biol. Chem.*, 1925, 65, 235—250).—On addition of bromine in excess to an ether extract of tissue, keeping in the cold for 2 days, and digesting the precipitate overnight with concentrated hydrochloric acid at 40°, an insoluble residue of octabromoarachidonic acid is obtained. Determined in this way, the content of arachidonic acid in the tissues of the whole rat was 0.075%; the figure was slightly reduced in rats on a diet deficient in ether-soluble substances; it was increased by feeding cod-liver oil, in the condition of beri-beri, after administration of phloridzin, and during that period of fasting when the stores of glycogen are exhausted, but those of fat still available. The increases were always more noticeable in the liver than in the whole tissues. The results indicate that arachidonic acid is essentially

an intermediate metabolic product of the higher fatty acids, and is not, as suggested by Hartley (A., 1909, ii, 597), derived from carbohydrates.  
C. R. H.

**Re-synthesis of Carbohydrates in the Muscle of Warm-blooded Animals.** S. JANSSON and H. JOST (*Z. physiol. Chem.*, 1925, 148, 41—61).—Resting muscle of warm-blooded animals absorbs small amounts of dextrose from the blood and returns to the circulation small amounts of lactic acid. If the amount of lactic acid in the blood be increased by infusion, absorption of it by the muscle increases. Immediately after stopping infusion, absorption stops, and a period of continuous washing out of lactic acid ensues, during which, however, the arterial content quickly sinks to normal. Since the kidney excretes but little lactic acid, it would appear that not the muscle, but more probably the liver, removes lactic acid from the circulation for use in the re-synthesis of carbohydrates.  
P. W. C.

**Metabolism of Galactose. II. Blood-sugar Curves.** A. W. ROWE and J. CHANDLER (*Endocrinology*, 1924, 8, 803—831).—The threshold tolerance for galactose averages 40 g. in women and 30 g. in men; any increased tolerance observed was not caused by a decreased rate of absorption. Hyperglycaemia and melituria are regarded as independent phenomena.  
CHEMICAL ABSTRACTS.

**Metabolism of Sulphur. IX. Effect of Repeated Administration of Small Amounts of Cystine.** H. B. LEWIS (*J. Biol. Chem.*, 1925, 65, 187—195).—Administration to rabbits of daily doses of 0.5—1 g. of cystine per kg. of body-weight caused an albuminuria, an increase in the urinary excretion of non-protein nitrogen, creatinine, and neutral sulphur, and an increase in the non-protein nitrogen of the blood. The increased urinary neutral sulphur did not represent cystine itself, but probably an intermediate oxidation product of the latter.  
C. R. H.

**Iron in Nutrition. I. Nutritional Anaemia on Whole Milk Diets; Utilisation of Inorganic Iron in Formation of Hæmoglobin.** E. B. HART, H. STEENBOCK, C. A. ELVEHJEM, and J. WADDELL (*J. Biol. Chem.*, 1925, 65, 67—80).—Young rabbits, if placed on a diet of whole cow's milk containing 0.3% of sodium citrate, develop an anaemia which ultimately proves fatal; the development of such an anaemia is not prevented by the addition of ferric oxide to the diet, but is prevented by the addition of cabbage, of ferric oxide together with an iron-free alcoholic extract of cabbage or of maize-meal, or by ferric oxide with iron-free chlorophyll.  
C. R. H.

**Effect of High and Low Protein Content on the Digestibility and Metabolism of Dairy Rations.** A. E. PERKINS and C. F. MONROE (*Ohio Sta. Bull.*, 1924, 376, 85—116).—High-protein rations are associated with increased intake and output of water of cows, and with storage of calcium; cows on low-protein rations excrete more calcium than they consume.  
CHEMICAL ABSTRACTS.



**Distribution of Nitrogen in Urine of Ruminants.** F. ROGOZINSKI and M. STARZEWSKA (*Bull. Inter. Acad. Polonaise, B*, 1924, 77—83).—When rations rich in protein are given to sheep, the increase in the nitrogen content of the urine is chiefly in the carbamide fraction, and to a less extent in the hippuric acid fraction. The excretion of other nitrogenous substances, in particular uric acid and creatinine, is scarcely affected by increase in the protein intake.  
G. W. R.

**Effect of Administration of Sodium Nitrate on the Alkalinity of the Urine of a Ruminant.** M. STARZEWSKA (*Bull. Inter. Acad. Polonaise, B*, 1924, 777—782).—Sodium nitrate added at the rate of 14.7 g. daily to the ration of a sheep results in increased alkalinity of the urine. About 10% of the sodium administered is excreted as nitrate, the other 90% appearing as sodium carbonate.  
G. W. R.

**Is Living Protoplasm Permeable to Ions ?** W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1925, 8, 131—146).—When cells of *Valonia macrophysa* are immersed in sea-water containing hydrogen sulphide, no penetration of the sulphide ion into the cell sap appears to take place. The protoplasm appears to be permeable only to undissociated molecules, and not to ions, since the concentration of sulphur inside the cell corresponds with the concentration of undissociated hydrogen sulphide outside the cell, as determined by the vapour pressure of the hydrogen sulphide above the solution.  
W. O. K.

**Electroendosmosis through Mammalian Serous Membranes. II. Comparison of the Hydrogen-ion Reversal Points with Acetate and with Citrate-Phosphate Buffers.** S. MUDD (*J. Gen. Physiol.*, 1925, 9, 73—79).—The hydrogen-ion reversal points (cf. this vol., i, 468) of human, dog, and cat serous membranes are 0.25 of a  $p_H$  unit higher for fat membranes and nearly 0.5 of a  $p_H$  unit higher for lean membranes when the determinations are made with acetate buffer solutions than when made with citrate-phosphate buffer solutions. The reversal points are characteristic for membranes and for species.  
H. J. C.

**Relation between the Chemical Structure of Bile Acids and their Effects on Animal and Plant Tissues.** D. I. MACHT, A. GROLLMAN, and O. R. HYNDMAN (*Amer. J. Physiol.*, 1924, 68, 141—142).—The depressant action of the bile acids for animal and plant protoplasm is attributed to the cholic acid component of the molecules.  
A. A. E.

**Effect of Excess of Calcium on the Skeleton.** V. KORENCHESKI (*Brit. Med. J.*, 1923, 1, 802—804).—Excess of calcium in a diet otherwise normal and containing 8% of butter and 2% of cod-liver oil increased the calcification of the skeleton scarcely at all. With incomplete exhaustion of vitamin-A in rats, a diet containing

excess of calcium slightly increases the calcium content of the skeleton.

CHEMICAL ABSTRACTS.

**Effect of Ultra-violet Light on Protein Metabolism.** S. YOSHINE (*Strahlenther.*, 1924, 18, 201—211; from *Chem. Zentr.*, 1925, ii, 63—64).—The positive nitrogen balance of irradiated dogs showed a slight rise when the exposure was short, changing to a negative balance on longer exposure. With increase in the positive balance, the excretion of amino-acids in the urine diminished somewhat. Longer periods of irradiation led to disturbance in the assimilation of nitrogenous substances in the intestine and to refusal of food. A. C.

**Effect of X-Rays on Cholesterol Content, Hydrogen-ion Concentration, Freezing-point Depression, and Surface Tension of Blood.** F. KONRICH and E. SCHELLER (*Strahlenther.*, 1924, 18, 263; from *Chem. Zentr.*, 1925, i, 2704).—The cholesterol content and the hydrogen-ion concentration of pathological human blood are not affected by X-radiation, the surface tension of the blood is practically unaltered, but the freezing-point depression of the serum is increased. X-Radiation of animals lowers the hydrogen-ion concentration and the surface tension, but has no effect on the cholesterol content of the blood. G. W. R.

**Perfuming and Flavouring Substances in Foods and Condiments. I. Effect of Ethyl Acetate and other Substances on the Nitrogen Excretion of Normal Dogs and those with Greatly Reduced Thyroid Glands.** A. G. BYLSMA (*Ber. staatl. Gesundheitspflege*, 1924, 696—746; from *Chem. Zentr.*, 1925, ii, 65).—Male and female animals with reduced thyroid glands under the influence of ethyl acetate showed an increased secretion of nitrogen in the urine; normal males also for the most part, but females showed a decrease. Amyl acetate and oil of cinnamon raise the nitrogen excretion of males. Coumarin has no distinct action. A. C.

**"Dulcitol" as Artificial Sugar Substitute from the Hygienic Point of View.** W. UGLOW (*Archiv Hyg.*, 1925, 95, 89—100; from *Chem. Zentr.*, 1925, ii, 99).—As opposed to saccharin, "dulcitol" is not bactericidal. A 0.02% solution destroys small crustaceans and with 0.007% their propagation is arrested. It inhibits the action of enzymes—pepsin weakly, pancreatic lipase and diastase strongly. It is destroyed by weak alkalis (0.5—1.0%) and acids (N/8—N/4-sulphuric or phosphoric) with formation of products which convert oxyhæmoglobin into methæmoglobin. It has been shown by means of colour reactions (red oxyazo, blue indophenol colours) that aminophenols are produced by the action of acids and alkalis on dulcitol, and to these the poisonous action of dulcitol on the blood is due. Aminophenols appear in the urine when dulcitol is introduced *per os*. Sickness, accompanied by methæmoglobin in the blood, occurs when experimental animals are given 0.1 g./kg. daily. Accordingly, dulcitol should be prohibited as injurious to health. A. C.

**Effect of Yellow Phosphorus (on Rats) with Varying Mineral Nutrition.** H. BERNHARDT and C. H. R. RABL (*Klin. Woch.*, 1925, 4, 758; from *Chem. Zentr.*, 1925, i, 2706—2707).—Administration of yellow phosphorus to white rats in sub-lethal doses results in rachitic changes in the bones, which are more marked in the case of rats receiving a diet low in calcium and phosphorus, when the ash content of the bones is decreased, the blood remaining normal. With rats normally fed, yellow phosphorus causes typical phosphorus sclerosis with increased ash content. Where an acid ration is given (addition of ammonium chloride), severe rachitic modifications are observed both with and without yellow phosphorus, the ash content of the bones decreasing most in rats which do not receive yellow phosphorus. Rats receiving acid rations show severe derangement of the tubular apparatus of the kidneys.

G. W. R.

**Lipin and Fat Metabolism of the Liver Cells of Fasting Animals and Animals Poisoned with Phosphorus. III. Course of the Fat-infiltration into Surviving Liver Tissue in Vitro.** I. SACCHETTO (*Arch. Sci. med.*, 1923, 46, 74—96; from *Chem. Zentr.*, 1925, ii, 63).—From experiments on surviving livers (dog), there is found to be a gradual increase in the lipins of fasting animals; those poisoned by phosphorus showed an accumulation of neutral fat in the peripheral zones and also an increase in the lipins before the setting in of autolysis. A. C.

**Toxicology of Hydrogen Sulphide.** H. W. HAGGARD (*J. Ind. Hyg.*, 1925, 7, 113—121).—Hydrogen sulphide, which is nearly as toxic as cyanogen or hydrogen cyanide, is a non-cumulative poison. It is rapidly oxidised in the blood to non-toxic products. It does not combine with or alter the hæmoglobin of the blood until the blood is completely reduced. Death may occur on inhalation of 0.09% hydrogen sulphide for less than 1 hr.; death occurs instantly on inhalation of 0.18% hydrogen sulphide.

CHEMICAL ABSTRACTS.

**Intravenous Silver Therapy. III. Solubility of Silver Salts in Blood.** K. VON NEERGAARD (*Arch. exp. Path. Pharm.*, 1925, 108, 295—312; cf. this vol., i, 1212).—The maximum possible concentration of silver ions in an organic fluid (e.g., blood, serum) is determined, as in inorganic solutions, by the concentration of chlorine ions, and the solubility product for silver chloride. On addition of dissociated silver salts to blood, the concentration of silver ions rises much more slowly than in an equivalent solution of electrolytes only, most of the silver forming a complex with the serum-albumins. The evidence indicates that this is an adsorption complex, following the usual logarithmic adsorption law. These investigations were made with the silver electrode described in A., 1924, ii, 124.

H. P. M.

**Enzyme Dialysis.** O. WALTER (*Bull. Acad. Sci. St. Pétersbourg*, 1917, [6], 1075—1088; from *Chem. Zentr.*, 1925, ii, 44).—Collodion bags of any desired degree of permeability and diminished pressure

in the outer solution are utilised. Using tryptase from yeast, a slight lowering of the activity of the solution (which might be caused by adsorption) was found after dialysis. The whole of the nitrogen capable of reacting with formaldehyde and 98.5% of the total nitrogen was removed. A. C.

**Temperature Coefficients of Enzymic Activity and Heat Destruction of Pancreatic and Malt Amylases.** D. H. COOK (*J. Biol. Chem.*, 1925, 65, 135—146).—At temperatures below that at which the rate of destruction of the enzyme becomes significant the rate of hydrolysis of starch by pancreatic or malt amylase is approximately doubled for every 10° rise in temperature. Pancreatic amylase is completely inactivated by heating for 15 mins. at 50°, whilst malt amylase retains a small amount of activity after 30 mins. at 60°. It is suggested that the inactivation of the enzyme by heat may consist in the coagulation of a protein accompanied by a hydrolysis. C. R. H.

**Malt Amylase. I. Determination of the Dextrin-forming and Saccharifying Action of Amylase. II. Influence of Different Experimental Conditions on the Action of Amylase. III. Influence of Adsorbents on the Dextrin-forming and Saccharifying Action of Amylase. IV. Influence of Caffeine and Aldehydes on the Dextrin-forming and Saccharifying Action of Amylase.** T. SABALITSCHKA and C. SCHULTZE (*Fermentforsch.*, 1925, 8, 428—473).—I. An improved colorimetric method of determining dextrin, comparing the colour produced with iodine with that of a series of 18 standard colours, is used. Maltose is determined by an extension of Willstätter and Schudel's hypiodide method for dextrose (*Ber.*, 1918, 51, 780).

II. Neither filtration nor 24 hrs' keeping has any effect on the activity of amylase solutions.

III. Dextrin and maltose formation from starch are considered not to be brought about by two separate constituents of malt amylase, since these functions are affected equally by partial adsorption of the enzyme by different adsorbents. When amylase is completely removed from solution by adsorption, the dextro-rotation of the solution remains unchanged. Amylase is therefore optically inactive.

IV. Caffeine in concentrations up to 0.3%, and sulphonal up to 0.06% have no action on amylase. Formaldehyde activates slightly up to 0.02%, inhibits above 0.06%. Acetaldehyde and propaldehyde inhibit above 0.06%. No differential action with regard to dextrin and maltose formation was observed. E. C. S.

**Decomposition of Arginine in *Lupinus luteus* by means of Enzymes.** O. WALTER (*Bull. Acad. Sci. St. Pétersbourg*, 1917, [6], 1071—1074; from *Chem. Zentr.*, 1925, ii, 44).—In an attempt to determine the arginine in *Lupinus luteus* by the Schultz method (A., 1899, i, 107) the author omitted to dry the material before preparing the aqueous extract. No arginine was found, since the amount of time taken in preparing the extract was sufficient for the enzyme to decompose the whole of the arginine. A. C.

**Invertase. X.** R. WILLSTÄTTER, K. SCHNEIDER, and E. BAMANN (*Z. physiol. Chem.*, 1925, **147**, 248—274).—Special fermentation methods previously described (see this vol., i, 1214) have been used to prepare a yeast of high invertase content, from which by fractional autolysis, followed by dialysis, an invertase preparation of very high activity has been obtained, associated with far smaller quantities of accompanying substance—yeast gum or peptide—than in any previous preparation. The invertase is further purified by a single adsorption on kaolin, yielding a product of high activity which is more stable than the previous very active preparations. Repeating the adsorption does not increase the purity of the product.  
H. D. K.

**Enzymic Hydrolysis of Glucosides.  $\beta$ -Glucosidase of Emulsin.** K. JOSEPHSON (*Z. physiol. Chem.*, 1925, **147**, 1—154).—The kinetics of the hydrolysis of the four  $\beta$ -glucosides, salicin, helicin,  $\beta$ -methylglucoside, and arbutin, by active specimens of emulsin prepared from almonds have been investigated. The dependence of the rate of hydrolysis on the acidity of the reaction medium is partly explained by the varying stability of the enzyme, and partly by the different rates of mutarotation of  $\alpha$ - and  $\beta$ -glucose at different hydrogen-ion concentrations (since  $\alpha$ - and  $\beta$ -glucose do not retard hydrolysis to the same extent). A method has been worked out for the evaluation of the enzymic activity of an emulsin preparation. The activity- $p_H$  curves for the hydrolysis of the four glucosides show fairly sharp maxima between  $p_H$  4 and 5. For arbutin the optimum  $p_H$  is about 4.1, for the other three glucosides, about 4.4. By calculation from the effect on the rate of hydrolysis of increasing concentration of the substrate, a value for the apparent dissociation or affinity constant of the enzyme-substrate complex has been derived. In one case, that of the salicin-emulsin complex, the effect of the acidity of the medium on the value of this constant has been followed. These results permit of the theoretical derivation of the activity- $p_H$  curve.

Not only  $\alpha$ - and  $\beta$ -glucose, but also the two similar metamerides of xylose inhibit the hydrolysis, each to a different extent. Galactose and arabinose are also inhibitory, but not so powerfully as dextrose or xylose, whilst lævulose and disaccharides do not retard the hydrolysis at all. The inhibitory effect of alcohols seems to be compounded of two actions, one depending on the affinity of enzyme for alcohol, and the other on a retardation in the rate at which the enzyme-substrate complex decomposes. The dissociation constant of the enzyme-alcohol complex is calculated from considerations of these inhibitory effects.

Salicin and arbutin are probably hydrolysed by the same enzyme.

In the hydrolysis of glucosides by enzymes both components of the glucoside play a part in the formation of the enzyme-substrate complex. The question of the method of combination of enzyme with substrate, and that of the specificity of enzymes which hydrolyse certain di- and poly-saccharides, receive detailed discussion.

H. D. K.

3 b 2

**Enzymic Synthesis of Glucosides.**  $\beta$ -Glucosidase of Emulsin. K. JOSEPHSON (*Z. physiol. Chem.*, 1925, **147**, 155—183).—The  $p_H$  of methyl alcohol–water mixtures up to a concentration of 40% of alcohol may be determined by the usual electrometric methods. The rate of synthesis is proportional to the amount of enzyme present. The activity– $p_H$  curve of the synthesis of  $\beta$ -methyl-glucoside corresponds with the hydrolysis curve almost exactly.

The effect of dextrose concentration on the rate of synthesis of  $\beta$ -methyl- and  $\beta$ -ethyl-glucoside again permits the calculation of the affinity constant of the sugar–enzyme complex. The constant is independent of the concentration and nature of the alcohol, and its value is very nearly equal to that determined by the methods described in the preceding abstract. The inhibitory effect of methyl alcohol on rate of synthesis is of the same order as the effect on hydrolysis.

In the case of  $\beta$ -phenylglucoside, the point of equilibrium under the action of emulsin is very near complete hydrolysis.

H. D. K.

**Laccase. V. Action of Hydrocyanic Acid.** P. FLEURY (*Bull. Soc. Chim. biol.*, 1925, **7**, 797—805).—Hydrocyanic acid, under appropriate conditions, retards the oxidation of guaiacol by laccase in concentrations of 0.5 mg. per litre. With increasing concentrations the effect increases logarithmically. The toxic effect varies with the  $p_H$  of the medium. In these respects, the action of hydrocyanic acid is similar to that of sodium chloride (this vol., i., 614). The retarding action of hydrocyanic acid, however, is most marked at the optimum  $p_H$  for laccase, falling off as the reaction becomes either more acid or more alkaline. This behaviour is explained on the assumption that the hydrocyanic acid affects both the power of combination of the enzyme and the speed of the oxidative process, the action on the former being greatest on the acid side and on the latter on the alkaline side. The activity of the laccase is restored by removal of the hydrocyanic acid by aëration.

H. P. M.

**Enzyme Action. XXXIII. Lipase Actions of Extracts of the Whole Rat at Different Ages.** K. G. FALK, H. M. NOYES, and K. SUGIURA (*J. Gen. Physiol.*, 1925, **8**, 75—88; cf. A., 1924, i., 696; this vol., i., 471; *J. Cancer Res.*, 1925, **9**, 105—129).—Various esters have been subjected to the action of extracts made of whole rats of various ages. It is found that whereas the esterase activity of an extract made from very young rats resembles that made from the Flexner–Jobling rat carcinoma or from several tumours of human origin, that made from adult rats is different, but the extracts made from the oldest rats again tend to revert to the embryonic type. Similar differences in action were not shown by protease preparations in their actions on several different proteins.

W. O. K.

**Tryptic and Ereptic Activity of the Pancreas.** E. WALDSCHMIDT-LEITZ and A. HARTENECK (*Z. physiol. Chem.*, 1925, **147**, 286—308).—Two proteolytic enzymes of the pancreas (extract of

the dried gland) have been separated from one another by the adsorption methods of Willstätter and Waldschmidt-Leitz. Trypsin is more basic than the pancreatic erepsin and is preferentially adsorbed by kaolin. Gelatin is used as substrate for the tryptic enzyme, leucylglycine for the ereptic component. The two enzymes seem to be definite distinguishable individuals, and not merely forms of the same enzymic substance reacting differently at different degrees of dispersion. The ereptic protease from the pancreas and the erepsin of the intestinal juice appear to be identical. Trypsin is more stable than pancreatic erepsin. H. D. K.

**Inactivation of Trypsin by X-Rays.** H. CLARK and J. H. NORTHROP (*J. Gen. Physiol.*, 1925, 9, 87—96).—The inactivation of trypsin solutions by X-rays increases with dilution and the reaction appears to be unimolecular. The inactivation is confined almost entirely to the free trypsin and seems to result from the electrical neutralisation of the trypsin ion. H. J. C.

**Peptidase Balance of Man and Animals.** I. H. PFEIFFER and F. STANDENATH (*Fermentforsch.*, 1925, 8, 327—358).—The peptidase content of serum and urine is measured by the rate of hydrolysis of glycytryptophan. For any species the peptolytic index of the serum is constant within narrow limits. Only in human urine does peptidase occur to any appreciable extent. The peptolytic index of urine varies with age, being marked in the first weeks after birth, and again between 20 and 30 years. Daily variations are correlated with digestive activity. Morning urine has the highest index. Individual variations are due to varying permeability of the rectum, which is the principal source of the enzyme, a further source being destroyed cells of the body. E. C. S.

**Formation of Pigments. III. Fermentative Micro-detection of 1- $\alpha$ -Amino-3:4-dihydroxyphenylpropionic Acid in the Presence of Tyrosine. Connexion between Constitution and Chromogenic Properties.** H. SCHMALFUSS and H. WERNER (*Fermentforsch.*, 1925, 8, 423—427; cf. A., 1924, i, 1263).—Pigment formation in the presence of hæmolymph of the meal worm, *Tenebrio molitor*, F., takes place much more rapidly with 1- $\alpha$ -amino-3:4-dihydroxyphenylpropionic acid than with tyrosine. This enables 0.007 mg. of the former to be detected in the presence of 0.5 c.c. of saturated tyrosine solution. E. C. S.

**Chemical Mechanism of the Principal Fermentations of Dextrose.** M. LEMOIGNE (*Bull. Soc. chim.*, 1925, [iv], 37, 1089—1106).

**Co-zymase. VII.** H. VON EULER and R. NILSSON (*Z. physiol. Chem.*, 1925, 148, 23—40).—When dextrose is fermented by means of dried yeast in phosphate solution of  $p_H$  6.0—6.5, the velocity is constant for the first third of the reaction, but then falls away considerably, due to the union of co-enzyme probably with the protoplasmic part of the yeast. Co-zymase is extracted only to a slight extent by washing from dried top yeast, but almost completely

from dried bottom yeast, and similar differences hold in respect to the phosphates. This confirms the experience of Euler and Myrbäck (A., 1924, i, 248, 693, 918). Co-zymase is extracted, however, on boiling. The decarboxylation of pyruvic acid by dried bottom yeast *H* is investigated. P. W. C.

**Effect of Growth of Yeast on Galactose on the Fermentability of the Latter by the Former. II.** E. ABDERHALDEN (*Fermentforsch.*, 1925, 8, 474—478; cf. A., 1924, i, 1265).—The power of yeast to decompose galactose, once acquired, remains unaltered for a considerable time. It is unaffected by drying and passage through solutions of other carbohydrates, but may be diminished by secondary causes such as infection. E. C. S.

**Effect of Hydrogen Peroxide on certain Groups of Bacteria. Microbic Catalases. Autolytic Phenomena.** G. PETROVANU (*Compt. rend. Soc. Biol.*, 1925, 92, 459—460; from *Chem. Zentr.*, 1925, i, 2700).—Bouillon cultures of a large number of bacteria decompose hydrogen peroxide. Their behaviour in respect of clearing of the cultures (lysis) is different. *Cholera vibrio*, the microbes of typhoid, paratyphoid, and dysentery, *Bacillus coli*, *B. anthracis*, Metschnikoff vibrio, *B. prodigiosus*, and two different saprophytic organisms, all showed complete lysis with hydrogen peroxide. Staphylococci, *B. pyocyaneus*, *B. proteus* X<sub>19</sub>, diphtheria bacilli, and streptococci suffered partial lysis, whilst the bacilli of whooping cough and a saprophytic coccus showed no lysis. The cleared cultures can induce lysis in new cultures, and are remarkably specific. Heating at 60° destroys the ability to react with hydrogen peroxide. The catalase in living bacteria appears to be connected with the phenomenon of lysis. G. W. R.

**Production of Peroxide by Anaërobes in Presence of Oxygen.** J. W. McLEOD and J. GORDON (*J. Path. Bact.*, 1925, 28, 147—153).—Further indirect evidence is adduced to show that hydrogen peroxide is formed in anaërobic cultures. Catalase cannot promote the growth of anaërobes in direct contact with air, but it raises the level of growth in a deep agar tube almost to the surface. CHEMICAL ABSTRACTS.

**Relations between the Reducing Powers of Bacteria and their Capacity for forming Peroxide.** J. W. McLEOD and J. GORDON (*J. Path. Bact.*, 1925, 28, 155—164).—The formation of hydrogen peroxide is a necessary consequence of bringing a reducing mechanism, e.g., by bacteria which produce nascent hydrogen and are free from catalase, into contact with oxygen. A parallelism exists between the reduction of glutathione, the solution of cystine, and the production of hydrogen peroxide by bacteria. CHEMICAL ABSTRACTS.

**Decomposition of Carnosine by Intestinal Bacteria, and its Relation to Autointoxication.** J. HEFTER (*Z. physiol. Chem.*, 1925, 145, 276—289).—*Bacillus pyocyaneus* was the only micro-organism investigated which was found to attack carnosine with



the formation of harmless fatty acids (acetic, butyric, etc.) and ammonia. No histamine could be detected. H. P. M.

**Decomposition of Cholic Acid by *Bacillus coli*.** K. KAZIRO (*Z. physiol. Chem.*, 1925, **145**, 227—237).—*Bacillus coli* was grown in a medium containing cholic acid. After 60 days' incubation at 37°, the mixture was made just acid to Congo-red and filtered. The ethyl acetate extract of the concentrated filtrate yielded an optically active substance, probable formula  $C_{17}H_{28}O_3$ , m. p. 183—184°,  $[\alpha]_D^{30} + 40.09^\circ$ , mol. wt. 270. It is insoluble in alkali, forms with digitonin an additive compound soluble in chloroform, insoluble in alcohol, and gives with sulphuric acid and acetic anhydride a brown colour. Chromic anhydride in glacial acetic acid removes six hydrogen atoms, to form a crystalline substance of m. p. 150—151°. H. P. M.

**Rôle of Hydrogen-ion Concentration on the Development of Pigment in *Fusaria*.** C. P. SIDERIS (*J. Agric. Res.*, 1925, **30**, 1011—1019).—Development of pigment by *Fusaria* is mainly controlled by the hydrogen-ion concentration of the media. Practically all the species examined developed pigment in dextrose solutions maintained at constant hydrogen-ion concentrations between  $p_H$  3.5 and 5.5. When the  $p_H$  was allowed to vary under the influence of the organism, pigment was produced at  $p_H$  values ranging from 3.0 to 7.5. The pigment developed may be retained within the cell or it may escape through the plasmatic membrane and cell-wall. Localisation of reaction may occur, since hydrogen and hydroxyl ions produced in the metabolism of the organism move very slowly in solid media. O. O.

**Accumulation of Dye in *Nitella*.** M. IRWIN (*J. Gen. Physiol.*, 1925, **8**, 147—182; cf. *ibid.*, 1922—1923, **5**, 427).—When living cells of *Nitella* are placed in solutions of brilliant-cresyl-blue of varying concentrations but at a constant  $p_H$ , the rate of accumulation of dye in the cell sap and also the concentration in it at equilibrium increases with increase in the concentration of dye in the external solution. The results are in harmony with the view that accumulation in the cell sap takes place as a result of the combination of the dye with some constituent of the sap. W. O. K.

**Choline as the Hormone of Peristalsis. VIII. Does Intestinal Choline Originate from the Suprarenal Bodies? IX. Inability of Isolated Intestinal Wall to Produce Choline.** O. GIBNDT (*Pflüger's Archiv*, 1925, **207**, 464—468, 469—475; from *Chem. Zentr.*, 1925, i, 2703; cf. *Pflüger's Archiv*, 1923, **195**, 390).—The choline content of the duodenum is not decreased by extirpation of both suprarenal bodies.

After reduction of the choline content by prolonged washing with Tyrode solution, no determinable replacement in the isolated intestinal wall is observed. Choline does not result from the degeneration of the intestinal mucosa. G. W. R.

**Insulin and Cholesterol Metabolism.** I. I. NITZESCU and I. CADARIU (*Compt. rend. Soc. Biol.*, 1925, **92**, 296—298; from *Chem. Zentr.*, 1925, ii, 52).—The power possessed by the lungs and liver to retain and destroy cholesterol is almost or entirely lost on depancreatisation, but is restored under the influence of insulin.  
A. C.

**Lactic Acid Metabolism in Diabetes and the Effect of Insulin.** J. A. COLLAZO and I. LEWICKI (*Deut. med. Woch.*, 1925, **51**, 600—603; from *Chem. Zentr.*, 1925, i, 2708).—The average content of lactic acid (in the blood) in both fasting diabetic and normal persons is 14.2—15.9 mg.%. The increase in lactic acid content after oral administration of sucrose is greater, sets in earlier, and persists longer in diabetic than in normal individuals. Administration of sugar together with injection of insulin causes in both cases hyperlactacidæmia. Insulin alone administered to fasting men generally causes hypolactacidæmia.  
G. W. R.

**Action of Pancreatic Extract of *Acanthias vulgaris* (Dog-fish) Compared with that of Beef Insulin.** E. DUCLOUX and G. CORDIER (*Compt. rend.*, 1925, **181**, 342—344).—The pancreatic extract of dog-fish lowers the blood-sugar concentration of guinea-pigs and rabbits when injected, the hypoglycæmia being more marked when injections are made directly into the blood-stream. No relation was detected between the amount of extract injected and the fall in blood-sugar concentration, nor any relation between the latter and the weight of the animal.  
L. F. H.

**Active Extract from External Parathyroid Glands of the Ox.** A. M. HJORT, S. C. ROBISON, and F. H. TENDICK (*J. Biol. Chem.*, 1925, **65**, 117—128).—Comparison of the effects of parenteral injection into dogs of extracts of the parathyroid glands of the ox made in various ways showed that those preparations obtained by extracting with aqueous or alcoholic hydrochloric acid, particularly boiling hydrochloric acid, had the power of raising the concentration of calcium in the serum of normal and parathyroidectomised animals. Active extracts were obtained from glands previously freed of their lipid constituents, and proteins could be removed from the extracts by precipitation at the isoelectric point and addition of alcohol to 80% concentration without appreciable loss of activity. Preparations in 0.1*N*-hydrochloric acid retained their activity on keeping for 16 months in the ice-chest (cf. Collip, this vol., i, 754).  
C. R. H.

**Internal Secretion of the Parathyroid Glands.** J. B. COLLIP (*Proc. Nat. Acad. Sci.*, 1925, **11**, 484—485).—A note on work previously reported (cf. this vol., i, 754).  
H. J. C.

**Physiological Determination of Vitamin-A.** M. JAVILLIER, P. BAUDE, and S. LÉVY-LAJEUNESSE (*Bull. Soc. Chim. biol.*, 1925, **7**, 831—841).—White rats about 7 weeks old, and 35—55 g. in weight, are fed on a basal diet consisting of 55 g. of potato starch, 15 g. of heated arachis oil, 15 g. of washed caseinogen, 4 g. of Bertrand-Benyon salt mixture, 7 g. of cellulose, and 4 g. of dried brewer's

yeast. The rats continue to grow until their reserves of vitamin-A are exhausted (after about 22 days), when rapid loss of weight ensues. When the rats have lost 10% of their weight (in another 5–6 days), the diet is supplemented by graded doses of the substance to be tested for vitamin-A. A certain "maintenance" dose can be found, which will just maintain the body-weight constant, without causing growth. As the physiological unit of vitamin-A, is suggested the amount, over and above the "maintenance" dose, required to produce a 30% increase in weight in 30 days.

H. P. M.

**Physical and Chemical Properties of Biosterin (Vitamin-A) and its Physiological Significance.** K. TAKAHASHI, Z. MAKAMIYA, K. KAWAKAMI, and T. KITASATO (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1925, **3**, 81–146).—Further purification of the product separated from cod-liver oil (cf. A., 1923, i, 968) has been achieved by (a) extracting the light petroleum solution with methyl alcohol, (b) crystallisation from acetone at  $-65^{\circ}$ , and (c) fractional distillation in a vacuum. The final purified product was a reddish-yellow, viscous oil,  $d_{25}^{20}$  0.9561;  $n_D^{20}$  1.52517; optically inactive; b. p.  $147^{\circ}/0.2$  mm.; mol. wt. 375 approx.; iodine value 178; acetyl value 137; suggested formula  $C_{27}H_{42}(OH)_2$ . It forms a *mono-benzoate* (m. p.  $125^{\circ}$ ) and *monophthalate* (m. p.  $90^{\circ}$ ) and takes up 3 mols. of bromine. It is soluble in alcohol, ether, chloroform, light petroleum; insoluble in water. Rats were maintained in health for several weeks by administration of 0.001 mg. daily as sole source of vitamin-A. The substance exhibited toxic properties when given in amounts greater than 10 mg. daily.

P. E.

**Effect of Bacterial Flora on Biological Test for Vitamin-B.** V. G. J. HELLER, C. H. MCELROY, and B. GARLOCK (*J. Biol. Chem.*, 1925, **65**, 255–264).—Experimental animals on a diet free from vitamin-B live longer if they have access to their faeces than if the latter are removed; bacterial examinations of the faeces of the two groups of animals support the view suggested by this observation, that the spore-bearing organisms of the intestinal tract synthesise and store vitamin-B, hence serving as a source of the latter to those animals which can eat their own excrement.

C. R. H.

**Scurvy and the Antiscorbutic Value of Orange and Lemon Juices.** D. LIOTTA (*Arch. Farm. speriment. Sci. aff.*, 1925, **39**, 202–224).—A summary is given of our knowledge of scurvy and the antiscorbutic vitamin, and experiments are described which show that orange or lemon juice containing 0.5% of chlorine may be kept under ordinary conditions without undergoing either attack by mould or fermentation. Daily doses of 5–6 c.c. of this juice, administered to guinea-pigs under ordinary diet, produce no poisonous effects. Such doses delay, but do not prevent, the death of the animals fed on a scorbutic diet; similar behaviour is shown by lemon juice concentrated in a vacuum at a low temperature, either with or without previous treatment with chlorine.

T. H. P.

**Experimental Rickets. XXVI. Diet of Purified Food-stuffs for Use in Vitamin-D Studies.** E. V. MCCOLLUM, N. SIMMONDS, J. E. BECKER, and P. G. SHIPLEY (*J. Biol. Chem.*, 1925, **65**, 97—100).—Modified rickets-producing diets are described which, being composed for the most part of purified substances, are free from the variability of action of the diet previously recommended (A., 1921, i, 757) for this purpose. C. R. H.

**Rôle of Different Nitrogenous Compounds as Sources of Nitrogen for Higher Plants in Pure Cultures.** V. BIALOSUKNIA (*Bull. Inter. Acad. Polonaise*, B, 1924, 715—727).—Experiments on the availability of the nitrogen of different compounds for the nutrition of mustard and cabbage seedlings in sterile water cultures show that, in addition to nitrates, the following compounds are also able to serve as sources of nitrogen: ammonium salts, in the presence of calcium carbonate, nitrites, and asparagine. Carbamide, glycine, and lecithin serve as sources of nitrogen only in the presence of sugars. Peptone, gelatin, egg-yolk, and amino-acids, except glycine, give no growth. G. W. R.

**Cyanamide, its Derivatives, and Hexamethylenetetramine as Sources of Nitrogen for Wheat, Cabbage, and White Mustard in Pure Cultures.** V. BIALOSUKNIA (*Bull. Inter. Acad. Polonaise*, B, 1924, 729—737).—Calcium cyanamide acts as a poison to plants in sterile water cultures owing to the liberation of free ammonia, acetylene, and hydrogen sulphide (from impurities). Dicyanodiamide, though not poisonous, cannot serve as a source of nitrogen except in the presence of sugar (dextrose). Preliminary unsuccessful experiments using hexamethylenetetramine as a source of nitrogen are recorded. G. W. R.

**Sodium Nitrate in the Nutrition of the Tomato.** P. WORK (*Cornell Agric. Exp. Sta. Memoir*, 1924, **75**, 86 pp.).—The optimal application of sodium nitrate for increase of vegetation and fruit is 32 g. per 35.5 cm. cubical box, a small quantity in small doses being preferable to a single application. It is supposed that the injurious effect of excess of sodium nitrate is due to a reduction in the availability of water in the environment rather than to internal poisoning. Green leaves of tomato plants contain 0.173—0.390% of nitrogen, a value above 0.30% being essential for vigorous vegetation and fruiting. Stems contain up to 0.206% of nitrogen, at least 0.120% in vigorous plants. There is no relation between the amount of nitrate applied to the soil and the concentration of total carbohydrates in the plants. Green leaves contain 0.92—5.97% of carbohydrate and stems 1.42—8.21%, the high values referring to nitrogen-starved plants. The carbohydrate in vigorous plants ranged from 0.92% to 3.66% in leaves and 1.42% to 3.30% in stems.

CHEMICAL ABSTRACTS.

**Comparative Growth of Pineapple Plants with Ammonium and Nitrate Nitrogen.** G. R. STEWART, E. C. THOMAS, and J. HORNER (*Soil Sci.*, 1925, **20**, 227—241).—In water culture, the pineapple can assimilate all its nitrogen in the form of ammonium

salts, but the best growth is obtained in normal culture solution containing nitrates. Probably, under field conditions, nitrogen is taken up in both forms. The cultures containing ammonium salts changed rapidly towards a more acid reaction during the growth of the plants.

C. T. G.

**Determination of Nitrate Nitrogen in Plants.** R. C. BURRELL and T. G. PHILLIPS (*J. Biol. Chem.*, 1925, **65**, 229—234).—Determination of nitrate nitrogen by reduction with Devarda's alloy is not applicable to plant extracts owing to the presence of amide nitrogen, which causes low results. The determination is best carried out by the colorimetric method of Chamot and others (A., 1911, ii, 331), an 80% alcoholic extract of the plant being first freed from coloured impurities and chlorides by successive treatment with lead acetate, silver sulphate, and a mixture of copper sulphate and calcium hydroxide.

C. R. H.

**Growth of Potato Plants in Sand Cultures treated with the "Six Types" of Nutrient Solutions.** E. S. JOHNSON (*Maryland Agric. Exp. Sta. Bull.*, 1924, **270**, 54—86).—There is a direct relationship between growth and the presence of nitrogen in the nutrient solutions. Potassium or calcium nitrate is preferable to magnesium nitrate; magnesium in high concentration is toxic. The most favourable solutions contained the following atomic proportions: N, 4—6; P, 2—4; K, 2—4; S, 1—2; Ca, 3—1; Mg, 2—1.

CHEMICAL ABSTRACTS.

**Rôle of Carbohydrates and Nitrogen in the Growth of Summer Shoots of the Apple.** E. M. HARVEY (*Oregon Agric. Exp. Sta. Bull.*, 1923, **200**, 51 pp.).—Moisture, soluble solids, phloridzin, and nitrogen, which decrease through the growing season, are most abundant in the shoot tips and least in the base; the reverse is the case for insoluble solids, sugars, polysaccharides, and total carbohydrates. In the upper part of the shoot, defoliation is accompanied by increase of the former group, but decrease of the latter and the carbohydrate-nitrogen ratio, and ringing by the reverse type of change.

CHEMICAL ABSTRACTS.

**Changes Produced in Apple Trees by Various Types of Pruning.** H. D. HOOKER (*Missouri Agric. Exp. Sta. Research Bull.*, 1924, **72**).—With late pruning nitrogen was translocated in the spring from the older wood to the tips of the shoots. Sodium nitrate, applied in the spring, increased the nitrogen content of the tips and decreased it in the middle of the one-year-old wood. Heading increased carbohydrate consumption and thinning conserved the nitrogen and carbohydrate supplies in the tree.

CHEMICAL ABSTRACTS.

**Selective Absorption of Ions by Seeds.** W. RUDOLFS (*Soil Sci.*, 1925, **20**, 249—252).—When maize or soya-bean seeds are immersed in dilute solutions of aluminium sulphate or nitrate, there is a rapid lowering of the  $p_H$  value of the solution, followed by a slower rate of change to higher values, until an equilibrium is reached. The changes noted are less marked with maize than with soya-bean,

and, in both cases, are greater in degree in the nitrate than in the sulphate solution. The differential absorption of ions is greatly affected by the character and amount of the proteins present in the seed.

C. T. G.

**Effect of Seeds on Hydrogen-ion Concentration Equilibrium in Solution.** W. RUDOLFS (*J. Agric. Res.*, 1925, **30**, 1021—1026).—Seeds of maize (*Zea mays*), lupin (*Lupinus albus*), beans (*Phaseolus vulgaris*), and soya beans (*Soja maxima*) immersed in solutions of a number of inorganic and organic acids and mineral salts change the reaction of the solution. Providing the immersion is sufficiently prolonged, a definite  $p_H$  value is reached which remains reasonably constant. The rate of attainment of this equilibrium is slightly less for dry seeds than for fresh seeds. The equilibrium  $p_H$  value for any kind of seeds is practically the same for all the solutions in which it is immersed. The approximate values given are: maize, 4.0; beans, 5.7—5.8; except in acetic acid, in which the values are much lower.

O. O.

**Effect of the Plant on the Reaction of the Culture Solution.** D. R. HOAGLAND (*California Agric. Exp. Sta. Tech. Paper*, 1923, **12**).—The absorption of nitrate is favoured when the culture solution has an acid reaction, and an increased absorption of cations when the reaction is alkaline. When grown in solutions of ammonium sulphate, ammonium chloride, potassium sulphate, sodium sulphate, or potassium dihydrogen phosphate, barley, peas, and cucumbers cause an increase of acidity with consequent injury. The relation between ion absorption and hydrogen-ion concentration is briefly discussed.

CHEMICAL ABSTRACTS.

**Effects of Seasonal Conditions on the Chemical Composition of American Grape Juices.** J. S. CALDWELL (*J. Agric. Res.*, 1925, **30**, 1033—1076).—The juices of grapes of sixty-six different varieties grown over a 5-year period have been analysed. Sucrose is of widespread but very irregular occurrence. Although generally associated with immature fruit, it is often found in mature or over-ripe grapes. Its presence cannot be associated with any other factor, such as temperature or water supply. There is a definite correlation between climatic conditions and the total sugar, total astringency, and titratable acidity of the fruit: under the experimental conditions the number of days of sunshine occurring between March 1st and September 30th is proportional to the total sugar content and inversely proportional to the total astringency and titratable acidity.

O. O.

**Relation between the Development, Structure, and Functioning of the Nodules on *Vicia faba* as Influenced by the Presence or Absence of Boron in the Nutrient Medium.** W. E. BRENCHLEY and H. G. THORNTON (*Proc. Roy. Soc.*, 1925, **B**, **98**, 373—399).—The number of nodules reaching macroscopic size is much reduced in plants grown without boron; their vascular supply is defective, the strands being either entirely absent or running only a short way into the nodule; there is reduced develop-

ment of "bacteroid" forms; and the amount of nitrogen fixation is much below normal. In such nodules the bacteria tend to become parasitic, attacking the protoplasm of the host cell.

C. P. S.

**Japanese Plants. III. Chemical Development in the Growth of Bamboo Shoots.** S. KOMATSU and C. TANAKA (*Mem. Coll. Sci. Kyōtō*, 1925, 9[A], 1—14).—Shoots of the bamboo *Phyllostachys quilioli* cut into five parts (numbered from I at the base to V at the top of the shoot) contained more than 90% of water. Of the dried material, the aqueous extract contained about 1% of pentoses; 15.82% (I), 18.35% (II), decreasing to 8.9% (V) of hexoses; and 1.34% (I) to 3.03% (V) of nitrogen. Alcohol extracted from the residue a green fraction containing 3.58% (I) to 5.76% (V) of fatty compounds and small quantities of nitrogen. The remainder contained 29.58% (I) to 8.50% (V) of cellulose, also lignin, pentosan, and 6.06% (I) to 15.56% (V) of protein. The chief constituents of the ash were sodium and potassium oxides (about 55%), and phosphoric and silicic acids. The young active shoots are the richest in protein and phosphorus and contain some iron and manganese which apparently catalyse the growth; the older wood contains more mono- and poly-saccharides and more silica, used for protecting the reserve materials.

B. W. A.

**Glycuronic Acid in Plants.** W. PALLADIN and W. LEWTSCHENKO (*Bull. Acad. Sci. St. Pétersbourg*, 1916, [6], 1267—1276; from *Chem. Zentr.*, 1925, i, 2630).—The ethereal extract of the plant dissolved in aqueous hydrochloric acid gives a bluish-violet coloration with naphthoresorcinol when glycuronic acid is present. The reaction is given by fresh leaves of *Taraxacum officinale*, by the germinating seeds of beans and barley, by the etiolated leaves of the bean plant, and by *Aspergillus niger*. A series of other plants did not give the reaction and many glucosides and enzymes also gave a negative test.

R. B.

**Asperuloside, a Glucoside obtained from Odoriferous Asperula.** H. HÉRISSEY (*Compt. rend.*, 1925, 180, 1695—1697; cf. A., 1920, i, 586).—By alcoholic extraction of odoriferous *Asperula*, 0.05% of a glucoside, *asperuloside*, colourless needles, m. p. 126—127°,  $[\alpha]_D^{20}$  —204.4°, *M*, cryoscopic in water, 410, is obtained. On hydrolysis with acids or emulsin, a dextrorotatory reducing sugar, with reducing power 43—45% of that of dextrose, and a brown precipitate, *asperuligenol*, are obtained. The properties of asperuloside are similar to those of aucubin.

L. F. H.

**Irisin and the Enzymic Hydrolysis of Polyfructosides.** H. VON EULER and H. ERDTMAN (*Z. physiol. Chem.*, 1925, 145, 262—275).—Irisin, prepared from an aqueous extract of iris root by precipitation with alcohol, has mol. wt. 10,300, m. p. 208—210°, and  $[\alpha]_D^{20}$  —52.10°. Acetylation in presence of pyridine gives a *triacetate* of mol. wt. 2220, corresponding with the formula  $7.7 \times$

$C_6H_7O_5(OMe)_3$ , m. p. 206—208°, and  $[\alpha]_D^{20} - 22.70^\circ$ . This in turn gives, on heating with phenylhydrazine, a substance of the approximate formula  $18C_6H_{10}O_5$  (mol. wt. 3200), and  $[\alpha]_D^{20} - 49^\circ$ . Irisin is hydrolysed by dilute acid at about the same rate as sucrose and inulin, but is unattacked by taka-diastrase, which hydrolyses inulin slowly.

H. P. M.

**isoLichenin and the Hydrolysis of Starch.** P. KARRER (*Z. physiol. Chem.*, 1925, **148**, 62—64).—Reply to Pringsheim (this vol., i, 1029); cf. Karrer and Joos (*ibid.*, i, 1028).

P. W. C.

**Nitrogenous Constitution of the Juice of the Alfalfa (Lucerne). IV. Betaine Fraction.** H. B. VICKERY. V. **Basic Lead Acetate Precipitate.** H. B. VICKERY and C. G. VINSON (*J. Biol. Chem.*, 1925, **65**, 81—89, 91—95).—IV. From the betaine fraction of the "alfalfa filtrate" (cf. A., 1924, i, 1393) have been isolated trimethylamine, choline, betaine, and stachydrine in amounts of 0.0069, 0.063, 0.0052, and 0.785% of the dried plant, respectively.

V. "Alfalfa filtrate" was treated with basic lead acetate, and the mixture of substances, recovered in the usual way from the precipitate, was submitted to hydrolysis with sulphuric acid; from the resulting solution were isolated adenine, arginine, lysine, aspartic acid, tyrosine, and stachydrine.

C. R. H.

**Incrustative Substances of Plants. VI.** E. SCHMIDT, W. HAAG, and L. SPERLING (*Ber.*, 1925, **58**, [B], 1394—1403; cf. A., 1922, i, 206).—The action of chlorine dioxide on aromatic compounds containing a free hydroxyl group is restricted and simplified by the presence of vanadium chloride; under these conditions, carbonic, oxalic, and maleic acids are the main products formed from *o*-nitrophenol, pyrocatechol, resorcinol, pyrogallol, phloroglucinol, salicylic acid, *m*-hydroxybenzoic acid, gallic acid, and furfuraldehyde. Cystine is oxidised to cystinic acid.

The successive action of chlorine dioxide and sodium sulphite on the cell membranes of flax and hemp has been investigated, whereby soluble oxidation products and carbohydrate, chiefly galacturonic acid, are formed. The latter cannot be ascribed to the hydrolytic action of the hydrochloric acid produced or to direct oxidation of carbohydrates. A part of the polysaccharides must be assumed to be united chemically to the susceptible components of the cell membrane. This view is confirmed by the observation that the products which are dissolved during the after-treatment with sodium sulphite are convertible by chlorine dioxide into polysaccharides of acidic character. The incrustation must therefore be regarded, not as the non-hydrolysable portion of the cell membrane, but as that portion which is attacked by successive treatment with chlorine dioxide and sodium sulphite.

The polysaccharides united to the susceptible portion of the cell membrane are distinguished from those attached to cellulose



or chitin in the skeleton substance by the lower stability of their union. Instead therefore of regarding the cell membrane as composed of incrustation, hemicelluloses or pentosans, and cellulose or chitin, it is preferable to consider only two components and to regard one part of the hemicellulose ( $H_i$ ) as attached to the susceptible component and a second part ( $H_s$ ) as attached to chitin or cellulose. The hemicelluloses,  $H_i$  and  $H_s$ , both contain carboxyl groups derived from glycuronic and galacturonic acids, respectively. The cell membrane is to be regarded as an ester, the alcohol of which is cellulose or chitin in the skeleton substance and the part susceptible to chlorine dioxide in the incrustation. H. W.

**Aluminium Content of the Soil Solution and its Relation to Soil Reaction and Plant Growth.** O. C. MAGISTAD (*Soil Sci.*, 1925, 20, 181—225).—The solubility curve for aluminium oxide in water at various reactions is almost identical with that obtained when the solvent is the displaced soil solution from soils at various reactions. The solubility is at a minimum at the neutral point. More than 3 parts per million of aluminium oxide can be present in a soil solution only when the  $p_H$  value is less than 4.7 or more than about 8.0. In soil solutions from acid and alkaline soils, the aluminium is in true solution as shown by dialysis experiments. The growth of a number of different plants in sand cultures, supplied with nutrient solutions at various reactions, in presence and absence of aluminium, indicated that toxicity due to aluminium is apparent only above and below a certain range of  $p_H$  which varies with different plants. Whether the beneficial action of lime on acid soils is attributable mainly to a reduction of acidity, or mainly to a reduction of the amount of soluble aluminium, or equally to both these effects, will depend on the original reaction of the soil and on the crop under cultivation. [Cf. *B.*, Nov. 27th.] C. T. G.

**Determination of Nutritive Requirements [of Soil] by Mitscherlich's Method and some Remarks on Neubauer's Method.** DENSCH and PFAFF (*Z. Pflanz. Düng.*, 1925, 4 B, 321—339).—Mitscherlich's method is compared with the method of direct field trials and the limitations of the two methods are discussed. Results are quoted to show that for nitrogen, phosphoric acid, and potash, Mitscherlich's procedure is satisfactory for oats and barley when the straw is neglected. When the straw is considered, the results are not so satisfactory. For crops grown in soils analysed by the Neubauer method, Mitscherlich's method is suitable for potash, but not so useful for phosphoric acid. The effect of low lime-content and excess of iron on the method is discussed. O. O.

**Availability of Organic Nitrogen Compounds in Pot Experiments.** E. M. CROWTHER (*J. Agric. Sci.*, 1925, 15, 300—302).—The nitrogen recovery in two successive crops from a series of nitrogenous substances added to soil is recorded. A. G. P.

**Effect of Straw on Accumulation of Nitrates [in Soil] and Crop Growth.** T. L. MARTIN (*Soil Sci.*, 1925, 20, 159—164).—Addition of finely-cut wheat straw to a loam soil proved, in general, detrimental to nitrification and retarded accumulation of nitrates, the effect increasing with the amount of straw used. Crop yields were correspondingly depressed. After 12 months, however, nitrification was stimulated in the soil with treated straw.

C. T. G.

**Absorption of Phosphate by Pasteur-Chamberland Filters.** F. W. PARKER (*Soil Sci.*, 1925, 20, 149—158).—The phosphorus content of solutions containing not more than 1 part per million of phosphate may be appreciably increased or decreased by filtration through a Pasteur-Chamberland filter which has been used for preparing soil extracts. New filter-candles also contain some soluble phosphorus. Treatment of used filters with strong hydrochloric acid and subsequent ignition did not completely destroy the phosphate-absorbing power. The determinations of phosphate were made by the cœruleo-molybdate method of Denigès (cf. A., 1920, ii, 770), using a somewhat modified procedure. C. T. G.

**Effect of Removing the Soluble Humus from a Soil on its Productiveness.** E. M. CROWTHER (*J. Agric. Sci.*, 1925, 15, 303—306).—A continuation of experiments initiated by Weir (*ibid.*, 1915, 7, 246) is recorded. Removal of soluble humus by extraction of soils with alkali reduced productiveness over a series of crops. The case of initially increased productiveness recorded by Weir was merely temporary.

A. G. P.

**Interaction between Soil and Dilute Acids.** A. N. PURI (*J. Agric. Sci.*, 1925, 15, 334—342).—It is shown that chlorine ions are removed from solutions of hydrochloric acid by soil free from carbonates. Similar effects were noted in the case of sulphuric, nitric, acetic, citric, and phosphoric acids, and the equilibrium between soil and solution could be expressed by Freundlich's equation  $y/m = KC^{1/n}$ . Characteristic values of  $n$  for the different acids were obtained. The various soil fractions exhibited similar equilibrium relationships with the acid solutions, but their power to react with acid varied inversely with the size of the particles. Evidence in support of the view that the reaction is a surface phenomenon is thus obtained.

A. G. P.

**Colloidal Behaviour of Soils and Soil Fertility. I. Suction Force of Soils as an Index of their Colloidal Content.** J. S. JOFFE and H. C. McLEAN (*Soil Sci.*, 1925, 20, 169—175).—A preliminary paper giving data indicating that the suction force of a soil, as measured by the method of Kornev (cf. *Russ. J. Exp. Agron.*, 1924, 22, 105; *Soil Sci.*, 1924, 17, 428), can be utilised as an index of the colloid content of the soil under the conditions of the experiment since it is the adsorption of water by the colloidal material which produces the suction force. [Cf. B., 1925, 858.]

C. T. G.

## Organic Chemistry.

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**Absorption of Ethylene by Ortho-, Pyro-, and Meta-phosphoric Acid.** A. MÜLLER (*Ber.*, 1925, **58**, [B], 2105—2109).

—Ethylene is absorbed by heated ortho-, pyro-, or meta-phosphoric acid at rates which depend greatly on the temperature and amount of gas already absorbed; at the optimum temperature, 140°, the initial ratios for the rate of absorption of the gas by the ortho-, pyro-, and meta-acids are 21 : 80 : 50. The reaction is remarkably catalysed by cuprous oxide, which, if present to the extent of 1.5%, causes orthophosphoric acid at the atmospheric temperature to absorb ethylene three times as quickly as at 140° in the absence of catalyst and increases the rate of absorption by the pyro- or meta-acid at 140° to four or sixty-seven times that observed without catalyst. Silver sulphate has a very similar action. Sulphuric acid slightly accelerates, whereas aluminium oxide retards, the absorption. Ethyl dihydrogen orthophosphate is formed from ethylene and orthophosphoric acid, possibly also from pyrophosphoric acid. The absorbed ethylene is for the most part evolved at 170°.

H. W.

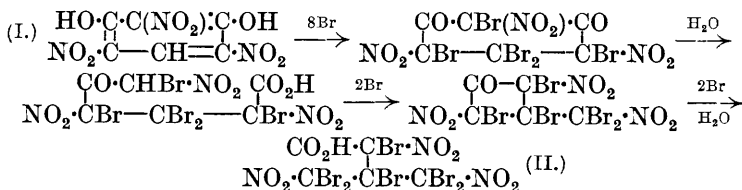
**Marine-animal Oils. Squalene and Spinacene.** E. ANDRÉ and H. CANAL (*Compt. rend.*, 1925, **181**, 612—614).—Liver oil from *Cetorhinus maximus* (yielding squalene, cf. Tsujimoto, A., 1916, i, 786; 1920, i, 261) contains unsaturated hydrocarbons from which two *hydrochlorides*,  $C_{28}H_{46}, 6HCl$ , m. p. 107—108°, and  $C_{30}H_{50}, 6HCl$ , m. p. 144—145°, were isolated. From the unsaturated hydrocarbons from *Scymnus licha* (yielding spinacene, cf. Chapman, T., 1917, **111**, 56; 1918, **113**, 458) two *hydrochlorides*,  $C_{30}H_{50}, 6HCl$ , m. p. 107—108°, and  $C_{31}H_{52}, 6HCl$ , m. p. 143—145°, were obtained. On mixing the two hydrochlorides of m. p. 107—108°, no depression of the freezing point was obtained, but on mixing the two hydrochlorides of m. p. 143—145°, the mixture had m. p. 139—140°. It is considered that squalene and spinacene are not chemical individuals.

L. F. H.

**Homologues of  $\gamma$ -Phenylpropinene.** L. BERT, P. C. DORIER, and R. LAMY (*Compt. rend.*, 1925, **181**, 555—556; cf. Bourguet, A., 1923, i, 429).—Acetylenic hydrocarbons are obtained by the action of sodamide on aromatic  $\gamma$ -chloroallyl compounds (this vol., i, 803), and are colourless liquids with penetrating odours, giving insoluble silver and cuprous compounds.  $\delta$ -Phenylbutinene, b. p. 83°/15 mm.,  $d^{20}_4$  0.918,  $n^{20}_D$  1.518,  $\gamma$ -o-tolylpropinene, b. p. 80°/15 mm.,  $d^{20}_4$  0.940,  $n^{20}_D$  1.532,  $\gamma$ -p-tolylpropinene, b. p. 83°/15 mm.,  $d^{20}_4$  0.947,  $n^{20}_D$  1.533,  $\gamma$ -3 : 4-dimethylphenylpropinene, b. p. 95°/15 mm.,  $d^{20}_4$  0.941,  $n^{20}_D$  1.534,  $\gamma$ -2 : 4-dimethylphenylpropinene, b. p. 98°/15 mm.,  $d^{20}_4$  0.939,  $n^{20}_D$  1.531,  $\gamma$ -4-isopropylphenylpropinene, b. p. 101°/15 mm.,

$d_4^{25}$  0.924,  $n_D^{25}$  1.523,  $\gamma$ -2-methyl-5-isopropylphenylpropinene, b. p. 115°/15 mm.,  $d_4^{25}$  0.919,  $n_D^{25}$  1.525, are described. L. F. H.

**So-called "Dibromonitroethylene" and the Mechanism of the Formation of Bromo- and Chloro-picrins from Polynitrophenols.** H. WIELAND and H. JUNG (*Annalen*, 1925, **445**, 82—92).—Merz and Zetter's "dibromonitroethylene" (A., 1879, 717, 721), m. p. 116—117°, prepared in 40% yield by the action of bromine on an aqueous suspension of trinitroresorcinol (I), is shown to be hexabromo- $\alpha\gamma\gamma'$ -trinitroisovaleric acid (II), its formation being represented by the scheme:



The compound readily loses carbon dioxide in cold alcohol or ether or in warm xylene, giving bromopicrin, b. p. 72—74°/14 mm., and  $\alpha\beta\gamma$ -tribromo- $\alpha\gamma$ -dinitropropylene, whilst in boiling water the latter compound is hydrolysed to hydrobromic acid, nitrous acid, and  $\alpha\beta$ -dibromoacrylic acid, m. p. 86°. By the action of aniline in cold alcohol or ether, there are obtained carbon dioxide, 2 mols. of dibromonitromethane, *p*-bromoaniline (the  $\beta$ -bromine atom being replaced by hydrogen), and bromonitroethylideneaniline, m. p. 156°, which is synthesised by bromination of nitroethylideneaniline (Meister, A., 1907, i, 885) with bromine water and alkali, and is converted by hot dilute mineral acid into bromonitromethane, b. p. 44°/14 mm., aniline, and formic acid. Phenylhydrazine similarly yields bromonitroacetaldehydophenylhydrazone, m. p. 166°.

Although no chlorine analogue of (II) can be isolated, the formation of chloropicrin from polynitrophenols is probably due to the same type of reaction. C. H.

**Halogenated Allyl Halides.** J. VON BRAUN and M. KÜHN (*Ber.*, 1925, **58**, [B], 2168—2173).—The primary halogen atom is very loosely united in halogenated allyl halides, which are therefore well adapted to a variety of synthetic purposes (*e.g.*, with Grignard's reagents), and the compounds so obtained contain a halogen atom attached at an unsaturated linking and therefore available for further changes.

$\gamma$ -Bromoallyl bromide, b. p. 156°,  $d_4^{25}$  2.061, is prepared in 35—40% yield by the action of phosphoryl bromide on dibromohydrin; tribromohydrin is simultaneously produced. Replacement of phosphoryl bromide by the corresponding chloride has little effect on the yield, but the product then contains 1—2% of chlorine. With trimethylamine,  $\gamma$ -bromoallyl bromide yields an additive compound,  $\text{C}_6\text{H}_{13}\text{NBr}_2$ , m. p. (indefinite) 190° after softening at 140° (chloroplatinate of corresponding chloride, decomp. 250°).

$\gamma$ -Chloroallyl chloride and trimethylamine give the compound  $C_6H_{13}NCl_2$ , m. p. (indefinite) 130—175°.

The action of magnesium aryl bromides on halogenated allyl halides yields the following compounds:  $\beta$ -bromoallylbenzene, b. p. 94—95°/14 mm.; *p*- $\beta$ -bromoallylanisole, b. p. 140—145°/14 mm.;  $\gamma$ -bromoallylbenzene, b. p. 106°/13 mm.;  $\gamma$ -chloroallylbenzene, b. p. 76°/13 mm.; 1- $\beta$ -bromoallylnaphthalene, b. p. 165—170°/12 mm.  $\gamma$ -Bromoallylbenzene is transformed by successive treatment with magnesium and carbon dioxide into  $\gamma$ -phenylcrotonic acid, m. p. 45—50°, whereas  $\beta$ -bromoallylbenzene affords  $\alpha$ -benzylacrylic acid, m. p. 73°.

$\beta\gamma$ -Dibromoallyl bromide is converted by trimethylamine into a mixture of two isomeric substances,  $C_6H_{12}NBr_3$ , m. p. 215° and 165—170°, respectively, and by pyridine into two compounds,  $C_8H_8NBr_3$ , m. p. 203° and 106—107°, respectively, whereby the expected *cis-trans* isomerism among allyl derivatives of this type appears to be realised experimentally for the first time. When, however, any of the quaternary bromides is distilled, the regenerated  $\beta\gamma$ -dibromoallyl bromide appears to consist of the equilibrium mixture of isomerides.

H. W.

**Preparation of Alcohol by Catalytic Reduction of Acetaldehyde.** K. NEGOSHI (*Rep. Osaka Ind. Res. Lab.*, 1924, 5, No. 6, 1—361).—The most effective nickel catalyst is obtained by soaking pumice with nickel nitrate up to 30% of nickel, and heating for 6 hrs. at 500° in hydrogen passed at a rate of 100 c.c. per min. When nickel from nickel nitrate is used, the reduction of the aldehyde is best effected at 140°; nickel from the oxide is best employed at 100°. The corresponding optimal rates for passing the acetaldehyde are, respectively, 60—70 c.c. per min. and 150—170 c.c. per min. With a sevenfold excess of hydrogen during reduction a 90% yield of alcohol was obtained.

CHEMICAL ABSTRACTS.

**Configurational Relationships between  $\beta$ -Hydroxy-acids and  $\alpha$ -Hydroxy-acids and between the Latter and Secondary Alcohols.** P. A. LEVENE and H. L. HALLER (*J. Biol. Chem.*, 1925, 65, 49—53).—As a first step in the determination of the above relationships, *l*- $\alpha\beta$ -dihydroxypropane has been prepared from *l*- $\beta$ -hydroxybutyric acid, by a series of reactions which took place without marked racemisation. Methyl *l*- $\beta$ -hydroxybutyrate,  $[\alpha]_D^{20} -20.9^\circ$ , was converted into *l*- $\beta$ -hydroxybutyrylhydrazide, m. p. 129—130°,  $[\alpha]_D^{21} -29.3^\circ$  in alcohol; *s*-di- $\beta$ -hydroxypropylcarbamide, prepared from the latter substance, had m. p. 49—51°,  $[\alpha]_D^{25.5} +18.5$  in alcohol, and was converted (cf. Levene and Scheidegger, A., 1924, i, 1049) into *l*- $\beta$ -hydroxypropylamine, of which the hydrochloride had  $[\alpha]_D^{26} -31.2^\circ$  in water; on treatment with silver nitrite and hydrochloric acid this gave a solution which was laevorotatory and contained no amino nitrogen.

C. R. H.

**Acetylenic Derivatives of Glycerol.** LESPIEAU (*Compt. rend.*, 1925, 181, 557—558).— $\delta\epsilon$ -Dichloro- $\Delta^a$ -pentinen- $\gamma$ -ol (this vol., i, 225), on treatment with 10% potassium hydroxide, is converted

into the acetylenic *epichlorohydrin*,  $\begin{array}{c} \text{CH:C}\cdot\text{CH} \\ \text{CH}_2\text{Cl}\cdot\text{CH} \end{array} > \text{O}$ , b. p. 58—60°,  $d^{23}_4$  1.1592,  $n^{23}_D$  1.472, which becomes hydrated when left in contact with water for some days, yielding  $\epsilon$ -chloro- $\Delta^a$ -*pentinene- $\gamma$  $\delta$ -diol*, b. p. 131—132°/16 mm.,  $d^{16}_4$  1.289,  $n^{16}_D$  1.504, which on treatment with sodium methoxide gives  $\epsilon$ -methoxy- $\Delta^a$ -*pentinene- $\gamma$  $\delta$ -diol*, b. p. 100°/3 mm.,  $d^{17}_4$  1.120,  $n^{17}_D$  1.4720. The monochlorohydrin and methoxy compound yield insoluble *silver* and *cuprous* compounds.  $\delta$ - $\epsilon$ -Dichloro- $\Delta^a$ -*pentinen- $\gamma$ -ol*, when treated with anhydrous potassium hydroxide in ethereal solution, yields a yellow, amorphous *compound*, mol. wt. 462, free from chlorine.

L. F. H.

**Experiments with Thiocarbonyl Chloride.** W. AUTENRIETH and H. HEFNER (*Ber.*, 1925, **58**, [B], 2151—2156; cf. Autenrieth and Bölli, this vol., i, 1468).—The principle of the Schotten-Baumann method of benzoylation can be extended with advantage to thiocarbonyl chloride, phenoxyphosphoryl dichloride, and diphenoxyphosphoryl chloride; addition of sodium hydroxide is unnecessary with primary and, probably, also with secondary bases.

Thiocarbonyl chloride is conveniently prepared by a modification of the method of Helfrich and Reid (*A.*, 1921, i, 300), whereby carbon disulphide is exhaustively chlorinated in bright sunlight, yielding a mixture of sulphur chloride and chlorothioltrichloromethane,  $\text{CCl}_3\cdot\text{SCl}$ . The mixture is added cautiously to water, whereby sulphur chloride is decomposed, washed thoroughly with water, dried, heated for a short time at 100°, and finally twice distilled with steam. After everything volatile below 146° has been removed from the distillate, the residue, consisting mainly of chlorothioltrichloromethane, is reduced by stannous chloride and hydrochloric acid, thereby yielding thiocarbonyl chloride, b. p. 73—73.5°. The following compounds are prepared from it: ethyl chlorothioformate,  $\text{Cl}\cdot\text{C}(\text{:S})\cdot\text{OEt}$ , b. p. 136°; diphenyl thiocarbonate,  $\text{S}\cdot\text{C}(\text{OPh})_2$ , m. p. 106°; *di- $\beta$ -naphthyl thiocarbonate*, m. p. 212°; *pyrocatechyl thiocarbonate*,  $\text{S}\cdot\text{C} < \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \end{array} > \text{C}_6\text{H}_4$ , m. p. 154°; diphenyl trithiocarbonate,  $\text{S}\cdot\text{C}(\text{SPh})_2$ , m. p. 95°; *di-p-tolyl trithiocarbonate*, m. p. 115°; thiocarbodihydrazide, m. p. 168°; thiocarbanilide, m. p. 153—154°; *o*-phenylenethiocarbamide, m. p. 295—298° after darkening at 270°; *diphenylenedithiocarbamide*,  $\text{S}\cdot\text{C} < \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \end{array} > \text{C}_6\text{H}_3\cdot\text{C}_6\text{H}_3 < \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \end{array} > \text{CS}$ , m. p. 233°. In general, the tendency of thiocarbonyl chloride to yield cyclic derivatives appears less marked than that of phenoxyphosphoryl dichloride or phenoxythiophosphoryl dichloride (cf. *loc. cit.*).

Phenoxyphosphoryl dichloride and aqueous aniline afford phenoxyphosphoryl dianilide,  $\text{O}\cdot\text{P}(\text{OPh})\cdot(\text{NHPh})_2$ , m. p. 125°, whereas diphenoxyphosphoryl chloride yields *diphenoxyphosphoryl anilide*, m. p. 129°. Either chloride is converted by phenol in dilute, alkaline solution into triphenyl phosphate. H. W.

**Preparation of the Alkaline-earth Salts of Alkylsulphonic Acids.** CHEMISCHE FABRIK VORM. SANDOZ (Swiss Pats. 101817 and 105845—7; from *Chem. Zentr.*, 1925, ii, 760).—Alkyl sulphates or the alkali alkyl sulphates are converted by warming with ammonium sulphite into ammonium alkylsulphonates, which with calcium or barium hydroxide yield the corresponding alkaline-earth salt. The reaction with dialkyl sulphates proceeds in two stages, the ammonium alkylsulphonate and the ammonium alkyl sulphate being formed in equimolecular proportions. The latter is unchanged in the cold, but on warming is converted into ammonium sulphate and a second molecule of ammonium alkylsulphonate. Calcium methylsulphonate, *calcium ethylsulphonate*, barium methylsulphonate, and barium ethylsulphonate are described. R. B.

**Oxidation of Unsaturated Fatty Acids.** A. GRÜN and F. WITTKA (*Chem. Umschau*, 1925, 32, 257—259).—In order to avoid the mixed products of the oxidation of an olefinic acid by potassium permanganate or chromic acid, the acid is converted into the di-bromo-saturated acid and from this the corresponding acetylenic acid is obtained by the action of alcoholic potassium hydroxide. The acetylenic acids are oxidised by 2% alkaline permanganate to give nearly theoretical yields of pure oxidation products, from which the structure of the original olefinic acid can be determined. Thus stearolic acid yields azelaic and *n*-nonoic acids, no suberic acid being formed. When chromic acid is used as the oxidising agent, the products are not so pure. R. W. W.

**Oil Films or "Oxyns." II. Autoxidation during the Drying of a Fatty Oil; Walton Process Linoxyn.** A. EIBNER and G. RIED (*Chem. Umschau*, 1925, 32, 233—249).—That the linoxyn prepared by the Walton process (scrim oil) exists in a less mature condition than that which constitutes a dried oil film is shown by its low acid value (79.4), high iodine value (59), and by the presence of a liquid phase, which if in excess produces syneresis with a tendency to liquefaction incorrectly attributed to over-oxidation. No hydroxy-acids could be obtained from Walton linoxyn by extraction, and their absence is further proved by the low acetyl value (83.8) of the acids obtained by saponification. The latter included about 25% of unoxidised acids, consisting chiefly of oleic but also of  $\beta$ -linoleic acid. It is evident that this modification is poorer in free energy than the  $\alpha$ -form, and is probably the *trans*-form. The oxy-acids, which constitute 65% of the total acids, form, unlike hydroxy-acids, a brown syrup from which no crystallisable product could be obtained except a small amount of azelaic acid, attributable to partial hydrolysis of peroxides. Both the oxyn and the free acids contain about the same quantity, 3%, of active oxygen, showing the presence of peroxides and their stability. The oxy-acids of linoxyn would appear to be transformation products of these peroxides, and to possess little or no hydroxylic character. The mol. wt. of Walton linoxyn obtained by the b. p. method is 952, which does not indicate extramolecular polymerisation. Details are given of the swelling and solubility

of this linoxyn in various organic solvents. [Cf. *B.*, 1925, 679, 930.]  
G. L. L.

**Addition of Alkali Alkoxide to Esters.** F. ADICKES (*Ber.*, 1925, 58, [B], 1992—1999).—Ethyl oxalate and alcohol-free sodium ethoxide in dry ethereal solution give the additive *compound*,  $\text{CO}_2\text{Et}\cdot\text{C}(\text{ONa})(\text{OEt})_2$ , decomp. about  $115^\circ$ , which is obtained as a white, very hygroscopic, unstable powder after removal of ether in a vacuum. On exposure to moist air, it yields sodium ethyl oxalate. Water converts it into sodium oxalate and oxalic ester, whereas anhydrous acids yield ethyl oxalate and the sodium salt of the acid. With carbon dioxide, it gives sodium ethyl carbonate. It does not yield an ester of semiortho-oxalic acid when treated with ethyl bromide or methyl sulphate. Its constitution is established by the observations that the additive *compounds* from methyl oxalate and sodium ethoxide and from ethyl oxalate and sodium methoxide are decomposed by carbon dioxide into methyl ethyl oxalate and dimethyl or diethyl ester and a mixture of sodium methyl and ethyl carbonates and, further, on exposure to moisture lose (in effect) methyl ethyl ether and leave a mixture of sodium methyl and ethyl oxalate. The addition of more than 1 mol. of sodium ethoxide to ethyl oxalate does not appear to be possible. The compound obtained by means of potassium ethoxide is much less stable than the sodium derivative.

The properties of the additive compounds derived from ethyl oxalate differ widely from those obtained by Claisen (*A.*, 1887, 574) from benzoic esters. Re-examination of the product obtained by heating ethyl benzoate with sodium ethoxide at  $100^\circ$  shows it to be a mixture of sodium benzoate and sodium ethoxide, although the possible production of a small proportion of additive compound is not excluded. Claisen's compounds must therefore be regarded as non-existent (cf. Tischtschenko, *A.*, 1907, i, 282; 1912, i, 268).

H. W.

**Photolysis of Ethylenic Dibasic Acids.** VOLMAR (*Compt. rend.*, 1925, 181, 467—469; cf. *A.*, 1924, ii, 244; this vol., ii, 575).—Unsaturated dibasic acids undergo photochemical decomposition more rapidly than their saturated analogues. The photolysis of *cis*-compounds is five or six times as rapid as that of the *trans*-isomerides, the latter behaving like monobasic acids, whilst in the *cis*-acids the carboxyl groups exert a mutually enhancing effect on photochemical change. Itaconic acid behaves like succinic acid. On prolonged exposure to ultra-violet light, the *trans*- and *cis*-isomerides behave identically owing to common equilibrium reached by them.

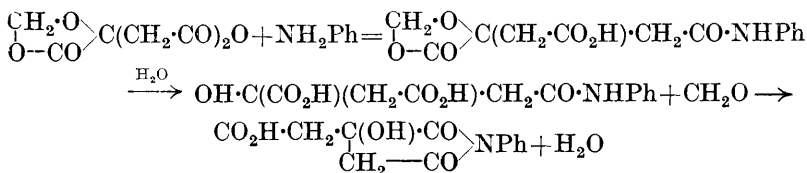
L. F. H.

**Fission of Ring Systems.** R. KUHN and F. EBEL (*Ber.*, 1925, 58, [B], 2088—2094; cf. Kuhn and Ebel, this vol., i, 780).—In reply to Meisenheimer (this vol., i, 1335), a series of examples is quoted from the literature in favour of the authors' view that trans-fission of cyclic systems is always a possibility and that a new arrangement of radicals is not "completely excluded" even when those



atoms which form the stereochemical centre of the molecule do not appear to be involved in the reaction. H. W.

**Methylenecitric Anhydride. Aniline Derivatives of Citric and Aconitic Acids.** C. A. NAU, E. B. BROWN, and J. R. BAILEY (*J. Amer. Chem. Soc.*, 1925, **47**, 2596—2606).—Methylenecitric anhydride (cf. van Ekenstein and Lobry de Bruyn, A., 1900, i, 619; 1901, i, 120) combines with aniline to form an *anilide*, m. p. 148° (decomp.), which hydrolyses to citroanilic acid (cf. Pebal, *Annalen*, 1852, **82**, 92); *aniline salt*, m. p. 139°. The methylenecitric anhydride cannot, however, possess the unsymmetrical structure this reaction implies, since *dimethyl methylenecitrate*, m. p. 69·5°, hydrolyses to *s*-dimethyl citrate, which with para-formaldehyde yields a product identical with that obtained by esterification of methylenecitric acid with methyl alcohol. The mechanism of conversion of the methylenecitric anhydride into the unsymmetrical anil of citric acid is as follows :



Contrary to the patent literature (D.R.-P. 186659, 1907), methylenecitric anhydride reacts with alcohols to form mono- and not di-alkyl esters of methylenecitric acid. The action of phosphorus pentachloride on citroanilic acid or its ethyl ester yields aconite-monoanil, m. p. 189°, and methyl and ethyl esters, m. p. 149° and 123°, respectively (Bertram, A., 1905, i, 465, gives 143° and 112°). The following compounds, which do not seem to have been previously obtained, were prepared in the course of the investigation : *phenylhydrazoanilide* of citric acid, m. p. 118° [phenylhydrazone salt, m. p. 132° (decomp.)], *monoethyl methylenecitrate*, m. p. 109°; *ethyl monoamidomonoanilidocitrate*, m. p. 183°; *citrodianilidemonoamide*, m. p. 185°; *monoanilidocitroamic acid*, m. p. 171°; *normal potassium ethyl citroanilide*, m. p. 121° (softens 70°); *hydrogen salt*, m. p. 153°; *ethyl citroanilide*, m. p. 108°. J. W. B.

**d-Glycuronic Acid.** F. EHRLICH and K. REHORST (*Ber.*, 1925, **58**, [B], 1989—1992).—Menthylglycuronic acid is hydrolysed with dilute sulphuric acid at 100° and the menthol is removed. The solution is treated with an excess of barium hydroxide or carbonate and, after removal of barium sulphate, is concentrated and treated with alcohol, whereby barium glycuronate is precipitated. The salt is decomposed by rather less than the calculated quantity of sulphuric acid, and to the filtrate, after removal of sulphate, a large excess of alcohol is added. After filtration from a small amount of barium glycuronate and concentration, *d-glycuronic acid*, C<sub>6</sub>H<sub>10</sub>O<sub>7</sub>, m. p. 154°, [ $\alpha$ ]<sub>D</sub><sup>20</sup> +11·73° to +36·26° in water, is obtained. The positive mutarotation indicates the existence of  $\alpha$ - and  $\beta$ -

modifications of the acid. The acid is transformed in boiling aqueous solution into the corresponding lactone. H. W.

**Lactone Formation from Mono- and Di-carboxylic Sugar Acids.** P. A. LEVENE and H. S. SIMMS (*J. Biol. Chem.*, 1925, **65**, 31—47).—The rate of lactone formation by certain sugar acids in 0.25*M* aqueous solution at 25° has been studied polarimetrically. Monocarboxylic acids of the type of gulonic acid form simultaneously two lactones, one with a five-membered and the other with a six-membered ring; the latter is formed to the extent of about 30% or less, equilibrium being reached in a few hours; the former is produced to the extent of 75—80%, equilibrium being attained in the course of several hundred hours. In the case of certain methyl derivatives of these acids which can form but one lactone, the latter is formed to the extent of 20—30% with rapid attainment of equilibrium if a six-membered ring, and to 75% with slow attainment of equilibrium if a five-membered one. A similar study, by titration, of lactone formation by dicarboxylic acids such as saccharic acid showed no marked difference in the rates of formation of the various lactones corresponding with the different physical properties of these lactones; rates were somewhat slower than those of the formation of five-membered ring lactones from the monocarboxylic acids. The dissociation constant of gulonic acid is  $10^{-3.68}$  (corrected for the activities of the ions). C. R. H.

**Constitution of the Sulphonation Products of the Higher Unsaturated Fatty Acids.** H. POMERANZ (*Chem. Umschau*, 1925, **32**, 259—261).—A theoretical discussion whereby it is reasoned that the sulphonation of the higher unsaturated fatty acids is best represented by the addition of 2 mols. of sulphur trioxide to the double linking:  $\cdot\text{HC}\cdot\text{CH}\cdot \rightarrow \cdot\text{CH} \begin{smallmatrix} \text{CH}\cdot\text{O} \\ \text{SO}_2\cdot\text{O} \end{smallmatrix} \text{SO}_2$ . The anhydride so obtained is readily decomposed on washing the sulphonated acid with water to give the acid  $\cdot\text{CH}(\text{SO}_3\text{H})\cdot\text{CH}(\text{O}\cdot\text{SO}_3\text{H})\cdot$ , which is in turn hydrolysed by the dilute acid to give  $\cdot\text{CH}(\text{SO}_3\text{H})\cdot\text{CH}(\text{OH})\cdot$ . R. W. W.

**Influence of Constitution on the Transformation of Phenylhydrazones of Unsaturated Compounds into Pyrazolines.** II. K. VON AUWERS and A. KREUDER.—(See i, 1454.)

**Action of Sulphites and Hydrogen Sulphites on Aldehydes and Ketones and its Application to the Quantitative Determination of these Compounds.** G. ROMEO and E. D'AMICO (*Annali Chim. Appl.*, 1925, **15**, 320—330).—Tiemann and Krüger, (A., 1899, i, 247) and Romeo (A., 1918, i, 265) have shown that, with aliphatic aldehydes having double bonds in the carbon chain, sodium hydrogen sulphite or, better, a mixture of this with normal sulphite produces hydrosulphonic derivatives by addition at the double bond as well as at the aldehyde group. In the case of ketones, the same action takes place more slowly: ketones with a methyl

group linked to the carbonyl react most easily, whilst the presence of a tertiary carbon atom directly linked to the carbonyl group may inhibit the addition. The above hydrosulphonic derivatives react neutral to rosolic acid. Hence the determination of an aldehyde or ketone may be carried out as follows: 2 g. of the substance are neutralised with standard sodium hydroxide in the presence of rosolic acid and then 50 c.c. of standard sulphite-hydrogen sulphite solution added. If the substance is insoluble in water, heating is necessary. The reaction requires  $\frac{1}{4}$  hr. to 5 hrs. The mixture is titrated with standard sodium hydroxide solution. Knowing the number of hydrosulphonic groups introduced into the molecule, the proportion of aldehyde or ketone is calculated from the observed diminution of the acidity.

The method is inapplicable to benzaldehyde, menthone, and carvone. Applied to the determination of cinnamaldehyde and pulegone in essential oils, it is claimed to be superior to the methods used hitherto (cf. Burgess, A., 1904, ii, 371; Bennett and Donovan, A., 1922, ii, 535).

W. E. E.

**Action of Halogen on the Enolates of Glutacondialdehyde and Synthesis of 3-Halogenopyridines.** P. BAUMGARTEN (*Ber.*, 1925, **58**, [B], 2018—2023; cf. Baumgarten, A., 1924, i, 1166).—The action of chlorine on  $\delta$ -benzoyloxy- $\Delta^{\alpha\gamma}$ -butadienealdehyde affords  $\gamma$ -chloro- $\delta$ -benzoyloxy- $\Delta^{\alpha\gamma}$ -butadienealdehyde, m. p. 127°, whereas in carbon tetrachloride solution benzoyl chloride and  $\alpha$ -chloroglutacondialdehyde [isolated as the corresponding *dianilide hydrochloride*,  $\text{CH}(\text{NHPh})\cdot\text{CCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}\cdot\text{HCl}$ , m. p. 119° (decomp.)] are produced. The compound is also prepared by the chlorination of the sodium derivative of  $\delta$ -hydroxy- $\Delta^{\alpha\gamma}$ -butadienealdehyde in methyl-alcoholic solution. The dianilide is transformed by alcoholic hydrogen chloride into 3-chloro-1-phenylpyridinium chloride. The sodium derivative of  $\delta$ -hydroxy- $\Delta^{\alpha\gamma}$ -butadienealdehyde can be brominated in aqueous or methyl-alcoholic solution, but the bromoaldehyde cannot be isolated as such and is characterised as  $\gamma$ -bromo- $\delta$ -benzoyloxy- $\Delta^{\alpha\gamma}$ -butadienealdehyde, m. p. 107.5°, or as the *dianilide hydrobromide*, m. p. 135—136° (decomp.). The crude bromoaldehyde is converted by distillation from alkaline solution with steam into 3-bromopyridine, b. p. 169°/762 mm. [*chloroplatinate*, m. p. 175° (decomp.)]. Decomposition of the dianilide hydrobromide affords 3-bromo-1-phenylpyridinium iodide, m. p. 247° (decomp.).  $\gamma$ -Iodo- $\delta$ -hydroxy- $\Delta^{\alpha\gamma}$ -butadienealdehyde, m. p. about 90° (decomp.), is prepared from the sodium derivative of  $\delta$ -hydroxy- $\Delta^{\alpha\gamma}$ -butadienealdehyde and iodine-potassium iodide in aqueous solution.  $\gamma$ -Iodo- $\delta$ -benzoyloxy- $\Delta^{\alpha\gamma}$ -butadienealdehyde, m. p. 127°, and  $\gamma$ -iodo- $\delta$ -anilino- $\Delta^{\alpha\gamma}$ -butadienealdehydeanil dihydriodide, m. p. 133—135° (decomp.), are described. The latter compound passes in boiling aqueous-alcoholic solution into 3-iodo-1-phenylpyridinium iodide, m. p. 272° (decomp.). The sodium derivative of  $\gamma$ -iodo- $\delta$ -hydroxy- $\Delta^{\alpha\gamma}$ -butadienealdehyde is converted into 3-iodopyridine, m. p. 53.5°; the corresponding *hydrochloride* and *chloroplatinate*, m. p. 211° (decomp.), are described.

H. W.

3 c\*

**Electrolytic Reduction of Oximes. II.  $\gamma$ -Oximinovaleic Acid and  $\alpha$ -Oximinopropionic Acid.** M. ISHIBASHI (*Mem. Coll. Sci. Kyōtō*, 1925, 9, 37—42).—In part already abstracted (cf. A., 1924, i, 621). Electrolytic reduction of  $\gamma$ -oximinovaleic acid at 6—8° with lead electrodes yields  $\gamma$ -aminovaleic acid, m. p. 217—218° (previously accepted value, 193°), in 94% yield, the current density being 2 amp./dm.<sup>2</sup>, and the cathode solution containing 5% of sulphuric acid and 3% of oximinovaleic acid. Increase of sulphuric acid, decrease of current density, and increase of temperature lower the yield of amino-acid and increase that of lævulic acid formed by hydrolysis. Best results are obtained with mercury as cathode, followed by lead and tin. B. F.

**Formation of *d*-Sorbitose and *d*-Gulose by Oxidation of *d*-Sorbitol with Bromine Water.** H. W. TALEN (*Rec. trav. chim.*, 1925, 44, 891—893).—The preparation described by Votoček and Lukes (this vol., i, 773) is improved by removing dextrose and lævulose from the mixture of products by alcoholic fermentation. The gulose and sorbose remaining then yield pure sorbosephenylsazone with phenylhydrazine. G. M. B.

**Dihydrazines. VI. Further Experiments in the Sugar Group with Diphenylmethanedimethyldihydrazine.** J. VON BRAUN and O. BAYER (*Ber.*, 1925, 58, [B], 2215—2222).—Diphenylmethanedimethyldihydrazine,  $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{NH}_2)_2$ , is very serviceable for preparatory purposes in the sugar series, since it does not react with ketoses and only with aldoses in which at least two of the three  $\cdot\text{CH}\cdot\text{OH}$  groups following the aldehydic group have the same spatial arrangements and follow one another in sequence. Even in the presence of a large excess of the reagent 1 mol. of the latter reacts predominately with 2 mols. of sugar, but the formation of derivatives from equal numbers of molecules does not limit the utility of the reagent, since both types of condensation product are practically insoluble in the media used. Regeneration of the sugars from the hydrazones is readily effected by the use of formaldehyde solutions containing much pyridine. Mannose is readily isolated as the diphenylmethanedimethyldihydrazone from the equilibrium mixture of mannose, lævulose, and dextrose obtained by the action of sodium hydroxide on either of the two latter sugars, the yield being 4—5%, in agreement with the observations of Lobry de Bruyn; from invert-sugar the yield is lower and the hydrazone less pure. In this instance, mannose is the only sugar capable of reacting with the hydrazine. A more interesting example is afforded by the isomerisation of *d*-galactose to *d*(—)-talose by lead hydroxide; in this instance, both sugars are precipitable by the hydrazine, and removal of the unchanged *d*-galactose from the equilibrium mixture is therefore effected by fermentation with yeast, after which *talose-bisdiphenylmethanedimethyldihydrazone*, m. p. 185°, is isolated. *d*(—)-Talose is obtained from the latter compound as a syrup,  $[\alpha]_D -21.4^\circ$ . Substitution of lactose for galactose as initial material for the preparation of talose offers no advantage.

The following compounds are incidentally described : the phenylhydrazone, m. p. 178° (decomp.), *p*-bromophenylhydrazone, m. p. 205°, phenylbenzylhydrazone, m. p. 199°, and phenylmethylhydrazone, m. p. 220—222°, of *d*(-)-talose; galactosemonodiphenylmethanedimethyldihydrazone,  $\text{C}_6\text{H}_{12}\text{O}_5 \cdot \text{N} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{NH}_2$ , m. p. 175°; arabinosemonodiphenylmethanedimethyldihydrazone, m. p. 155°.

H. W.

**Sugars obtained from Gein.** H. HÉRISSEY and J. CHEYMOL (*Compt. rend.*, 1925, **181**, 565—566).—On hydrolysis with gease gein (this vol., i, 487) yields vicianose (Bertrand and Weisweiler, A., 1911, i, 15), which, on treatment with acids, gives 1 mol. each of dextrose and arabinose.

L. F. H.

**Octaethylcellobiose and its Acetolysis, compared with Cellobiose and Octa-acetylcellobiose.** K. HESS and G. SALZMANN (*Annalen*, 1925, **445**, 111—122; cf. this vol., i, 641).—*Heptaethyl-β-ethylcellobioside*, m. p. 64—66°, b. p. 185—190°/0.5 mm.,  $[\alpha]_D^{20} -2.06^\circ$  in chloroform,  $[\alpha]_D^{22} -3.07^\circ$  in water, is obtained in 61% yield by the action of ethyl sulphate on hepta-acetyl-β-ethylcellobioside in suspension in aqueous sodium hydroxide at 65° (cf. Hess, Wittelsbach, and Messmer, A., 1921, i, 710). Whilst both α- and β-octa-acetylcellobioses are unattacked by a mixture of equal proportions of acetic acid and acetic anhydride in presence of sulphuric acid, except that a portion of the β-form is converted into the α-isomeride, and whilst cellobiose also resists fission under similar conditions, the above octaethyl derivative is completely converted by the reagent mentioned into triethylglucose diacetate and tetraethylglucose acetate, a result indicating that the sensitiveness of compound sugars to hydrolytic fission is influenced by the nature of the radicals substituting the hydroxyl groups. Hydrolysis of the octaethyl derivative with boiling 5% alcoholic hydrogen chloride affords a mixture of tri- and tetra-ethylethylglucosides, from which, by hydrolysis with aqueous hydrochloric acid, the corresponding triethylglucose (A., 1921, i, 710) and (?) βγδ-*tetraethylglucose*, m. p. 61—64°, b. p. 138—139°/0.5 mm.,  $[\alpha]_D^{20} +65.3^\circ$  in water, are obtained. The latter does not exhibit mutarotation, indicating the probable existence of the equilibrium mixture in the distilled substance. Hydrolysis of the above-mentioned acetolysis product also yields the two ethylglucoses, and the tetraethyl derivative was only isolated from the product of this hydrolysis. *Heptamethyl-β-benzylcellobioside*, m. p. 71—72.5°,  $[\alpha]_D^{19} -32.5^\circ$  in chloroform, is obtained by the action of methyl sulphate, at 75°, on a suspension in aqueous alkali hydroxide of β-*benzylcellobioside*, m. p. 187°,  $[\alpha]_D^{18} -35.57^\circ$  in water, prepared by the action of cold methyl-alcoholic ammonia on the corresponding hepta-acetate (cf. Zemplén, A., 1920, i, 559). The ease with which the above methylation, and the earlier mentioned ethylation, proceed to the fully alkylated derivatives is discussed in reference to the results of Haworth and Hirst (T., 1921, **119**, 193) and of Karrer and Widmer (A., 1921, i, 310, 397), and the possibility of complete methylation of cellobiose and of methylcellobioside by means of methyl sulphate in one stage is suggested

(cf. Hess and Weltzien, this vol., i, 517). The lowering of specific rotation in passing from heptamethyl- $\beta$ -methylcellobioside to the ethyl homologue is in line with the similar regularity observed among the aliphatic esters of carbohydrates (cf. Hess and Messmer, A., 1921, i, 305).

F. G. W.

**Synthesis of Disaccharides from Sugar Derivatives containing Sulphur and Selenium and their Oxidation Products.**

F. WREDE and W. ZIMMERMANN (*Z. physiol. Chem.*, 1925, **148**, 65—82).—Tetra-acetyl- $\alpha$ -bromoglucose is converted into disaccharide by means of silver oxide only with difficulty, but on treatment with potassium sulphide or selenide, it readily gives  $\alpha\alpha'$ -diglucosyl sulphide and selenide. Tetra-acetyl- $\zeta$ -bromoglucose gives  $\zeta\zeta'$ -diglucosyl sulphide and selenide. Attempts to replace the sulphur or selenium with oxygen by treatment with mercuric oxide failed. When the reaction is carried out in aqueous solution, dextrose but no disaccharide results. In alcoholic solution, little dextrose and no disaccharide is obtained, the chief product being the  $\beta$ -ethylglucoside;  $\alpha\alpha'$ -diglucosyl selenide gives  $\beta$ -ethylglucoside (acetate, m. p. 106°). The reaction also fails when the sulphur or selenium compound is acetylated and treated with mercuric oxide in boiling benzene or toluene. The acetylated  $\alpha\alpha'$ - and  $\zeta\zeta'$ -dihexose sulphides are readily converted into sulphones on oxidation with permanganate; *octa-acetyl- $\alpha\alpha'$ -diglucosylsulphone*, m. p. 189°,  $[\alpha]_D^{20}$  —45·5° in ethyl acetate;  *$\alpha\alpha'$ -diglucosylsulphone*, m. p., hydrated, 118°, anhydrous, 129°,  $[\alpha]_D^{20}$  —38·1° in water; *octa-acetyl- $\alpha\alpha'$ -digalactosylsulphone*, needles from methyl alcohol, m. p. 175°,  $[\alpha]_D^{20}$  —5·32° in benzene; plates from benzene, m. p. 149°,  $[\alpha]_D^{20}$  —8·48° in benzene;  *$\alpha\alpha'$ -digalactosylsulphone*, m. p. 182° (decomp.),  $[\alpha]_D^{20}$  —2·16° in water; *tetradeca-acetyl- $\alpha\alpha'$ -dicellosylsulphone*, m. p. 238° after softening at 162°,  $[\alpha]_D^{20}$  —19·9° in chloroform;  *$\alpha\alpha'$ -dicellosylsulphone*, m. p. above 100°, decomp. 150°,  $[\alpha]_D^{20}$  —35·4° in water; the *hexa-acetyldimethylglucoside of  $\zeta$ -diglucosylsulphone*, m. p. 232—233°. The  $\alpha\alpha'$ -selenides do not give oxidation products similar to the sulphones, the selenium being eliminated from the sugar residue. The hexa-acetyldimethylglucoside of  $\zeta$ -diglucosyl selenide gives, however, the corresponding *selenium oxide*, m. p. 231°,  $[\alpha]_D^{20}$  —19·0° in chloroform.

P. W. C.

**Chemistry of Substances of High Molecular Weight. I. An Anhydride of Cellobiose.** M. BERGMANN and E. KNEHE (*Annalen*, 1925, **445**, 1—17; cf. Hess, A., 1921, i, 12; Hess, Weltzien, and Messmer, A., 1924, i, 142).—When a chloroform solution of cellulose acetate, prepared by the method of Skraup (A., 1906, i, 68) or Ost (B., 1919, 355A), is treated for 3 hrs. at 20° with saturated hydrobromic-acetic acid, and then with solid silver acetate in acetic acid at 45—50° to replace bromine by the acetyl group, a mixture of acetates results, from which, by fractionation with methyl alcohol, a small quantity of crystalline *tetra-acetylcellobiose anhydride*,  $C_{12}H_{16}O_{10}Ac_4$ , may be isolated. This compound sinters at 155°, becoming transparent at 165°, and melting to a thin liquid at 185°. The mol. wt. in acetic acid is normal at concentrations below 0·5%,

becoming higher as the concentration increases; in phenol, it is 10% too high, in bromoform and camphor, much higher. Acetylation in pyridine converts the compound into *hexa-acetylcellobiose anhydride*, sintering at 178—216°, clear at 225°, and liquid at 229°, which has a normal mol. wt. in acetic acid at concentrations below 1%. With acetic anhydride and sulphuric acid, both the tetra-acetate and the hexa-acetate yield  $\alpha$ -octa-acetylcellobiose, m. p. 224°. The tetra-acetate is hydrolysed by cold alcoholic potassium hydroxide, giving a *cellobiose anhydride*,  $[\text{C}_{12}\text{H}_{20}\text{O}_{10}]_x$  (sinters above 200°, darkens at 285°), which may be reprecipitated unchanged by acidifying its solution in warm alkali; it reduces Fehling's solution but not hypiodites. It is easily reconverted into the tetra-acetate by acetic anhydride in cold pyridine. Cellobiose anhydride is a true high-molecular carbohydrate, showing the same insolubility as cellulose. The bearing of these results on the polymerisation theory of high-molecular compounds (Pringsheim, "Die Polysaccharide," 1923, p. 177) is discussed. C. H.

**Constitution of Lichenin and Cellulose.** H. PRINGSHEIM, W. KNOLL, and E. KASTON (*Ber.*, 1925, 58, [B], 2135—2143).—Lichenin becomes depolymerised when heated in glycerol at 240° to *lichosan*,  $\text{C}_6\text{H}_{10}\text{O}_5$ , which, according to cryoscopic determinations of its mol. wt. in water supported by similar determinations of the mol. wt. of its *triacetate* ( $[\alpha]_D^{20}$  —32.70° or —31.7° in chloroform) in phenol, is regarded as a glucose anhydride. In aqueous solution, it somewhat rapidly polymerises to lichenin, which, according to the Röntgen spectrum, is completely identical with the natural material. It therefore appears probable that lichosan is the unit substance of lichenin, in which the units are united only by subsidiary valencies. The optical inactivity of lichenin and lichosan in water is remarkable and apparently due to compensation of the activity of the aldehydic carbon atom by that of the four remaining asymmetric carbon atoms; in any case, it is established that the optical inactivity of lichenin, and obviously also of cellulose, is not due to colloid-chemical causes. Acetolysis of lichosan affords octa-acetylcellobiose, m. p. 224°,  $[\alpha]_D^{20}$  +40.0° in chloroform. In contrast with the glucose anhydrides described previously, lichosan cannot be hydrolysed by dialysed malt extract to dextrose; attempts to transform it into cellobiose by cellobiase-free malt extract did not give definite results on account of experimental difficulties. Since lichenin is converted by methylation into  $\beta\gamma\delta$ -trimethyl-

glucose, the constitution 
$$\begin{array}{c} \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \\ \text{O} \end{array}$$

may be assigned to lichosan if the structural relationship of the two substances is regarded as established. Lichosan, like lichenin, after four methylations is converted into a dimethyl derivative, thus showing that difficulty in methylation is not due to the degree of polymerisation, but to the disposition of the main valencies of the compounds.

The behaviour of lichenin and cellulose towards cold, concentrated

hydrochloric acid affords new evidence of the analogous chemical behaviour of the polysaccharides. Lichenin is converted by hydrochloric acid (37%) at the atmospheric temperature during 4 hrs. into a *biose A*,  $C_{12}H_{22}O_{11}$ ,  $[\alpha]_D^{20} +34.51^\circ$  or  $+36.35^\circ$  in water (*acetate*,  $C_{28}H_{38}O_{19}$ ,  $[\alpha]_D^{20} +43.5^\circ$  in chloroform), which is stable towards yeast maltase and emulsin, but partly converted into cellobiose by dialysed malt extract, whereas, after 4 days, a *biose B*,  $C_{12}H_{22}O_{11}$ ,  $[\alpha]_D^{20} +108.7^\circ$  or  $+112.0^\circ$  in water (*acetate*,  $C_{28}H_{38}O_{19}$ ,  $[\alpha]_D^{20} +114.6^\circ$  in chloroform), is produced. Cellulose is not affected by ordinary fuming hydrochloric acid, but after being treated with the acid ( $d\ 1.23$ ) at  $14^\circ$ , gives with 37% acid exclusively the *biose B* just described. If, however, the cellulose is obtained by precipitation from "cuprammonium" solution with hydrochloric acid, it is converted by short treatment with hydrochloric acid (37%) into *biose A* and by more prolonged treatment into *biose B*.

Depolymerisation of unprepared cellulose in glycerol does not appear to occur, whereas cuprammonium cellulose gives indefinite results; cellulose *A*, however, affords a non-reducing depolymeride, soluble in water.

H. W.

**Methylation of Polysaccharides.** L. SCHMID (*Ber.*, 1925, 58, [B], 1963—1965).—Cellulose does not react with diazomethane. Lichenin, inulin, and soluble starch scarcely react with diazomethane in anhydrous ether, but become methylated if water is added in small quantity. Starch yields two fractions, separable by alcohol, containing, respectively, 21.51% and 22.24% OMe; methylation proceeds therefore beyond the monomethyl stage, but more highly methylated derivatives cannot be obtained. Similarly, lichenin affords apparently a *monomethyl-lichenin* (17.37% OMe), insoluble in alcohol, and a soluble fraction containing 21.62% OMe. Inulin yields a product with 25.24% OMe equivalent to three methoxyl groups for two  $C_6H_{10}O_5$  residues. The methylated compounds do not reduce Fehling's solution.

H. W.

**Alkali Compounds of Carbohydrates.** L. SCHMID and B. BECKER (*Ber.*, 1925, 58, [B], 1966—1968).—Well-defined compounds in which one atom of alkali metal displaces an atom of hydrogen are obtained when sodium or potassium reacts with inulin, lichenin, soluble starch, mannitol, or  $\alpha$ -methylglucoside in the presence of liquid ammonia. Attempts to introduce more than one atom of alkali metal into the carbohydrate molecule yield ill-defined products which are very sensitive to air. Calcium does not appear to react with carbohydrates under these conditions.

H. W.

**Cryoscopic Determinations of Molecular Weight in Liquid Ammonia.** L. SCHMID and B. BECKER (*Ber.*, 1925, 58, [B], 1968—1971).—Determinations of the mol. wt. of inulin in freezing ammonia give for dilute solutions values in agreement with the composition,  $C_{12}H_{20}O_{10}$ ; in more concentrated solution, higher values are found, possibly due to the non-applicability of Raoult's laws at these concentrations. The constant for the solvent is deduced from determinations with mannitol and acetanilide, and does not



agree with that calculated theoretically. Starch is soluble in liquid ammonia only to a slight extent, and separates with the solid ammonia, so that its mol. wt. cannot be determined in this solvent.  
H. W.

**Depolymerisation of Cellulose.** E. HEUSER (*Z. Elektrochem.*, 1925, **31**, 498—502).—Determinations of the mol. wts. of the methyl derivatives of various forms of cellulose (containing 2.0 to 2.5 methoxyl groups per  $C_6H_{10}O_5$ ) in aqueous solution have been made by the cryoscopic method. The results vary from 6000 to 8000 with cotton wool, to 900 with cellulose dextrin I. The mol. wts. decrease with increasing hydration temperature, at which the methyl derivative is precipitated from aqueous solution on heating, and increase with increasing softening temperature. The results show that the alterations in the properties of cellulose brought about by various treatments are due to depolymerisation, and conversely that cellulose is a polymerised substance.

N. H. H.

**Sodium Hydroxide and Cellulose.** J. D'ANS and A. JÄGER (*Cellulosechem.*, 1925, **6**, 137—151).—The absolute values for sodium hydroxide absorbed per unit weight of cellulose are considerably higher at 2° than at 23°, although the two curves are of the same shape, and show flattenings between the same limits of concentration. Further, the solubility of the cellulose in the sodium hydroxide liquor may have a perceptible influence on the calculated values. Solubility increases with rise in concentration of sodium hydroxide up to a maximum point situated at about 12 g. per 100 c.c. at 23° and at 10.4 g. per 100 c.c. at 2°, the solubility at the lower temperature being always considerably greater. With further rise in concentration, the solubility rapidly falls, that at 2° sometimes even falling below that at 23°. The addition of salts to the sodium hydroxide has no effect on the absorption up to a concentration of about 12 g. of sodium hydroxide per 100 c.c.; above that concentration, the presence of sodium chloride or sodium carbonate increases the absorption values. Swelling or hydration of the cellulose is regarded as being proportional to the solubility. The hydration may be taken into account by a study of the ternary system: cellulose-sodium hydroxide-water, according to the principles of the phase rule, and the equilibria have been worked out diagrammatically on a triangular system of three co-ordinates. The influence of alcohol on this system has also been studied. [Cf *B.*, 1925, 984.]  
J. F. B.

**Lignin.** K. KÜRSCHNER (*Bernnstoff-Chem.*, 1925, **6**, 117—125, 158—162, 177—180, 188—194, 208, 304—311).—Lignin, as free from cellulose and with as little decomposition as possible, is obtained by the following modification of Willstätter's procedure: pine shavings, previously freed from resins and fats by extraction during several hours with a mixture of alcohol and benzene, are shaken for 15 mins. with ten times their weight of fuming hydrochloric acid ( $d$  1.222), then poured into excess of hot water, thoroughly

stirred, and at once diluted with a large excess of cold water. The lignin settles first, and the lighter and more finely dispersed cellulose precipitate is separated from it by decantation followed by filtration through muslin. The residue is extracted twice with fuming hydrochloric acid (10 mins.' shaking each time with 5 and then with  $2\frac{1}{2}$  times its weight of acid), and finally washed with water and dried. The product is free from cellulose. The lignin thus prepared is only very slightly soluble in boiling phenol, and in general is resistant to the action of solvents. It dissolves at once, however, in trichloroacetic acid, giving a violet-brown solution, from which it is reprecipitated by water in a form which is soluble in alkalis, acetone, etc. It dissolves with difficulty in hot sulphite solutions, but addition of cellulose greatly facilitates solution. It acts on a photographic plate in the dark more strongly than lignin prepared by other methods. The product still contains pentosans (about 8%) the greater part of which is shown probably to be combined chemically with the lignin.

An examination of the available experimental evidence throws doubt on the existence of acetyl groups in lignin. The acetic acid produced when lignin undergoes hydrolytic decomposition probably originates in the carbohydrate content of the lignin. This is confirmed by experiments on the amount of acetic acid produced when wood, cellulose, sugars, and lignin are treated with fuming hydrochloric acid. The reactions of lignin showing the presence in it of hydroxyl and methoxyl groups, of a double linkage, and of an aldehyde group are discussed. Lignin prepared by the author's method reduces ferric chloride and colours Schiff's reagent, but does not reduce Fehling's solution. From the frequent occurrence of vanillin in products obtained by the action of various reagents on wood, it is concluded that this substance plays an important part as an intermediate product in the transformations undergone by lignin.

The views of previous workers on the aromatic nature of lignin are critically discussed. The presence of benzene derivatives, *e.g.*, vanillin, pyrocatechol, etc., in the decomposition products of lignin is not necessarily a proof of the aromatic character of lignin itself.

At 200°, pine lignin, prepared by the author's method, gave about 60% of its weight as a sublimate of vanillic acid with some vanillin. Other samples of lignin and many related substances gave similar sublimates. The vanillic acid and vanillin are produced as a result of the oxidation of the lignin, for in an inert atmosphere neither is produced. The residue appears to be a decomposition product of dextrose, and further evidence is considered supporting the assumption that lignin possesses a glucosidic structure. At 200°, it splits into dextrose, or its decomposition products, and a substance yielding vanillin, or vanillic acid, on oxidation. It thus appears to be closely related to coniferin.

Lignin is regarded as a colloidal coniferin complex, with some free coniferin adsorbed on its surface. The elementary composition and methoxyl content of lignin isolated by the author's method

are in accord with this hypothesis when account is taken of the unavoidable hydrolysis which occurs during the treatment with fuming hydrochloric acid. So also is the yield of vanillic acid on sublimation at  $200^{\circ}$ , which agrees with that obtained from coniferin after treatment with acid. The hypothesis is further confirmed by a comparison of the action of various reagents, *e.g.*, trichloroacetic acid, sulphite solution, fused potassium hydroxide, etc., on lignin and coniferin, respectively; by the presence of sugars in lignin; and by the widespread occurrence of coniferin in lignified tissues and the presence of its decomposition products in the tar and liquor from wood distillation.

A. B. M.

**Properties and Constitution of Coal Ulmins. Composition of Coal.** W. FRANCIS and R. V. WHEELER (*J. Chem. Soc.*, 1925, 127, 2236—2245; cf. this vol., i, 372).—Bituminous coal consists essentially of a matrix of insoluble ulmins in which organised plant tissues are dispersed. Mild oxidation renders the ulmins soluble in alkalis without altering the internal arrangement of the molecules. The carboxyl groups produced by the oxidation enable insoluble salts of barium, iron, silver, and copper to be formed. From the last named, a value of 170 for the equivalent has been obtained, and the molecular unit is assumed to be 680, containing one hydroxyl group, one atom of nitrogen, and four carboxyl groups. Cautious oxidation with dilute nitric acid yields oxalic, succinic, picric, pyromellitic, and probably trimellitic acids, indicating that the nuclei of the ulmin molecules consist of compact systems of benzenoid groupings connected together by heterocyclic ring structures such as pyrrole and furan or their derivatives.

B. W. A.

**Methiodides of  $\alpha\gamma$ -Di-dimethylaminopropan- $\beta$ -ol.** J. CALLEN (U.S. Pat. 1526627).— $\alpha\gamma$ -Di-dimethylaminopropan- $\beta$ -ol and methyl iodide yield the *dimethiodide*, m. p.  $270-275^{\circ}$  (decomp.). Various iodine compounds of this type may be prepared from the corresponding chloride or bromide, or from  $\alpha\gamma$ -di-iodohydrin with trialkylamines.

CHEMICAL ABSTRACTS.

**Relation between Constitution and Taste of  $\alpha$ -Amino-acids. II. Relation between "Degree of Sweetness" and Concentration of Aqueous Solutions of Amino-acids.** A. HEIDUSCHKA and E. KOMM (*Z. angew. Chem.*, 1925, 38, 941—945; cf. *B.*, 1925, 374).—The "degree of sweetness" and "molecular degree of sweetness" of aqueous glycine and *dl*-alanine diminish with increasing concentration, and the sweet taste increases much less rapidly than the concentration. Graphs connecting "degree of sweetness" with concentration for glycine and *dl*-alanine, are most nearly parallel between concentrations of 5% and 7.5%, so that comparisons are best made with 5—10% solutions.

W. T. K. B.

**Optical Activity of Cystine. Oxidation of Cystine.** J. C. ANDREWS (*J. Biol. Chem.*, 1925, 65, 147—159, 161—164).—Determinations were made of the specific rotation of cystine in presence

of various acids and in different dilutions; at concentrations below 0.2% of cystine, the rotation is determined by the  $p_H$ ; at higher concentrations, the different acid ions show specific effects. The effect of dilution with water of a solution of cystine in a given acid on the rotation indicates an increased dissociation of the acid salt of cystine with dilution; no such evidence of electrolytic dissociation was obtained in the case of cystine picrate. It is suggested that the specific effects of the various ions are due to their different degrees of hydration, which influence the internal pressure of the solution and hence the shape of the cystine molecule. In 1% solution in *N*-hydrochloric acid, cystine has  $[\alpha]_D^{20} -215.5^\circ$ , the temperature coefficient between  $20^\circ$  and  $29^\circ$  being  $-1.7^\circ [\alpha]_D$  per  $1^\circ$ .

The change in the optical rotation of cystine in strongly alkaline solution is as rapid in an atmosphere of nitrogen as in one of oxygen; further, alkaline solutions of sodium sulphide show a similar rate of absorption of oxygen to solutions of cystine in alkali; these results indicate that the oxidation of cystine in alkaline solution by atmospheric oxygen (cf. Mathews and Walker, A., 1909, i, 698) is in reality an absorption of oxygen by the alkaline sulphide formed from the cystine.

C. R. H.

### Taurine. I. Methylation and Acetylation of Taurine.

M. TERAOKA (*Z. physiol. Chem.*, 1925, **145**, 238—243).—Taurine can be methylated by boiling with ammonium iodide in the presence of sodium carbonate and magnesium oxide, a complex salt containing 2 mols. of dimethyltaurine, 1 mol. of ammonium iodide, and 5 mols. of water being formed. The free base, m. p.  $315\text{--}316^\circ$ , is obtained by removing the ammonium iodide with silver oxide, or by recrystallising from hot methyl alcohol. Similarly, the sodium salt of acetyltaurine, m. p.  $233\text{--}234^\circ$ , is obtained by the action of acetic anhydride on taurine, in the presence of alcoholic sodium hydroxide.

H. P. M.

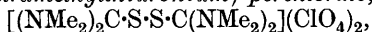
### Constitution of Thiocarbamide and of Thiuronium Salts.

II. H. LECHER [with F. GRAF, C. HEUCK, K. KOBERLE, F. GNADINGER, and F. HEYDWEILLER] (*Annalen*, 1925, **445**, 35—61; cf. Lecher and Heuck, A., 1924, i, 1051).—That the acid hydrogen in salts of thiocarbamides is attached to the sulphur atom (*loc. cit.*) is further proved by the formation of a disulphide when *s*-tetramethylthiocarbamide is treated with bromine in acetic acid. According to the position of the positive charge in the thiuronium ion, the salts may be of the sulphonium, carbonium, or immonium type:  $(NR_2)_2C^+SR$ ,  $(NR_2)_2\overset{+}{C}SR$ , or  $(NR_2)(SR)\cdot C^+NR_2$ . A reinvestigation of Taylor's supposed ammonium-sulphonium isomerism in the case of *S*-benzyl- $\psi$ -thiocarbamide salts (T., 1917, **111**, 650; 1920, **117**, 6; Lecher and Heuck, *loc. cit.*) shows that it is non-existent; such an isomerism, on Lecher's views, could only be of the type of valency-isomerism. The ready formation of a methiodide from tetramethylthiocarbamide, but not from dithiourethanes and trithiocarbonic esters, is opposed to the carbonium theory. In the series guanidines— $\psi$ -thiocarbamides—formimidodithioethers

$[(RS)_2C:NR]$ , the basicity decreases as the number of sulphur atoms increases, which is opposed to the sulphonium theory. The carbonium salts should exhibit optical isomerism; no separation into enantiomorphs could be observed when the bromocamphor-sulphonate of *N*-phenyl-*N'*:*N'*:*S*-trimethyl-*N*-ethylthiuronium was fractionated, but this is not conclusive evidence. The immonium theory implies geometrical isomerism in certain cases; no instance of this was observed, and the immonium constitution must be regarded as disproved.

Thus the carbonium and sulphonium theories are shown to be improbable and the static immonium theory is disproved. It becomes probable, therefore, that the basic function is shared between the two nitrogen atoms. The ionic charge may be regarded as divided between them or as alternating from one to the other, the latter view being favoured as more in accordance with the strong basicity exhibited. A similar suggestion is applied to the nitrogen of amidine bases and the oxygen of carboxylic acids. The oscillation occurs only in the ionised molecule, the usual structures being adopted for undissociated molecules.

*Dehydrobis(N-tetramethylthiuronium) perchlorate,*



results when a solution of bromine in acetic acid is added to a solution of *N*-tetramethylthiocarbamide and perchloric acid in acetic acid. Trimethylamine and dimethylthiocarbamyl chloride do not react to give the expected tetramethylthiocarbamide methochloride, both substances being recovered unchanged. Ethyl methylamino- and dimethylamino-dithioformates were prepared by Delépine's method (A., 1902, i, 702); the former has m. p. 30—32°, b. p. 103—104°/3 mm. Methyl trithiocarbonate does not give an additive compound with methyl iodide. *Carbodimethyldi-imide*,  $C(NMe)_2$ , prepared by oxidation of *s*-dimethylthiocarbamide with mercuric oxide, polymerises when distillation in a vacuum is attempted. Its ethereal solution gives a *picrate*,  $(NO_2)_3C_6H_2 \cdot NMe \cdot CO \cdot NHMe$ , m. p. 169° (decomp.). *Carbodi-n-propyldi-imide* (Chancel, A., 1893, i, 297), b. p. 53°/10 mm., dissolves in dilute hydrochloric acid and in part may be recovered unchanged if the solution is made alkaline immediately. It does not form a methiodide, but gives a *semi-picrate*, m. p. 166—169° (decomp.), which by treatment with concentrated hydrochloric acid is converted into *N-picryldi-n-propylcarbamide*, m. p. 176—177°.  $\alpha\alpha'$ -*Dimethyl-ββ'-diethylthiocarbamide*, b. p. 124—125°/12 mm., is obtained in 50% yield by the action of thiocarbonyl chloride on methylethylamine in light petroleum at 100° in sealed tubes. *N-Phenyl-N':S-dimethyl-N-ethyl-ψ-thiocarbamide*, b. p. 118—120°, is prepared by methylation of phenylmethylethylthiocarbamide with methyl sulphate. Its *methiodide*, the corresponding *picrate*, m. p. 87—88°, and *d-α-bromocamphor-π-sulphonate* ( $[\alpha]_D^{20} + 3.78^\circ$ ,  $l=2$ ) are described. *N:N':S-Trimethyl-N:N'-diethylthiuronium iodide*, m. p. 80.5—83° (*picrate*, m. p. 52.5—53.5°), is prepared by methylation either of *N:S-dimethyl-N:N'-diethyl-ψ-thiocarbamide*, or of *N:N'-dimethyl-N:N'-diethylthiocarbamide*. *S-Benzylthiuronium chloride*,

$[\text{CH}_2\text{Ph}\cdot\text{S}\cdot\text{C}(\text{NH}_2)_2]\text{Cl}$ , from thiocarbamide and benzyl chloride, is dimorphous; it separates usually in the stable form, m. p. 172.5—174°; the metastable form has m. p. 146—148°. The hydrogen sulphate, m. p. 146—147.5°, and sulphate, m. p. 184—188° (decomp.), are described. C. H.

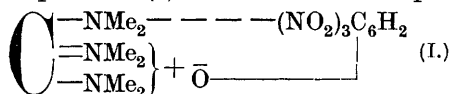
### Constitution of Thiocarbamide and of Thiuronium Salts.

III. H. LECHER and F. HEYDWEILLER (*Annalen*, 1925, **445**, 77—82; cf. preceding abstract).—If Werner's structure (T., 1912, **101**, 2185) for thiocarbamides is correct, a third isomeride,  $\text{NMe}\cdot\text{C} < \begin{smallmatrix} \text{NMe}_3 \\ \text{S} \end{smallmatrix}$ , of tetramethylthiocarbamide should be obtainable

by the action of trimethylamine on methylthiocarbamide. This has not been observed. At the ordinary temperature no reaction occurs, and at 100—110° the only product is a little tetramethylammonium thiocyanate. This substance is formed in larger amount from trimethylamine and methyl thiocyanate, and thus confirms the thiocyanate rather than the thiocarbimide structure for the latter.

The formula,  $+\begin{Bmatrix} \text{NR}_2 \\ \text{NR}_2 \end{Bmatrix} > \text{C}\cdot\text{S}^-$ , of Lecher and Heuck (A., 1924, i, 1051) is brought into line with the fact that many of the *N*-alkylated thiocarbamides do not show the physical properties of internal salts, by assuming an equilibrium between the amphoteric ionic form and the thiocarbamide form,  $\frac{\text{NR}_2}{\text{NR}_2} > \text{C}\cdot\text{S}$ . C. H.

**Peralkylated Guanidines.** III. H. LECHER and F. GRAF [in part with F. GNÄDINGER] (*Annalen*, 1925, **445**, 61—77; cf. A., 1924, i, 1081, and preceding abstracts).—The dynamic formula suggested for thiuronium salts is applied to the guanidinium ion. The positive charge oscillates amongst the three nitrogen atoms, only two of which are thus at any instant basic in character, the third being unconcerned in the oscillation. It is to this third nitrogen atom that hexamethylguanidinium picrate owes its capacity for combining with a second molecule of picric acid, with sodium picrate, and with trinitrobenzene, through the secondary valencies of the nitro group; indeed the monopicrate has probably the nature of an internal complex salt (I). In the search for possible valency



isomerides amongst guanidinium salts, it is found that whilst hexamethyl- and pentamethylethyl-guanidinium picrates etc. are single individuals, trimethyltriethylguanidinium picrate and chloroplatinate are apparently mixtures of isomerides.

The preparation of methylethylamine and its reactions with methyl- and ethyl-thiocarbimides are described. Methylation of *s*-dimethylthiocarbamide with methyl sulphate gives *N* : *N'* : *S*-trimethyl-*ψ*-thiocarbamide, m. p. 53.5—54.5°, b. p. 90°/14 mm. *N* : *N'* : *S*-Trimethyl-*N*-ethyl-*ψ*-thiocarbamide, b. p. 79—80°/18 mm.

(corr.), is obtained by methylation of dimethylethylthiocarbamide; methyldiethylthiocarbamide similarly gives  $N : \bar{S}$ -dimethyl- $N : N'$ -diethyl- $\psi$ -thiocarbamide, b. p.  $80^\circ$  (corr.)/13 mm. The following penta-alkylguanidines are described:  $N : N' : N'' : N'''$ -tetramethyl- $N$ -ethyl-, b. p.  $61.5$ – $63^\circ$  (corr.)/13 mm.;  $N : N : N'$ -trimethyl- $N'' : N''$ -diethyl-, b. p.  $71$ – $72^\circ$ /15 mm.;  $N : N'' : N'$ -trimethyl- $N : N'$ -diethyl-, b. p.  $68$ – $69^\circ$  (corr.)/12 mm.;  $N : N'$ -dimethyl- $N : N'' : N'''$ -triethyl-, b. p.  $80$ – $81^\circ$  (corr.)/19 mm.

Hexamethylguanidinium picrate, m. p.  $120$ – $121^\circ$ , forms molecular compounds with picric acid, m. p.  $68.5$ – $71.5^\circ$ ; with sodium picrate, m. p.  $165$ – $166.5^\circ$ , and with 1 : 3 : 5-trinitrobenzene, m. p.  $73.5$ – $75^\circ$ . The chloroplatinate has m. p.  $181.5$ – $182^\circ$  (corr., decomp.). An attempt to prepare hexamethylguanidinium ethoxide from the chloride and sodium ethoxide was unsuccessful.

Pentamethylethylguanidinium tri-iodide, m. p.  $58$ – $59.5^\circ$ , from the iodide (*loc. cit.*) and iodine in methyl alcohol, and picrate, m. p.  $96$ – $99^\circ$  (corr.), are described.  $N : N : N'$ -Trimethyl- $N' : N'' : N'''$ -triethylguanidinium iodide, decomp. without melting above  $230^\circ$ , is prepared by the action of ethyl iodide on  $N : N : N'$ -trimethyl- $N'' : N''$ -diethylguanidine or  $N : N'' : N'$ -trimethyl- $N : N'$ -diethylguanidine, or of methyl iodide on  $N : N'$ -dimethyl- $N : N'' : N'''$ -triethylguanidine. The tri-iodide, m. p.  $50$ – $54^\circ$ , is not separated into isomerides by fractional crystallisation, but the picrate is at first oily, and a pure product, m. p.  $41.5$ – $44.5^\circ$ , is obtained only with difficulty. The chloroplatinate, m. p.  $186.5$ – $188.5^\circ$  (corr.), shows similar signs of being a mixture of isomerides. C. H.

**Action of Phenylcarbimide on Methylcarbamide.** H. BILTZ and A. BECK (*Ber.*, 1925, **58**, [B], 2187–2190).—Re-examination of the action between phenylcarbimide and methylcarbamide (Biltz and Jeltsch, A., 1923, i, 1074) has shown the product of the change to be a mixture of  $\omega$ -phenyl- $\omega$ -methylbiuret, m. p.  $133^\circ$  (cf. Gatewood, this vol., i, 805), and  $\omega$ -phenyl-*ms*-methylbiuret,  $\text{NHPh}\cdot\text{CO}\cdot\text{NMe}\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $183^\circ$ ; addition of the phenylcarbimide occurs mainly at the free amino group of methylcarbamide, to a minor extent at the substituted amino group. Nitrous acid converts  $\omega$ -phenyl- $\omega$ -methylbiuret into  $\omega$ -nitroso- $\omega'$ -phenyl- $\omega$ -methylbiuret, decomp.  $126^\circ$ , whereas it is without action on  $\omega$ -phenyl-*ms*-methylbiuret. Methylcarbimide and phenylcarbamide react in a complex manner, as do phenylcarbimide and ethylcarbamide. H. W.

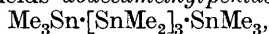
**Decomposition of Liquid Hydrocyanic Acid.** M. WALKER and D. N. ELDERED (*Ind. Eng. Chem.*, 1925, **17**, 1074–1081).—Commercially pure liquid hydrogen cyanide maintained at 50–200 lb. pressure by heating in a bomb, after a period of 40–160 hrs. decomposes with explosive violence, yielding a solid polymeride containing an excess of carbon, and ammonia and other gases. Decomposition is hastened by the presence of hydroxyl ions. Accidental explosions of this substance stored in closed containers are due to the same reaction proceeding under conditions such that

the heat developed gradually is not dissipated by radiation. [Cf. *B.*, 1925, 917.] C. I.

**Labile Prussic Acid (isoHydrocyanic Acid).** C. J. ENKLAAR (*Rec. trav. chim.*, 1925, **44**, 889—890; cf. *A.*, 1923, ii, 811).—By means of the base mercuric methyl hydroxide,  $\text{MeHg}\cdot\text{OH}$ , the existence of two isomerides of hydrocyanic acid has been demonstrated. The base (m. p.  $95.5\text{--}97^\circ$ ) reacts with ordinary hydrocyanic acid (from potassium cyanide and dilute acid) to give *mercuric methyl cyanide*, m. p.  $90^\circ$ , which yields the same hydrocyanic acid when heated with stearic acid. Mercuric methyl iodide is converted by silver cyanide in alcoholic solution into *mercuric methylcarbylamine*, m. p.  $60^\circ$ , which yields when heated with stearic acid an *isohydrocyanic acid*, since this reacts with mercuric methyl hydroxide to regenerate the cyanide of m. p.  $60^\circ$ . The cyanide of m. p.  $90^\circ$  is slowly converted on keeping at  $6^\circ$  into its isomeride of lower m. p. The new form of hydrocyanic acid is also obtained by the action of hydrogen sulphide on silver cyanide, or, better, a solution of silver cyanide in potassium cyanide, on mercuric cyanide and on palladium cyanide. Cadmium and lead cyanides, on the other hand, yield with hydrogen sulphide only ordinary hydrocyanic acid. The isomeric form also results when sodium ferrocyanide is decomposed by the gradual addition of sulphuric acid.

G. M. B.

**Tin Dimethyl Group and Some of its Reactions.** C. A. KRAUS and W. N. GREER (*J. Amer. Chem. Soc.*, 1925, **47**, 2568—2575).—A number of derivatives of the tin dimethyl radical have been prepared and the great tendency of the tin atoms to form chains has been demonstrated. The reactions are carried out in liquid ammonia solution. Tin dimethyl dibromide (prepared by the bromination of tin trimethyl bromide, cf. Kraus and Sessions, this vol., i, 1253), on treatment with 1 atom of sodium for each atom of bromine, yields a *polymeride* of the tin dimethyl radical, another *polymeride* being obtained by the action of tin dimethyl dibromide on disodium dimethyl stannide (below). Both are yellow solids and oxidise readily, the latter being spontaneously inflammable. When three atomic equivalents of sodium have been added to the tin dimethyl dibromide, *disodium tetramethyldistannane*,  $(\text{NaSnMe}_2)_2$ , is formed, whilst further addition up to four equivalents of sodium yields *disodium dimethylstannane*. On treatment of 2 mols. of the latter with 1 mol. of tin dimethyl dibromide, *disodium hexamethyltristannane* is produced. This on treatment with ethyl bromide yields *hexamethyldiethyltristannane*, and with tin trimethyl bromide yields *dodecamethylpentastannane*,



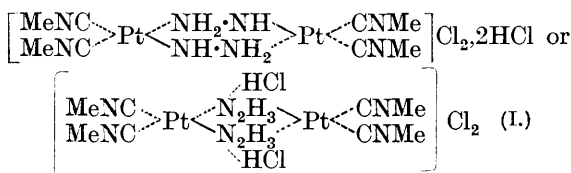
both compounds being difficultly volatile liquids which oxidise in the atmosphere. On treatment of disodium dimethylstannane with methylene chloride, the reaction  $2\text{Na}_2\text{SnMe}_2 + \text{CH}_2\text{Cl}_2 = 2\text{NaCl} + (\text{NaSnMe}_2)_2\text{CH}_2$  probably first occurs, whilst further addition of methylene chloride yields *dimethylmethylenestannane*,  $\text{Me}_2\text{Sn}\cdot\text{CH}_2$ , which oxidises slowly in air, is reactive towards halogens, and with



hydrochloric acid yields tin trimethyl chloride and tin dimethyl dichloride. Its properties undergo change with time, probably due to polymerisation, the mol. wt. in benzene indicating a high but varying degree of polymerisation. J. W. B.

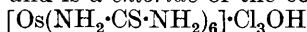
**Antimonial Analogues of the Cacodyl Series.** G. T. MORGAN and G. R. DAVIES (*Nature*, 1925, **116**, 499).—The thermal decomposition:  $\text{SbMe}_3\text{X}_2 = \text{SbMe}_2\text{X} + \text{MeX}$  yields dimethylstibine chloride, bromide, and iodide; dimethylstibine oxide and cyanide have also been prepared. Further demethylation yields a series of compounds containing only one methyl group. A. A. E.

**Hydrazine Carbylamine Complexes of Platinum.** L. TSCHUGAEV, M. SKANAVY-GRIGORJEVA, and A. POSNJAK (*Z. anorg. Chem.*, 1925, **148**, 37—42).—The complex compounds of methyl- and ethyl-carbylamine with platinum and hydrazine are of interest because, although they contain two nuclei, they are comparatively stable. They are compounds of bivalent platinum, having a co-ordination number of six, and the hydrazine molecule occupies only one co-ordination position. By the action of methyl-carbylamine and hydrazine hydrate on potassium chloroplatinate, a red *complex chloride*,  $[(\text{MeNC})_4\text{Pt} \cdot [\text{N}_2\text{H}_3]_2 \cdot \text{Pt} \cdot (\text{CNMe})_4]\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ , is obtained. The corresponding *perchlorate*, *iodide*, and *azide* were also prepared. When the red chloride is treated with concentrated



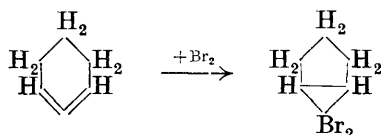
hydrochloric acid a portion of the methylcarbylamine is lost and a yellow *chloride* (I) is obtained. From ethylcarbylamine, the *nitrate*, *chloride*, *iodide*, *perchlorate*, and *chloroplatinite* of the red series were prepared, and the *chloride* of the yellow series. A. G.

**Complex Base of Osmium.** L. TSCHUGAEV [with E. FRITZ-MANN] (*Z. anorg. Chem.*, 1925, **148**, 65—68).—When sodium chlorosmate is boiled with thiocarbamide in the presence of a little hydrochloric acid, an intense red colour is produced; this may be used as a test for osmium and is sensitive to 1 part of osmium in 100,000 parts of water. By cooling and adding concentrated hydrochloric acid and solid lithium chloride, a mixture of two crystalline substances is precipitated. The principal constituent is soluble in alcohol and is a *chloride* of the constitution



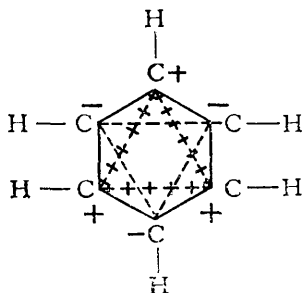
or  $[(\text{NH}_2 \cdot \text{CS} \cdot \text{NH}_2)_6\text{Os} \overset{\text{OH}}{\underset{\text{OH}}{\text{O}}} \text{Os}(\text{NH}_2 \cdot \text{CS} \cdot \text{NH}_2)_6]\text{Cl}_6$ . The freezing-point depression of water and the electrical conductivity correspond with four ions per atom of osmium. A. G.

**Structure of the Dihydrobenzenes and Some Related Compounds.** C. W. A. LELY (*Chem. Weekblad*, 1925, **22**, 501—507).—On the assumption of synchronous rotation advanced for aromatic compounds, the three isomeric dibromocyclohexanes should each be capable of existence in *cis* and *trans* forms. Consideration of all possible ways of removing hydrogen bromide indicates that three isomeric dihydrobenzenes ( $\Delta^{1,2}$ ,  $\Delta^{1,3}$ , and  $\Delta^{1,4}$ ) should exist; earlier results are discussed from this point of view, and present theory is shown to be inconsistent.  $\Delta^{1,2}$ -cyclo-Hexadiene gives by addition of bromine the well-known dibromide, m. p.  $108^\circ$ ; the others give tetrabromides, one of which is solid and the other liquid (Markovnikov, *Annalen*, 1898, **302**, 30, 31; Baeyer, *ibid.*, 1893, **278**, 96, etc.). The properties of the dibromide, particularly its resistance to further addition, are explained by the triangular formula:



The different properties of the two pairs of hydrogen atoms in benzoquinone, and of the two pairs of chlorine atoms in tetrachlorobenzoquinone are similarly quoted in support of the triangular formula. S. I. L.

**Constitution of Benzene and Substitution Processes in the Benzene Nucleus.** M. GIUA and R. PETRONIO (*J. pr. Chem.*, 1925, [ii], **110**, 289—308).—The lability of certain *ortho*- and *para*-substituents in polysubstituted benzene derivatives is discussed in relation to the benzene nucleus. The



observed phenomena are in accordance with the annexed representation of benzene, in which the difference between the 1:4- and 1:3-positions is accentuated, and on which basis the lability of *ortho*- and *para*-substituents can be ascribed to the disarrangement of the symmetrical valency system. Graphical representations of typical derivatives containing labile groups are appended, for details of which the original should be consulted.

1-Chloro-2:4-dinitrobenzene reacts with cyanamide in aqueous-alcoholic solution, with formation of 2:4-dinitrophenylcyanamide, yellow, m. p.  $168-169^\circ$ . This yields a reddish-violet solution in fuming nitric acid, the colour changing to yellowish-red on keeping, when the solution deposits, on dilution,  $\beta$ -nitro- $\alpha$ -(2:4-dinitrophenyl)-carbamide (cf. Reudler, A., 1914, i, 521), m. p.  $146-147^\circ$  (decomp.). Alcoholic hydrogen chloride converts 2:4-dinitrophenylcyanamide into dinitrophenylcarbamide, m. p.  $178^\circ$  (cf.

Reudler, *loc. cit.*).  $\gamma$ -Trinitrotoluene reacts similarly with cyanamide, with formation of 4:6-dinitro-*m*-tolylcyanamide, golden-yellow, m. p. 161—162°, which can be converted as above into 4:6-dinitro-*m*-tolylcarbamide, pale yellow, m. p. 205—206° (decomp.), and  $\beta$ -nitro- $\alpha$ -(4:6-dinitro-*m*-tolyl)-carbamide, flesh-coloured, m. p. 168—169° (decomp.). The action of cyanamide on  $\beta$ -trinitrotoluene affords a yellow substance, decomp. about 300°, which, when heated with concentrated hydrochloric acid, yields 2:4-dinitro-*m*-tolylcarbamide, pale yellow, m. p. 224—225°, with brown coloration.

Picrylsemicarbazide, yellow, m. p. 218—219° (decomp.), and picrylsemioxamazine, yellow, m. p. 249—250° (decomp.), are obtained by the action of picryl chloride on semicarbazide and semioxamazine, respectively, in alcoholic solution (cf. Giua, A., 1924, i, 338). When  $\beta$ -trinitrotoluene is warmed with benzylideneethylamine in alcoholic solution, 2:4-dinitroethyl-*m*-toluidine, yellow, m. p. 68—69°, is obtained (cf. Giua, A., 1923, i, 455).  $\gamma$ -Trinitrotoluene affords similarly 4:6-dinitroethyl-*m*-toluidine, yellow, m. p. 125—126°; trinitro-*p*-xylene yields in the same way 3:5-dinitroethyl-*p*-xylidine, m. p. 132—133° (cf. Blanksma, A., 1905, i, 425), whilst 2:3:5-trinitro-*p*-toluic acid gives 3:5-dinitro-2-ethylamino-*p*-toluic acid, pale yellow, m. p. 190—191°. The following compounds, obtained analogously from  $\beta$ - and  $\gamma$ -trinitrotoluenes and benzylidenealkylamines, are described: 2:4-dinitro-*n*-propyl-*m*-toluidine, pale yellow, m. p. 64—65°; 4:6-dinitro-*n*-propyl-*m*-toluidine, yellow, m. p. 106—107°; and 4:6-dinitro-isoamyl-*m*-toluidine, yellow, m. p. 87—88°. 4:6-Dinitromethyl-*m*-toluidine has m. p. 172—173°, not 165°, as previously reported (A., 1923, i, 455).

F. G. W.

**Nitro Compounds with Special Reference to the Nitration of *m*-Chloronitrobenzene and *p*-Chlorotoluene.** H. H. HODGSON (*J. Soc. Dyers and Col.*, 1925, **41**, 327—329).—The reaction conditions for the formation of *p*-chloro-*o*- and -*m*-nitrotoluene from *p*-chlorotoluene have been examined with a view to the production of a predominance of either one of the isomerides. The results of Holleman (A., 1909, i, 18) on the nitration of *p*-chlorotoluene at 0° are not in agreement with Fry's theory ("The Electronic Conception of Valence"), nor are the expectations of this theory satisfied when *m*-chloronitrobenzene is nitrated. Instead of a mixture of chloro-3:5- and -3:4-dinitrobenzenes, only the latter was obtained on nitrating *m*-chloronitrobenzene under the conditions employed in nitrating nitrobenzene to obtain *m*-dinitrobenzene. This on treatment with potassium hydroxide should yield *p*-chloro-*o*-nitrophenol according to Fry's theory, whilst *m*-chloro-*o*-nitrophenol is the product actually obtained. *p*-Chlorotoluene was obtained from *p*-toluidine in 88—89% yield. Attention is directed to the contrast of this result with that of Wynne (T., 1892, **61**, 1072) for *o*-chlorotoluene. *p*-Chloro-*o*- and -*m*-nitrotoluenes, similarly prepared from the corresponding nitrotoluidines, even after repeated purifications, could not be obtained in the purity

described by Holleman. The *o*-nitro compound had m. p. 37° (Holleman, 38.2°), the *m*-nitro had setting point 4° (Holleman, 5.8°). On reduction with sodium trisulphide (cf. this vol., 532, 1104), the *o*-nitro compound gives *p*-chloro-*o*-toluidine quantitatively, whilst the *m*-nitro isomeride gives *p*-thiol-*m*-toluidine. Holleman's method of nitration of *p*-chlorotoluene at 0° was repeated and his results were confirmed. The addition of concentrated sulphuric acid to the reaction medium favours the formation of the *o*-nitro isomeride; with 10% excess of nitric acid and five times the weight of sulphuric acid (on the *p*-chlorotoluene), a product was obtained, setting point 14°, which contained 64—65% of *p*-chloro-*o*-nitrotoluene (Holleman, 58%). In presence of acetic anhydride and phosphorus pentoxide, the proportion of *m*-nitro compound is raised from 42% to 50%.  
A. C.

**Dissociation Constants of Organic Complexes.** H. LEY and R. GRAU.—(See ii, 1159.)

**"Fluorenone Hydrate."** R. KUHN and A. WASSERMANN (*Ber.*, 1925, 58, [B], 2230—2231).—The compound described by Schmidt and Mezger (*A.*, 1907, i, 43) as 9 : 9'-dihydroxyfluorene (prepared by the action of concentrated hydrochloric acid on  $\alpha$ -9-acetoxyfluorene) is identified as 9-chlorofluorene, m. p. 91.5°.  $\alpha$ -9-Acetoxyfluorene is most conveniently prepared by the action of acetic anhydride on 9-hydroxyfluorene dissolved in pyridine.

H. W.

**Mechanism of Substitution Reactions in the Aromatic Nucleus.** V. E. DE B. BARNETT, J. W. COOK, and M. A. MATTHEWS (*Rec. trav. chim.*, 1925, 44, 894—899; cf. this vol., i, 648, 900).—The behaviour of 1 : 5 : 9-trichloroanthracene dichloride,  $C_6H_3Cl \begin{smallmatrix} CCl_2 \\ \diagup \quad \diagdown \\ CHCl \end{smallmatrix} C_6H_3Cl$ , m. p. 162°, with a number of reagents, chiefly bases, is described. With water, alcohol, sodium acetate, diethylamine, and piperidine a *meso*-substituted anthrone derivative of the type  $C_6H_3Cl \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CHX \end{smallmatrix} C_6H_3Cl$  results, where X is a group introduced in place of the chlorine atom, whilst aniline and mono- or di-methylaniline causes the re-establishment of the bridge linking, the products being of the type  $C_6H_3Cl \begin{smallmatrix} CX \\ \diagup \quad \diagdown \\ CX \end{smallmatrix} C_6H_3Cl$ .

1 : 5 : 9 : 10-Tetrachloroanthracene, m. p. 195°, obtained by the action of alcoholic potassium hydroxide on 1 : 5 : 9-trichloroanthracene dichloride, is oxidised by chromic acid to 1 : 5-dichloroanthraquinone. This tetrachloroanthracene is also produced by the action of tripropylamine on the dichloride. 1 : 5 : 9-Trichloroanthracene dichloride is converted by boiling in acetone solution with water and calcium carbonate into 1 : 5 : 9-trichloroanthrone and 1 : 5-dichloro-9-hydroxyanthrone, the latter being the main product if the reaction is prolonged. Anhydrous sodium acetate in glacial acetic acid furnishes 1 : 5-dichloroanthronyl acetate, and boiling absolute alcohol gives 1 : 5-dichloroanthronyl ethyl ether,

m. p. 159°, converted by hydrogen chloride in alcoholic solution into 1 : 5 : 9-trichloroanthrone. 1 : 5-Dichloro-9-diethylaminoanthrone, m. p. 194°, results from the action of diethylamine on the dichloride in benzene solution, and 1 : 5-dichloro-9-piperidinoanthrone, m. p. 239°, by a similar reaction using piperidine, a small amount of 1 : 5 : 9 : 10-tetrachloroanthracene being also formed in each case. 1 : 5-Dichloro-9 : 10-dianilinoanthracene, m. p. 254°, 1 : 5-dichloro-9 : 10-dimethyldianilinoanthracene, not melted at 310°, and 1 : 5-dichloro-9 : 10-tetramethyldianilinoanthracene, not melted at 300°, are produced by the action at 100° of aniline, methylaniline, and dimethylaniline, respectively. The dichloride reacts with pyridine to yield 1 : 5 : 9-trichloroanthranilpyridinium chloride, yellow needles (*picrate*, m. p. 253°).

1 : 5 : 9-Trichloroanthracene with bromine in carbon tetrachloride solution yields either 1 : 5 : 9-trichloro-9-bromoanthracene, m. p. 224°, or 1 : 5-dichloro-9-bromoanthrone. G. M. B.

**Directive Influence of Substituents in the Benzene Ring.**  
**IV. Partial Bromination of Derivatives of Aniline.** A. W. FRANCIS (*J. Amer. Chem. Soc.*, 1925, **47**, 2588—2596).—In continuation of previous investigations (cf. Francis, Hill, and Johnston, this vol., i, 1141, 1261), the partial bromination curves (yields of highest brominated product plotted against the relative amounts of bromine solution added) of forty-two derivatives of aniline have been obtained. The mathematical analyses of the curves for *meta* and *para* derivatives of aniline previously given (*loc. cit.*) are summarised, and the more complicated curve for *ortho* derivatives is worked out. Except for the nitroanilines, the same curve is obtained for all *m*-amino compounds (in which three atoms of bromine are substituted) as for aniline itself. Similarly, a second curve is obtained for all *o*-substituted compounds, and another for all *p*-substituted compounds (in which only two atoms of bromine are substituted), irrespective of the *m*- or *o* : *p*-directing influence of the substituent, indicating that although the substituent may greatly affect the absolute velocity of bromination, it affects the rate in each position to the same extent, the ratios remaining unchanged; hence the directive influence must be distributed symmetrically around the ring. The curve for the *m*-diamines is a straight line indicating simultaneous substitution of all the bromine. In the case of the nitroanilines, the last bromination is much slower than the preceding ones. The stepwise curve obtained for these compounds is more characteristic of phenolic compounds than of amines. The three nitrophenols, on the other hand, have curves of the characteristic amine type, the nitro group apparently reversing certain properties of the amino and hydroxyl groups.

J. W. B.

**Velocity of Benzylation of certain Amines.** II. D. H. PEACOCK (*J. Chem. Soc.*, 1925, **127**, 2177—2180; cf. A., 1924, i, 1297; Preston and Jones, T., 1912, **101**, 1931).—The benzylation of various bases takes place more quickly with *m*-nitrobenzyl

chloride than with *p*-nitrobenzyl chloride, which has a lower energy of activation. With benzyl chloride, *m*-nitroaniline reacts faster than *p*-nitroaniline, and *p*-toluidine faster than *m*-toluidine. These results agree with the alternate polarity hypothesis. The effect of concentration on the velocity coefficient and energy of activation depends on the character of the base employed; with dimethylamine, the value of  $k_1$  is lowered when the concentration is increased. It is suggested that the formation of a loose molecular complex between the base and the halogen compound precedes activation; this would explain why the nitrobenzyl chlorides are less reactive than benzyl chloride. B. W. A.

**Nitration of Phthal- and Succin-*p*-tolil.** O. 'L. BRADY, W. G. E. QUICK, and W. F. WELLING (*J. Chem. Soc.*, 1925, **127**, 2264—2267).—The nitration of succinyl-, phthalyl-, 3-nitrophthalyl-, and tetrachlorophthalyl-anilide with fuming nitric acid yielded chiefly *p*-nitroaniline; the corresponding derivatives of *p*-toluidine gave 76—84% of 2-nitro-*p*-toluidine, the influence of the acyl group enabling the methyl group to take control. B. W. A.

**Imino-aryl Ethers. III. Molecular Rearrangement of *N*-Phenylbenzimidio Phenyl Ether.** A. W. CHAPMAN (*J. Chem. Soc.*, 1925, **127**, 1992—1998).—On heating *N*-phenylbenzimidio phenyl ether [prepared similarly to *N*-phenylbenzimidio *m*-hydroxyphenyl ether (T., 1922, **121**, 1679)] at 240° for 1 hr., only unchanged material is recovered (cf. Mumm, Hesse, and Volquartz, A., 1915, i, 244), but 2 hrs.' heating at 270—300° effects complete transformation into benzyldiphenylamine, without production of by-products. By means of the freezing-point curve of mixtures of the two components, the progress of the transformation is followed, and is found to agree with that required by the unimolecular formula;  $k \times 10^3$  at 262° = 5.5. The velocity coefficients at different temperatures are recorded, and the mean temperature coefficient. *N*-Phenylbenzimidio *o*-chlorophenyl ether, m. p. 88°, is similarly converted into benzoyl-*o*-chlorodiphenylamine, m. p. 95—96°, which is also prepared by benzylation of *o*-chlorodiphenylamine, b. p. 300—303°/753 mm., obtained from *o*-chlorophenylanthranilic acid on heating at 300—320° for 5 hrs. (cf. Ullmann, A., 1907, i, 842). *N*-Phenylbenzimidio *p*-chlorophenyl ether, m. p. 92—93°, is converted into benzoyl-*p*-chlorodiphenylamine, m. p. 109—110°, which is also prepared by benzylation of *p*-chlorodiphenylamine (*benzoyl-m*-chlorodiphenylamine has m. p. 101—102°). It is concluded that the mobile group must have become attached to the nitrogen atom by the nuclear carbon atom originally attached to the oxygen.

The absence of by-products could be accounted for by regarding the dissociation as ionic. The specific conductivity of *N*-phenylbenzimidio phenyl ether remains constant so long as no appreciable isomeric change occurs, but, at a higher temperature, isomeric change and increase in conductivity occur simultaneously and finally the conductivity of benzyldiphenylamine is reached. According to the ionic hypothesis, reaction occurs in the following

stages, of which the first, a comparatively slow change, gives the unimolecular character:  $\text{PhC} \begin{smallmatrix} \text{NPh} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} \rightarrow \text{PhC} \begin{smallmatrix} \text{NPh} \\ \diagup \diagdown \\ \text{O} \cdots \end{smallmatrix} + \text{Ph} \cdots \rightarrow$

$\text{PhC} \begin{smallmatrix} \text{NPh} \cdots \\ \diagup \diagdown \\ \text{O} \end{smallmatrix} + \text{Ph} \cdots \rightleftharpoons \text{PhC} \begin{smallmatrix} \text{NPh}_2 \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ . The observed conductivity change is unlikely to be due to a by-product, since different samples of benzoyldiphenylamine show the same conductivity.

N-*p*-Tolylbenzimidido *p*-tolyl ether, m. p. 65—66°, is converted into benzoyldi-*p*-tolylamine, m. p. 124—125° (also prepared from di-*p*-tolylamine). On heating *N*-phenylbenzimidido phenyl ether and *N*-*p*-tolylbenzimidino *p*-tolyl ether at 290°, equimolecular proportions of benzoyldiphenylamine and benzoyldi-*p*-tolylamine are produced, but no benzoylphenyl-*p*-tolylamine, whence it is concluded that the isomeric change of an imino-ether into a substituted amide is not ionic in character.

F. M. H.

**Methylenecitric Anhydride. Aniline Derivatives of Citric and Aconitic Acids.** C. A. NAU, E. B. BROWN, and J. R. BAILEY. —(See i, 1379.)

**Tenacity of Organic Radicals. III.** J. VON BRAUN, R. FUSSGÄNGER, and M. KUHN (*Annalen*, 1925, **445**, 201—224; cf. A., 1924, i, 632).—Whilst in general the firmness with which radicals so far examined are attached to nitrogen is greater the greater their mol. wt. and the more their atom chains are branched, allyl and benzyl derivatives show considerably less tenacity than would be expected, and it is suggested that this is due to the unsaturated nature of the group attached to the end carbon atom, which attracts an appreciable proportion of the affinity of this atom to itself, leaving correspondingly less available for the linkage to nitrogen, sulphur, oxygen, or halogen. This conclusion is supported by the results of the following investigation on derivatives containing the unsaturated (or reactive) propargyl, cyclopropylmethyl ("trimethylenyl"), cyclobutylmethyl ("tetramethylenyl"),  $\alpha$ -thienylmethyl ("α-thenyl"), and furfuryl ("α-furo-methyl") groups, the tenacity of the allyl,  $\alpha$ -thienylmethyl, furfuryl, benzyl, propargyl and cyclopropylmethyl, methyl, ethyl (and propyl) and cyclobutylmethyl, and butyl being in this order, in general agreement with the known properties of these radicals.

Methylaniline reacts with  $\beta$ -bromoallyl bromide at the ordinary temperature with formation of methyl- $\beta$ -bromoallylaniline, b. p. 136—138°/13 mm. (the hydrochloride, picrate, and methiodide are oily), which when boiled with aqueous-alcoholic potassium hydroxide yields methylpropargylaniline, b. p. 108—110°/13 mm. (hydrochloride, m. p. 142°; methiodide, m. p. 130—132°; picrate, oily; silver salt, yellow, flocculent). This reacts with cyanogen bromide in ether with formation of phenylmethylecyanamide, m. p. 28°, b. p. 137°/12 mm., and propargyl bromide, the latter combining with excess of the original base to form the quaternary phenyl-methylpropargylammonium bromide, m. p. 170°. Benzylmethyl- $\beta$ -bromoallylamine, b. p. 126—130°/15 mm. (hydrochloride, m. p. 140°; picrate, m. p. 124°; methiodide, yellow, m. p. 141°), yields similarly

*benzylmethylpropargylamine*, b. p. 101—103°/11 mm. (*silver salt*, orange; *hydrochloride*, m. p. 155°; *picrate*, oily), which on treatment with cyanogen bromide yields benzyl bromide and *methylpropargylcyanamide*, b. p. 90°/12 mm. The tenacity of the propargyl group towards nitrogen thus falls between that of methyl and that of benzyl, whilst the non-formation of propargylphenol by heating phenyl propargyl ether (cf. Powell and Adams, A., 1920, i, 381) indicates that the propargyl group is more firmly attached to oxygen than is the allyl group. *Cyanocyclopropane* (cf. Henry, *Bull. Acad. roy. Belg.*, 1899, [3], 37, 17; Dalle, A., 1902, i, 525) affords, on reduction with sodium and alcohol, *cyclopropylmethylamine*, the *benzoyl* derivative of which, m. p. 74—75°, b. p. 186—187°/11 mm., yields, when treated with phosphorus tribromide, *cyclopropylmethyl bromide* (cf. Demjanow and Dojarenko, A., 1908, i, 156), together with benzonitrile and dibromobutanes. *cyclopropylmethyl bromide* is unaffected when mixed with bromine and kept. Its pungent odour and destructive effect on the mucous membrane, as well as the ease with which it is hydrolysed by warm water, indicate the unsaturated nature of the *cyclopropylmethyl* group, and its analogy rather to the allyl than to the corresponding alkyl group. On treatment with *benzylmethylamine*, *cyclopropylmethyl bromide* yields *cyclopropylmethylbenzylmethylamine*, b. p. 105—106°/11 mm. (*hydrochloride*, oily; *picrate*, m. p. 88°), which affords, when treated with cyanogen bromide, benzyl bromide and *cyclopropylmethylmethylcyanamide*, pale yellow, b. p. 80—83°/11 mm. *cyclopropylmethylmethylaniline*, b. p. 113—114°/12 mm. (*hydrochloride*, *picrate*, and *methiodide*, oily), obtained similarly, is converted by the action of cyanogen bromide into phenylmethylcyanamide and *cyclopropylmethyl bromide*. *Phenyl cyclopropylmethyl ether*, m. p. 214°, b. p. 95°/12 mm., obtained by the action of *cyclopropylmethyl bromide* on phenol in acetone solution in presence of potassium carbonate (cf. Claisen, A., 1913, i, 1175), does not undergo isomerisation into the corresponding substituted phenol when heated in a sealed tube at 250°. Interaction of ammonium thiocyanate and *cyclopropylmethyl bromide* in aqueous-alcoholic solution affords *cyclopropylmethyl thiocyanate*, b. p. 65—67°/12 mm., which shows no tendency to isomerise to the corresponding thio-carbimide. These reactions place the tenacity of the *cyclopropylmethyl* radical above that of allyl and benzyl and below that of methyl. Reduction of *cyclobutylacetonitrile* with sodium and alcohol affords *cyclobutylmethylamine* (cf. Freund and Gudemann, A., 1888, 1271), the *benzoyl* derivative of which, m. p. 102°, b. p. 191—193°/12 mm., yields, when treated with phosphorus tribromide, *cyclobutylmethyl bromide*, b. p. 81—83°/125 mm.,  $d_4^{25}$  1.360. This is indifferent to bromine, much less readily hydrolysed by water than the above corresponding *cyclopropyl* derivative, and has an odour much less pungent than the latter or allyl bromide, but not so sweet as that of the alkyl bromides. It combines slowly with alcoholic trimethylamine with formation of *cyclobutylmethyltrimethylammonium bromide*, hygroscopic, m. p. 214°, and condenses with methylaniline to form *cyclobutylmethylmethylaniline*, b. p. 135°/12



mm. (*hydrochloride*, *picrate*, and *methiodide*, oily; *chloroplatinate*, ochre-yellow, decomp.  $178^{\circ}$ ). The latter reacts with cyanogen bromide to form *phenylcyclobutylmethylcyanamide*, b. p.  $158-160^{\circ}$ . *cycloButylmethyl-n-butylaniline*, pale yellow, b. p.  $161-162^{\circ}/13$  mm. (*hydrochloride*, oily; *picrate*, orange, m. p.  $128^{\circ}$ ), yields similarly *phenyl-n-butylcyanamide*, b. p.  $165-168^{\circ}/13$  mm. These reactions place the tenacity of the *cyclobutylmethyl* radical between that of methyl and that of butyl.  $\alpha$ -*Thienylmethyl* bromide, b. p.  $80-82^{\circ}/150$  mm., is obtained in 90% yield by the action of phosphorus tribromide on the corresponding alcohol in cold chloroform solution. Its odour is slightly less irritant than that of benzyl bromide, whilst it resembles furfuryl bromide in its lack of stability, as it becomes deeply coloured when kept more than 24 hrs., evolving hydrogen bromide and finally being transformed into a dark resin. It is readily hydrolysed by water, and is rapidly converted by the action of trimethylamine into  $\alpha$ -*thienylmethyltrimethylammonium bromide*, very hygroscopic, m. p.  $172^{\circ}$ . By reaction with benzylmethylamine, it yields  $\alpha$ -*thienylmethylbenzylmethylamine*, b. p.  $148-152^{\circ}/12$  mm. (*picrate*, m. p.  $95^{\circ}$  after sintering at  $92^{\circ}$ ; *methiodide*, m. p.  $165^{\circ}$ ), which, on treatment with cyanogen bromide, affords  $\alpha$ -thienylmethyl bromide, identified by conversion into  $\alpha$ -*thienylmethyltrimethylammonium chloroplatinate*, yellow, decomp. at  $179^{\circ}$  after turning grey at  $155^{\circ}$ .  $\alpha$ -*Thienylmethylallylaniline*, b. p.  $161-165^{\circ}/10$  mm. (*hydrochloride*, oily; *picrate*, m. p.  $124-125^{\circ}$ ), obtained similarly, yields allyl bromide when treated with cyanogen bromide.  $\alpha$ -Thienylmethyl bromide reacts with ammonium thiocyanate in aqueous alcohol, with formation of  $\alpha$ -*thienylmethylthiocarbimide*, b. p.  $141-142^{\circ}/20$  mm., which reacts with aniline with formation of *phenyl- $\alpha$ -thienylmethylcarbamide*, m. p.  $123^{\circ}$ . The analogy between the allyl and  $\alpha$ -thienylmethyl radicals is thus established (cf. A., 1923, i, 1193), as well as the position of the latter slightly higher than allyl in the tenacity series. *Furfurylbenzylmethylamine*, b. p.  $131-133^{\circ}/13$  mm. (*hydrochloride* and *picrate*, oily; *methiodide*, m. p.  $135^{\circ}$ ), obtained by the action of benzyl chloride on furfurylmethylamine, affords, on treatment with cyanogen bromide, the very unstable *furfuryl bromide* (identified by conversion into the quaternary salt by the action of trimethylamine), indicating the smaller tenacity of the furfuryl group towards nitrogen, as compared with benzyl.  $\alpha$ -*Thienylmethylfurfurylmethylamine*, b. p.  $132-135^{\circ}/14$  mm. (*picrate*, m. p.  $78^{\circ}$ ; *methiodide*, m. p.  $110^{\circ}$ ), obtained by treating furfurylmethylamine with  $\alpha$ -thienylmethyl bromide, yields  $\alpha$ -thienylmethyl bromide on treatment with cyanogen bromide, thus placing the furfuryl group above the  $\alpha$ -thienylmethyl group in the tenacity series. F. G. W.

**Aluminium Oxide as a Condensing Agent and the Rôle of Carriers in Catalysis.** K. W. ROSENMUND and A. JOITHE (*Ber.*, 1925, 58, [B], 2054-2058).—In solvents of high b. p. such as nitrobenzene or tetrahydronaphthalene, benzyl alcohol is converted by ammonia in the presence of aluminium oxide into a mixture of mono-, di-, and tri-benzylamine. The catalyst is pre-

pared by heating aluminium hydroxide at  $400^{\circ}$ ; technical aluminium oxide is not uniform in its action. The quantity of aluminium oxide used has a very marked influence on the yield; its catalytic action at the relatively low temperature is not completely unfolded, since decomposition of the hydrate after attainment of equilibrium is slow. For the same reason, increase in the pressure of ammonia accelerates the change only until the aluminium oxide has attained equilibrium with the hydrate. Thorium dioxide, prepared from the oxalate at  $400^{\circ}$ , causes more vigorous evolution of water in the above reaction than does aluminium oxide, but the main product is dibenzyl ether, only about 8% of mixed bases being obtained. Benzyl alcohol and aniline in the presence of aluminium oxide and tetrahydronaphthalene afford benzylaniline in 81% yield.  
H. W.

**Stereochemistry of Aromatic Compounds. Isomerism of the 9-Aminofluorenes.** R. KUHN and P. JACOB (*Ber.*, 1925, 58, [B], 2232; cf. this vol., i, 1260).—Kerp's 9-aminofluorene, m. p.  $161^{\circ}$  (A., 1896, i, 239), is identified, not as  $\gamma$ -9-fluorylcarbamic acid (Kuhn and Jacob, *loc. cit.*), but as  $\gamma$ -9-aminofluorene acetate. The unstable  $\gamma$ -9-aminofluorene has m. p.  $46-46.5^{\circ}$ , which rapidly rises when the compound is preserved in a desiccator.

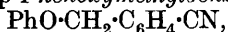
The possibility of *cis-trans* isomerism in the naphth- and *iso*-naphth-thioxin group is suggested.  
H. W.

**Transformations of Benzyl Ethers. II.** P. SCHORIGIN (*Ber.*, 1925, 58, [B], 2028—2036; cf. A., 1924, i, 1188).—The previous conclusion that the transformation of ethers into carbinols under the influence of sodium is peculiar to such compounds as contain the benzyl group is confirmed; the change is ascribed to the relative feebleness of the bond between the benzyl group and oxygen. *p*-Tolyl benzyl ether decomposes in the presence of sodium wire at  $100^{\circ}$  in two directions, yielding toluene and *p*-cresol, and phenyl-*p*-tolylcarbinol, m. p.  $53-54^{\circ}$ . cycloHexyl benzyl ether, b. p.  $146^{\circ}/17$  mm.,  $d_4^{20}$  0.9856, prepared from cyclohexanol, sodium, and benzyl chloride in the presence of benzene, affords a little toluene and cyclohexylphenylcarbinol, m. p.  $50-51^{\circ}$ . Dibenzyl ether yields toluene, benzyl alcohol, phenylbenzylcarbinol, m. p.  $62-63^{\circ}$ , benzoic acid, and, probably, stilbene. Somewhat unexpectedly, *o*-tolyl benzyl ether is transformed into toluene, *o*-cresol, and *o*-hydroxydibenzyl, m. p.  $84-85^{\circ}$  (6-benzyl-*o*-cresol, prepared for purposes of comparison from sodium *o*-tolyl oxide and benzyl chloride in boiling toluene, has b. p.  $187-188^{\circ}/15$  mm., m. p.  $51-52^{\circ}$ ). 4-m-Xylol benzyl ether, b. p.  $186-187^{\circ}$  (corr.)/18 mm.,  $d_4^{20}$  1.0455, is converted by sodium into toluene, xylene, *m*-4-xylol, and 6-hydroxy-3-methyldibenzyl (characterised as the phenylurethane, m. p.  $114-115^{\circ}$ ). Phenyl *o*-tolyl ether affords benzene, toluene, phenol, and *o*-cresol, the fission proceeding mainly in such direction as to give phenol; isomerisation is not observed. Decomposition of *o*-tolyl ethyl ether at  $260^{\circ}$  gives mainly *o*-cresol, ethylene, and ethane; toluene or a transformation product does not appear to be formed. Phenyl  $\beta$ -phenylethyl

ether, b. p.  $180^{\circ}/22$  mm.,  $d_4^{20}$  1.0501, prepared from potassium phenoxide and  $\beta$ -phenylethyl chloride in the presence of alcohol, is converted exclusively into ethylbenzene and phenol.

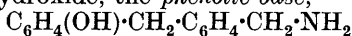
Phenyl benzyl sulphide, m. p.  $41.5-42^{\circ}$ , b. p.  $197^{\circ}$  (corr.)/27 mm., prepared in 90% yield from thiophenol, potassium hydroxide, and benzyl chloride in the presence of alcohol, is converted by sodium into toluene and thiophenol; benzyl thioethers do not therefore appear capable of isomerisation to thiocarbinols. H. W.

**Syntheses in the Aliphatic-aromatic Series. XVI. Chlorinated Amines and Amino-acids.** J. VON BRAUN and H. REICH (*Annalen*, 1925, **445**, 225—246).—When phenyl benzyl ether is heated with 5 parts of 38% hydrochloric acid in a sealed tube at  $100^{\circ}$  for several hours, 4-hydroxydiphenylmethane, m. p.  $84^{\circ}$ , and probably the 2-hydroxy isomeride, together with 2 : 4-dibenzylphenol, b. p.  $253-255^{\circ}/12$  mm., are obtained (cf. Sintenis, *Annalen*, 1872, **111**, 329), the formation of benzyl chloride not being observed. The same products are obtained similarly from a mixture of benzyl chloride and phenol. *p*-Tolyl benzyl ether, b. p.  $165^{\circ}/12$  mm., benzyl  $\alpha$ -naphthyl ether, m. p.  $61^{\circ}$ , b. p.  $200^{\circ}/12$  mm., benzyl  $\beta$ -naphthyl ether, m. p.  $95^{\circ}$ , and *p*-diphenoxymethylbenzene,  $C_6H_4(CH_2 \cdot OPh)_2$ , m. p.  $142^{\circ}$ , behave analogously, chlorinated derivatives not being obtained in any case. *p*-Phenoxymethylbenzonitrile,



m. p.  $65^{\circ}$ , b. p.  $205^{\circ}/12$  mm., obtained by the action of sodium phenoxide on *p*-bromomethylbenzonitrile (cf. Banse, A., 1894, i, 574), is reduced by hydrogen under pressure at  $120^{\circ}$  in presence of nickel in decalin solution, to benzyl *p*-phenoxymethylamine, m. p. about  $78^{\circ}$ , indefinite owing to absorption of atmospheric carbon dioxide (benzoyl derivative, m. p.  $116^{\circ}$ ; hydrochloride, m. p.  $260^{\circ}$ ; picrate, m. p.  $197^{\circ}$ ), together with di-*p*-phenoxymethylbenzylamine, decomp. on distillation. *p*-Phenoxymethylbenzyl alcohol, m. p.  $106^{\circ}$ , b. p.  $215-220^{\circ}/12$  mm., and *p*-phenoxymethylbenzyl bromide, b. p.  $210^{\circ}/13$  mm., lachrymatory, are described (cf. von Braun and Zobel, A., 1923, i, 1199). Treatment of the *p*-phenoxymethylbenzylamine with fuming hydrochloric or hydrobromic acid at  $130^{\circ}$  affords a phenolic base,  $C_{14}H_{32}ON$ , halogen derivatives not being obtained. *p*-Ethoxymethylbenzonitrile, b. p.  $135^{\circ}/13$  mm. (cf. von Braun and Zobel, A., 1923, i, 371), is reduced similarly to *p*-ethoxymethylbenzylamine, b. p.  $135^{\circ}/13$  mm., a strong base (hydrochloride, hygroscopic, m. p.  $235^{\circ}$ ; picrate, m. p.  $150^{\circ}$ ), and di-*p*-ethoxymethylbenzylamine, b. p.  $255^{\circ}/12$  mm. (hydrochloride, m. p.  $226^{\circ}$ ; picrate, m. p.  $152^{\circ}$ ; nitroso and benzoyl compounds, oily). *p*-Ethoxymethylbenzyl alcohol, b. p.  $152^{\circ}/13$  mm., *p*-ethoxymethylbenzyl bromide, b. p.  $148^{\circ}/13$  mm., and *p*-ethoxymethylphenylacetone, b. p.  $165^{\circ}/12$  mm., were prepared. The last-named yields, on reduction as above,  $\beta$ -*p*-ethoxymethylphenylethylamine, b. p.  $145-147^{\circ}/13$  mm. (hydrochloride, m. p.  $180^{\circ}$ ; picrate, m. p.  $130^{\circ}$ ), and di-( $\beta$ -*p*-ethoxymethylphenylethyl)amine, b. p.  $270-275^{\circ}/13$  mm. (hydrochloride, m. p.  $250^{\circ}$ ; nitroso compound, m. p.  $58^{\circ}$ ). Whilst treatment of the above *p*-ethoxymethylbenzylamine and *p*-ethoxymethylphenyl-

ethylamine with hydrochloric acid under pressure above  $100^{\circ}$  leads to deep-seated decomposition, smooth reaction is obtained by passing dry hydrogen chloride through boiling alcoholic solutions of the bases. The former base is thus converted into *p*-chloromethylbenzylamine hydrochloride, m. p. not below  $300^{\circ}$  (chloroplatinate, ochre-yellow, m. p.  $226^{\circ}$ ; picrate, m. p.  $185^{\circ}$ ), the phenylethylamine yielding similarly  $\beta$ -*p*-chloromethylphenylethylamine hydrochloride, m. p. not below  $300^{\circ}$  (chloroplatinate, m. p. not below  $300^{\circ}$ ; picrate, m. p.  $145^{\circ}$ ). The free bases change, on isolation, into viscous, halogen-free, non-purifiable oils, resembling the analogous transformation product derived from  $\zeta$ -heptylamine (cf. von Braun and Müller, A., 1907, i, 28). The following *meta* derivatives, obtained similarly, are described: *m*-bromomethylbenzonitrile, m. p.  $93^{\circ}$ ; *m*-phenoxymethylbenzonitrile, m. p.  $51^{\circ}$ , b. p.  $183$ – $185^{\circ}/12$  mm.; *m*-phenoxymethylbenzylamine, b. p.  $220^{\circ}/16$  mm. (hydrochloride, m. p.  $170^{\circ}$ ; picrate, m. p.  $170^{\circ}$ ), affording, on treatment with aqueous sodium hydroxide, the phenolic base,



(platinum salt, decomp.  $197^{\circ}$ ); *di*-*m*-phenoxymethylbenzylamine, b. p.  $290^{\circ}/16$  mm.; *m*-ethoxymethylbenzonitrile, b. p.  $133^{\circ}/12$  mm.; *m*-ethoxymethylbenzylamine, b. p.  $150$ – $152^{\circ}/15$  mm. (hydrochloride, m. p.  $156^{\circ}$ ; picrate, m. p.  $131^{\circ}$ ); *m*-ethoxymethylbenzyl alcohol, b. p.  $140$ – $142^{\circ}/11$  mm.; *di*-*m*-ethoxymethylbenzylamine, b. p.  $250^{\circ}/14$  mm. (picrate, m. p.  $212^{\circ}$ ); *m*-ethoxymethylbenzyl bromide, b. p.  $140$ – $145^{\circ}/12$  mm.; *m*-ethoxymethylphenylacetoneitrile, b. p.  $155^{\circ}/11$  mm.;  $\beta$ -*m*-ethoxymethylphenylethylamine, b. p.  $145^{\circ}/11$  mm. (hydrochloride, m. p.  $107^{\circ}$ ; picrate, m. p.  $182^{\circ}$ ); *di*-( $\beta$ -*m*-ethoxymethylphenylethyl)amine, b. p.  $240$ – $245^{\circ}/11$  mm. (hydrochloride, m. p.  $135^{\circ}$ ); *m*-chloromethylbenzylamine hydrochloride, m. p.  $169^{\circ}$  (chloroplatinate, m. p.  $219^{\circ}$ ; picrate, m. p.  $173^{\circ}$ ), and  $\beta$ -*m*-chloromethylphenylethylamine hydrochloride, decomp.  $177^{\circ}$  (picrate, m. p.  $172^{\circ}$ ).

The benzoyl derivative, m. p.  $92^{\circ}$ , of the above *m*-chloromethylbenzylamine affords, on treatment with aqueous-alcoholic potassium cyanide, the corresponding benz-*m*-cyanomethylbenzylamide, m. p.  $89^{\circ}$ , which, on hydrolysis with concentrated hydrochloric acid at  $115^{\circ}$ , yields the hydrochloride of  $\beta$ -*m*-aminoethylphenylacetic acid, m. p.  $165^{\circ}$ , the free acid, m. p.  $210^{\circ}$ , being obtained from the salt by the action of silver oxide. When heated, the acid chars, lactam formation not being observed.

Reduction of *o*-ethoxymethylphenylacetoneitrile (cf. A., 1923, i, 371) affords  $\beta$ -*o*-ethoxymethylphenylethylamine, b. p.  $140^{\circ}/11$  mm. (hydrochloride, hygroscopic, m. p.  $117^{\circ}$ ; picrate, reddish-yellow, m. p.  $163^{\circ}$ ), and *di*-( $\beta$ -*o*-ethoxymethylphenylethyl)amine, b. p.  $250^{\circ}/11$  mm., the salts of which are oily. *o*-Phenoxymethylbenzylamine yields, when treated above  $100^{\circ}$  with hydrochloric or hydrobromic acid, a phenolic base,  $\text{C}_{14}\text{H}_{25}\text{ON}$ , m. p.  $158$ – $159^{\circ}$ , b. p.  $225$ – $235^{\circ}/14$  mm. with slight decomposition, which, on exhaustive methylation, affords the methiodide,  $\text{C}_{18}\text{H}_{24}\text{ONI}$ , m. p.  $181$ – $183^{\circ}$ .

-Chloromethylbenzylamine hydrochloride, m. p.  $222^{\circ}$  (chloroplatinate, m. p.  $218^{\circ}$ ; picrate, m. p.  $187^{\circ}$ ), and  $\beta$ -*o*-chloromethylphenylethyl-

amine hydrochloride, m. p. 209° (*p*-nitrobenzoyl derivative, m. p. 120—121°), are described. Treatment of di-( $\beta$ -*m*-ethoxymethylphenylethyl)amine with hydrochloric acid affords di-( $\beta$ -*m*-chloromethylphenylethyl)amine hydrochloride, m. p. 220° (benzoyl derivative, m. p. 95°). Di-( $\beta$ -*o*-chloromethylphenylethyl)amine hydrochloride, m. p. 154°, is obtained similarly. The similar action of hydrochloric acid on di-*o*-ethoxymethylbenzylamine affords the hydrochloride of the corresponding primary chloroamine, together with *o*-chloromethylbenzyl chloride.

Benzoylation of *o*-chloromethylbenzylamine affords the corresponding benz-*o*-chloromethylbenzylamide, m. p. 119°, which reacts with aqueous-alcoholic potassium cyanide to form the corresponding cyano derivative, m. p. 135°. This is hydrolysed by hydrochloric acid at 115° to *o*-aminomethylphenylacetic acid, decomp. 202° (hydrochloride, m. p. 154°; hydrochloride of the ethyl ester, m. p. 167°). When heated at 160—170° under reduced pressure, the acid decomposes with formation of the corresponding lactam,  $C_6H_4 \begin{smallmatrix} < CH_2 \cdot CO \\ CH_2 \cdot NH \end{smallmatrix}$  ("benzopiperidone"), m. p. 150°, which can be recrystallised unchanged from hot aqueous sodium hydroxide or hydrochloric acid, but yields, on long boiling with the latter reagent, the above ester hydrochloride. Benz- $\beta$ -*o*-cyanomethylphenylethylamide, b. p. 290—300°/12 mm., affords similarly, on hydrolysis with hydrochloric acid, *o*-aminoethylphenylacetic acid, decomp. 228° (hydrochloride, m. p. 218°), which decomposes below 200° when heated under 12 mm. pressure, with formation of the corresponding lactam, m. p. 159°. *o*- $\gamma$ -Chloropropylbenzonitrile (cf. von Braun and Bartsch, A., 1913, i, 197) reacts with potassium phthalimide at 200°, giving the corresponding phthalimido derivative, m. p. 138°, which is hydrolysed by hydrochloric acid at 150° with formation of *o*- $\gamma$ -aminopropylbenzoic acid, m. p. 213—214°. Lactamisation of this acid begins when its aqueous solution is evaporated, but is only completed by heating the acid at 195° under a pressure of 15 mm., at which temperature the lactam, m. p. 100°, distils. F. G. W.

**Derivatives of ar-Tetrahydro- $\beta$ -naphthol.** CHEMISCHE FABRIK VON HEYDEN AKT.-GES. (D.R.-P. 414261; from *Chem. Zentr.*, 1925, ii, 615).—ar-Tetrahydro- $\beta$ -naphthol and benzenesulphochloride in pyridine yield ar-tetrahydro- $\beta$ -naphthyl benzenesulphonate, m. p. 95°; ar-tetrahydro- $\beta$ -naphthyl *p*-toluenesulphonate, m. p. 79—80°, is similarly obtained. Dimethylaniline and carbonyl chloride in benzene followed by treatment with ammonia give ar-tetrahydro- $\beta$ -naphthyl carbamate, m. p. 150°; carbonyl chloride alone in dilute sodium hydroxide yields the carbonate, m. p. 119°. The *p*-nitrobenzoate has m. p. 113°, and the *p*-aminobenzoate, m. p. 154°. Fusion with salicylic acid at 160° followed by treatment with phosphoryl chloride at 130° yields ar-tetrahydro- $\beta$ -naphthyl salicylate, m. p. 55°, which has therapeutic properties. R. B.

**New Hydroxyurethanes and Chromoisomeric Silver Salts of their Acyl Derivatives. III.** R. E. OESPER and W. BROKER (*J. Amer. Chem. Soc.*, 1925, 47, 2606—2608).—The study of the

chromoisomeric silver salts of the benzoyl esters of aliphatic carbalkyloxyhydroxamic acids (cf. Oesper and Cook, this vol., i, 523) has been extended to analogous aromatic acids. In all cases, the silver is directly united to the nitrogen, since hydrolysis of the product obtained by the interaction with alkyl iodides yields  $\beta$ -substituted hydroxylamines. The following compounds were prepared by the methods previously described (*loc. cit.*), but improved yields of the benzoyl esters are obtained by refluxing ethereal solutions of the hydroxamic acid and benzoyl chloride in the presence of the equivalent quantity of potassium carbonate: *carbophenoxyhydroxamic acid*, m. p.  $102\cdot5^\circ$  [benzoyl ester, m. p.  $105\cdot5^\circ$ , giving silver salt, m. p.  $150$ — $155^\circ$  (decomp.), white and yellow forms, and N-ethyl derivative, m. p.  $45^\circ$ ]; o-, m-, and p-*carbotoxyloxyhydroxamic acid*, m. p.  $116^\circ$ ,  $67\cdot5^\circ$ , and  $99^\circ$ , respectively (benzoyl esters, m. p.  $76\cdot5^\circ$ ,  $102\cdot5^\circ$ , and  $92^\circ$ , respectively, giving white silver salts and N-ethyl derivatives, oils; *dibenzoyl* ester of the o- and p-compounds, m. p.  $54\cdot5^\circ$  and  $90^\circ$ , respectively); *carbo-o-* and *-p-chlorophenylhydroxamic acid*, m. p.  $127^\circ$  and  $119^\circ$ , respectively (benzoyl ester of p-compound, m. p.  $100^\circ$ ); *carbo-m-nitrophenoxyhydroxamic acid*, m. p.  $130\cdot5^\circ$  (benzoyl ester, m. p.  $99^\circ$ ).

J. W. B.

**Chlorocarbonates [Chloroformates] Derived from Aromatic and Dihydric Alcohols.** R. E. OESPER, W. BROKER, and W. A. COOK (*J. Amer. Chem. Soc.*, 1925, **47**, 2609—2610).—A large number of chloroformates have been prepared by the action of alcohols on the additive product of carbonyl chloride and anti-pyrene (D.R.-PP. 117624, 118536, 118537) or by addition of a base to a non-aqueous solution of carbonyl chloride and the alcohol (cf. D.R.-P. 251805, A., 1913, i, 5). In the former case, the yields range only from 40% to 60% and in the latter from 75% upwards, dialkylated anilines being especially trustworthy. The method is applicable to dihydric alcohols. The following new compounds are obtained: o- and p-*chlorophenyl chloroformate*, b. p.  $113^\circ/27$  mm. and  $114^\circ/20$  mm., respectively; o-*chlorophenyl carbamate*, m. p.  $142^\circ$ ; m-*nitrophenyl chloroformate*, b. p.  $158^\circ/18$  mm.; m-*nitrophenyl carbonate*, m. p.  $168\cdot5^\circ$ ;  $\alpha$ -*naphthyl chloroformate*, b. p.  $132^\circ/15$  mm.; *ethylene dichloroformate*, b. p.  $122^\circ/37$  mm., *carbamate*, m. p.  $165^\circ$  (Gattermann, A., 1888, 574, gives  $147$ — $149^\circ$ ); trimethylene dichloroformate, b. p.  $122^\circ/37$  mm. (*carbamate*, m. p.  $167^\circ$ ); m-*phenylene dichloroformate*, m. p.  $100^\circ$ ; o-*tolyl carbamate*, m. p.  $160^\circ$ .

J. W. B.

**Nitrosation of Phenols. II. Nitrosation of 3-Bromo-, 2-Bromo-, 3-Iodo-, and 2-Iodo-phenol. Evidence for the Nitroso Formula of 4-Nitrosophenol.** H. H. HODGSON and F. H. MOORE (*J. Chem. Soc.*, 1925, **127**, 2260—2264; cf. T., 1923, **123**, 2499).—Nitrosation of 3-bromophenol yielded 3-*bromo-4-nitrosophenol*, m. p.  $139^\circ$  (decomp.), which in any solvent except ether formed 3-*bromo-p-benzoquinone-4-oxime*, orange, m. p.  $188^\circ$  (decomp.); acidification of a cold alkali solution of this compound produced the pale yellow geometrical isomeride, m. p.  $189$ — $190^\circ$ ,

crystallisation of which from dilute hydrochloric acid caused reversion into the orange isomeride. 2-Bromo-4-nitrosophenol, m. p.  $150^{\circ}$ , did not form a quinoneoxime, whereas 3-iodo-p-benzoquinone-4-oxime (deep yellow *syn*-form and straw-coloured *anti*-form, decomp.  $185\text{--}195^{\circ}$ ) was unobtainable in the nitroso modification. 2-Iodo-4-nitrosophenol, decomp.  $152^{\circ}$ , was obtained by a special method; no quinoneoxime was formed. Oxidation to the corresponding halogenated nitrophenols established the 4-positions of the nitroso groups, and the lower m. p. of the true nitroso compounds distinguish them from the quinoneoximes. A very pure specimen of nitrosophenol was prepared, having m. p.  $133^{\circ}$ .

B. W. A.

**Nitration Products of *o*'-Nitrotoluene-*p*'-sulpho-*p*-phenetide.** F. REVERDIN (*Helv. Chim. Acta*, 1925, 8, 602—608; cf. A., 1922, i, 537).—Nitration of *o*'-nitrotoluene-*p*'-sulpho-*p*-phenetide, m. p.  $129\text{--}130^{\circ}$ , with nitric acid, *d* 1.4, in acetic acid (or nitric acid *d* 1.18 in alcoholic solution) yields 3-nitro-*o*'-nitrotoluene-*p*'-sulpho-*p*-phenetide, m. p.  $135\text{--}136^{\circ}$  (hydrolysed to 3-nitro-*p*-aminophenol), together with 3:5-dinitro-*o*'-nitrotoluene-*p*'-sulpho-*p*-phenetide, m. p.  $163^{\circ}$  (cf. Reverdin and Fürstenberg, A., 1913, i, 850), which is also obtained by the action of nitric acid, *d* 1.15, on the mononitro compound in acetic acid solution. Under described conditions in the absence of acetic acid and employing nitric acid, *d* 1.5, the mononitro compound is converted into 2:3-dinitro-*o*'-nitrotoluene-*p*'-sulpho-*p*-phenetide, m. p.  $163^{\circ}$  (mixed m. p. with the 3:5-compound  $144^{\circ}$ ), which by the action of nitric acid, *d* 1.4, readily yields 2:3:5-trinitro-*o*'-nitrotoluene-*p*'-sulpho-*p*-phenetide, m. p.  $233\text{--}234^{\circ}$  (decomp.). The orientation of each derivative is established by hydrolysis to the corresponding nitro-*p*-phenetide. With ammonia, diethylamine, and aniline at about  $30^{\circ}$ , the 2:3-dinitro compound yields unstable additive compounds, difficult to isolate in the pure state; the first two have m. p.  $175^{\circ}$  and  $174^{\circ}$ , respectively. Similarly, the 2:3:5-trinitro compound yields compounds, m. p. below  $100^{\circ}$  (decomp.  $110^{\circ}$ ),  $141^{\circ}$ ,  $155\text{--}158^{\circ}$ , respectively. Aniline at  $95^{\circ}$  reacts, yielding 2-nitro-3-anilino-*o*'-nitrotoluene-*p*'-sulpho-*p*-phenetide, m. p.  $142^{\circ}$  (+1 mol. of acetic acid of crystallisation, m. p.  $126^{\circ}$ ), and 3:5-dinitro-2-anilino-*o*'-nitrotoluene-*p*'-sulpho-*p*-phenetide, m. p.  $198^{\circ}$ .

J. W. B.

**Alcoholysis of Trinitroanisole and Trinitrophenetole.** O. L. BRADY and H. V. HORTON (*J. Chem. Soc.*, 1925, 127, 2230—2233).—When 2:4:6-trinitroanisole (m. p.  $68^{\circ}$ ) is crystallised from ethyl alcohol, a mixture, m. p.  $58^{\circ}$ , of trinitroanisole and trinitrophenetole separates, whilst trinitrophenetole crystallised from methyl alcohol gives a mixture, m. p.  $52^{\circ}$ . The binary fusion diagram of the two substances shows that an unstable additive compound is formed, consisting of 3 mols. of trinitroanisole to 2 mols. of trinitrophenetole. By heating with dry alcohol, up to 35% of trinitroanisole is converted into trinitrophenetole.

B. W. A.

**Photographic Developers. III. Preparation of *p*-Aminophenol Sulphate from  $\beta$ -Phenylhydroxylamine.** M. HORII and K. KOMORI (*Report Osaka Ind. Research Lab.*, 1924, 5, No. 13, 1—21).—The optimal conditions include the use of a large excess of sulphuric acid, and a temperature above 70°; the yield is 73%. [Cf. *B.*, 1925, 901.]

CHEMICAL ABSTRACTS.

**Phenols Alkylated in the Nucleus.** L. CLAISEN (D.R.-P. 412169; from *Chem. Zentr.*, 1925, ii, 94).—Metallic compounds of phenols are treated with alkyl halides (or their homologues or substitution products) the halogen of which is particularly reactive, in media which do not cause dissociation (cf. *A.*, 1923, i, 1094). 3-Allyl-*p*-cresol has b. p. 112°/12 mm. *o*-Benzylphenol (*o*-hydroxydiphenylmethane) has m. p. 52°, b. p. 171°/13 mm.; phenylurethane, m. p. 118°. 3-Benzyl-*p*-cresol (phenyl-6-hydroxy-*m*-tolylmethane), b. p. 180—182°/12 mm., is obtained on heating sodium *p*-tolyl-oxide, suspended in toluene, with benzyl chloride; phenylurethane, m. p. 145°. Further benzylation gives 3:5-dibenzyl-*p*-cresol, b. p. 251°/12 mm. *o*-Benzhydrylphenol (*o*-hydroxytriphenylmethane),  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHPh}_2$ , a viscid oil, is obtained by the action of diphenylmethyl bromide on a suspension of sodium phenoxide in toluene. It couples with diazo salts, giving yellow- to orange-coloured azo dyes.

A. C.

**Catalytic Dehydration of Phenol-Alcohol Systems. II. Naphthol-Alcohol Systems.** W. PLÜSS (*Helv. Chim. Acta*, 1925, 8, 507—512; cf. this vol., i, 248).—The action of methyl alcohol on a mixture of potassium naphthalenesulphonate and alumina at 420° gave a small amount of a substance, m. p. 144—145°.  $\beta$ -Naphthol and methyl alcohol under the influence of alumina, as previously described, furnish a mixture of trimethylnaphthalenes of b. p. 102—150°/12 mm. and the tetramethylnaphthalene of m. p. 107—108°. Nitration of the trimethylnaphthalene fraction gives a mononitrotrimethylnaphthalene, m. p. 142—143°, reduced to the corresponding aminotrimethylnaphthalene, b. p. 198—200°/12 mm., m. p. 115—116°. When ethyl, butyl, or amyl alcohol is used in place of methyl alcohol, the products contain oxygen and cannot be isolated in a state of purity. With  $\alpha$ -naphthol in place of  $\beta$ -naphthol, a mixture of liquid hydrocarbons is produced.

G. M. B.

**meso-Thioanthracene Derivatives. II. Dianthranyl Disulphide and Dianthranyl Tetrasulphide.** W. H. COOKE, I. M. HEILBRON, and G. H. WALKER (*J. Chem. Soc.*, 1925, 127, 2250—2255; cf. Heilbron and Heaton, *T.*, 1923, 123, 173).—The action of sodium hydrosulphide in excess on 9:10-dibromoanthracene in amyl-alcoholic solution gives 30—40% of dianthranyl disulphide (m. p. 223°), 9:10-dithiolanthracene and 9-anthranyl mercaptan being intermediate products. In addition, some dianthranyl oxide, m. p. 213°, is often formed, which on reduction yields both anthranol and anthracene. When less than one equivalent of the hydrosulphide is used, a yield of 80—90% of dithioheptacyclene is



obtained. Dibromoanthracene is completely converted into this latter substance when heated in an autoclave with sodium sulphide. Sodium disulphide acting on dibromoanthracene yields 60% of dianthranyl disulphide, but the same reactants heated in an autoclave produce a yellow, insoluble, amorphous compound, presumably *ms-dibromodiheptacyclene disulphide*. *Dianthranyl tetrasulphide*, m. p.  $190^{\circ}$ , is formed by the action of sodium polysulphides on dibromoanthracene, and is identical with the "dithiodianthranone disulphide" of Heilbron and Heaton; alcoholic potassium hydroxide converts this into 9-anthranyl mercaptan and dianthranyl disulphide.

B. W. A.

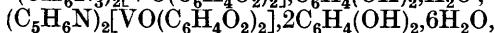
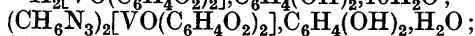
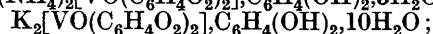
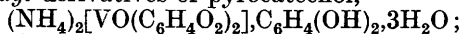
**Formation of Metallic Phenoxides by Metals.** F. ZETZSCHE, H. SILBERMANN, and G. VIRLI (*Helv. Chim. Acta*, 1925, **8**, 596—602).—A large number of phenoxides of metals other than the alkali metals have been prepared by the direct action of the finely divided metals on the phenol dissolved in an organic solvent (alcohol, toluene, xylene, or nitrobenzene). In carefully dried media, very little formation of the phenoxide occurs even at the b. p., but in the presence of a small quantity of water the action may become exothermic, an optimum yield being obtained in toluene solution containing 2.5% of 96% alcohol, and with a 10% solution of the phenol in 72% alcohol. The reaction velocity of the metals used decreases in their electromotive series order; the magnesium compound of salicylaldehyde, for example, reacts with aniline to yield the anil of salicylaldehyde and magnesium hydroxide, whilst the corresponding copper compound yields the copper salt of the anil. The following compounds are described: *magnesium* salts of 8-hydroxyquinoline, salicylaldehyde, 2-aceto- $\alpha$ -naphthol, 1-hydroxyxanthone; *cobalt* salts of 8-hydroxyquinoline, salicylaldehyde; *copper* salts of 8-hydroxyquinoline, salicylaldehyde, *o*-hydroxybenzylideneaniline, m. p.  $222$ — $226^{\circ}$ ; *zinc* salts of 8-hydroxyquinoline, salicylaldehyde; *ferrous* salts of 8-hydroxyquinoline, m. p.  $120^{\circ}$  (with loss of colour), salicylaldehyde, m. p.  $144^{\circ}$ , *o*-vanillin, m. p.  $156$ — $158^{\circ}$ . The ferrous compounds were obtained by the addition of freshly prepared ferrous disalicylate (obtained by the direct action of finely divided iron on salicylic acid in an inert atmosphere) on the phenol. The following compounds are also described: 8-hydroxyquinoline *p*-nitrobenzoate, m. p.  $174$ — $175^{\circ}$ ; 2-*p*-nitrobenzoyloxybenzaldehyde, m. p.  $123$ — $124^{\circ}$  (*phenylhydrazone*, m. p.  $210$ — $211^{\circ}$ ).

J. W. B.

**Salts and Complex Compounds of Quadrivalent Vanadium.** A. ROSENHEIM and H. YÜ MONG (*Z. anorg. Chem.*, 1925, **148**, 25—36).—Alkali vanadyl sulphates decompose in boiling sulphuric acid according to the equation  $2V^{IV} = V^{III} + V^V$ , yielding a crystalline vanadium sulphate,  $V_2O_3(SO_4)_2$ , and a series of insoluble double sulphates,  $MV(SO_4)_2$ , where  $M = K, Na, \text{ or } NH_4$ . All these substances differ in properties from sulphates of the same composition previously described. Vanadyl sulphate probably decomposes in a similar way.

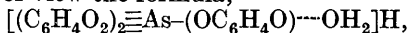
The following complex organic compounds are described:

*Ammonium* (+4H<sub>2</sub>O) and *potassium* (+3H<sub>2</sub>O) *vanadyl hydroxynaphthoates*; *ammonium*, *potassium*, *guanidine*, *pyridine*, and *thallium vanadyl* derivatives of pyrocatechol,



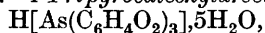
and  $\text{Ti}_2[\text{VO}(\text{C}_6\text{H}_4\text{O}_2)_2]_2 \cdot 2\text{C}_6\text{H}_4(\text{OH})_2$ ; *vanadyl acetylacetonate*,  $\text{VO}(\text{C}_5\text{H}_8\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , and its *ammonium*, *pyridine*, and *quinoline* derivatives. The existence of the complex vanadyl tartrates and salicylates of Barbieri (A., 1915, i, 380, 887) is confirmed. A. G.

**Optically Active Tripyrocatechylarsenic Acids.** A. ROSENHEIM and W. PLATO (*Ber.*, 1925, 58, [B], 2000—2009).—Weinland and Heingler's pyrocatechol semiarsenate,  $\text{AsO}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{OH})_3 \cdot 4\text{H}_2\text{O}$  (cf. A., 1919, i, 442; 1920, i, 778), is resolvable into its optical antipodes, thus rendering untenable the constitution ascribed to it by these authors. The simplest mode of formulation lies in the assumption that three pyrocatechol molecules are arranged at six co-ordination positions around the central quinquevalent arsenic atom. No account is thereby rendered of the tenacity with which a molecule of water is retained in the acid and all its salts, and from this point of view the formula,



proposed by Reihlen (cf. this vol., i, 912), is to be preferred.

*r*-Tripyrocatechylarsenic acid is conveniently resolved into its optical antipodes by crystallisation of the normal cinchonine salt from boiling alcohol; under these conditions, the *r*-acid is converted quantitatively into cinchonine *l*-tripyrocatechylarsenate, owing to the gradual racemisation of the *d*-acid, which would otherwise remain in solution, and continuous withdrawal of the *l*-acid as the cinchonine salt. *l*-Tripyrocatechylarsenic acid,



has  $[\alpha]_D -446.4^\circ$  in aqueous acetone. The following salts are described: *cinchonine* salt,  $[\alpha]_D -253.5^\circ$  in acetone; *potassium* salt,  $\text{K}[\text{As}(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot \text{H}_2\text{O}$ ,  $[\alpha]_D -459.9^\circ$  in aqueous acetone; *ammonium* salt (+H<sub>2</sub>O),  $[\alpha]_D -570.9^\circ$  in aqueous acetone; *barium* salt (+10H<sub>2</sub>O),  $[\alpha]_D -417.5^\circ$  in water; *quinidine* salt,  $[\alpha]_D -168^\circ$  in acetone.

*d*-Tripyrocatechylarsenic acid,  $[\alpha]_D +408.7^\circ$  in aqueous acetone, is prepared by resolution of the *r*-acid in alcoholic solution by quinine or cinchonidine. The *quinine* salt (+H<sub>2</sub>O),  $[\alpha]_D +250.2^\circ$  in acetone, *cinchonidine* salt (+H<sub>2</sub>O),  $[\alpha]_D +287.2^\circ$  in acetone, *potassium* salt (+H<sub>2</sub>O),  $[\alpha]_D +413.4^\circ$  in aqueous acetone, and *barium* salt (+10H<sub>2</sub>O),  $[\alpha]_D +418.7^\circ$  in water, are described.

*r*-Tripyrocatechylarsenic acid could not be resolved by the normal *strychnine* salt,  $[\alpha]_D -61.9^\circ$  in acetone, normal *brucine* salt (+H<sub>2</sub>O),  $[\alpha]_D -41.4^\circ$  in acetone, *cinchonine hydrogen* salt (+2H<sub>2</sub>O),  $[\alpha]_D +62.5^\circ$  in acetone, *cinchonidine hydrogen* salt (+2H<sub>2</sub>O), *quinine hydrogen* salt (+2H<sub>2</sub>O), or *quinidine hydrogen* salt (+2H<sub>2</sub>O).

The optically active tripyrocatechylarsenic acids are very stable

towards racemisation in alkaline solution; they are slowly inactivated in neutral solution, but are very sensitive towards hydrogen ions.

H. W.

**Piperonyl Bromide.** CHEMISCHE FABRIK FLORA (Swiss Pat., 107617; from *Chem. Zentr.*, 1925, ii, 612).—Piperonyl bromide is obtained by the action of dry hydrogen bromide on piperonyl alcohol in benzene at 0°.

R. B.

**Formation of Safroegenol [3-Hydroxy-4-ethoxyallylbenzene] and isoSafroegenol [3-Hydroxy-4-ethoxypropenylbenzene] from Safrole and isoSafrole.** K. KAFUKU (*Acta Phytchim.*, 1925, 2, 113—118).—On treatment with hot concentrated solutions of magnesium methyl iodide for 5 hrs., safrole and iso-safrole undergo rupture of their methylenedioxy rings. Safrole yields *safroegenol* [3-hydroxy-4-ethoxyallylbenzene], b. p. 111—112°/1.5 mm.,  $d_4^{20}$  1.03422,  $n_D^{20}$  1.52992 (benzoate, b. p. 200°/6 mm.,  $d^{20}$  1.0944,  $n_D^{20}$  1.5595; *phenylurethane*, m. p. 57.5—59°). *isoSafrole* apparently yields *cis-isoSafroegenol* [3-hydroxy-4-ethoxypropenylbenzene], m. p. 86° (acetate, m. p. 67—68.5°; benzoate, m. p. 59°; *methyl ether*, m. p. 63.5°; *phenylurethane*, m. p. 121—123°), the *trans-compound*, m. p. 35—36°, being formed when safroegenol is heated with potassium hydroxide. The *trans-form* may be changed to the *cis* by heating the solid with solid potassium hydroxide. The formulæ attributed to safroegenol and its *iso-form* are confirmed by the identity which exists between *trans-isoSafroegenyl methyl ether* and *isoeugenyl ethyl ether*, the latter being prepared by the method of Puxeddu (A., 1909, i, 225—226). An attempt to prepare *isoeugenyl ethyl ether* from eugenol, ethyl iodide, and sodium ethoxide in the hot led to an unknown substance, m. p. 60.5°. On catalytic reduction, safroegenol and its *iso-form* yield *dihydrosafroegenol* [3-hydroxy-4-ethoxypropylbenzene], m. p. 42.6°, b. p. 114.3—115.4°/3 mm.,  $d^{25}$  1.0095 (liquid),  $n_D^{25}$  1.5172 (liquid) (*phenylurethane*, m. p. 79—81°), which is also formed from dihydrosafrole and magnesium methyl iodide. On treatment with hot alkali, betelphenol [3-hydroxy-4-methoxyallylbenzene] is converted into *isobetelphenol* [3-hydroxy-4-methoxypropenylbenzene], m. p. 91° (*ethyl ether*, m. p. 50°).

B. F.

**Derivatives of *m*- and *o*-Dicresol [Dihydroxyditolyl].** W. STEINKOPF [with E. ZEMISCH, H. WINKLER, and G. POHL] (*J. pr. Chem.*, 1925, [ii], 110, 354—358).—*m*-Nitrotoluene is obtained in 43% yield by adding concentrated sulphuric acid (40 g.) gradually to a boiling solution of *m*-nitroacet-*p*-toluidide (10 g.) in 96% alcohol (40 g.), cooling to 10—15°, and, ignoring the separation of crystals, diazotising the product, decomposing the diazonium compound by gentle warming, extracting the *m*-nitrotoluene with ether, and purifying the product by vacuum distillation (b. p. 99—104°/16 mm.). When *m*-tolidine hydrochloride is treated in aqueous solution with gaseous nitrous acid at 18—20°, and the resulting mixture diluted and boiled with nitric acid, a tetranitro derivative, probably 3 : 5 : 3' : 5'-tetranitro-4 : 4'-dihydroxy-2 : 2'-di-

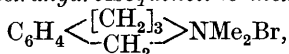
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*tolyl*, yellow, m. p. 299° (*ammonium* salt, deep yellow; *sodium* salt, reddish-golden), separates in 97% of the theoretical yield. When boiled with tin and hydrochloric acid, the tetranitro derivative affords the *chlorostannate* of 3 : 5 : 3' : 5'-*tetra-amino-4 : 4'-dihydroxy-2 : 2'-ditolyl*,  $C_{26}H_{36}O_4N_8 \cdot 8HCl, SnCl_4$ , from which the corresponding *tetra-acetamido* derivative ( $+2H_2O$ ) is obtained by the action of acetic anhydride. When dinitro-*o*-cresol is boiled with tin and hydrochloric acid until reduction is complete, and the cooled, filtered mixture saturated with hydrogen chloride, 5 : 5'-*diamino-4 : 4'-dihydroxy-3 : 3'-ditolyl dihydrochloride*, decomp. 230°, is obtained.

Aniline chlorostannate can be diazotised directly, with formation of *benzenediazonium chlorostannate*, light grey flocks.  $\alpha$ -Naphthylamine chlorostannate yields similarly  $\alpha$ -*naphthalenediazonium chlorostannate* as a greenish-yellow precipitate.

F. G. W.

**Syntheses in the Fatty-aromatic Series. XV. *o*- $\gamma$ -Bromopropylbenzyl Bromide.** J. VON BRAUN and W. KAISER (*Ber.*, 1925, **58**, [B], 2162—2164).—*o*- $\gamma$ -Chloropropylbenzonitrile is readily converted by alcoholic sodium ethoxide into *o*- $\gamma$ -ethoxypropylbenzonitrile, b. p. 150°/16 mm., which, in decahydronaphthalene at 100° and 30 atm., is readily hydrogenated to a mixture of *o*- $\gamma$ -ethoxypropylbenzylamine, b. p. 155—158°/16 mm. (*hydrochloride*, m. p. 112°), and, apparently, *di-o*- $\gamma$ -ethoxypropylbenzylamine; the latter substance when distilled under diminished pressure decomposes into *o*- $\gamma$ -ethoxypropylbenzylamine and 2-ethoxy-1 : 2 : 3 : 4-*tetrahydronaphthalene*. The primary base is transformed by sodium nitrite into *o*- $\gamma$ -ethoxypropylbenzyl alcohol, b. p. 165—170°/15 mm., which, in a difficult operation, is converted by hydrobromic acid (60%) at 100° during 22 hrs. into *o*- $\gamma$ -bromopropylbenzyl bromide, b. p. 175°/15 mm. The latter compound is converted by dimethylamine into *as-homotetrahydroisoquinoline methobromide*,



m. p. 241—242°.

H. W.

**Leprosy. XXXVII. Fractionation of Chaulmoogra Oil. II. Evidence of the Existence of a Highly Unsaturated Optically Active Acid.** R. WRENSHALL and A. L. DEAN (*U.S. Pub. Health Service Bull.*, 1924, **141**, 12—23).—Fractionation of the liquid acid residue of chaulmoogra acids, and application of the lead salt-ether method to the highly unsaturated fraction, yield an acid, probably  $C_{17}H_{29} \cdot CO_2H$ ,  $d^{20}_D$  0.9322,  $n^{28}_D$  1.4735,  $\alpha^{27}_D$  +53.1°, acid number 201.2, iodine number (Hübl) 168.3, rising to 180.4. Catalytic hydrogenation of the acid yields dihydrochaulmoogric acid.

CHEMICAL ABSTRACTS.

**Leprosy. XXXVIII. Catalytic Reduction of Chaulmoogric and Hydnocarpic Acids.** A. L. DEAN, R. WRENSHALL, and G. FUJIMOTO (*U.S. Pub. Health Service Bull.*, 1924, **141**, 24—27; cf. preceding abstract and T., 1904, **85**, 838, 851).—*Dihydrochaulmoogric acid*, m. p. 71—71.5°, iodine number 0.76—0.83, acid number

199.8,  $\alpha_D$  (5% solution in chloroform)  $-0.12^\circ$  to  $+0.57^\circ$  (*ethyl ester*, m. p.  $16.5^\circ$ ), is obtained by reduction for 48 hrs. with hydrogen and colloidal platinum-palladium catalyst of a solution of chaulmoogric acid (17%) in 95% alcohol, additional catalyst being added after 16–24 hrs. Esterification occurs simultaneously. *Dihydrohydno-carpic acid*,  $C_{15}H_{29} \cdot CO_2H$ , m. p.  $63^\circ$ , optically inactive, is obtained similarly.

CHEMICAL ABSTRACTS.

**Influence of Phosphorus Oxychloride on the Catalytic Reduction of Acid Chlorides.** F. ZETZSCHE and O. ARND (*Helv. Chim. Acta*, 1925, 8, 591–597).—In view of the conflicting results concerning the deleterious effect of phosphorus oxychloride on the catalytic reduction of acid chlorides (cf. Busch and Stöve, A., 1916, ii, 534; Rosenmund and Zetzsche, A., 1918, i, 300), the effects of varying concentrations of phosphorus oxychloride, temperature, and duration of heating on the reduction have been studied. If, in the reduction of benzoyl chloride in xylene solution with a palladium catalyst at  $115^\circ$ , a current of the oxychloride be passed into the reaction mixture, no benzaldehyde and only a trace of benzoic acid is formed, 98.8% of the chloride remaining unchanged, whilst in phosphorus oxychloride solution the whole of the acid chloride is recovered unchanged; hence phosphorus oxychloride itself, even in low concentrations, is a contact poison. With increasing concentration of the oxychloride, the production of the aldehyde, ester, and acid is in turn suppressed and the secondary formation of non-volatile hydrocarbons favoured. The same effect is observed, using smaller concentrations of the oxychloride, as the duration of heating is increased. The explanation of these phenomena by the theory of the “complex” mechanism of catalysis (cf. Rosenmund and Zetzsche, A., 1921, ii, 320) is discussed. Superimposed on the poisoning effect of the oxychloride is a secondary reaction by which it alters the existing complexes, or produces new ones, so that a reaction unfavourable to aldehyde formation sets in even after the removal of the oxychloride from the system. With increase in temperature, the arresting influence of the oxychloride decreases, but is still considerable at a temperature  $90^\circ$  above its b. p. For the synthesis of aldehydes, therefore, the acid chloride should be free from phosphorus oxychloride.

J. W. B.

**Glycol Esters of certain Aromatic Acids.** L. H. CRETCHER and W. H. PITTENGER (*J. Amer. Chem. Soc.*, 1925, 47, 2560–2563).—Glycol esters of various aromatic acids are prepared in 70–80% of the theoretical yield by the action of the anhydrous sodium salt of the acid on 3 mols. of ethylene chlorohydrin in the presence of a small concentration of diethylamine at  $130$ – $160^\circ$  for several hours. The following  $\beta$ -hydroxyethyl esters are thus obtained: benzoate, b. p.  $173^\circ/21$  mm.,  $d_{15}^{15}$  1.0937 (D.R.-P. 245532, 1910, gives m. p.  $45^\circ$ , but samples obtained showed no tendency to crystallise), giving a *phenylurethane*, m. p.  $115^\circ$ ; salicylate, b. p.  $172^\circ/12$  mm.,  $d_{15}^{15}$  1.2537 (cf. D.R.-P. 173776, 1905); *phenylcinchoninate*, m. p.  $90^\circ$ ; *p*-nitrobenzoate, m. p.  $77^\circ$  (D.R.-P. 245532, 1910, gives  $63^\circ$ ), which on reduction with iron and dilute hydrochloric acid yields the *p*-amino-

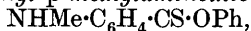
benzoate, m. p.  $132^{\circ}$  [*hydrochloride*, m. p.  $162$ — $163^{\circ}$  (decomp.)]. On heating, or distilling under ordinary pressure, the glycol monoesters are converted almost quantitatively into the di-esters and ethylene glycol and thus are obtained, *ethylene disalicylate*, m. p.  $78.5^{\circ}$ , and *di-p-nitrobenzoate*, m. p.  $140^{\circ}$ .  $\beta$ -Hydroxyethyl *p*-aminobenzoate is not suitable as a local anæsthetic. J. W. B.

**"Bromonovocaine."** J. FREJKA and J. VITHA (*Spisy Přírodovědeckou Fak. Masarykovy Univ.*, 1925, No. 48, 1—22).—2:4-Bromonitrotoluene, m. p.  $77$ — $78^{\circ}$ , obtained in 90% yield by refluxing *p*-nitrotoluene with bromine and ferrous bromide, when oxidised for 15 hrs. below the b. p. with 30% nitric acid and a small amount of mercury and potassium chlorate, yields 2-bromo-4-nitrobenzoic acid, m. p.  $166$ — $167^{\circ}$  (97% yield). Reduction with ferrous sulphate and barium hydroxide at  $50^{\circ}$  or with iron and hydrochloric acid at  $70^{\circ}$  yields 2-bromo-4-aminobenzoic acid, m. p.  $201$ — $202^{\circ}$  in 83% yield (*silver salt*, m. p.  $234^{\circ}$ ; *lead salt*, m. p. above  $300^{\circ}$ ; *ethyl ester*, m. p.  $125^{\circ}$ ). Condensation of the acid with ethylene chlorohydrin gives *chloro-o-bromo-p-aminobenzoylethanol*, m. p.  $123$ — $124^{\circ}$ , which when heated in a sealed tube with 2 mols. of dimethylamine affords *dimethylamino-o-bromo-p-aminobenzoylethanol*, m. p.  $130$ — $131^{\circ}$ . The following compounds were also prepared: 2-bromo-4-nitrobenzoyl chloride, m. p.  $132$ — $133^{\circ}$ ; *chloroethyl* and *ethylene 2-bromo-4-nitrobenzoate*, m. p.  $59$ — $60^{\circ}$  and  $134$ — $135^{\circ}$ , respectively; 3:3'-dibromoozobenzene-4:4'-dicarboxylic acid, m. p. above  $300^{\circ}$ , formed by air-oxidation of the hydrazine produced by reduction of the nitro compound with zinc and sodium hydroxide, when heated with ethylene chlorohydrin at  $110^{\circ}$  in a sealed tube, yields the *ethylene ester*.  
CHEMICAL ABSTRACTS.

**Action of Some Chlorides Derived from Carbonic Acid on Dimethylaniline.** H. RIVIER and P. RICHARD (*Helv. Chim. Acta*, 1925, 8, 490—500).—The action of a series of acid chlorides such as carbonyl chloride, thiocarbonyl chloride, and a number of derived chlorides on dimethylaniline is described. In most cases, substitution results in the *para* position of the dimethylaniline nucleus, but partial demethylation of dimethylaniline appears as a side reaction in some instances. The occurrence of isomeric thionic and thiolic esters of *p*-dimethylaminothiobenzoic acid is confirmed.

The action of carbonyl chloride on dimethylaniline at  $0$ — $10^{\circ}$  for several days yields *p*-dimethylaminobenzoyl chloride, m. p.  $147$ — $149^{\circ}$ , purified by removing the dimethylaniline hydrochloride in chloroform. By the action of sodium phenoxide, and of lead mercaptide and lead phenyl sulphides, this chloride furnishes *phenyl p*-dimethylaminobenzoate, m. p.  $180$ — $181^{\circ}$ , *ethyl p*-dimethylaminothiobenzoate,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{SEt}$ , m. p.  $61$ — $63^{\circ}$ , and *phenyl p*-dimethylaminothiobenzoate,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{SPh}$ , unstable (*picrate*, m. p.  $132$ — $133^{\circ}$ ). Thiocarbonyl chloride yields with dimethylaniline chiefly tetramethyldiaminodiphenyl thioetone and crystal-violet, but by conducting the reaction in carbon disulphide solution there is obtained a small yield of *p*-dimethylaminothiobenzoic acid,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{SH}$ , m. p.  $205$ — $208^{\circ}$  (decomp.), which is unstable but

yields coloured precipitates with solutions of salts of lead, iron, nickel, and cadmium. Ethyl chloroformate, phenyl chloroformate, and ethyl chlorothionformate give no condensation products with dimethylaniline, the base merely inducing decomposition with production of ethyl chloride and carbon dioxide, phenyl carbonate with carbon dioxide and hydrogen chloride, and ethyl chloride and carbon oxysulphide, respectively. Phenyl chlorothionformate, however, furnishes *phenyl p-methylaminothionbenzoate*,



yellow, m. p. 109—110°, methyl chloride being evolved in the reaction. Ethyl chlorothionformate also causes elimination of a methyl group, the product being *p-methylaminophenyl ethyl sulphide*, a pale yellow liquid, b. p. 154—156°/18 mm. (*picrate*, m. p. 130·5—131·2°), whilst phenyl chlorothionformate in an analogous manner produces *phenyl p-methylaminophenyl sulphide*, m. p. 65·5—66·5°, b. p. 345—350° (decomp.) (*picrate*, m. p. 140°; *nitrosoamine*, m. p. 160·5—161°). When dimethylaniline acts on ethyl or phenyl chlorodithioformate, the only products identified are ethyl and phenyl trithioformate and crystal-violet.

G. M. B.

**Mechanism of the Claisen Cinnamic Ester Synthesis.** H. SCHEIBLER and H. FRIESE (*Annalen*, 1925, **445**, 141—158).—In the synthesis of cinnamic acid by the interaction of benzaldehyde (1 mol.), ethyl acetate (2 mols.), and sodium or potassium (2 mols.) in ethereal solution (Claisen, A., 1890, 891), the yield of product is the same when the benzaldehyde is added to the freshly-prepared metal-ester condensation product, or added after the latter has been kept for 48 hrs., or when all three reactants are mixed in the solvent, indicating that the first phase of the reaction is the formation of the ethyl sodio- or potassio-acetate,  $\text{CH}_3\text{:C}(\text{ONa})\cdot\text{OEt}$ . Cinnamic acid is also formed by the action of benzaldehyde on the product obtained by dissolving metallic sodium in 10 parts of ethyl acetate (as in the acetoacetic ester synthesis) and removing excess of ester by evaporation under reduced pressure. Ethyl acetoacetate is not a by-product of this reaction, and benzaldehyde is without action on ethyl sodioacetoacetate under similar conditions. The use of sodium ethoxide in place of metallic sodium lowers the total yield of cinnamic ester and acid from 65% to 24%, the alcohol apparently preventing the reaction from proceeding to completion, since the yields of cinnamic derivatives can be increased by the following procedure, in which the alcohol formed during the reaction is removed. Sodium wire (9·2 g.) is added to a mixture of benzaldehyde (42·4 g.) and ethyl acetate (52·8 g.), the mixture being cooled at first, then boiled until solution of the metal is complete. Excess of ethyl acetate is then distilled off, any alcohol present being thereby removed, and the residue boiled with a further 40 c.c. of fresh ethyl acetate. This is again removed by distillation, treatment with fresh ethyl acetate repeated twice more, excess of the latter being finally removed by evaporation under reduced pressure. Treatment of the residue with cold dilute sulphuric acid, followed by extraction with ether, affords ethyl cinnamate (58 g., or 82·4%) and cinnamic

acid (8.2 g., or 13.9%). No advantage is gained by the application of excess of benzaldehyde, indicating that the reaction product, before hydrolysis, represents the end-product of the condensation. The presence of a small proportion of acetic acid in the hydrolysed product (cf. Stoermer and Kippe, A., 1905, i, 777) is to be ascribed to the formation of an additive product from the ethyl acetate and sodium ethoxide,  $\text{CMe}(\text{ONa})(\text{OEt})_2$  (I), hydrolysis of which may lead to either sodium or ethyl acetate, but it may undergo fission into ethyl alcohol and ethyl sodioacetate. Continuous removal of the alcohol by the above procedure favours this fission, as a result of which the proportion of (I) in the final condensation product is reduced to a minimum, and the ensuing formation of acetic acid avoided. The almost equally high yield of cinnamic acid, obtained when sodium ethoxide is used instead of metallic sodium, provided that the above method of removing alcohol is applied, affords additional evidence for the occurrence of the above fission, and indicates that the active agent in the acetoacetic ester and similar condensations is not (I) (cf. Claisen and Lowman, A., 1887, 583; 1888, 692), but the ethyl sodioacetate derived therefrom. The reaction between ethyl sodioacetate and benzaldehyde can be formulated

$$\text{CH}_2\text{:C}(\text{ONa})\cdot\text{OEt} + \text{Ph}\cdot\text{CHO} \rightarrow \begin{array}{c} \text{CH}_2 - \text{C}(\text{ONa})\cdot\text{OEt} \\ | \\ \text{CHPh}\cdot\text{O} \end{array} \rightarrow$$

$\text{CHPh}\cdot\text{CH}\cdot\text{C}(\text{OH})(\text{ONa})\cdot\text{OEt}$ , and the formation of both ester and acid from the sodium compound is due to the hydrolysis of the  $\cdot\text{C}(\text{OH})(\text{ONa})\cdot\text{OEt}$  group taking place in two directions simultaneously. Treatment of the sodium derivative with acetyl chloride affords a product which decomposes on distillation with formation of acetic and cinnamic acids and their ethyl esters, whilst benzyl iodide leads similarly to ethyl and benzyl alcohols and cinnamates. Condensation of benzyl acetate, benzaldehyde, and sodium in benzene affords a hygroscopic condensation product which yields benzyl cinnamate (73%) and cinnamic acid (20.8%) on hydrolysis, and on treatment with ethyl bromide affords a product which decomposes on distillation with formation of ethyl and benzyl alcohols and cinnamates. The analogous preparation of *p*-methoxycinnamic acid from *p*-anisaldehyde, ethyl acetate, and sodium, in ether, is described. Ethyl *isobutyrate* condenses with benzaldehyde and sodium in ether, with formation of  $\beta$ -phenyl- $\alpha\alpha'$ -dimethylhydracrylic acid (20%) and its ethyl ester (47.8%), the reaction being formulated



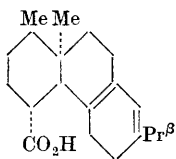
**Derivatives of Cinnamic Acid.** CHEMISCHE FABRIKEN VORM. WEILER-TER MEER (D.R.-P. 411955; from *Chem. Zentr.*, 1925, ii, 93).—*o*-Cyanocinnamic acid, m. p. 137°, is prepared by heating 1-nitroso- $\beta$ -naphthol with aqueous sodium hydroxide and *p*-toluenesulphochloride. Boiling with sodium hydroxide converts it into



*o*-carboxycinnamic acid, m. p. 183—184°, identical with the acid derived from the spatially isomeric *o*-cyanocinnamic acid of m. p. 254°. *Amyl o*-cyanocinnamate, m. p. 137°, distils without decomposition, whilst *methyl o*-cyanocinnamate has a considerably lower m. p. than the corresponding derivative of the above isomeride. A. C.

**Alkylamine Esters of Aromatic Amino-acids.** FARBEN-FABRIKEN VORM. F. BAYER & Co. (Austrian Pat. 99680; from *Chem. Zentr.*, 1925, ii, 772).— $\gamma$ -Dimethylamino- $\alpha\beta$ -dimethylpropyl *p*-nitrocinnamate, an oil, on reduction yields  $\gamma$ -dimethylamino- $\alpha\beta$ -dimethylpropyl *p*-aminocinnamate, b. p. 230—235°/8 mm. (hydrochloride). The *o*-nitrobenzoate and *o*-aminobenzoate (hydrochloride, m. p. 182°) of  $\gamma$ -dimethylamino- $\alpha\beta$ -dimethylpropyl alcohol and the hydrochloride, m. p. 100°, of the *m*-aminobenzoate are also described. R. B.

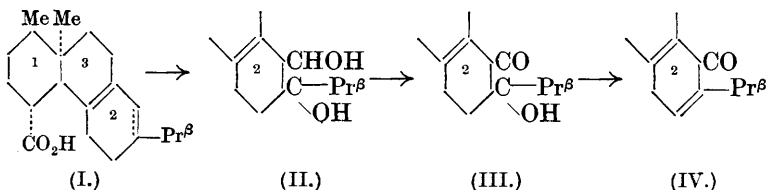
**Higher Terpene Compounds. XXV. Anhydride Formation and Nitric Acid Oxidation of Abietic Acid.** L. RUZICKA and M. PFEIFFER (*Helv. Chim. Acta*, 1925, 8, 632—636).—In opposition to the view of Knecht (A., 1923, i, 1202), it is shown that when purified abietic acid, obtained from American colophony, is heated for 8 days at 180° under a pressure of 12 mm. and then distilled in a high vacuum, the product has the formula  $C_{20}H_{30}O_2$ , no trace of anhydride formation being observed (cf. Ruzicka and Schinz, A., 1923, i, 1202). *l*-Pimaric acid from pine resin, similarly treated, yields only traces of water and carbon dioxide, the distilled product having the same composition. The indefinite melting points obtained by Knecht (*loc. cit.*) are probably due to the formation of isomerides. Oxidation of abietic acid with nitric acid, *d* 1.18, gives a 10% yield of trimellitic acid, the small yield being due to the complete destruction of the ring concerned in its production, thus confirming the annexed constitution for abietic acid (cf. Ruzicka, Schinz, and Meyer, A., 1924, i, 171; Virtanen, A., 1912, i, 669).



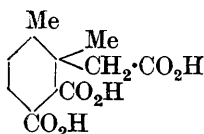
J. W. B.

**Higher Terpene Compounds. XXVI. Degradation of Abietic Acid by Potassium Permanganate and Ozone.** L. RUZICKA, J. MEYER, and M. PFEIFFER (*Helv. Chim. Acta*, 1925, 8, 637—650; cf. Ruzicka and Meyer, A., 1924, i, 172).—Oxidation of abietic acid with potassium permanganate (10 atoms of oxygen) yields an amorphous acid, insoluble in water, which, after purification through its methyl ester, yields a semicarbazide derivative corresponding with a dibasic acid of molecular formula  $C_{18}H_{26}O_4$  (cf. Aschan's "colophenic" acid, A., 1921, i, 512), but it is probably a mixture. The oxidation products soluble in water are isobutyric acid and (in small yield) a dimethylcyclohexanetricarboxylic acid, m. p. 224° (trimethyl ester, m. p. 75°), which is obtained in larger yield together with succinic acid when a quantity of potassium permanganate equivalent to 24 atoms of oxygen is used. The orientation of this acid relative to *o*- or *m*-xylene is not yet estab-

lished. Oxidation of methyl abietate with potassium permanganate (6 atoms of oxygen) in aqueous acetone solution yields a neutral *substance* (freed from a small quantity of a dibasic acid by means of sodium hydroxide solution), b. p. 225—235°/2 mm., of composition  $C_{21}H_{32}O_4$ , which on hydrolysis yields an amorphous *keto-acid*,  $C_{20}H_{30}O_4$  (III), [*semicarbazone*, amorphous, m. p. about 225° (decomp.)], which on heating for 15 hrs. with acetic anhydride and sodium acetate loses 1 mol. of water to yield an *acid*,  $C_{20}H_{28}O_3$ , (IV) (*semicarbazone*, amorphous, decomp. 240°). The formation of these products from the structure suggested for abietic acid is formulated thus:



Oxidation of abietic acid in carbon tetrachloride solution by ozone and hydrolysis of the ozonide yields no simple product which has been characterised with certainty (probably the same dicarboxylic acid as is obtained by permanganate oxidation) except *isobutyric acid*. By the action of ozone at 0° on methyl abietate in carbon tetrachloride solution, an *ozonide* was isolated, decomp. about 82°, which on analysis gives figures between those of a mono- and a di-ozonide, and on hydrolysis yields no product which could be characterised. The methyl ester was also treated with ozone in acetic acid solution (to attack the reactive double bond), the product of hydrolysis of the ozonide re-esterified and again treated with ozone (to attack the less reactive double bond). The final product was hydrolysed, converted into its methyl esters, and fractionally distilled. The fraction b. p. 132—137°/0.5



mm. on hydrolysis yields a tricarboxylic *acid*,  $C_{12}H_{18}O_6$ , m. p. 215—216°, which depresses the m. p. of the acid  $C_{11}H_{16}O_6$  obtained by permanganate oxidation, and is the next higher homologue of the latter, represented by the annexed formula or a position isomeride. These observations are all in accordance with the structure proposed for abietic acid (above), the double bond in juxtaposition to the *isopropyl* group being the reactive one.

J. W. B.

**Constituents of French and American Resins. II. E. KNECHT and E. HIBBERT** (*J. Soc. Dyers and Col.*, 1925, **41**, 329—333; cf. 1919, i, 338; 1923, i, 1202).—The work described in previous papers is continued and concluded. Reasons are given for adopting the name abietic acid for resin acids (m. p. 161°) of the formula  $C_{20}H_{30}O_2$  instead of pimaric acid. The yield of resin acids has been raised to 20%, but this is not considered the total

amount available from the original material. Acids having m. p. of  $130^{\circ}$  and  $145^{\circ}$  on repeated crystallisation from the same solvent had their m. p. raised to  $161^{\circ}$  (pure) by change of solvent. In regard to optical rotation very perplexing behaviour was met with, acids from French resin showing a positive and those from American resin of negative rotation changed about and gave the normal acid (m. p.  $161^{\circ}$ ) on purification. The rotation of a 2% solution of *l*-abietic acid (m. p.  $161^{\circ}$ ) in alcohol, heated at  $100^{\circ}$  for 1 hr., dropped to zero, and similarly with *d*-abietic acid (cf. Caillot, *Bull. Soc. chim.*, 1874, [ii], 21, 387). The acid sodium salt of *l*-abietic acid had  $[\alpha]_D -72^{\circ}$  and that of the *d*-acid,  $+72^{\circ}$ ; both had m. p.  $183^{\circ}$ . Purification of the acid through the sodium salt is recommended. Crystalline calcium and magnesium salts were prepared. The aluminium salt from sodium abietate and alum is non-crystalline and gives a liquid methyl ether. The nitrosites of *l*- and *d*-abietic acids,  $[\alpha]_D -50^{\circ}$  and  $+50^{\circ}$ , respectively, may be obtained in 95% yield from the resin itself. A solution of the resin in light petroleum is superposed on a solution of sodium nitrite and dilute hydrochloric acid gradually added. After a time the nitrosite separates as a blue, crystalline precipitate which becomes yellow on drying. The m. p. ( $98^{\circ}$ ) is only  $1^{\circ}$  below that of the nitrosite from pure abietic acid. The nitrosite from inactive abietic acid has m. p.  $137^{\circ}$ , possibly because abietic acid is dimeric. Attempts to determine the resin acids by the apparent insolubility of their nitrosites in light petroleum, or by making use of the fact that they behave as dibasic acids were unsuccessful. In the nitrometer, a pure nitrosite gives up one half of its nitrogen as nitric oxide, but not when mixed with fatty acids. Reduction by titanous chloride also gives uncertain results. The tribromo derivative of abietic acid (*loc. cit.*) is insoluble in sodium hydroxide, but when the acid is brominated in carbon tetrachloride and the solution shaken with aqueous potassium hydroxide, the tribromo compound loses 2 atoms of bromine, forming a yellow monobromo derivative. Abietic acid loses its power of crystallising after boiling with acetic anhydride. Vesterberg's *d*-pimaric acid (cf. A., 1922, i, 1020) reacts like abietic acid, taking up 6 atoms of bromine. It does not form a nitrosite. An optically inactive acid of mol. wt. 276 was obtained from the filtrate from Vesterberg's sodium pimarate. The composition of this acid is probably analogous to the colophenic acids resulting from the treatment of pinabietic acid with hydrogen peroxide (cf. Aschan, A., 1921, i, 512). From the great variation of the yields of the acid—greatest with *l*-abietic acid from French resin, whilst the *d*-acid from American resin sometimes contains none—it appears that *d*-pimaric acid is not a conversion product, but is present in small amount in the abietic acid itself. The pitch from the Pinion Pine (Rocky Mountains) shows a strong dextrorotation. An acid has been extracted from it having m. p.  $130$ – $140^{\circ}$  and  $[\alpha]_D -232^{\circ}$  which seems to be an analogue of Vesterberg's *l*-pimaric acid,  $[\alpha]_D -272^{\circ}$ . Air oxidation of the *d*-acid from American resin led to the separation of a small amount of an acid of composition  $C_{20}H_{30}O_2$ , m. p.  $198^{\circ}$ ,  $[\alpha]_D -60^{\circ}$ . After purification through the

sodium salt the m. p. was  $210^\circ$  and the rotation  $+63^\circ$ , indicating a change from the *l*- to the *d*-pimaric acid of Vesterberg.

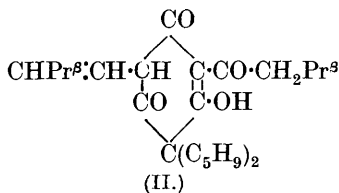
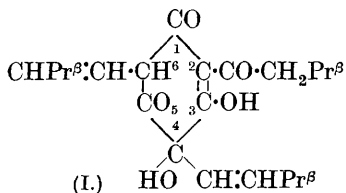
It is concluded that the particular American resins examined contain acids similar to Vesterberg's *d*- and *l*-pimaric acids but differ in showing opposite optical rotations, *i.e.*, there are two *dextro* and two *laevo* pimaric acids. To ensure constancy of results in the examination of the resin acids, it is considered necessary to have a guarantee of their exact source and mode of manufacture.

A. C.

**Abietic Acid.** J. FREIKA and F. BALAŠ (*Spisy Prirodovedeckou Fak. Masarykovy Univ.*, 1923, No. 29, 3—12; cf. Mach, A., 1895, i, 384).—On oxidation at  $0^\circ$  with potassium permanganate, sodium abietate prepared from American colophony by Mach's method yields isopropionic acid and a monobasic acid,  $C_{10}H_{16}O_3$ , m. p.  $89$ — $90^\circ$  (*lead*, *silver*, and *barium* salts; *oxime*, m. p.  $172^\circ$ ); Levy's tetrahydroxyabietic acid could not be detected.

CHEMICAL ABSTRACTS.

**Chemical Nature of the Resin Acids of Hops. II.** H. WIELAND, E. MARTZ, and H. HOEK (*Ber.*, 1925, **58**, [B], 2012—2017).—*isoHumulic* acid (Wieland, this vol., i, 276) is converted by hot potassium hydroxide solution into oxalic acid, methyl *isobutyl* ketone, methyl *isohexyl* ketone, *isovaleric* acid, and  $\delta$ -methylhexoic acid. The primary product of the action is therefore the diketone,  $Pr^{\beta} \cdot [CH_2]_3 \cdot CO \cdot CH_2 \cdot CO \cdot CH_2 \cdot Pr^{\beta}$ , which is hydrolysed to acid and ketone in each of the two possible directions. The constitution  $\begin{matrix} CO-CH([CH_2]_2 \cdot Pr^{\beta}) \\ CO-CH(CO \cdot CH_2 \cdot Pr^{\beta}) \end{matrix} > CO$  for *isohumulic* acid is therefore established. These results, considered in conjunction with those recorded previously (*loc. cit.*), permit the constitution (I)



to be assigned to humulon, in which only the position of the double linking in the side chain attached to carbon atom 6 is doubtful. This double linking is retained in humulic acid and in the hydrocarbon derived from it by Clemmensen's method (to which the constitution  $\begin{matrix} CH_2-CH(CH \cdot CHPr^{\beta}) \\ CH_2-CH(CH_2 \cdot CH_2 \cdot Pr^{\beta}) \end{matrix} > CH_2$  is now assigned). This linking cannot be present in the side chain attached to carbon atom 2, since if in the  $\alpha\beta$  position to the carbonyl group it would become hydrogenated during the formation of the hydrocarbon,  $C_{15}H_{28}$ , and if in the  $\beta\gamma$  position would become displaced towards the carbonyl group during the conversion of humulon into humulic acid by treatment with alkali. There remains only the third

side chain available for it in which the  $\alpha\beta$  position is excluded and the location is chosen (as shown) by analogy with other unsaturated substances. The optical activity of humulon is due to the asymmetry of carbon atom 4. This atom becomes a member of a carboxy group when humulon is transformed into the optically inactive humulic acid; during the process, enolisation also occurs at the two other asymmetric carbon atoms of humulon (assuming a triketonic structure).

The close relationship of humulon to lupulon (cf. Wöllmer, this vol., i, 690) allows the constitution (II), to be assigned to the latter.  
H. W.

**Ester of Salicylic Acid.** J. D. RIEDEL AKT.-GES. (D.R.-P. 414798; from *Chem. Zentr.*, 1925, ii, 771).—Phenyl salicylate is heated with *p*-propenylphenol and the fraction distilling at 180—230°/14 mm. yields *p*-propenylphenyl salicylate, m. p. 87°.

R. B.

**Synthesis of *p*-Hydroxyphenylglycine.** K. SHIMO (*Rep. Osaka Ind. Res. Lab.*, 1924, 5, No. 7, 1—13).—Commercial "formalin" (17 c.c.) is added to an ice-cooled solution of 30 g. of *p*-aminophenol hydrochloride in 140 c.c. of hot water, and 75 g. of 20% potassium cyanide solution are added dropwise. The nitrile,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CN}$  (95% yield), is dissolved (20 g.) in 100 c.c. of 10% potassium hydroxide solution and boiled with 50 c.c. of water for 15—20 mm. until no more ammonia is evolved. On neutralisation with dilute hydrochloric acid and acidification with acetic acid, *p*-hydroxyphenylglycine separates in 84.2% yield. The methyl and ethyl derivatives of *p*-hydroxyphenylglycine, and the acetyl and benzoyl derivatives of the nitrile are described.

CHEMICAL ABSTRACTS.

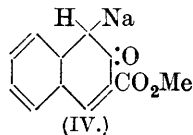
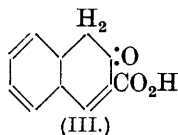
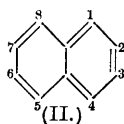
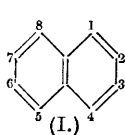
**Methylation of Tyrosine.** E. ABDERHALDEN and E. SCHWAB (*Z. physiol. Chem.*, 1925, 148, 17—22).—Tyrosine, treated with diazomethane in dry ether, yields methyl  $\alpha$ -amino- $\beta$ -*p*-anisylpropionate, a yellow oil, b. p. 158°/12 mm. (hydrochloride, m. p. below 100°), and methyl  $\alpha$ -methylamino- $\beta$ -*p*-anisylpropionate, which on distillation passes into the anhydride. In moist ether, methylation yields only small amounts of the above, the chief product being *p*-methoxybenzylbetaine, m. p. 222° (decomp.), hydrochloride, m. p. 107°, chloroplatinate, m. p. 232°.

P. W. C.

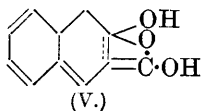
**Esters of Aromatic Alkyloxy- and Alkylamino-carboxylic Acids, containing Iodine in the Aliphatic Side-chain.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 412699; from *Chem. Zentr.*, 1925, ii, 613).—Esters of iodoalkyloxy- or iodoalkylamino-aromatic acids are obtained by esterification of the corresponding acids or from the hydroxyalkyloxy or hydroxyalkylamino acids by replacement of the hydroxyl group with halogen. Thus *p*- $\beta$ -hydroxyethoxybenzoic acid, m. p. 182° (from ethylenechlorhydrin and *p*-hydroxybenzoic acid; methyl ester, m. p. 65°), with phosphorus pentachloride yields *p*- $\beta$ -chloroethoxybenzoyl chloride, m. p. 42°, b. p. 180°/10 mm., from which *p*- $\beta$ -chloroethoxybenzoic acid,

m. p. 256°, and *p*-β-iodoethoxybenzoic acid, m. p. 181°, are successively obtained. The methyl ester of the latter acid has m. p. 70°. Similarly, *p*-β-chloroethoxybenzoyl chloride with benzyl alcohol yields benzyl *p*-β-chloroethoxybenzoate, m. p. 62°, which with sodium iodide in acetone gives benzyl *p*-β-iodoethoxybenzoate, m. p. 77–78°. Methyl *p*-β-hydroxyethoxybenzoate with phosphorus pentabromide yields methyl *p*-β-bromoethoxybenzoate, m. p. 68°, which can be converted into the iodoethoxy ester. Methyl *p*-hydroxybenzoate and isopropylenechlorohydrin yield, after hydrolysis, *p*-β-hydroxypropoxybenzoic acid, m. p. 150°, from which *p*-β-chloropropoxybenzoyl chloride, methyl *p*-β-chloropropoxybenzoate, b. p. 140–142°/1 mm., and methyl *p*-β-iodopropoxybenzoate, b. p. 156–159°/1 mm., are successively obtained. Ethyl *m*-aminobenzoate and ethylene bromide yield ethyl *m*-β-bromoethylaminobenzoate, converted by sodium iodide in acetone into ethyl *m*-β-iodoethylaminobenzoate, m. p. 123°. R. B.

**Constitution of Naphthalene and its Derivatives.** R. LESSER, E. KRANEPUHL, and S. SAD (*Ber.*, 1925, **58**, [B], 2109–2124).—In an attempt to discriminate between the symmetrical and unsymmetrical formulæ for naphthalene, (I) and (II), examination has been made of 2-hydroxynaphthalene-3-carboxylic acid, which, on account of the yellow colour of its alkali salts and those



of its esters, has been considered by Möhlau to be 2-keto-1 : 2-dihydronaphthalene-3-carboxylic acid, (III) and (IV). Since, however, methyl 1-bromo-2-hydroxynaphthalene-3-carboxylate yields stable, coloured salts of the alkali metals, Möhlau's conception cannot be maintained in its entirety, since its application involves the presence of alkali and bromine in stable union to the same carbon atom. The presence of the quinonoid linking is, however, established and since it cannot lie between carbon atoms 1 and 2, it must be between the atoms 2 and 3 [cf. formula (II)]. The structure of the coloured derivatives is most readily explained by adopting the structure (V) based on the recent work of Anschütz (this vol., i, 666) on isomeric *O*- and *N*-acylsalicylamides. The strength of the subsidiary valency depends on the nature of the substituents in the carboxyl group and sinks to zero in the colourless anilide and colourless basic sodium salt



of free 2-hydroxynaphthalene-3-carboxylic acid, whereas compounds in which the hydrogen of the nuclear hydroxyl groups is replaced by another group are simply formulated in accordance with (II). In any case, it is certain that a double linking in 2-hydroxynaphthalene-3-carboxylic acid lies between carbon atoms 2 and 3, and thus definite evidence is adduced in favour of the

unsymmetrical structure (II) for naphthalene. The adoption of this constitution affords a simple explanation of the observations of Willstätter (A., 1912, i, 545; 1913, i, 353; 1923, i, 771) on the hydrogenation of naphthalene, if it be assumed that in the production of tetrahydronaphthalene the double linkings between carbon atoms 5 and 6 and 7 and 8 (or the conjugate linking between 5 and 8) are ruptured and the remaining benzene nucleus offers great resistance to hydrogenation, whereas in the perhydrogenation the primary addition takes place at carbon atoms 2 and 3, thus leaving a cyclic structure with uniform conjugate double linkings which therefore readily undergoes complete hydrogenation without production of isolable intermediate compounds.

Whether the unsymmetrical structure of naphthalene persists in all its derivatives cannot at present be decided definitely, but this appears to be the case in so far as products containing substituents in only one nucleus are concerned. This conclusion appears to be contrary to the evidence of von Weinberg (A., 1921, i, 781), who, however, worked exclusively with naphthalene derivatives symmetrically substituted in both nuclei. Since, however, experimental evidence is now adduced in favour of the symmetrical disposition of the double linkings in 2:7-dihydroxynaphthalene, it appears probable that the symmetrical structure (II) is to be generally ascribed to such compounds.

The following compounds are incidentally described: 2-hydroxy-3-naphthoyl chloride, m. p. 95—96°; 2-hydroxy-3-naphthamide, m. p. 217—218°; 2-acetoxy-3-naphthoic acid, m. p. 184—186°; 2-benzoyloxy-3-naphthoic acid, m. p. 208—209°; 2-acetoxy-3-naphthamide, colourless needles, m. p. (indef.) 180—190° after becoming yellow at 160°, which readily becomes isomerised to 2-hydroxy-3-naphthoacetamide, yellow plates, m. p. 185°; 2-acetoxy-3-naphthoacetamide, m. p. 159—160°; 1-bromo-2-acetoxy-3-naphthoic acid, m. p. 183°; 1-bromo-2-acetoxy-3-naphthamide, apparent m. p. 204—206° after becoming yellow at about 180° (actually m. p. of the isomeric *N-acetyl* derivative, into which it is converted by heat or by prolonged treatment with boiling, glacial acetic acid); 1-bromo-2-hydroxy-3-naphthamide, m. p. 258—259°; 2-acetoxy-3-naphthonitrile, m. p. 118°; 2-hydroxy-3-naphthonitrile, m. p. 188—189°; methyl 2-methoxy-3-naphthoate, b. p. 197—198°/11 mm., m. p. 63—65°; 2-methoxy-3-naphthoic acid, m. p. 134—135°; 2-methoxy-3-naphthamide, m. p. 172—173°; 2-methoxy-3-naphthonitrile, m. p. 132—133°; methyl 1-bromo-2-hydroxy-3-naphthoate, m. p. 115°. Methyl 2-hydroxy-3-naphthoate yields an intensely yellow *potassium* salt,  $C_{12}H_9O_3K$ ; the analogous *sodium*, *rubidium*, *cadmium*, *mercury*, and *silver* salts are described. Methyl 1-bromo-2-hydroxy-3-naphthoate similarly yields intensely yellow *sodium*, *potassium*, *rubidium*, and *cadmium* salts. The *potassium* salt of 1-bromo-2-hydroxy-3-naphthamide and the *silver* and *potassium* salts of 2-hydroxy-3-naphthonitrile are described; the *silver* salt is transformed by methyl iodide into 2-methoxy-3-naphthonitrile, m. p. 132—133°. 2-Acetoxy-3-naphthoyl chloride is converted by aluminium chloride and benzene into *phenyl* 2-hydroxy-3-naphthyl

ketone, m. p. 161—162° (the orange-red *potassium* salt is described). 2-Hydroxy-3-naphthomethylanilide has m. p. 192—193°.

2:7-Dihydroxynaphthalene is converted by acetic anhydride and sodium hydroxide solution into a *monoacetyl* derivative, m. p. 171—172°, and by benzoyl chloride into the *monobenzoyl* compound, m. p. 199°; acetylation of the benzoyl compound or benzylation of the acetyl derivative yields the same *benzoyloxyacetoxy-naphthalene*, m. p. 136—137°. The action of diphenylcarbamyloxy chloride on 2:7-dihydroxynaphthalene gives the corresponding *diphenylcarbamyloxy* compound, m. p. 261°, which is converted by benzoyl chloride into 2-benzoyloxy-7-diphenylcarbamyloxy-naphthalene, m. p. 179°, identical with the substance obtained by the action of diphenylcarbamyloxy chloride on the monobenzoyl derivative. 2-Hydroxy-7-benzoyloxy-naphthalene has m. p. 151—152°. The preparation of monoacetyl or monobenzoyl derivatives of 2:6- or 1:5-dihydroxynaphthalene could not be effected. H. W.

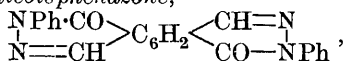
**Preparation of  $\beta$ -Naphthol-4-carboxylic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 413836; from *Chem. Zentr.*, 1925, ii, 614).— $\alpha$ -Naphthylamine-3-sulphonic acid is converted into 1-cyanonaphthalene-3-sulphonic acid (*potassium* salt, *barium* salt), which on boiling with dilute alkali yields 1-carboxynaphthalene-3-sulphonic acid. This acid, or the nitrile acid, on fusion with sodium hydroxide at 220—230°, yields  $\beta$ -naphthol-4-carboxylic acid, m. p. 241—242°; fission of the substituted ring does not take place. Diazotised *p*-nitroaniline yields a dark red azo dye with  $\beta$ -naphthol-4-carboxylic acid. R. B.

**Action of Benzilic and Anisilic Acids on Thiophenols.** A. BISTRZYCKI and J. RISI (*Helv. Chim. Acta*, 1925, 8, 582—591).—In contrast to the reaction of the alkyl ethers of thiophenol previously described (A., 1922, i, 33), it is found that thiophenol itself reacts with benzilic acid in glacial acetic acid solution on addition of sulphuric acid at 40—45° to yield  $\alpha$ -phenylthioldiphenylacetic acid,  $\text{C}_6\text{H}_5(\text{SPh})\cdot\text{CO}_2\text{H}$ , m. p. 126—128° (*sodium* and *barium* salts described), which also results from the direct action of thiophenol on diphenylchloroacetic acid in benzene solution. This acid loses carbon dioxide when its solution in pyridine is boiled, with production of *phenyl benzhydryl sulphide*,  $\text{CHPh}_2\cdot\text{SPh}$ , m. p. 76—78.5°. Oxidation of the acid with chromic anhydride in acetic acid solution gives no sulphone, but a little benzophenone. Its *acid chloride*, m. p. 45—50°, heated with anhydrous zinc chloride, undergoes an internal condensation to give 1:1-diphenyl-2-keto-1:2-dihydrothionaphthen,  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{CPh}_2$ , m. p. 145—146°. The following compounds are prepared by analogous reactions:  $\alpha$ -*p*-tolylthioldiphenylacetic acid, m. p. 155° (after sintering at 135°), from thio-*p*-cresol;  $\alpha$ -phenylthioldi-*p*-anisylacetic acid, m. p. 106—107°, from anisilic acid and thiophenol (*barium* salt described), which loses carbon dioxide at 140° to give *phenyl 4:4'-dimethoxybenzhydryl sulphide*,  $(\text{MeO}\cdot\text{C}_6\text{H}_4)_2\text{CH}\cdot\text{SPh}$ , m. p. 50.5—51.5°. No similar



condensation results between thiophenol and mandelic,  $\alpha$ -hydroxy-isobutyric,  $\alpha$ -bromoisobutyric,  $\alpha$ -bromopropionic,  $\beta$ -chloro- or  $\beta$ -iodopropionic, or bromomalonic acids. Incidentally, it is found that  $\alpha$ -bromopropionic acid and bromomalonic acid, when heated with stannous chloride in benzene solution, yield  $\alpha\beta$ -dimethylsuccinic and succinic anhydrides, respectively. G. M. B.

**Derivatives of Cumidic and Pyromellitic Acids.** H. DE DIESBACH and G. ZURBRIGGEN (*Helv. Chim. Acta*, 1925, 8, 546—556).—Bromine vapour, introduced by means of a stream of carbon dioxide into the dinitrile of  $\beta$ -cumidic acid (cf. A., 1923, i, 798) above its m. p. (209·5—210°), yields as a first product the *dinitrile* (m. p. 163°) of 1:4-di(bromomethyl)benzene-2:5-dicarboxylic acid, which itself decomposes without melting at 339—340° and was isolated by the action of formic acid on its *dibromide*, m. p. 117—117·5°, obtained by a similar bromination of  $\beta$ -cumidoyl chloride (m. p. 116°). (*Diethyl ester*, m. p. 163—163·5°, described.) By heating the dinitrile with hydrogen chloride in glacial acetic acid at 180° or with 70% sulphuric acid, or by dissolving the free acid in sodium carbonate solution, or by elimination of 2 mols. of ethyl bromide from the diethyl ester above its m. p., *p*-pyromellitide [the *dilactone* of 1:4-di(hydroxymethyl)benzene-2:5-dicarboxylic acid], decomp. 338—339°, is produced, which is oxidised by permanganate to pyromellitic acid. More prolonged bromination of  $\beta$ -cumidic dinitrile yields the *dinitrile* (m. p. 221°) of 1:4-di(dibromomethyl)benzene-2:5-dicarboxylic acid, decomp. 259—260°, itself prepared by the action of formic acid on its *dibromide*, m. p. 147°, the product of further bromination of the dibromo-dibromide of m. p. 117—117·5° *diethyl ester*, m. p. 142—142·5°, also described). This acid is converted by boiling with calcium carbonate and water into 1:4-dialdehydobenzene-2:5-dicarboxylic acid, m. p. 257·5—258·5° (decomp.) (*dioxime*, decomp. 153°), which yields with phenylhydrazine *pyromelliticbisphenazone*,



m. p. 352°.

The dinitrile (m. p. 144—145°) of  $\alpha$ -cumidic acid brominated at 165° furnishes 1:3-di(bromomethyl)benzene-4:6-dicarboxylic *dinitrile*, m. p. 114°, converted by hot 70% sulphuric acid into *m*-pyromellitide [the *dilactone* of 1:3-di(hydroxymethyl)benzene-4:6-dicarboxylic acid], m. p. 277·5—278·5° (decomp.). Bromination of  $\alpha$ -cumidoyl dichloride (m. p. 82°) at 160° yields the *dibromide* (m. p. 104°) of 1:3-di(dibromomethyl)benzene-4:6-dicarboxylic acid, m. p. 224—225° (decomp.) (*diethyl ester*, m. p. 93°), the dibromide being converted further by complete hydrolysis into 1:3-dialdehydobenzene-4:6-dicarboxylic acid, m. p. 246—247° (decomp.).

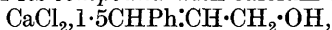
*p*-Pyromelliticdi-imidine [the *dilactam* of 1:4-di(aminomethyl)benzene-2:5-dicarboxylic acid], a white powder not melted at 350°, results from the action of ammonia gas on an alcoholic solution of the corresponding dibromo-diethyl ester, whilst aniline produces

the *dianil*, not melted at 360°. The *m*-*pyromelliticdi-imidine* is similarly obtained and decomposes at 340–350°. G. M. B.

**Substitution in Vicinal Trisubstituted Benzene Derivatives.**

III. L. RUBENSTEIN (*J. Chem. Soc.*, 1925, **127**, 2268–2269; cf. Davies and Rubenstein, *T.*, 1923, **123**, 2839).—The nitration of 3-methoxy-2-ethoxybenzaldehyde yields a mixture of 5- and 6-nitro-3-methoxy-2-ethoxybenzaldehydes, which is found to contain 60% of the 5-nitro and 40% of the 6-nitro compound. A complete separation of the mixture of 5- and 6-nitro-2 : 3-diethoxybenzaldehydes, obtained in the nitration of 2 : 3-diethoxybenzaldehyde, has not been effected. In both these nitrations the 4-nitro-aldehyde is formed in small quantity. B. W. A.

**Mixed Cannizzaro Reaction.** III. C. ENDOH (*Rec. trav. chim.*, 1925, 866–875).—Simple and mixed Cannizzaro reactions have been obtained with cinnamaldehyde alone and with acetaldehyde, in the presence of aluminium ethoxide as condensing agent, the products being cinnamyl cinnamate in the former case and a mixture of ethyl cinnamate with *cinnamyl acetate*, b. p. 142–144°/12 mm., in the latter. Cinnamyl alcohol was isolated, after hydrolysis, by means of its *compound* with calcium chloride,



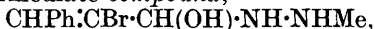
m. p. 157°, and obtained in 41% yield of crystalline product of m. p. 33°. G. M. B.

**Action of Aldehydes on Grignard's Reagent.** III. J. MARSHALL (*J. Chem. Soc.*, 1925, **127**, 2184–2188; cf. *T.*, 1914, **105**, 527; 1915, **107**, 509).—It has been shown (*loc. cit.*) that, where the aldehyde is in excess in a Grignard reaction, along with the primary and secondary alcohols obtained, the ketone corresponding with the secondary alcohol is also formed, with the condensation products of this ketone with the aldehyde used. The suggestion that the mechanism is analogous to Cannizzaro's reaction is borne out by the formation, besides cinnamyl alcohol, of styryl methyl ketone when cinnamaldehyde reacts with magnesium methyl iodide, and of styryl ethyl ketone when magnesium ethyl iodide is used (cf. Meisenheimer, this vol., i, 527; Hess, *A.*, 1924, i, 859). Magnesium phenyl bromide, reacting with excess of trioxymethylene, yielded chiefly benzyl bromide and, as expected, some benzaldehyde. B. W. A.

**Derivatives of Phenylpropionaldehyde and  $\alpha$ -Bromocinnamaldehyde.** K. VON AUWERS and B. OTTENS (*Ber.*, 1925, **58**, [B], 2060–2071).—Phenylpropionaldehyde, b. p. 105–108°/10 mm.,  $d_4^{15.3}$  1.0639,  $n_D^{15.8}$  1.60717, is converted by semicarbazide in faintly acid, neutral, or faintly alkaline aqueous-alcoholic solution into a mixture of the labile *semicarbazone*, m. p. 193–194°, and stable semicarbazone, m. p. 132–134° (cf. Driessen, *Diss.*, Kiel, 1898; Moureu and Delange, *A.*, 1904, i, 650). Transformation of the former into the latter substance is effected by glacial acetic acid or by mineral acid in alcoholic solution. The semicarbazones are hydrolysed by 2*N*-sulphuric acid at 100°, the phenylpropiol-

aldehyde being identified as the *p*-nitrophenylhydrazone, m. p. 133—135°. Oxidation of the semicarbazones by potassium permanganate in aqueous acetone affords benzoic acid. [Benzaldehydesemicarbazone is stable towards permanganate at 0°; it is converted by nascent nitrous acid into benzaldehyde. Cinnamaldehydesemicarbazone is readily oxidised by permanganate to benzoic acid.] Attempts to convert phenylpropionaldehydesemicarbazone into a pyrazole derivative were unsuccessful. Similar experiments are recorded with the compound, b. p. 158—160°/14 mm.,  $d_4^{25}$  0.9937,  $n_D^{25}$  1.51665, obtained by Lieske (*Diss.*, Kiel, 1908) by the action of sodium ethoxide on phenylpropionaldehyde diethylacetal and regarded by him as  $\beta$ -ethoxycinnamaldehyde diethylacetal, but now shown to be  $\alpha$ -ethoxycinnamaldehydediethylacetal, since the semicarbazone, m. p. 151—152° (obtained by Lieske from the free aldehyde), is hydrolysed to an  $\alpha$ -monosemicarbazone,  $C_{10}H_{11}O_2N_3$ , m. p. 168—169°, which is converted by semicarbazide into a disemicarbazone, m. p. 238°, identical with benzylglyoxaldisemicarbazone described by Dakin and Dudley (*A.*, 1914, i, 907). The rule that in the addition of HX to a compound containing the group  $>C:C<$  or  $-C:C-$  the radical X becomes attached to the carbon atom poorest in hydrogen appears to be valid only in the absence of negative substituents; these cause X to enter in a position as remote from them as possible, and in those cases in which two such substituents are present the more strongly negative one has the directing influence.

Attempts to convert the mixture of stereoisomeric phenylpropionaldehydephenylhydrazones (cf. Driessen, *loc. cit.*; Lieske, *loc. cit.*) into 1:5-diphenylpyrazole were unsuccessful. On the other hand, phenylpropionaldehyde and methylhydrazine yield 5-phenyl-1-methylpyrazole, b. p. 142—143°/22 mm., with such ease that the isolation of the primarily formed methylhydrazone appears impossible. Similarly,  $\alpha$ -bromocinnamaldehyde and methylhydrazine yield ultimately 5-phenyl-1-methylpyrazole (von Auwers and Schmidt, this vol., i, 586), reaction occurring through the unstable intermediate compound,



m. p. 45—50°, which is hydrolysed by cold mineral acid to  $\alpha$ -bromocinnamaldehyde and methylhydrazine; decomposition of this substance appears to yield 4-bromo-5-phenyl-1-methylpyrazoline hydrobromide, m. p. 129—130°, or in the presence of ether gives 5-phenyl-1-methylpyrazole,  $\alpha$ -bromocinnamaldehyde, and methylhydrazine.

Phenylpropionaldoxime very readily suffers ring closure, and even under the mildest conditions appears to be converted by acetic anhydride into phenylpropionitrile, m. p. 38—40°; the constitution  $\begin{array}{c} CPh:C\cdot CH \\ | \\ HO\cdot N \end{array}$  may therefore be assigned to it. On the

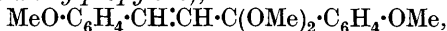
other hand,  $\alpha$ -bromocinnamaldoxime, m. p. 144°, cannot be converted into an isomeric cyclic compound and is transformed by cautious treatment with acetic anhydride into the *acetate*, m. p. 81—82°, from which the original oxime can be regained; boiling

acetic anhydride transforms it into  $\alpha$ -bromocinnamonnitrile, b. p.  $155^\circ/30$  mm.,  $144\text{--}145^\circ/15$  mm.,  $d_4^{19.3}$  1.4656,  $n_{\text{He}}^{19.3}$  1.63169. The oxime probably has the constitution  $\text{CHPh}\cdot\text{CBr}\cdot\overset{\text{N}\cdot\text{OH}}{\underset{|}{\text{CH}}}$ . According

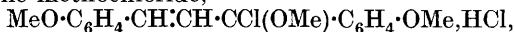
to this view, water is more readily lost from the *anti*- than from the *syn*-oxime, so that Meisenheimer's views on the Beckmann transformation of ketoximes appear capable of extension to intramolecular reactions of aldoximes. *Cinnamonnitrile*, prepared from cinnamaldehyde for purposes of comparison, has b. p.  $135^\circ/18$  mm.,  $d_4^{20.2}$  1.0304,  $n_{\text{He}}^{20.2}$  1.59467.

$\alpha$ -Bromocinnamaldehydesemicarbazone, m. p.  $206\text{--}207^\circ$ , could not be transformed into a cyclic compound. Similar results are recorded with  $\alpha$ -bromocinnamaldehydephenylhydrazone,  $\alpha$ -ethoxycinnamaldehydephenylhydrazone, and  $\alpha$ -methylcinnamaldehydephenylhydrazone. H. W.

**Distyryl Ketone and Triphenylmethane. XII. The Dimethylacetal and Methochloride of *p*-Anisyl *p*-Methoxystyryl Ketone.** F. STRAUS and W. HEYN (*Annalen*, 1925, **445**, 92—110).— $\alpha\gamma$ -Dichloro- $\alpha\gamma$ -di-*p*-anisylpropylene (Straus, Krier, and Lutz, A., 1910, i, 565), m. p.  $73\text{--}77^\circ$ , is prepared by an improved method by the action of oxalyl chloride on anisyl *p*-methoxystyryl ketone in benzene or chloroform. It reacts with sodium methoxide in methyl alcohol in a glass-lined autoclave at  $100^\circ$  to give the dimethylacetal of *p*-anisyl *p*-methoxystyryl ketone ( $\gamma\gamma$ -dimethoxy- $\alpha\gamma$ -di-*p*-anisylpropylene),



b. p.  $228\text{--}230^\circ/0.8\text{--}0.9$  mm.,  $d_{20}^{20}$  1.130,  $n_D^{21.2}$  1.57572.  $\alpha$ -Chloro- $\gamma$ -methoxy- $\alpha\gamma$ -dianisylpropylene (Straus, Krier, and Lutz, *loc. cit.*) is probably formed intermediately, and it is shown that this compound, which decomposes at the ordinary temperature with evolution of heat into methyl chloride and anisyl methoxystyryl ketone, undergoes isomerisation in the presence of a trace of hydrogen chloride, with migration of the  $\gamma$ -methoxyl and a corresponding change in position of the double linking:  $\text{C}\text{ArCl}\cdot\text{CH}\cdot\text{CH}\text{Ar}\cdot\text{OMe} \rightarrow \text{C}\text{ArCl}(\text{OMe})\cdot\text{CH}\cdot\text{CH}\text{Ar}$  (cf. Ziegler, Richter, and Schnell, this vol., i, 915).  $\gamma\gamma$ -Dimethoxy- $\alpha\gamma$ -dianisylpropylene is very sensitive to acids, which convert it into the parent ketone, m. p.  $102.5\text{--}103^\circ$ . Reduction with palladium and hydrogen (cf. Straus and Ehrenstein, this vol., i, 535) gives  $\gamma\gamma$ -dimethoxy- $\alpha\gamma$ -di-*p*-anisylpropane (dimethylacetal of anisyl  $\beta$ -anisylethyl ketone), b. p.  $217\text{--}218^\circ/0.6\text{--}0.7$  mm.,  $d_{20}^{20}$  1.098,  $n_D^{21.2}$  1.54439, which is readily hydrolysed to the corresponding ketone (semicarbazone, m. p.  $148\text{--}149.5^\circ$ ). By the action of hydrogen chloride in carbon disulphide at the ordinary temperature, the unsaturated acetal gives an unstable *hydrochloride* of the ketone methochloride,



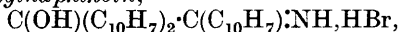
which readily passes into the ketone on contact with a trace of water, and regenerates the acetal by treatment with sodium methoxide. The dimorphous *mercuric chloride* compound ( $\text{HgCl}_2$  in place of  $\text{HCl}$ ), prepared in red or brown modifications by adding

hydrogen chloride and mercuric chloride, each dissolved in dry ether, to a solution of the acetal in dry ether, is much more stable.

*p*-Anisyl *p*-methoxystyryl ketone, with hydrogen chloride in carbon disulphide, yields crystals of a *monohydrochloride*,  $\text{CHAr}:\text{CH}\cdot\text{CArCl}\cdot\text{OH}$ , but no evidence of a dihydrochloride analogous to the methochloride hydrochloride could be obtained. The *mercuric chloride* compound,  $\text{CHAr}:\text{CH}\cdot\text{CArCl}\cdot\text{OH}\cdot\text{HgCl}_2$ , however, is easily prepared. A *monohydrobromide* is also described.

The abnormal ketochloride of dianisylideneacetone (Straus, Krier, and Lutz, *loc. cit.*) is converted by sodium methoxide, probably after a similar isomerisation of an intermediate chloromethoxy compound, into  $\alpha\alpha$ -dimethoxy- $\alpha\epsilon$ -di-*p*-anisyl- $\beta\delta$ -pentadiene (dimethylacetal of *pp'*-dimethoxycinnamylideneacetophenone), b. p. 241—243°/0.2—0.6 mm. This, treated with hydrogen chloride in carbon disulphide, gives crystals of a *compound*, which is probably the ketone methochloride hydrochloride; or it may be hydrolysed with methyl-alcoholic hydrogen chloride to the ketone, *pp'*-dimethoxycinnamylideneacetophenone, m. p. 112.5—113°. C. H.

**Action of Methyl Cyanoformate on Organo-magnesium Compounds.** H. FINGER and R. GAUL (*J. pr. Chem.*, 1925, [ii], **111**, 54—61).—Methyl cyanoformate (1 mol.) reacts vigorously with magnesium methyl iodide or magnesium ethyl iodide (3 mols.) in ethereal solution with formation of 2-methylbutan-2-ol-3-one (cf. Schmidt and Austin, A., 1903, i, 2) or 3-ethylhexan-3-ol-4-one (cf. Blaise and Maire, A., 1907, i, 749; 1909, i, 85), respectively. Magnesium phenyl bromide yields similarly phenylbenzoin, together with a large proportion of triphenylcarbinol, whilst magnesium  $\alpha$ -naphthyl bromide affords the *imide hydrobromide* of the corresponding *naphthyl-naphthoin*,



yellow, m. p. 205—210° (decomp.). The latter is not readily hydrolysed to the corresponding ketone, and yields brown, amorphous *substances*, together with ammonia, on treatment with hot concentrated acids, whilst treatment in alcoholic solution with concentrated aqueous potassium hydroxide affords the *imide hydroxide*, as a *hydrate*, m. p. 135—138° (decomp.), from which the *hydrochloride*, pale yellow, m. p. 185—190°, *nitrate*, yellow, m. p. 135—136°, and *picrate*, yellow, m. p. 165—166°, were prepared. The anhydrous *imide hydroxide*, m. p. 150—151° (decomp.), cannot be prepared by heating the above hydrated product, but is obtained by heating the hydrochloride or hydrobromide at 110—120° in a current of ammonia. F. G. W.

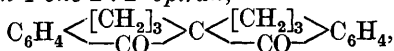
**Acetopyrocatechol Dibenzyl Ether.** E. MERCK, CHEM. FABRIK (D.R.-P. 414142; from *Chem. Zentr.*, 1925, ii, 612).—The *dibenzyl ether* of acetopyrocatechol, m. p. 93—94°, is obtained by heating acetopyrocatechol and benzyl bromide in a solution of sodium ethoxide at 100°. R. B.

**Electrolytic Reduction of Oximes. III. Benzildioxime.** M. ISHIBASHI (*Mem. Coll. Sci. Kyōtō*, 1925, **8**, 383—389; cf. A., 1924, i, 183).—A 5% solution of  $\beta$ -benzildioxime in 5% aqueous

alcoholic (40 : 60 by volume) sulphuric acid was reduced electrolytically, using a lead cathode, current density 1.5 amp./dm.<sup>2</sup>, at 16—18°, and yielded a mixture of the *racemic* and *meso* forms of  $\alpha\beta$ -diamino- $\alpha\beta$ -diphenylethane. Combination with acids of either form appears to lead to identical salts (*carbonate* of mixture, m. p. 108°). Chemical reduction yields only the *racemic* form. As by-products, due to hydrolysis of the dioxime, there are formed a *stilbene hydrate* (iso), m. p. 61—62°, differing from the known form; 2 : 3 : 5 : 6-tetraphenylpyrazine (for which a possible mechanism of formation is suggested); benzoinpinacone : deoxybenzoinpinacone; hydrobenzoin; *isohydrobenzoin*;  $\beta$ -hydroxy- $\alpha\beta$ -diphenylethylamine and its *iso* form. Electrolysis in sodium hydroxide solution reduces the yield of diamine.  $\alpha$ - and  $\gamma$ -Benzil-dioxime behave similarly to the  $\beta$  form. B. F.

**Spirans. XII. Preparation of Dibenzo- $\Delta^6$ -suberen-1-one-2 : 2'-spiran.** H. LEUCHS and P. SANDER (*Ber.*, 1925, 58, [B], 2200—2202).—The synthesis of a spiran containing a seven-membered heterocyclic ring from di- $\beta$ -phenoxyethylmalonyl chloride has been recorded previously (A., 1924, i, 972). An analogous compound with homocyclic rings is derived from di- $\gamma$ -phenylpropylmalonyl chloride. Since in each case the yields are very small, it appears that the spiran arrangement does not favour the formation of seven-membered rings.

Ethyl malonate is converted successively into ethyl  $\gamma$ -phenylpropylmalonate, b. p. 190—192°/13 mm., and *ethyl di- $\gamma$ -phenylpropylmalonate*, b. p. 262°/13 mm., m. p. 56—57°. Hydrolysis of the latter ester occurs with difficulty, yielding *ethyl hydrogen di- $\gamma$ -phenylpropylmalonate*, m. p. 86—87° (*potassium* and *sodium* salts) and *di- $\gamma$ -phenylpropylmalonic acid*, m. p. 165—166° (decomp.) after softening at 160°. The acid is transformed by successive treatment with phosphorus pentachloride and ferric chloride into *dibenzo- $\Delta^6$ -suberen-1-one-2 : 2'-spiran*,



m. p. 142—144°.

H. W.

### **Influence of Mercury on the Sulphonation of Anthraquinone.**

A. COPPENS (*Rec. trav. chim.*, 1925, 44, 907—930).—A repetition of the work of Roux and Martinet (A., 1921, i, 257) shows that, contrary to their statements, anthraquinone-1-sulphonic acid is not affected by heating at 180° with sulphuric acid, and that sulphonation of anthraquinone at 160° in presence of mercury yields as main product, not the 2-, but the 1-acid. Their theory of the reaction is rejected and the facts are simply accounted for by the assumption that sulphonation in the 2-position always proceeds independently and is unaffected when mercury or one of its salts is added, but that the mercury salts catalyse sulphonation in the 1-position.

The methods hitherto used to distinguish between the isomeric sulphonic acids are shown to be untrustworthy, and a new method

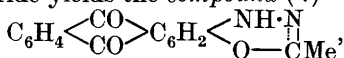
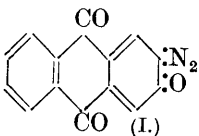
has been worked out. The alkyl esters of these acids are not sufficiently stable to give a satisfactory m. p. curve: ethyl anthraquinone-2-sulphonate has m. p. 138—141° (as compared with the value 125° found by Heffter, A., 1895, i, 671). The *methyl* ester, m. p. 163·2—164·2°, and the *methyl* ester of anthraquinone-1-sulphonic acid, m. p. 192—193°, are obtained by the action of methyl sulphate on the dry sodium salts of the respective acids. The proximate analysis of the mixed sulphonation products depends on their conversion by a boiling solution of sodium chlorate and hydrochloric acid into 1-chloro-, m. p. 161°, and 2-chloro-anthraquinone, m. p. 209·5°, the proportion in the mixture being determined from the m. p. curve (eutectic point at 144° and 24% of 1-chloroanthraquinone). A small amount of 2-acid escapes chlorination and is weighed as barium salt and included in the result.

The yields of 1- and 2-sulphonic acid obtained by sulphonation of anthraquinone with fuming sulphuric acid at 156° and 132° in the presence of varying proportions of mercurous sulphate have been determined. The yield of 2-sulphonic acid at 156° is 97·8% in the absence of mercury, but falls gradually to 16·1% as proportions of mercurous sulphate are added increasing to 1% or more, the remainder of the product being the 1-sulphonic acid with only a trace of disulphonic acid. The figures obtained at 132° are similar, so that the change of temperature must affect the two reactions equally. The influence of mercury is limited by the small solubility of mercuric sulphate in the fuming acid, so that the addition of more than 1% of mercury salts has no further effect. Within the range where the mercury salt dissolves immediately, and assuming the velocity of formation of the 2-acid to remain constant, the velocity of formation of the 1-acid is found to be proportional to the amount of mercury present. At the end of the sulphonation, the mercury is all to be found in the recovered unsulphonated anthraquinone, where it is present as an anthraquinone-mercury compound from which it is not removed by boiling dilute acids. Partly successful attempts have been made to prepare such a compound. No direct mercuration of anthraquinone results when it is heated with mercuric chloride or acetate at temperatures up to 300°, but mercuric sulphate in presence of a little fuming sulphuric acid at 140—170° yields a substance which gives with hydrogen sulphide an orange-brown precipitate from which black mercuric sulphide is produced by heating with water. Impure specimens of *anthraquinone*-1- and -2-*mercurichlorides* are obtained by the action of mercuric chloride on the 1- and 2-sulphonic acids in aqueous alcoholic solution. These substances resemble, in their reactions, those present in the pyridine extract of the anthraquinone recovered from the sulphonations, and both are as efficient catalysts of the sulphonation as free mercury salts. The following reactions are therefore probably involved in the formation of anthraquinone-1-sulphonic acid:  $C_{14}H_8O_2 + HgSO_4 = (C_{14}H_7O_2)HgSO_4H$ ;  $(C_{14}H_7O_2)HgSO_4H + SO_3 = C_{14}H_7O_2 \cdot SO_3H + HgSO_4$ .

G. M. B.

**9 : 10-Anthraquinone-2 : 3- and -1 : 2-quinonediazides and their Derivatives.** M. TANAKA (*Ber.*, 1925, **58**, [B], 1986—1988).

—3-Nitroanthraquinone-2-diazonium sulphate, decomp. 133°, is converted when cautiously heated with acetic anhydride at 95° into 9 : 10-anthraquinone-2 : 3-quinonediazide (I), decomp. 227° after darkening at 160°; the compound is reduced by alkaline sodium hyposulphite solution to 2-hydroxyanthraquinonyl-3-hydrazine, decomp. 330—340°, which with acetic anhydride yields the compound (?)



m. p. 314°. Similarly, 1-nitro-2-aminoanthraquinone affords successively 1-nitroanthraquinone-2-diazonium sulphate and 9 : 10-anthraquinone-1 : 2-quinonediazide. H. W.

**Univalent Oxygen.** IV. S. GOLDSCHMIDT, A. VOGT, and M. A. BREDIG (*Annalen*, 1925, **445**, 123—141; cf. A., 1924, i, 1062).—Whilst the action of sodium alkoxides on 9-chloro-10-hydroxyphenanthrene does not lead to crystalline products (cf. Schmidt, A., 1909, i, 34), dichlorophenanthrene yields, when treated at 0° with dry sodium phenoxide in absolute alcohol, 9 : 9'-diphenoxy-10-keto-9 : 10-dihydrophenanthrene, m. p. 136—137° (decomp.), together with a mixture of by-products, at least one constituent of which appears to give rise to a free radical, and on oxidation gives only a small yield of phenanthraquinone. When the above diphenoxy derivative is reduced with zinc dust and glacial acetic acid, it yields phenanthraquinol monophenyl ether, m. p. 140—141°, which on oxidation with alkaline potassium ferricyanide affords 9-phenoxy-10-phenanthryl peroxide, m. p. 166—167° (decomp.). The latter gives colourless solutions in cold chloroform and pyridine, which turn red at the b. p., indicating dissociation of the peroxide into the free univalent oxygen radical, and become colourless again on cooling. Nitric acid and bromine convert the peroxide into phenanthraquinone.

When dichlorophenanthrene is treated with phenol at 50°, hydrogen chloride is evolved and 9 : 9'-bis-p-hydroxyphenyl-10-keto-9 : 10-dihydrophenanthrene, m. p. 248°, is obtained in quantitative yield. o-Cresol affords similarly the corresponding bis-p-hydroxy-m-tolyl derivative, m. p. 291—293° (decomp.).

The production of phenanthrol by the action of hydrazine hydrate on phenanthraquinone (cf. Dutt and Sen, T., 1923, **123**, 3420) is not confirmed. In boiling alcoholic solution, phenanthraquinol is obtained, whilst when phenanthraquinone (5 g.) and hydrazine hydrate (1.7 g.) are mixed in alcohol (30 c.c.) and water (3 g.), and, after evolution of nitrogen has ceased, heated at 180° in a sealed tube, phenanthrazine,  $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{N} : \text{C} \cdot \text{C}_6\text{H}_4$ , m. p. about 450°, is obtained.

Phenanthrol is obtained in satisfactory yield by the reduction of dichlorophenanthrene or of chlorophenanthrol with stannous chloride in glacial acetic acid solution. On oxidation with aqueous



alkaline potassium ferricyanide, or with lead peroxide in ether, it affords an amorphous, reddish-brown *substance*, the action of which on hydrazobenzene indicates the presence of a compound containing univalent oxygen, but yields a *product* not identical with phenanthrol. 9-Bromo-10-hydroxyphenanthrene, m. p. 124—125°, is obtained by the action of bromine on phenanthrol in chloroform in presence of pyridine. On oxidation with lead peroxide in chloroform at -20°, it yields 9-bromo-10-phenanthryl peroxide, m. p. 107—109° (decomp.), unstable in sunlight, solutions of which in benzene, chloroform, or pyridine, colourless at first, quickly assume a pink to red shade, and then, except in the case of pyridine solutions, become colourless again. The peroxide cannot be recovered from its solutions. Measurements of the dissociation of bromophenanthryl peroxide by means of hydrazobenzene titrations indicate that the influence of temperature on the equilibrium between the peroxide and the free radical is remarkably small, the difference between the dissociation constant at 0° ( $5.6 \times 10^{-4}$ ) and that at 20° ( $5 \times 10^{-4}$ ) being less than the error of the method of determination, whilst the intensity of colour of a solution of the peroxide at 20° is only 1.3 times that at -20°.

F. G. W.

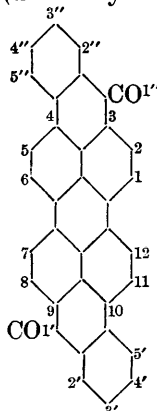
### Dibenzoylxylenes and Dinaphthanthraquinones. III.

H. DE DIESBACH and K. STREBEL (*Helv. Chim. Acta*, 1925, **8**, 556—566; cf. A., 1924, i, 1082).—The observation of Thörner and Zincke (*Ber.*, 1877, **12**, 1479) that chlorine at 120° converts phenyl *o*-tolyl ketone into anthraquinone dichloride has been extended to a number of tolyl ketones, the method being modified by the use of bromine at a higher temperature in a solution in either acetic acid (becoming bromoacetic acid during the reaction) or nitrobenzene. The anthraquinone derivatives are either directly obtained or result from the action of sulphuric acid on acidic intermediate products. Bromination of the nucleus also occurs in many cases. Phenyl *o*-tolyl ketone gives a 20% yield of anthraquinone when acted on by bromine in nitrobenzene at 180°. *o*-Tolyl *p*-tolyl ketone, b. p. 300—303°, from *o*-toluoyl chloride and toluene in presence of aluminium chloride, by the action of bromine in acetic acid solution, oxidation with potassium permanganate, and finally heating in concentrated sulphuric acid at 160—180°, yields 3-bromoanthraquinone-2-carboxylic acid, decomp. above 310°. *o*-Tolyl anisyl ketone, b. p. 325—330°, from *o*-toluoyl chloride and anisole, is converted by bromine in acetic acid into an acid which hot concentrated sulphuric acid transforms into 1 : 4-dibromo-2-hydroxyanthraquinone, m. p. 218°, identical with the product of bromination of the hydroxyanthraquinone in aqueous solution. 3 : 4-Dimethoxyphenyl *o*-tolyl ketone, m. p. 75°, from *o*-toluoyl chloride and veratrole, gives no definite product when treated with bromine. 2 : 5-Dibenzoyl-1 : 4-dimethylbenzene with bromine in nitrobenzene solution at 170—180° gives dinaphthanthraquinone in 50% yield. If the bromine is used in glacial acetic acid solution, a similar result is obtained after heating the product in concentrated sulphuric acid. 2 : 5-(2' : 5' : 2'' : 5''-Tetrachlorodibenzoyl)-1 : 4-dimethylbenzene is similarly converted into tetra-

chlorodinaphthanthradiquinone. 2 : 5-Di-*p*-toluoyl-1 : 4-dimethylbenzene with bromine in acetic acid, followed by oxidation with potassium permanganate and solution in hot concentrated sulphuric acid gave an impure specimen of *dinaphthanthracene-5 : 7 : 12 : 14-diquinone-3 : 10-dicarboxylic acid*, not melted at 340°, which was synthesised for comparison by the action of concentrated sulphuric acid at 200° on 2 : 5-di-*p*-carboxybenzoyltetraphthalic acid, decomp. above 340° (*barium* salt described), obtained by oxidation of the diketone with dilute nitric acid at 200°. 2 : 5-Di-*p*-anisoyl-1 : 4-dimethylbenzene furnished, under the action of bromine in glacial acetic acid, a *tetrabromo-2 : 5-di-p-hydroxybenzoyltetraphthalic acid*, converted by hot concentrated sulphuric acid into a *tetrabromo-2 : 9-dihydroxydinaphthanthra-5 : 7 : 12 : 14-diquinone*, not melted at 330°. 2 : 5-(3' : 3'' : 4' : 4''-Tetramethoxydibenzoyl)-1 : 4-dimethylbenzene, m. p. 245°, from the acid chloride of  $\beta$ -cumidic acid and veratrole, 4 : 6-di-*p*-toluoyl-1 : 3-dimethylbenzene, m. p. 118°, 4 : 6-di-*p*-anisoyl-1 : 3-dimethylbenzene, m. p. 95°, and 4 : 6-(3' : 3'' : 4' : 4''-tetramethoxydibenzoyl)-1 : 3-dimethylbenzene, m. p. 137°, prepared from the acid chloride of  $\alpha$ -cumidic acid and toluene, anisole, and veratrole, respectively, give similar reactions, but no pure products have been isolated.

G. M. B.

**Perylene and its Derivatives. X.** A. ZINKE and K. FUNKE [with J. MATSCHER, O. WOLFBauer, and N. LORBER] (*Ber.*, 1925, **58**, [B], 2222—2227; cf. this vol., i, 383, 819).—The yield of *isoviolanthrone* prepared by the action of aluminium chloride on 3 : 9-dibenzoylperylene may be increased to 45% by the addition of finely-divided manganese dioxide. The oxidising agent, however, sometimes causes undesirable complications either by direct oxidation or by interacting with the liberated hydrogen chloride with production of chlorine. Thus 3 : 9-di-*p*-methoxybenzoylperylene, m. p. 319.5°, is converted by aluminium chloride into a mixture of *dimethoxyisoviolanthrone* and *dihydroxyisoviolanthrone* (due to hydrolytic action of hydrogen chloride); in the presence of manganese dioxide, the yield of the dimethoxy derivative is increased, but *chlorodimethoxyisoviolanthrone* appears to be produced simultaneously.



(I.)

4 : 10-Dichloro-3 : 9-di-*o*-toluoylperylene, m. p. 351°, is converted by potassium hydroxide in the presence of boiling quinoline into 2' : 2''-dimethylisoviolanthrone (cf. I). Similarly, 4 : 10-dichloro-3 : 9-di-*p*-toluoylperylene, m. p. 345°, affords 4' : 4''-dimethylisoviolanthrone, whereas 3' : 3'' (or 5' : 5'')-dimethylisoviolanthrone is obtained from 4 : 10-dichloro-3 : 9-di-*m*-toluoylperylene, m. p. 334°. The naphthoyl chlorides yield only 4 : 10-dichloro-3- $\alpha$ -naphthoylperylene, m. p. 275°, and 4 : 10-dichloro-3- $\beta$ -naphthoylperylene, m. p. 293°, respectively, which are transformed by potassium hydroxide and boiling quinoline into dark products which do not yield vats.

H. W

**Dimethylaminoethylimide of Camphoric Acid.** FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 414262; from *Chem. Zentr.*, 1925, ii, 613—614).—The anhydro base of the aminoethylimide of camphoric acid is heated at 100° with formic acid and formaldehyde, and the *dimethylaminoethylimide* separates on addition of potassium carbonate as a bright yellow oil, b. p. 164°/15 mm. (*hydrochloride*, m. p. 214°). R. B.

**Camphor Oils. V. Sesquiterpenes and Sesquiterpene Alcohols of Japanese Camphor Oil.** K. ONO (*Mem. Coll. Sci. Kyōtō*, 1925, 8, [A], 1—10).—From the high-boiling fraction of camphor oil a new dicyclic *sesquiterpene alcohol*,  $C_{15}H_{26}O$ , b. p. 170—174°/10 mm.,  $n_D^{20}$  1.5084,  $[\alpha]_D +66.58^\circ$ , was isolated. This alcohol was treated with potassium hydrogen sulphate, and the corresponding *sesquiterpene*, b. p. 139—142°/10 mm.,  $d^{20}$  1.5050, obtained. Both these compounds, when dehydrogenated by boiling with sulphur, yielded cadalene (1 : 6-dimethyl-4-isopropyl-naphthalene, Ruzicka, A., 1922, i, 560). The sesquiterpene probably contains conjugated double linkings. B. W. A.

**Occurrence of Borneol in Spruce Turpentine.** A. S. WHEELER and C. R. HARRIS (*J. Elisha Mitchell Sci. Soc.*, 1924, 40, 111).—*l*-Borneol constitutes 1% of the total cymene residue from spruce turpentine. CHEMICAL ABSTRACTS.

**Examination of Some Gum Enzymes.** G. J. FOWLER and M. A. MALANDKAR (*J. Indian Inst. Sci.*, 1925, 8 [A], 221—239).—Observations made in isolating the gum from the gum-oleoresin of *Boswellia serrata* (*ibid.*, 1921, 4, 27) indicated that this gum contained an oxydase. The gum, separated by extraction of the oleoresin with hot or cold alcohol, has now been compared with myrrh, gum arabic, the gums from *Cochlospermum gossypium* and *Moringa pterigospermum*, and the gum kino from *Butea frondosa*. Only the first three substances, namely, myrrh, gum arabic, and the gum from *Boswellia*, contained enzymes to any noteworthy extent. An oxydase is present; quantitative tests, by Bunzel's method and by determination of the amount of purpurogallin formed in the action on pyrogallol, showed that the *Boswellia* gum and myrrh resemble one another in oxydase activity, and that both are much stronger than gum arabic. There are indications that a pyrocatechol-like compound is present in *Boswellia* gum and in myrrh, Onslow's theory (A., 1919, i, 361) being thus supported. Tyrosinase is absent. Manganese is present in the gums in traces only; 0.0095% was found in the *Boswellia* gum, and slightly more in myrrh and gum arabic. Accompanying the oxydase in all three gums is a diastatic enzyme. The diastatic power was found to be 3.7 for the *Boswellia* gum, 3.6 for myrrh, and less than 1.0 for gum arabic. The conversion of starch into maltose by this diastase comes almost to an end when 50% is transformed. The enzymes have no action on unchanged starch or gum, nor on hemicelluloses. *Boswellia* gum contains 3.03%, myrrh 3.02%, and gum arabic 0.16% of nitrogen.

The enzymes convert tannins into non-tannins. This fact may be of importance in relation to the theory of gum-formation.

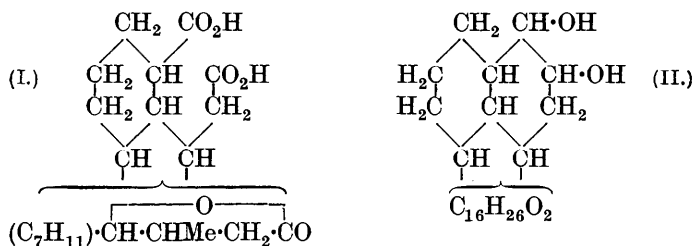
W. A. S.

**Chemical Constitution of the Gum from *Boswellia serrata*.**

M. A. MALANDKAR (*J. Indian Inst. Sci.*, 1925, **8**, [A], 240—243).—On hydrolysis the gum, previously freed from oleo-resins by extraction with hot alcohol, yields a mixture of sugars containing as identified constituents arabinose (chiefly), xylose, and galactose, and a mixture of acids the mol. wt. of which decreases on repeated mild hydrolysis.

W. A. S.

**Gitonin and its Degradation Products.** A. WINDAUS and O. LINSERT (*Z. physiol. Chem.*, 1925, **147**, 275—285).—Gitonin, a glucoside occurring in association with digitalin, gives, on acid hydrolysis, a dihydric alcohol, gitogenin,  $C_{26}H_{42}O_4$ , which is very similar in composition to digitogenin,  $C_{26}H_{42}O_5$ , obtained from digitonin in the same way. On further oxidation, gitogenin yields gitogenic acid,  $C_{26}H_{40}O_6$ , which, if again oxidised with hot concentrated nitric acid, gives a substance having the constitution (I).



This on distillation with acetic anhydride gives a keto-lactone, which on further oxidation yields a dibasic acid,  $C_{21}H_{30}O_6$ . Gitogenin appears to have the formula (II). The same complicated four-ring system is present in gitogenin as in digitogenin, the only difference being the replacement of a  $\text{CH}_2$  group in the former by a  $\text{CH} \cdot \text{OH}$  group in the latter.

H. D. K.

**Primeverosidase and Primeverase in Emulsin from Almonds.** M. BRIDEL (*Compt. rend.*, 1925, **181**, 523—524; cf. this vol., i, 760).—On prolonged treatment with emulsin from almonds monotropitoside yields, not merely primeverose, but also its hydrolytic products, dextrose and xylose, indicating the presence of primeverosidase and the true *primeverase*; the existence of the latter has not previously been demonstrated.

L. F. H.

**"Hesperidine" from Various Plants.** O. A. OESTERLE and G. WANDER (*Helv. Chim. Acta*, 1925, **8**, 519—536).—Recorded cases of isolation of hesperidine from various plants are reviewed; the identity of the substance was in many cases not proved conclusively, whilst the hesperidine-like substances from hyssop and *Capsella bursa pastoris* have been proved to be distinct (A., 1922, i, 849). The substances described as hesperidine have been isolated

from the following species or drugs : *Scrophularia nodosa*, *Hyssopus officinalis*, fol. Bucco, fruct. Conii, herb. Conii, Penny Royal, *Mentha crispa*, *M. pulegium*, *Toddalia aculeata*, and *Linaria genistifolia* and are found to be identical with each other but distinct from hesperidine, being insoluble in aqueous ammonia and most organic solvents. The name *diosmin* is adopted for this glucoside and the word "hyssopin" is to be abandoned. It has the composition  $C_{34}H_{44}O_{21} \cdot 2H_2O$ , m. p. 276—280°, and is hydrolysed by means of alcoholic sulphuric acid at 130—140° with production of rhamnose (1 mol.), dextrose (2 mols.), and *diosmetin* (1 mol.), m. p. 253—255° (*acetate*, m. p. 193—195°, *methyl ether*, m. p. 191—192°), which is identical with luteolin methyl ether (5 : 7 : 3'-trihydroxy-4'-methoxy-flavone; cf. A., 1917, i, 703), and has also been obtained by ring closure from hesperitin, the corresponding trihydroxyphenyl 3-hydroxy-4-methoxystyryl ketone. The structure of *diosmetin* prepared from *diosmin* is established by its disruption by means of concentrated potassium hydroxide into *acetoisovanillone*, *isovanillic acid*, and *phloroglucinol*, and its demethylation by hydriodic acid to yield luteolin (*acetate* described, m. p. 221°). The genetic relationship of hesperitin and *diosmetin* to the natural colouring matters of the flavone and anthocyan series is discussed.

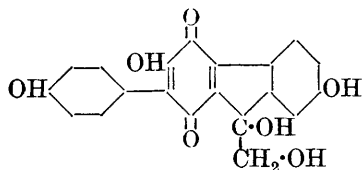
G. M. B.

**Fluorescence of Vegetable Colouring Matters.** L. MEUNIER and A. BONNET (*Compt. rend.*, 1925, **181**, 465—467; cf. this vol., ii, 738).—Although possessing the same general structure as *fisetin*, *morin*, *quercetin*, *rhamnetin*, and *luteolin* are not fluorescent. Acetylation of the hydroxyl groups in *fisetin* removes the fluorescence, which is regained on hydrolysis. Plant extracts containing *berberine* possess a yellow fluorescence (cf. Bayle, Fabre, and George, this vol., ii, 260), which is also given by the alkaloid adsorbed on cellulose etc. *Berberine* gives lakes when treated with tannins or with *fisetin*, and although the components are fluorescent the lakes are not. Precipitation of *fisetin* and *berberine* by potassium mercury iodide etc. results in disappearance of the fluorescence from both precipitate and supernatant liquid. Extracts of turmeric, *anatto wood*, *log-wood*, and *saffron* do not exhibit fluorescence, whilst *alkanet roots* and *orchil* give a white fluorescence. These properties assist identification of commercial wood extracts.

L. F. H.

**Colouring Matters of Fungi. III. Atromentin. II.** F. KÖGL and J. J. POSTOWSKY (*Annalen*, 1925, **445**, 159—170; cf. this vol., i, 50, 1083).—The hydrocarbon obtained by distilling *atromentin* with zinc dust has now been identified as *p*-diphenylbenzene (terphenyl), m. p. 206°. Treatment of *atromentin dimethyl ether* with acetic anhydride, sodium acetate, and zinc dust affords *penta-acetyl-leucoatromentin dimethyl ether*, m. p. 260—261° after sintering at 251—252°. Reduction of *penta-acetyl-atromentin* with zinc dust and acetic acid yields a colourless compound,  $C_{30}H_{26}O_{12}$ , m. p. 251—252°, whilst oxidation with chromic acid in acetic acid affords *p*-acetoxybenzoic acid, which is also obtained

similarly from hepta-acetyl-leucoatromentin. Oxidation of atromentin with hydrogen peroxide in alkaline solution yields *p*-hydroxybenzoic acid, whilst treatment with hot 18% nitric acid affords *m*-nitro-*p*-hydroxybenzoic acid, picric acid, and *dinitroatromentin*,  $C_{19}H_8O_{16}N_2$ , m. p. not below  $300^\circ$  [*triacetate*, m. p.  $282$ – $284^\circ$  (decomp.)]; cf. Thörner, A., 1880, 47]. Reduction of atromentin with hydriodic acid and phosphorus in acetic acid, or with aqueous sodium hyposulphite in alcoholic suspension, affords leucoatromentin, which on acetylation yields the hepta-acetate previously described. When steam is blown through a solution of atromentin in strong aqueous potassium hydroxide, a substance,  $C_{13}H_{10}O_5$ , m. p.  $200$ – $202^\circ$  (decomp.) after softening at  $110$ – $114^\circ$ , is obtained on acidification. When kept in 0.1*N*-alkaline solution for 24 hrs. and reprecipitated, it crystallises with 2 mols. of water and has m. p.  $110$ – $114^\circ$  (decomp.); on keeping, without changing in weight, it gradually returns to the first-given m. p. Dehydration over phosphorus pentoxide in a vacuum at  $100^\circ$  affords the anhydrous substance, m. p.  $156^\circ$ , hygroscopic. Its reactions appear to indicate keto-enol tautomerisation.



When heated with 50% aqueous potassium hydroxide at  $150$ – $160^\circ$ , it yields the hydroxy-acid,  $C_{11}H_{10}O_3$ , m. p.  $183^\circ$ , previously obtained. The reactions so far examined are in accordance with the annexed formula, provisionally assigned to atromentin.

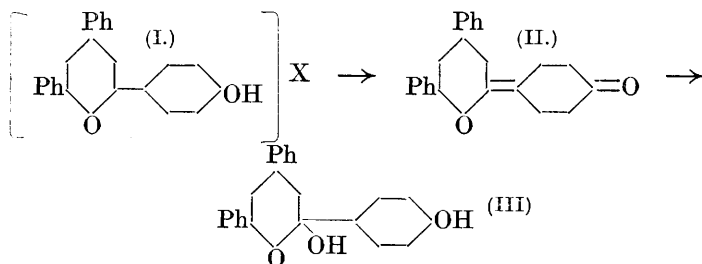
F. G. W.

**Colouring Matters of Fungi. IV. Xylindein, the Colouring Matter of the Green Mould of Decayed Wood.** F. KÖGL and G. VON TAEUFFENBACH (*Annalen*, 1925, 445, 170–180).—The only satisfactory solvent for the extraction of xylindein from the green mould of decayed wood, *Peziza aeruginosa*, is phenol (cf. Liebermann, *Ber.*, 1874, 7, 1102), applied preferably as “phenolum liquefactum” containing the minimum quantity of water, at  $60^\circ$ , from which the colouring matter crystallises in dichroic, yellow, pale green, or deep brown, rhombic plates, of plane angle  $79^\circ$ , angle of extinction  $30^\circ$ , of empirical formula  $C_{34}H_{26}O_{11}$ . Treatment with cold aqueous sodium hydroxide affords an amorphous sodium salt, insoluble in alkali, but soluble in water, when freshly prepared, to a deep, bluish-green solution, and apparently identical with Rommier’s “water-soluble xylindein” (*Compt. rend.*, 1868, 66, 108). Xylindein dissolves in concentrated sulphuric acid with dark green coloration. The finely divided material precipitated on the addition of water dyes wool direct in neutral aqueous suspension a deep bottle-green, a shade unaffected by previous mordanting of the fibre, and not removed by hot water. Plain unmordanted cotton is scarcely tinted. Xylindein also behaves as a vat dye, giving under these conditions olive-green shades on cotton and wool. The absorption spectrum in chloroform shows shading to  $631.6$ , indistinct bands from  $612.4$  to  $584.6$ , absorption finishing

at 426; in phenol, very indistinct bands from 627 to 603; in concentrated sulphuric acid, shading to 590·3, then light shading, deepening to a distinct band 573·2 to 558·1, a further band at 510·4 to 449·5, absorption finishing at 474·2; in the same solvent at great dilution, indistinct bands at 572·2 to 561·0 and 510 to 500·3. The sodium salt in aqueous solution shows shading to 622·2, lessening to 600, then a broad indistinct band to 572·2, absorption finishing at 430. The dye dissolves in acetic anhydride in presence of sulphuric acid to a violet solution which turns brown on boiling, with formation of *tetra-acetylxylindein*, yellow. Treatment with diazomethane in a mixture of ether and chloroform affords *xylindein dimethyl ether*, bluish-violet, further methylation yielding a non-crystalline product. Boiling acetic anhydride in presence of sodium acetate converts the dimethyl ether into *diacetylxylindein dimethyl ether*, yellowish-green, m. p. 294—295° (indistinct) after sintering at 260°. In presence of zinc dust, the dimethyl ether yields similarly *diacetyl-leucoxylindein dimethyl ether*, m. p. 293—295° after sintering.

F. G. W.

**Pyrylium Compounds. XV. Arylated Pyridines. VII. *m*-Substituted Triphenylpyrylium Compounds.** W. DILTHEY and W. RADMACHER (*J. pr. Chem.*, 1925, [ii], **111**, 153—166; cf. this vol., i, 153).—The ease of hydrolysis of various *m*-substituted triphenylpyrylium salts compared with that of the corresponding *p*-compounds, shows only small differences when R=OMe; but the *p*-hydroxy-salt is much more stable to water than the *m*-compound, which has the same order of stability as the methoxy derivatives. The  $\psi$ -base (III) is formed by hydration of the violone (II), which results directly from the pyrylium salt by loss of acid:



4 : 6-Diphenyl-2-*m*-nitrophenylpyrylium ferrichloride, m. p. 218° ( $\psi$ -base and its *picrate*, m. p. 251°, and *perchlorate*, m. p. 276—277°, described), prepared from *m*-nitroacetophenone and phenyl styryl ketone, is converted by ammonia into 4 : 6-diphenyl-2-*m*-nitrophenylpyridine, m. p. 141—142° (*picrate*, m. p. 184°; *perchlorate*, m. p. 176°). Reduction in alcoholic suspension with stannous chloride and hydrochloric acid yields 4 : 6-diphenyl-2-*m*-amino-phenylpyridine, m. p. 151° [*dipicrate*, m. p. 207°; *monoperchlorate* (pyridinium salt), m. p. 235°; *diperchlorate*, m. p. 170—171°; *benzoyl* derivative, m. p. 224—225°]. 2 : 6-Diphenyl-4-*m*-nitro-

*phenylpyrylium ferrichloride*, m. p. 237—238° ( $\psi$ -base, m. p. 135°, and its *picrate*, m. p. 248°, and *perchlorate*, m. p. 268°, described), is converted by ammonia into 2:6-diphenyl-4-m-nitrophenylpyridine, m. p. 150—151° (*picrate*, m. p. 188°; *perchlorate*, m. p. 271—272°), which is reduced to the corresponding *amine*, m. p. 168—169° (*dipicrate*, m. p. 209°). From phenyl *m*-aminostyryl ketone and acetophenone is obtained 2:6-diphenyl-4-m-amino-phenylpyrylium diperchlorate, m. p. 281—282° [ $\psi$ -base, m. p. 132—133°; *hydrobromide*, decomp. above 290°; *dipicrate*, m. p. 232—233°; yellow *monopicrate* (ammonium salt), m. p. 231°; red *monopicrate* (pyrylium salt), m. p. 236—237°]. 4:6-Diphenyl-2-m-anisylpyrylium perchlorate, m. p. 194°, gives by demethylation 4:6-diphenyl-2-m-hydroxyphenylpyrylium perchlorate, m. p. 193—194°, which is also synthesised from phenyl styryl ketone and *m*-hydroxyacetophenone. The corresponding 2-*p*-anisyl and 2-*p*-hydroxyphenyl derivatives melt at 235—236° and 278—280°, respectively. C. H.

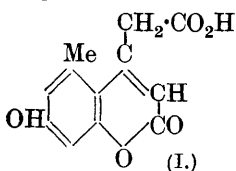
**Preparation of 6-Methylcoumarin and its Derivatives.** T. J. THOMPSON and R. H. EDEE (*J. Amer. Chem. Soc.*, 1925, **47**, 2556—2559).—When equimolecular quantities of fumaric acid and *p*-cresol are heated with 72% sulphuric acid at 160—180° until the evolution of carbon monoxide ceases (2 hrs.) an 80% yield of 6-methylcoumarin is obtained. This on hydrolysis yields 6-methylcoumaric acid (*sodium*, *potassium*, *silver*, and *nickel* salts described). 6-Methylcoumarin forms a *dibromide*, m. p. 65—66°, *mercurichloride*, m. p. 189—190°, *chloroplatinate*, m. p. 65°, an unstable *hydriodide-periodide*, and a *potassium iodide-periodide*, m. p. 89—90°. On treatment with phosphorus trisulphide it yields 6-methylthiocoumarin, m. p. 148° [*mercurichloride*, m. p. 225° (decomp.)]. On reduction, it yields *dihydro*-6-methylcoumarin, m. p. 225° (decomp.). When *p*-cresol is condensed with succinic acid in a similar manner a *compound*, m. p. 71—72°, not 6-methyldihydrocoumarin, is obtained. J. W. B.

**3:4-Diphenylcoumarins.** G. BARGELLINI (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 178—182).—A number of *o*-hydroxybenzophenones have been condensed with sodium phenylacetate in presence of acetic anhydride, and the acetoxy coumarins so obtained hydrolysed by cold concentrated sulphuric acid. The following compounds are described: 7-hydroxy-3:4-diphenylcoumarin, m. p. 290° (*acetyl* derivative, m. p. 220°); 7:8-dihydroxy-3:4-diphenylcoumarin, m. p. 271—273° [*diacetyl* derivative, m. p. 253° (decomp.)], with previous decomp. beginning at 220°; 5:7-dihydroxy-3:4-diphenylcoumarin, m. p. 260—265° (*diacetyl* derivative, m. p. 190°); and 7-hydroxy-3-phenyl-4-*p*-anisylcoumarin, m. p. 255° (decomp.) (*acetyl* derivative, m. p. 220—222°). F. G. T.

**Formation of Coumarins from Citric Acid and Phenols.** A. MÜLLER (*Ber.*, 1925, **58**, [B], 2202—2209).—4:7-Dimethylcoumarin, m. p. 132° (corr.) (cf. Fries and Klostermann, A., 1906, i, 276), is prepared by the condensation of crystalline citric acid



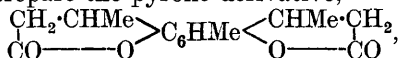
with *m*-cresol in the presence of sulphuric acid (*d* 1.84) at 110—130°; under analogous conditions, the condensation proceeds less satisfactorily with *o*- or *p*-cresol. The mechanism of the change has been studied more fully in the case of orcinol, which, with sulphuric and citric acids at 110—130°, readily yields a mixture



of 5-methylumbelliferone-4-acetic acid (I), m. p. about 250° after softening at 215°, and orcinaurin. The constitution of the acid is established by its production from acetonedicarboxylic acid, orcinol, and sulphuric acid, and its conversion at 300—310° into the known 4:5-dimethylumbelliferone, m. p. 249°, which is conveniently prepared from ethyl acetoacetate, orcinol, and sulphuric acid (73—75%) at 75—80°.

It therefore appears probable that citric acid in this reaction is converted first into acetonedicarboxylic and formic acids, which, with orcinol, yield 5-methylumbelliferone-4-acetic acid and orcinaurin, respectively (the direct production of the dye from orcinol, formic acid, and sulphuric acid at 120—130° is established). The reactions just described render the formation of 4:5-dimethylumbelliferone from citric and sulphuric acids very improbable and an experimental investigation of the reaction yielded only very small amounts of products very similar to orcinaurin and 5-methylumbelliferone-4-acetic acid.

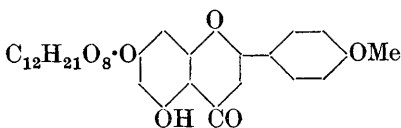
Attempts to prepare the pyrone derivative,



from orcinol and ethyl acetoacetate or acetonedicarboxylic acid were unsuccessful. H. W.

**Acaciin, a New Flavone Glucoside from the Leaves of *Robinia pseudacacia*, L.** S. HATTORI (*Acta Phytochim.*, 1925, 2, 99—112).—A new flavone glucoside, *acaciin*,  $\text{C}_{28}\text{H}_{32}\text{O}_{13}\cdot 4\text{H}_2\text{O}$ , colourless needles sintering at 250°, m. p. 260° (decomp.) (*heptaacetyl* derivative, m. p. 135—140°; *heptabenzoyl* derivative, m. p. 180—181°), is obtained by extracting the leaves of *Robinia pseudacacia*, L., with hot water (crude yield, 1.3%). Like apiin, *acaciin* tends to separate from organic solvents as a jelly. Crystallisation is difficult, but is eventually induced by repeated extraction with chloroform from an aqueous-alcoholic solution. The pure product is readily crystallised from boiling water. It is readily soluble in alkali hydroxides, and soluble in ammonia and alkali carbonates on warming. It gives a deep reddish-brown colour with ferric chloride. It is reduced by magnesium powder and hydrochloric acid, giving, like apigenin, an orange colour. Hydrolysis with hot, dilute sulphuric acid gives *acacetin*, m. p. 258—259° (cf. Perkin, T., 1900, 77, 423) [*diacetyl* derivative, m. p. 203° (cf. Perkin, *loc. cit.*, m. p. 195—198°; Vongerichten, A., 1901, i, 40, 646, m. p. 198—200°); *dibenzoyl* derivative, m. p. 201°; *dibromoacacetin*, m. p. 254—255°], and rhamnose. Thus,  $\text{C}_{28}\text{H}_{32}\text{O}_{13} + 2\text{H}_2\text{O} \rightarrow \text{C}_{16}\text{H}_{12}\text{O}_5 + 2\text{C}_6\text{H}_{12}\text{O}_5$ . The identity of *acacetin* with Vongerichten's apigenin 4'-methyl ether (*loc. cit.*) was established by a mixed m. p. of these

substances. The absorption spectrum of acaciin with two bands having their maxima at 3000 and 3800, respectively, shows no marked differentiation from that of acacetin. It is, therefore, concluded that the dirhamnose residue must occupy the position least



affecting light absorption, and the annexed formula is, accordingly, suggested. Attempts to methylate the remaining hydroxyl were unsuccessful—a result in accordance with the supposition

that the latter is *ortho* to the carbonyl group of the pyrone ring. Diacetylacacetin, where both hydroxyl groups are substituted, has an entirely different absorption spectrum, almost identical with that of 4'-methoxyflavone. Comparison of the spectra of these two substances with that of flavone shows that the first absorption band of the latter is displaced towards the red, whilst the second band completely disappears on substitution of methoxyl in the *para* position of the side-chain. The first band now reaches a maximum at 3150 instead of 3500. 4'-Methoxyflavanone, m. p. 91–92°, is readily obtained by addition of excess of aqueous sodium hydroxide (1.5%) to a warm alcoholic solution of *o*-hydroxyphenyl *p*-methoxystyryl ketone (A., 1924, i, 1221). It is converted by phosphorus pentachloride in presence of boiling benzene into 4'-methoxyflavone, m. p. 158.5°. The latter gives no coloration with ferric chloride. M. J.

### Absorption Spectra of Vegetable Dyes of the Flavone Series.

II. Influence of Methoxy-substitution on the Absorption Spectra of Flavones and Flavonols. T. TASAKI (*Acta Phytochim.*, 1925, 2, 119–128; cf. A., 1923, ii, 360; this vol., ii, 838).—Replacement of the hydroxyl groups of flavones by methoxyl produces no marked alteration in the absorption spectra observed in *M*/10,000-alcoholic solution. Chrysin and *chrysin dimethyl ether*, m. p. 115–117°, show almost identical spectra. Apigenin trimethyl ether differs from apigenin only in that the second band is shifted very slightly towards the red.

In the flavonols, methylation of the hydroxyls results in a marked displacement of the first band towards the blue. The second band is usually unaltered in position, whilst becoming less deep. In certain cases, either the first or the second band may disappear altogether. *Galangin trimethyl ether*, m. p. 165–166°, shows only a horizontal part of the curve in the neighbourhood of 3200 instead of the first band of galangin at 2650. *Kaempferide trimethyl ether*, m. p. 114–116°, and myricetin hexamethyl ether show a displacement of the first band in each case from 2650 to 3000. Morin pentamethyl ether, instead of bands with maxima at 2750 and 3900, shows one band only at 3250. The curve is horizontal in the region of 4200. Quercetin pentamethyl ether gives a similar shift of the first band from 2650 to 3050 with simultaneous flattening of the second band into a horizontal region at 4200.

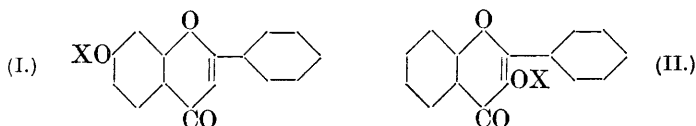
It is suggested that the bathochromic effect of introduction of

hydroxyl into the pyrone ring of flavones is due to the possibility of tautomerism in the flavonols, whereby an  $\alpha$ -diketone or *ortho*-quinonoid form is produced. Stabilisation of the hydroxyl group by methylation reverses this effect, so that the methylated flavonols again become more nearly like the corresponding flavones.

M. J.

### Absorption Spectra of Vegetable Dyes of the Flavone Series.

**III. Absorption Spectra of certain Flavone and Flavonol Glucosides.** T. TASAKI (*Acta Phytchim.*, 1925, 2, 129—137).—The flavone glucosides, like the flavones themselves, show in *M*/10,000-alcoholic solution, two characteristic bands in the ultra-violet. They fall, however, into two distinct groups. It is suggested that those in which the absorption spectrum shows no marked difference from that of the parent flavone are of type (I), whilst those in which important modification of the flavone spectrum occurs are of type (II). The first group includes toringin,



apiin, acaciin, and rutin, showing absorption spectra closely resembling those of chrysin, apigenin, acacetin, and quercetin, respectively. The second group includes quercitrin, robinin and kaempferitrin, and myricitrin derived from quercetin, kaempferol, and myricetin. In each of these, there is marked displacement of the first band towards the blue, giving new maxima at 2900—3000 instead of 2650. The second band is unaltered in position, whilst both bands become less deep.

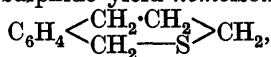
The character of the absorption spectrum is determined by the position of the sugar residue in the molecule and not by the individual sugar or sugars present in the glucoside.

M. J.

**Cyclic Sulphides.** **III.** J. VON BRAUN, O. BAYER, and W. KAISER (*Ber.*, 1925, 58, [B], 2165—2168).—The deciding factor in the formation of cyclic sulphides from open-chain compounds appears to be the immediate attachment of the sulphur atom to the aromatic nucleus and not the number of links in the open chain. This observation is in direct contrast with that made in the formation of benzopolymethyleneimines, and is the more surprising since the behaviour of the thiol group appears substantially the same whether it is attached to an alkyl or aryl group, whereas the basicity of the amino group is influenced greatly by these factors.

*o*-Xylylene sulphide,  $C_6H_4<\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}>S$ , b. p. 108°/14 mm., m. p. 26°,  $d_4^{20}$  1.143, is readily obtained in 40% yield by the action of sodium sulphide on *o*-xylylene bromide in aqueous-alcoholic solution; the corresponding methiodide has m. p. 175°. *o*- $\beta$ -Chloro-ethylaniline is converted by successive treatment with sodium nitrite and potassium xanthate followed by alcoholic potassium

hydroxide into 2:3-dihydrothionaphthen, b. p. 104°/13 mm.,  $d_4^{21}$  1.129, the yield being quantitative; it is dehydrogenated by sulphur at 200° to thionaphthen and oxidised by permanganate to the corresponding *sulphone*, m. p. 98°. *o*- $\gamma$ -Bromopropylbenzyl bromide and sodium sulphide yield *homoisothiochroman*,



b. p. 141—145°/14 mm., m. p. 95—96° (yield 40%); the corresponding *methiodide*, m. p. 154°, and *sulphone*, m. p. 176°, are described.

H. W.

**New Synthesis of Ricinine. IV.** E. SPÄTH and G. KOLLER (*Ber.*, 1925, **58**, [B], 2124—2130; cf. Späth and Tschelnitz, *A.*, 1922, i, 571; Späth and Koller, *A.*, 1923, i, 594; 1924, i, 204).—Ricinine (3-cyano-4-methoxy-1-methyl-2-pyridone) is synthesised along the following lines. Ethyl 4:6-dihydroxy-2-methylpyridine-5-carboxylate is converted by diazomethane into ethyl 4:6-dimethoxy-2-methylpyridine-5-carboxylate, from which (?) 4:6-dimethoxy-2-methylpyridine-5-carboxylic acid, m. p. 174—176° (decomp.), is obtained in not very satisfactory yield. Better results are obtained by converting ethyl 4:6-dihydroxy-2-methylpyridine-5-carboxylate by alcoholic ammonia at 130° into 4:6-dihydroxy-2-methylpyridine-5-carboxylamide, m. p. 280—281° (decomp.), which is transformed by phosphoryl chloride at 100° into 4:6-dichloro-5-cyano-2-methylpyridine, m. p. 101—102°. Oxidation of the latter compound to the carboxylic acid does not proceed smoothly, and it is therefore transformed by benzaldehyde and zinc chloride at 125° into 4:6-dichloro-5-cyano-2-styrylpyridine, yellow needles, m. p. 168—169° (which even in diffused daylight readily passes into a colourless *dimeride*, m. p. 213—214.5° after softening). The styryl derivative is oxidised by permanganate in the presence of acetone to 4:6-dichloro-5-cyanopyridine-2-carboxylic acid, m. p. 180°, which loses carbon dioxide and suffers simultaneously almost total decomposition when heated above its m. p. The acid is therefore transformed by sodium methoxide into 5-cyano-4:6-dimethoxypyridine-2-carboxylic acid, m. p. 205—206° after softening at 204°, which when cautiously distilled under atmospheric pressure affords 3-cyano-2:4-dimethoxypyridine, m. p. 145—146°, identical with the compound prepared previously (*A.*, 1924, i, 205) from 2:4-dichloro-3-cyanopyridine. The conversion of the compound into ricinine is effected as described previously (*loc. cit.*). H. W.

**Therapeutic Compounds. [Esters of Benzoyl-*l*-ecgonine and Similar Compounds.]** THE WELLCOME FOUNDATION, LTD., W. H. GRAY, and T. A. HENRY (Brit. Pat. 239985).—Benzyl and phenylethyl esters of benzoyl-*l*-ecgonine are prepared by heating the last with a mixture of alkali, pyridine, and the aralkyl chloride. The benzyl ester of benzoyl-*l*-ecgonine, an oil, forms a *nitrate*,  $\text{C}_{23}\text{H}_{25}\text{O}_4\text{N}\cdot\text{HNO}_3$ , m. p. 163°, and a *hydrochloride*, m. p. 171°. *o*-Acetoxybenzyl chloride, an oil, b. p. 135°/14 mm., obtained by treating *o*-acetoxybenzyl alcohol with thionyl chloride in presence of diethylaniline, is used for obtaining the *o*-hydroxybenzyl ester of

benzoyl-*l*-ecgonine. The *phenylethyl* ester of benzoyl-*l*-ecgonine has m. p. 100° and its *hydrochloride* m. p. 196°. In a similar manner, esters of acyl- $\psi$ -ecgonines can be obtained. The products have local anæsthetic properties.

E. H. R.

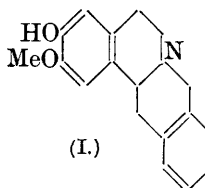
**Lupine Studies. IV. Isolation of *d*-Lupanine from *Lupinus Kingii* (S. Watson).** J. F. CROUCH (*J. Amer. Chem. Soc.*, 1925, 47, 2584—2587).—The alkaloid isolated from the American lupine, *Lupinus Kingii* (0.83% calculated on basis of the weight of dried plant), is shown by a comparison of a large number of its derivatives to be identical with *d*-lupanine, which has not hitherto been found in a native American annual lupine.

J. W. B.

**Calycanthine.** E. SPÄTH and W. STROH (*Ber.*, 1925, 58, [B], 2131—2132).—Calycanthine, obtained from *Calycanthus floridus*, has m. p. 245° (in an evacuated tube),  $[\alpha]_D^{25} +684.3^\circ$  in absolute ethyl alcohol. Determinations of mol. wt. by Rast's method in boiling benzene, and by Bleier and Kohn's method in boiling phenanthrene, indicate that the formula assigned to it by Gordin (*A.*, 1905, i, 295; 1906, i, 35; 1911, i, 903) must be doubled and that its composition is therefore  $C_{22}H_{28}N_4$ . It appears to be converted by methyl iodide in an evacuated tube at 100° into the compound  $C_{22}H_{26}N_4Me_2 \cdot 2MeI$ , m. p. 261—262° (slight decomp.), whereas Gordin describes a substance  $C_{24}H_{28}ON_3I \cdot H_2O$ . H. W.

**Corydalis Alkaloids. V. Constitution of Corypalmine.**

E. SPÄTH and E. MOSETTIG (*Ber.*, 1925, 58, [B], 2133—2135).—Corypalmine is converted by nascent diazoethane into *corypalmine*



*ethyl ether*, which in faintly alkaline suspension is oxidised by potassium permanganate to 7-methoxy-6-ethoxy-1-keto-1:2:3:4-tetrahydroisoquinoline (cf. Späth and Dobrowsky, this vol., i, 1086). Since corypalmine affords tetrahydropalmatine when methylated, the constitution (I) is established for it. The same constitution is

assigned to tetrahydrojatrorrhizine (Späth and Duschinsky, unpublished work), so that corypalmine is to be regarded as *d*-tetrahydrojatrorrhizine.

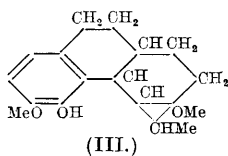
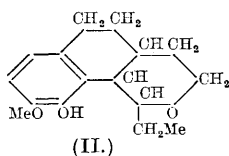
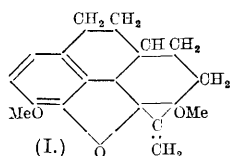
H. W.

**Aconite Alkaloids. IV. Oxonitin and Some New Derivatives Thereof.** R. MAJIMA and H. SUGINOME (*Ber.*, 1925, 58, [B], 2047—2051; cf. *A.*, 1924, i, 1224, 1225).—Japaconitine-*A*,

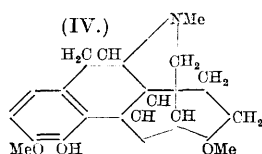
-*A*<sub>1</sub>, -*A*<sub>2</sub>, -*B*, -*B*<sub>1</sub>, and aconitine-*A* and -*C* are converted by cautious oxidation with potassium permanganate in acetone solution into the same oxonitin,  $C_{25}H_{33}O_{10}N$ , decomp. 282°,  $[\alpha]_D -41.0^\circ$  to 42.7° in chloroform (for different specimens), identical with the product obtained by Carr (*T.*, 1912, 101, 2241), Barger (*T.*, 1915, 107, 231), and Brady (*T.*, 1913, 103, 1821). The compound contains three methoxyl groups, but the *N*-methyl group of aconitine is removed during the oxidation. When cautiously heated at 282° under diminished pressure in an atmosphere of hydrogen, oxonitin

of all origins loses 1 mol. of acetic acid and gives *pyroxonitin*,  $C_{23}H_{29}O_8N$ , m. p.  $231^\circ$ ,  $[\alpha]_D^{20} -128.9^\circ$  in ethyl alcohol (the compound +  $CHCl_3$  is described), in which three methoxyl groups are present. Hydrolysis with barium hydroxide in aqueous-alcoholic solution converts *pyroxonitin* into benzoic acid and *pyroxonin*,  $C_{16}H_{23}O_6N$ , decomp.  $273-274^\circ$ . H. W.

**Morphine Alkaloids. IV. Constitution of Thebaine.** H. WIELAND and M. KOTAKE (*Ber.*, 1925, 58, [B], 2009—2012; cf. this vol., i, 1093).—The methiodide of dihydrode-*N*-methyldihydrothebaine is converted by Hofmann's method into the nitrogen-free ether (I) which, when catalytically hydrogenated in acid-free alcohol



in the presence of sodium hydrogen carbonate passes into the *dimethyl ether* (III), m. p.  $168-169^\circ$ ; the persistence of the *cyclopropane* ring is unusual among reduced derivatives of thebaine. When warmed with acid, the dimethyl ether passes into the *keto-phenol* (II), m. p.  $148-150^\circ$ . The latter substance is converted



by methyl sulphate and potassium hydroxide into its *methyl ether*,  $C_{18}H_{24}O_3$ , m. p.  $111-112^\circ$  (*benzylidene* derivative, m. p.  $128-130^\circ$ ).

Hydrogenation of thebaine in a medium completely free from acid appears also to leave the *cyclopropane* ring intact, yielding the *substance* (IV) as a non-crystallisable oil which is transformed by acids into dihydrothebainone.

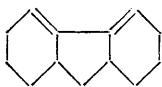
Hydrogenation of the cyclic ether (II) by the method described previously (*loc. cit.*) gives, in addition to the *keto-phenol* (II), an isomeric *ketone*,  $C_{17}H_{22}O_3$ , b. p.  $180-185^\circ/4$  mm. H. W.

**Quinine Compounds [Quinine Salicylosalicylate].** MERCK AND CO., New York (Brit. Pat. 241109).—*Quinine salicylosalicylate*,  $C_{20}H_{24}O_2N_2 \cdot 2C_{14}H_{10}O_5$ , m. p.  $86-88^\circ$ , is prepared by mixing solutions of quinine hydrogen sulphate and sodium salicylosalicylate. Owing, among other reasons, to its sparing solubility in water, it has advantages for therapeutic purposes over other quinine salts. [Cf. *B.* Dec. 24th.] E. H. R.

**$\beta$ -Isoquinine and Niquine.** J. SUSZKO (*Rocz. Chem.*, 1925, 5, 358—385).— $\beta$ -isoQuinine, colourless prisms, m. p.  $186^\circ$ , is prepared by the action of sodium methoxide on hydriodoquinine dihydriodide, and is shown to be (3-ethylidene-8-quinuclidyl)-(6'-methoxy-4'-quinolyl)-methanol. The following derivatives are prepared: *methyl iodide* derivative, m. p.  $178-180^\circ$ ,  $[\alpha]_D^{20} -161^\circ$ ; *di-methyl iodide* compound, orange prisms, m. p.  $135-138^\circ$ ;  $\beta$ -iso-

*quinine aminoxide*, colourless needles, m. p. 192—193°; *acetyl-β-isoquinine*, oil, by the action of acetic anhydride at 60—80°; *β-isoquinotoxin*,  $C_{20}H_{24}O_2N_2$ , oil, by heating *β-isoquinine* in a sealed tube with 25% acetic acid, the toxin being shown to be *β-(3-ethylidene-4-piperidyl)-ethyl 6'-methoxy-4'-quinolyl ketone*; its *picrolonate*,  $(C_{20}H_{24}O_2N_2)_2 \cdot C_{10}H_8O_5N_4$ , yellow crystals, m. p. 187—188°, and *p-bromophenylhydrazone*, yellow, amorphous powder, m. p. 90—95°, the *picrolonate*, orange crystals, m. p. 184—188°, and *picrate*, red prisms, m. p. 199—200°, of the *p-bromophenylhydrazone*; *N-methyl-β-isoquinotoxin*, oil, by the action of sodium hydroxide on *β-isoquinine methyl iodide* compound; *dibromo-β-isoquinine*, tetragonal plates, m. p. 210—212°, and *β-isoquinine hydrochloride*, colourless prisms, m. p. 192°, the bromine and hydrogen chloride in the two latter substances adding on to the ethylidene group; *apoquinine hydrochloride*, cubic crystals, m. p. 182—183°; *apoquinine methyl iodide* compound, colourless crystals, m. p. 248—250°, and *apoquinine methyl ether*, m. p. 175—176°. Niquine, formed as a by-product in the preparation of *β-isoquinine*, has probably the formula  $C_{19}H_{24}O_2N_2$ , and is a secondary-tertiary base, possessing one double linking and probably a free hydroxyl group. The following derivatives of niquine are prepared: *benzoylniquine*, oil; its *hydrochloride*, prisms, m. p. 192—194°; *N-methylniquine*, needles, m. p. 132—134°,  $[\alpha]_D^{25} -157.5^\circ$ ; its *methyl iodide* compound, oily mass; the *picrolonate* of the latter, needles, 172—174°; *N-nitrosoniquine*, yellow powder, m. p. 90°; *dibromoniquine*, resinous mass, and its *hydrobromide*, white leaves, m. p. 235—236°. R. T.

**Hydrogenated Carbazoles.** J. VON BRAUN and L. SCHÖRNIG (*Ber.*, 1925, 58, [B], 2156—2161).—Doubts have been cast by Perkin and Plant (*A.*, 1924, i, 1104) on the constitution of the octahydrocarbazole obtained by von Braun and Ritter (*A.*, 1923, i, 142), considered by the latter to be 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole. The production of octahydrocarbazoles con-



(I.)

taining an intact pyrrole nucleus is, however, placed beyond doubt by the formation of the same octahydro derivative by the hydrogenation of 6 : 9-dimethyl-1 : 2 : 3 : 4-tetrahydrocarbazole and 3 : 9-dimethyl-1 : 2 : 3 : 4-tetrahydrocarbazole. The behaviour of the *N*-methyl derivative of Perkin and

Plant's octahydrocarbazole towards cyanogen bromide suggests that it has the constitution (I).

*cycloHexanone* is converted by successive treatment with *as-p*-tolylmethylhydrazine and dilute sulphuric acid into 6 : 9-dimethyl-1 : 2 : 3 : 4-tetrahydrocarbazole, m. p. 90°, which is hydrogenated in decahydronaphthalene at 240° to a mixture of 6 : 9-dimethyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole, b. p. 165—170°/12 mm., m. p. 36—37°, and dimethyldodecahydrocarbazole, b. p. 130°/12 mm. (the non-crystalline *hydrochloride* and *picrate* and the *methiodide*, m. p. 174—175°, are described). Similarly, phenylmethylhydrazine and 4-methylcyclohexanone afford 3 : 9-dimethyl-1 : 2 : 3 : 4-tetrahydrocarbazole, b. p. above 190°/12—13 mm., m. p. 74°, which is

catalytically hydrogenated to the octa- and dodeca-hydro compounds just described.

It does not appear possible to carry the hydrogenation of carbazole and its derivatives beyond the octahydro stage, and the production of dodecahydro compounds from tetrahydrocarbazoles (*v.s.*) is therefore somewhat remarkable. 9-Methyl-1:2:3:4-tetrahydrocarbazole, b. p.  $180^{\circ}/12$  mm., m. p.  $50-51^{\circ}$ , when energetically hydrogenated gives a mixture of unchanged material, 9-methyloctahydrocarbazole, m. p.  $94-95^{\circ}$ , and 9-methyl-dodecahydrocarbazole, b. p.  $125^{\circ}/12$  mm. (ethiodide, m. p.  $223^{\circ}$ ; *methiodide*, m. p.  $245^{\circ}$ ) (cf. Perkin and Plant, *loc. cit.*). It is remarkable that 9-methylhexahydrocarbazole is initially dehydrogenated to 9-methyltetrahydrocarbazole when treated with hydrogen in the presence of nickel. Hydrogenation of tetrahydrocarbazoles must therefore occur at the benzenoid nucleus.

H. W.

**Synthetic Experiments in the Indole Group. V. Synthesis of 3- $\beta$ -Amino- $\alpha$ -hydroxyethylindole.** R. MAJIMA and M. KOTAKE (*Ber.*, 1925, 58, [B], 2037—2041).—Addition of concentrated hydrochloric acid to a mixture of indole-3-aldehyde and aniline yields 3-anilinohydroxymethylindole hydrochloride, decomp.  $240-246^{\circ}$ , whereas if the mixture is warmed a monohydrated form of the compound, decomp. about  $200^{\circ}$ , is produced. The hydrochloride is converted by dilute alkali into indole-3-aldehyde-anil, m. p.  $126-127^{\circ}$ . The latter compound is converted by sodium acetate and acetic anhydride into 1-acetylindole-3-aldehyde, m. p.  $161-164^{\circ}$ , which is more simply obtained by acetylation of indole-3-aldehyde [the triacetyl compound,  $C_8H_5N\text{Ac}\cdot\text{CH}(\text{OAc})_2$ , m. p.  $154^{\circ}$ , is obtained as by-product]. 1-Acetyl-3-anilinohydroxymethylindole hydrochloride has m. p.  $191-194^{\circ}$ . Under unusually definite conditions, 1-acetylindole-3-aldehyde condenses with nitromethane in the presence of potassium hydrogen carbonate to 1-acetyl-3- $\beta$ -nitro- $\alpha$ -hydroxyethylindole, m. p.  $138.5-140.5^{\circ}$ , which is converted by acetic anhydride and sodium acetate at  $165^{\circ}$  into 1-acetyl-3- $\omega$ -nitrovinylindole, m. p.  $189-192^{\circ}$ . 1-Acetyl-3- $\beta$ -nitro- $\alpha$ -hydroxyethylindole is reduced by stannous chloride in the presence of acetic acid and hydrogen chloride to 1-acetyl-3- $\beta$ -amino- $\alpha$ -hydroxyethylindole hydrochloride, m. p. (anhydrous)  $163-166^{\circ}$ , m. p. (hydrated)  $53-55^{\circ}$ ; the corresponding chloroplatinate, decomp. about  $225^{\circ}$  after darkening at  $200^{\circ}$ , and picrate, m. p.  $174-176^{\circ}$  (decomp.), are described. The hydrochloride is converted by alkali into 3- $\beta$ -amino- $\alpha$ -hydroxyethylindole, which is very unstable and could be isolated only as the picrate, decomp.  $188^{\circ}$ . 1-Acetyl-3- $\beta$ -amino- $\alpha$ -hydroxyethylindole is transformed by acetic anhydride and sodium acetate into 1-acetyl-3- $\beta$ -acetamido- $\alpha$ -acetoxethylindole, m. p.  $68-71^{\circ}$ , which is converted by alcoholic potassium hydroxide into 3- $\beta$ -acetamido- $\alpha$ -acetoxethylindole, decomp.  $202-204^{\circ}$ .

H. W.

**Synthetic Experiments in the Indole Group. VI. New Synthesis of 3-Aminoalkylindoles.** R. MAJIMA and T. HOSHINO (*Ber.*, 1925, 58, [B], 2042—2046).—The cyano group appears to be



indifferent towards magnesium indolyl iodide, since acetonitrile and this reagent in the presence of anisole give a molecular compound which remains unchanged at 60—70°. Chloroacetonitrile and magnesium indolyl iodide in the presence of cold anisole yield a similar additive product which, when heated to 60—70°, and subsequently decomposed by water, affords  $\beta$ -indolylacetone, b. p. 160°/0.2 mm.; anisole in this instance may be replaced by ether. The nitrile is converted by potassium hydroxide solution into *indolyl-3-acetic acid*, decomp. 164.5—165° (*picrate*, decomp. 178°), and is reduced by sodium and alcohol to 3- $\beta$ -aminoethylindole, m. p. 114.5—115.5°, together with a little hydrogen cyanide and skatole; the *hydrochloride*, decomp. 248—249°, *picrate*, decomp. 242—243°, and *acetate*, m. p. 135—136° (*semihydrate*), of the base are described. 3-Indolylacetone is converted by zinc dust and acetic acid (95%) into 3-indolylacetamide, m. p. 150—151°.

In a similar manner, magnesium indolyl iodide and  $\beta$ -chloropropionitrile yield 3- $\beta$ -indolylpropionitrile, m. p. 67—68°, b. p. about 200°/1 mm. (*picrate*, m. p. 123.5—124.5°), which is hydrolysed to 3- $\beta$ -indolylpropionic acid, m. p. 133—134° (*picrate*, m. p. 141—143°). The nitrile is reduced by sodium and alcohol to the hygroscopic 3- $\gamma$ -aminopropylindole, m. p. 60—64°; the corresponding *hydrochloride*, m. p. 169—170°, the *picrate*, m. p. 155—156°, and its *trihydrate* are described.

H. W

**Action of Halogen on the Enolates of Glutacondialdehyde and Synthesis of 3-Halogenopyridines.** P. BAUMGARTEN.—(See i, 1381.)

**Quinoline Derivatives. I. Synthesis of Substituted 2-Phenyl-4-methylquinolines.** H. JOHN and F. NOZICZKA (*J. pr. Chem.*, 1925, [ii], **111**, 65—82).—Aniline does not condense with styryl methyl ketone under the conditions of Döbner and Miller's synthesis of 2-phenylquinoline from aniline and cinnamaldehyde (A., 1883, 1149). The best yield (12.8%) of 2-phenyl-4-methylquinoline results when a mixture of aniline hydrochloride (4.4 g.), styryl methyl ketone (5 g.), water (17 drops), and concentrated hydrochloric acid (3 drops) is heated for 5 hrs. in a sealed tube at 135°. The presence of an oxidant does not affect the yield appreciably.

The following substituted 2-phenyl-4-methylquinolines, prepared similarly from the hydrochlorides of *m*- and *p*-anisidines, *m*- and *p*-phenetidines, *m*- and *p*-aminophenols, and *m*- and *p*-toluidines, are described, together with the *hydrochloride*, *sulphate*, *mercuric chloride* compound, *ferrocyanide*, *chromate*, and *picrate* in each case: 5(or 7)-*Methoxy*-, m. p. 99.5°; 6-*methoxy*-, m. p. 129°; 5(or 7)-*ethoxy*-, m. p. 105.5°; 6-*ethoxy*-, m. p. 153°; 5(or 7)-*hydroxy*-, m. p. 228°; 6-*hydroxy*-, m. p. 211—212° (*n*-propyl ether, m. p. 110°, isobutyl ether, m. p. 104°; isoamyl ether, m. p. 117°, allyl ether, m. p. 96.5°, and phenacyl ether, m. p. 143°, are prepared); 5(or 7)-*methyl*-, oily; 6-*methyl*-, m. p. 93—93.3°. The yields are all below 20%.  $\beta$ -Naphthylamine hydrochloride gives, in 24.6% yield, 2-phenyl-4-methyl- $\beta$ -naphthaquinoline (lin. or ang.).

C. H.

**Quinoline Derivatives. II. Substituted 2-Phenyl-4-methylquinolines.** H. JOHN and G. WEBER (*J. pr. Chem.*, 1925, [ii], **111**, 83—99; cf. preceding abstract).—Styryl methyl ketone is condensed with *o*- and *p*-substituted arylamines under determined conditions, giving the following 2-phenylquinoline derivatives; in each case the *hydrochloride*, *sulphate*, *mercuric chloride* compound, *ferrocyanide*, *chromate*, and *picrate* are described, and in some instances the *periodide*: 4:8-*Dimethyl*-, m. p. 91.5° (*periodide*), from *o*-toluidine; 8-*chloro-4-methyl*-, m. p. 91.5° (*periodide*), from *o*-chloroaniline; 8-*hydroxy-4-methyl*-, m. p. 57—58° (*periodide*), from *o*-aminophenol; 8-*methoxy-4-methyl*-, m. p. 98° (*periodide*; *picrate*, m. p. 153°), from *o*-anisidine; 8-*ethoxy-4-methyl*-, m. p. 98° (*periodide*; *picrate*, m. p. 182°), from *o*-phenetidine; 6-*chloro-4-methyl*-, m. p. 91.5°, from *p*-chloroaniline; 6-*bromo-4-methyl*-, m. p. 100°, from *p*-bromoaniline; 6-*iodo-4-methyl*-, m. p. 50° (*sulphate* not prepared), from *p*-iodoaniline; 4-*methyl-6-ethyl*-, m. p. 74°, from *p*-aminoethylbenzene; 4:5:8-*trimethyl*-, m. p. 111.5° (*periodide*), from *p*-xylydine; 4:5:6:8-*tetramethyl*-, m. p. 128°, from  $\psi$ -cumidine; 6-*dimethylamino-4-methyl*-, m. p. 131—132°, from *p*-aminodimethylaniline. 2-*Phenyl-4-methylquinoline-8-carboxylic acid*, m. p. 201—202° (*hydrochloride*, *sulphate*, *mercuric chloride* compound, *ferrocyanide*, *picrate*, and the *sodium*, *potassium*, *magnesium*, *calcium*, *barium*, *mercuric*, *lead*, *iron*, *copper*, and *silver* salts are described), and the 6-*carboxylic acid*, m. p. 228° (*hydrochloride*, *sulphate*, *mercuric chloride* compound, *ferrocyanide*, *chromate*, *picrate*, and the *sodium* and *potassium* salts are described), are prepared from *o*- and *p*-aminobenzoic acids, respectively. 7-Amino-2-naphthol gives 8(or 5)-*hydroxy-2-phenyl-4-methyl- $\beta$ -naphthaquinoline*, m. p. 107—108° (*hydrochloride*, *sulphate*, *picrate*, and *sodium* and *potassium* compounds are described). The yields range from 1.5% to 15%. No quinolines could be obtained by condensing styryl methyl ketone with sulphanilic acid, *o*- and *p*-aminobenzaldehydes, phenylenediamines, amino-*p*-cresol, aminosalicyclic acid,  $\alpha$ -naphthylamine, tetrahydro- $\beta$ -naphthylamine,  $\beta$ -aminoanthracene, or  $\beta$ -aminoanthraquinone, and only traces from *o*- and *p*-nitroanilines. C. H.

**Preparation of Quinoline-4-aldehyde and its 2-Aryl Derivatives.** CHEM. FABRIK AUF AKTIEN (VORM. E. SCHERING) (Brit. Pat. 240051).—Quinoline-4-acrylic acid is oxidised with potassium permanganate in aqueous sodium carbonate solution at 0°, in presence of benzene to take up the aldehyde as formed, giving *quinoline-4-aldehyde*, m. p. 51°; *phenylhydrazone*, m. p. 170—171°. In the same way, 2-phenylquinoline-4-acrylic acid (obtained by hydrolysing the reaction product of 2-phenyl-4-methylquinoline and chloral) gives 2-*phenylquinoline-4-aldehyde*, m. p. 74°; *phenylhydrazone*, m. p. 130° (decomp.). [Cf. *B.*, 1925, 943.] E. H. R.

**3-*o*- and -*p*-Anisolesulphonyl- and -Phenetolesulphonyl-2-methylquinolines, their Derivatives, and their Behaviour towards Nascent Hydrogen.** J. TRÖGER and C. BROHM (*J. pr. Chem.*, 1925, [ii], **111**, 176—192; cf. Tröger and Menzel, *A.*, 1922, i, 269; Tröger and von Seelen, *A.*, 1923, i, 1127).— $\beta$ -Arylsulphonyl-

2-methylquinolines are oxidised with difficulty, but reduction with tin and hydrochloric acid eliminates the sulphonyl group as thiophenol, giving tetrahydro-2-methylquinoline. The aldehyde condensation products of these compounds are also stable to oxidants, but may be reduced to thiophenols and stilbazolines.

3-*o*-Anisolesulphonyl-2-methylquinoline, m. p. 159° (*hydrochloride*, *nitrate*, *hydrogen sulphate*, and *chloroplatinate* described), prepared from *o*-aminobenzaldehyde and *o*-anisolesulphonylacetone, is reduced by tin-foil and hydrochloric acid to *o*-methoxythiophenol (which is distilled off in steam and identified by oxidation with iodine to a disulphide, m. p. 120°) and tetrahydro-2-methylquinoline (benzoyl derivative, m. p. 118°). 2-Propenyl-3-*o*-anisolesulphonyl-2-methylquinoline, m. p. 216°, is prepared by condensation of the 2-methylquinoline with paraldehyde and zinc chloride at 150°; it is not oxidised by nitric acid (*d* 1.4) at 100°. The 2-styryl compound, m. p. 198° (*hydrochloride* described), prepared similarly from benzaldehyde, is reduced by tin and hydrochloric acid to *o*-methoxythiophenol and 2-β-phenylethyltetrahydroquinoline (von Grabski, A., 1902, i, 563).

The cinnamylidene derivative,  $C_6H_4 \begin{smallmatrix} \text{CH}:\text{C}:\text{SO}_2\cdot C_6H_4\cdot OMe \\ \text{N}=\text{C}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CHPh} \end{smallmatrix}$ , has m. p. 203°.

*p*-Anisolesulphonylacetone, m. p. 76.5° (*oxime*, m. p. 134°; *phenylhydrazone*, m. p. 140°), prepared from sodium *p*-anisolesulphinate and chloroacetone, condenses with *o*-aminobenzaldehyde to give 3-*p*-anisolesulphonyl-2-methylquinoline, m. p. 122° [*hydrochloride*, *nitrate*, *hydrogen sulphate*, and *chloroaurate*, m. p. 183° (decomp.)], described; *benzylidene* derivative, m. p. 200°; *cinnamylidene* derivative, m. p. 149°, which may be reduced to *p*-methoxythiophenol (disulphide, m. p. 45°) and tetrahydro-2-methylquinoline.

*o*-Phenetolesulphonylacetone, m. p. 59° (*oxime*, m. p. 122°), when condensed with *o*-aminobenzaldehyde, gives 3-*o*-phenetolesulphonyl-2-methylquinoline, m. p. 184° (*hydrochloride*, m. p. 213°, *hydrogen sulphate*, m. p. 186°, *nitrate*, and *chloroplatinate* described), which is converted by reduction into *o*-ethoxythiophenol (disulphide, m. p. 90°) and tetrahydro-2-methylquinoline.

From *p*-phenetolesulphonylacetone (*semicarbazone*, m. p. 179°) and *o*-aminobenzaldehyde is obtained 3-*p*-phenetolesulphonyl-2-methylquinoline, m. p. 113° [*hydrochloride*, *nitrate*, m. p. 135° (decomp.)], *hydrogen sulphate*, m. p. 173° (decomp.), and *mercuric chloride* compound, m. p. 135° (described), which on reduction gives *p*-ethoxythiophenol (disulphide, m. p. 49°). C. H.

**Barbituric Acid Derivatives.** J. D. RIEDEL A.-G. (Brit. Pat. 223221).—By condensing *isopropyl*barbituric acid with αβ-dibromo-Δ<sup>8</sup>-propylene in alcohol in presence of sodium ethoxide at 90–100°, *isopropyl*-β-bromoallylbarbituric acid, m. p. 181°, is obtained. Barbituric acid derivatives containing the β-bromoallyl group can also be obtained by condensing malonic acid derivatives containing this group with carbamide or *N*-substituted carbamides. Ethyl malonate is condensed with αβ-dibromo-Δ<sup>8</sup>-propylene in presence of sodium ethoxide in alcohol, giving a mixture of *ethyl*

$\beta$ -bromoallylmalonate, b. p. 122—125°/13 mm., and ethyl di- $\beta$ -bromoallylmalonate, b. p. 148—152°/12 mm. The latter when condensed with carbamide in presence of sodium ethoxide gives di- $\beta$ -bromoallylbarbituric acid. The new barbituric acid derivatives have powerful hypnotic properties. E. H. R.

**Influence of Constitution on the Transformation of Phenylhydrazones of Unsaturated Compounds into Pyrazolines.**

II. K. VON AUWERS and A. KREUDER (*Ber.*, 1925, **58**, [B], 1974—1986; Auwers and Voss, A., 1910, i, 70).—In general, pyrazolines result from the action of phenylhydrazines on unsaturated ketones, whereas unsaturated aldehydes yield the phenylhydrazones which may be isomerised to pyrazolines. The presence of the *p*-nitro group in phenylhydrazine diminishes the tendency towards pyrazoline formation, which is favoured by methylhydrazine. The usual colour reactions are inadequate for distinguishing between isomeric pyrazolines and phenylhydrazones; for this purpose, reduction of the compounds and identification of the aniline yielded by the phenylhydrazones is advocated for the simpler derivatives, whereas hydrolysis by a mixture of glacial acetic acid (3 parts) and sulphuric acid (60%, 1 part) gives the desired information with substituted phenylhydrazones. *p*-Nitrophenylhydrazones are distinguished from the corresponding pyrazolines by giving an intensely red or violet solution in alcoholic potassium hydroxide.

Acraldehyde and phenylhydrazine in cold ethereal solution give a mixture of acraldehydephenylhydrazone and 1-phenylpyrazoline, m. p. 51—52°. Crotonaldehyde and phenylhydrazine in the absence of solvent afford crotonaldehydephenylhydrazone, b. p. 165°/13 mm., m. p. 56—57° (cf. Wegscheider and Späth, A., 1911, i, 112); aldol gives the corresponding phenylhydrazone (cf. Wegscheider and Späth, *loc. cit.*; Trener, A., 1901, i, 232). Tiglic aldehyde yields the phenylhydrazone, b. p. 155—160°/9 mm., 163—168°/17 mm., m. p. 92—94°.  $\beta$ -Methyl- $\Delta^2$ -pentenal affords the phenylhydrazone, b. p. 171—175°/10.5 mm., m. p. 60°, which is very sensitive towards moist air, yielding ultimately *s*-formylphenylhydrazine, m. p. 141—142°, whereas  $\Delta^2$ -penten- $\beta$ -one,  $d_4^{18.6}$  0.8568,  $n_D^{18.6}$  1.44078, yields exclusively 1-phenyl-3:5-dimethylpyrazoline, b. p. 173—175°/25 mm. Mesityl oxide and phenylhydrazine under widely varied conditions give exclusively 1-phenyl-3:5:5-trimethylpyrazoline, b. p. 152—153°/16.5 mm. Mesityl oxide and *p*-nitrophenylhydrazine hydrochloride in cold aqueous alcoholic solution yield the *p*-nitrophenylhydrazone, m. p. 132—134°, whereas in boiling solution they afford 1-*p*-nitrophenyl-3:5:5-trimethylpyrazoline, m. p. 205—208° (also obtained by boiling the *p*-nitrophenylhydrazone with glacial acetic acid). Prolonged treatment of the substance with a boiling mixture of acetic anhydride and sulphuric acid in the presence of air gives 1-*p*-nitrophenyl-3:4:5-trimethylpyrazole, m. p. 116—116.5° (prepared also from the pyrazoline and bromine in boiling glacial acetic acid). The compound is prepared synthetically from methylacetylacetone and *p*-nitrophenylhydrazine hydrochloride, whereas

acetylacetone under similar conditions yields 1-*p*-nitrophenyl-3:5-dimethylpyrazole, m. p. 99.5—100.5°. Phorone yields 1-phenyl-5:5-dimethyl-3-isobutenylpyrazoline, b. p. 186—189°/17 mm., when boiled with phenylhydrazine in alcohol and acetic acid.

Styryl methyl ketone and methylhydrazine in boiling aqueous alcoholic solution afford 5-phenyl-1:3-dimethylpyrazoline, b. p. 123—124°/12 mm. (picrate, m. p. 128—130°), whereas *o*-tolylhydrazine gives the corresponding hydrazone, m. p. 176—178° (converted by boiling acetic acid into 5-phenyl-1-*o*-tolyl-3-methylpyrazoline, m. p. 82—83°), and *p*-tolylhydrazine yields styryl methyl ketone *p*-tolylhydrazone, m. p. 120—121° [transformed by distillation under diminished pressure or by boiling acetic acid into 5-phenyl-3-*p*-tolyl-1-methylpyrazoline, b. p. 215—219°/26 mm. (picrate, m. p. 111—112°)]. Styryl methyl ketone *p*-nitrophenylhydrazone, m. p. 165—167°, is isomerised in boiling aqueous-alcoholic or glacial acetic acid solution, but not in benzene or toluene, to 5-phenyl-1-*p*-nitrophenyl-3-methylpyrazoline, m. p. 149°. *o*-Chlorostyryl methyl ketone phenylhydrazone, m. p. 92—93°, 1-phenyl-5-*o*-chlorophenyl-3-methylpyrazoline, m. p. 87°, *o*-chlorostyryl methyl ketone *o*-tolylhydrazone, m. p. 92—93°, 5-*o*-chlorophenyl-1-*o*-tolyl-3-methylpyrazoline, m. p. 96—98°, 5-*o*-chlorophenyl-1-*o*-tolyl-3-methylpyrazole, m. p. 98—99°, *o*-chlorostyryl methyl ketone *p*-tolylhydrazone, m. p. 122—123°, and 5-*o*-chlorophenyl-1-*p*-tolyl-3-methylpyrazoline, b. p. 205—220°/17 mm., m. p. 77.5—78.5°, are described. *o*-Hydroxystyryl methyl ketone *p*-nitrophenylhydrazone, m. p. 218—220° (decomp.), is readily converted by acetic acid into 1-*p*-nitrophenyl-5-*o*-hydroxyphenyl-3-methylpyrazoline, m. p. 149—151° (decomp.).

Benzylidenepinacolone with *o*- or *p*-tolylhydrazine gives 5-phenyl-1-*o*-tolyl-3-*tert*.-butylpyrazoline, m. p. 94—95°, and 5-phenyl-1-*p*-tolyl-3-*tert*.-butylpyrazoline, m. p. 116—117°, respectively. Phenyl styryl ketone and *p*-nitrophenylhydrazine hydrochloride under a variety of conditions yield inseparable mixtures of hydrazone and pyrazoline; 3:5-diphenyl-1-*p*-nitrophenylpyrazoline, m. p. 177—177.5°, is prepared from the components in boiling alcoholic solution in the presence of concentrated hydrochloric acid. H. W.

**Action of Ammonia on Bisimmonium Bromides.** J. VON BRAUN and F. ZOBEL (*Annalen*, 1925, **445**, 247—266).—Piperidine condenses readily with  $\delta$ -chlorobutylbenzamide, with formation of *N*- $\delta$ -benzamidobutylpiperidine, m. p. 57—58°, b. p. 240°/12 mm., which, on hydrolysis with concentrated hydrochloric acid at 130°, affords *N*- $\delta$ -aminobutylpiperidine, b. p. 102—105°/12 mm.,  $d_4^{20}$  0.9075, identical with the base previously described (A., 1924, i, 427) as tetramethylenepentamethylenedi-imine. When treated with excess of benzenesulphonyl chloride, this yields the dibenzene-sulphonyl derivative previously described by Scholtz (A., 1898, i, 567). The constitution of the above aminobutylpiperidine is confirmed by the following synthesis: condensation of  $\epsilon$ -phenoxy-amylamine with  $\delta$ -chlorobutylbenzamide affords  $\delta$ -( $\epsilon$ -phenoxyamyl-amino)butylbenzamide hydrochloride, m. p. 171—173°, which yields, when heated with concentrated hydrochloric acid at 120°,  $\delta$ -( $\epsilon$ -chloro-

*amylamino*)butylamine dihydrochloride, m. p. 246—248°, this passing into the above piperidine derivative when warmed with excess of dilute aqueous sodium hydroxide. As  $\delta$ -aminobutylpiperidine is the product of the action of ammonia on piperidinepyrrolidinium bromide, the two stereoisomeric bases obtained similarly from coppelidylpyrrolidinium bromide (A., 1923, i, 840) must be actually  $\delta$ -aminobutylcoppellidines,  $\text{CH}_2 < \begin{smallmatrix} \text{CHEt} \cdot \text{CH}_2 \\ \text{CH} \cdot \text{CHMe} \end{smallmatrix} > \text{N}[\text{CH}_2]_4 \cdot \text{NH}_2$ .  $\delta$ -Phenoxybutylamine condenses with  $\varepsilon$ -chloroamylbenzamide with formation of  $\varepsilon$ -( $\delta$ -phenoxybutylamino)amylbenzamide hydrochloride, m. p. 160—162°, which on hydrolysis with concentrated hydrochloric acid at 115—120° yields  $\varepsilon$ -( $\delta$ -chlorobutylamino)amylamine dihydrochloride, m. p. 215—217° (chloroplatinate, m. p. 215—216°), and this is converted, by the action of dilute aqueous alkali, into *N*- $\varepsilon$ -aminoamylpyrrolidine (pyrrolidylpentamethylenediamine), b. p. 112—114°/15 mm.,  $d_4^{20}$  0.920 [hydrochloride, m. p. 150—152°; chloroplatinate, (+H<sub>2</sub>O), m. p. 212°; methiodide, m. p. 290°]. *N*- $\varepsilon$ -Benzamidoamylpiperidine (cf. von Braun and Steindorff, A., 1905, i, 206), m. p. 74°, b. p. 255°/10 mm., affords on hydrolysis  $\varepsilon$ -aminoamylpiperidine, b. p. 115°/13—14 mm., identical with the base previously described as "bispiperidine," but of which the dibenzenesulphonyl derivative, m. p. about 70°, could not be completely purified. Coniine and  $\varepsilon$ -chloroamylbenzamide yield similarly  $\varepsilon$ -aminoamylconiine, b. p. 145°/10 mm.,  $d_4^{19}$  0.898 (benzoyl derivative, b. p. 270—285° with slight decomp.), identical with the product previously obtained by the action of ammonia on piperidylconiinium bromide. *o*-Chloromethylbenzylbenzamide condenses analogously with dihydroisoindole, hydrolysis of the resulting benzoyl derivative yielding *o*-aminomethylbenzylidihydroisoindole, m. p. 72°, b. p. 220—225°/12 mm. (mono-*p*-nitrobenzoyl derivative; picrolonate, m. p. 230°; salicylidene derivative, m. p. 113°; monobenzenesulphonyl derivative, m. p. 154°), from which *o*-hydroxymethylbenzylidihydroisoindole, m. p. 114°, is obtained by the action of sodium nitrite and acetic acid. Treatment of *o*-chloromethylbenzylamine with warm aqueous alkali affords the above *o*-aminomethylbenzylidihydroisoindole, together with higher condensation products.  $\beta$ -*o*-Chloromethylphenylethylamine affords similarly tetrahydroisoquinoline and *o*- $\beta$ -aminoethylbenzyltetrahydroisoquinoline, b. p. 240—243°/12 mm. (picrolonate, m. p. 230°; phenylthiocarbamide, m. p. 162°; salicylidene derivative, m. p. 67°; mono-*p*-nitrobenzoyl derivative, m. p. 109°). The last-named nitrobenzoyl derivative is also obtained by heating tetrahydroisoquinoline with the *p*-nitrobenzoyl derivative of  $\beta$ -*o*-chloromethylphenylethylamine. *o*-Benzamidomethylbenzylpiperidine, m. p. 111° (hydrochloride, m. p. 221°), obtained from *o*-chloromethylbenzylbenzamide and piperidine, affords on hydrolysis the corresponding *o*-aminomethylbenzylpiperidine, b. p. 158—160°/11 mm. (picrate, m. p. 192°; monobenzenesulphonyl derivative, m. p. 94°). The dibenzenesulphonyl derivative (cf. Scholtz, *loc. cit.*) could not be obtained pure, but the base is otherwise identical with the product obtained by the action of ammonia on xylylenepiperidinium bromide.  $\varepsilon$ -Aminoamyl-di-

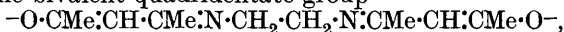
*hydroisoindole*, b. p.  $180^{\circ}/11$  mm. (*benzoyl* derivative, m. p.  $99^{\circ}$ ; *picrate*, m. p.  $140^{\circ}$ ; *monobenzenesulphonyl* derivative, m. p.  $123^{\circ}$ ), is obtained analogously. Treatment with nitrous acid affords a viscous, non-purifiable product.

When piperazinedipiperidinium bromide is heated for 12 hrs. with excess of concentrated aqueous ammonia at  $125$ – $130^{\circ}$ , it yields  $\beta$ -aminoethylpiperidine, piperidine, and piperazine, together with a mixture of several bases from which pure substances could not be isolated, but which has marked pharmacological activity

F. G. W.

**Residual Affinity and Co-ordination. XXV. A Quadridentate Group Contributing Four Associating Units to Metallic Complexes.** G. T. MORGAN and J. D. M. SMITH (*J. Chem. Soc.*, 1925, 127, 2030–2037).—The dienolic radical (*ec*) of ethylenediaminobisacetylacetone (Combes, A., 1889, 851) furnishes the first example of a quadridentate group in co-ordinated complexes. The ketone reacts with hexa-aquocobaltous chloride in presence of sodium hydroxide, giving bright orange-red prisms of *diaquo-cobaltous ethylenediaminobisacetylacetone*,  $[(H_2O)_2ecCo'']$ , readily decomposed by mineral acid into acetylacetone and cobaltous and ethylenediamine salts. The compound is oxidised by hydrogen peroxide in presence of ammonia and ammonium chloride, giving *diamminoethylenediaminobisacetylacetonecobaltic chloride dihydrate*,  $[(NH_3)_2Co'''ec]Cl \cdot (H_2O)_2$ , fawn needles, from which yellowish-brown needles of the anhydrous *bromide*, *iodide*, *chlorate*, *perchlorate*, *nitrite*, *nitrate*, and of the *d-camphorsulphonate* ( $+H_2O$ ) are prepared.

Five stereochemical arrangements of the groups present in this cobaltic co-ordination complex are possible, depending on the positions taken up on the octahedron by the ammonia molecules and by the bivalent quadridentate group



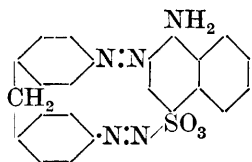
one inactive isomeride (*trans*) in which the two ammonia molecules are in the antipodal positions, one enantiomorphous pair (*cis-trans*) in which the two ammonia molecules are in contiguous positions whilst the oxygen atoms occupy antipodal positions, and one enantiomorphous pair (*cis-cis*) in which the oxygen atoms as well as the ammonia molecules occupy *cis* positions. The cobaltic co-ordination compound has been found to contain two racemoid modifications resolved through the *d-camphorsulphonate* into the corresponding *d-bromides*,  $[M] + 2097^{\circ}$  and  $[M] + 158^{\circ}$ . The *cis* form, in which no elements of symmetry persist, probably has the higher rotation. The active forms are spontaneously transformed on keeping into the single, inactive, and irresolvable form. M. J.

**Reactions of *p*-Phenylenediamine with Formaldehyde and Hydrogen Peroxide. (Comparison with the Reactions of Natural Peroxydases.)** B. LÄTT (*Fermentforsch.*, 1925, 8, 359–422).—The conditions governing the oxidation of *p*-phenylenediamine by a mixture of hydrogen peroxide and formaldehyde in equimolecular proportions were investigated by colorimetric determination of the pigment produced, which was identified as tetra-

aminodiphenyl-*p*-azophenylene (Erdmann, A., 1904, i, 935). Acids exert an inhibitory action; bases at a concentration of 1—2 mols. per mol. of *p*-phenylenediamine accelerate, at higher concentrations inhibit. Salts and colloidal substances influence only the rate of sedimentation of the pigment. Increase of temperature accelerates oxidation, but causes preferential formation of condensation products of formaldehyde with *p*-phenylenediamine. In the presence of phenols and aromatic amines, indophenols and indamines are formed. The action of formaldehyde in the system is compared with that of other aldehydes, milk peroxidase, and blood pigments. E. C. S.

**Search in the Diphenylmethane Series for the Isomerism Characteristic of certain Diphenyl Derivatives.** C. L. BUTLER, jun., and R. ADAMS (*J. Amer. Chem. Soc.*, 1925, **47**, 2610—2620).

—The properties of 4:4'-diaminodiphenylmethane have been investigated to discover whether the same type of isomerism exists as is found in substituted benzidines and the diphenic acids. Like benzidine, 4:4'-diaminodiphenylmethane forms ring structures through the two amino groups, but unlike benzidine it is impossible to cause one diazotised amino group to couple quantitatively before the other reacts; no isomeric 2:2'- or 3:3'-dinitro compounds could be obtained, and the various dicarboxylic acids could not be resolved. 4:4'-Diaminodiphenylmethane condenses with carbonyl chloride to yield *carbonyl-4:4'-diaminodiphenylmethane* (probably polymerised), m. p. above 340°; and with oxalic acid to yield (?) *oxalyl-4:4'-diaminodiphenylmethane*, m. p. above 340° (cf. also Kaufler and Borel, A., 1907, i, 794). Tetrazotised 4:4'-diaminodiphenylmethane couples with 2 mols. of  $\beta$ -naphthol to yield *diphenylmethane-4:4'-bisazo- $\beta$ -naphthol*, m. p. 259—260°, and with 2 mols. of naphthionic acid to yield *diphenylmethane-4:4'-bisazonaphthionic acid*, not melting below 340°. With 1 mol. of naphthionic acid an intermediate compound (annexed formula) was isolated but not purified; this on boiling with dilute alkali yielded *sodium 4-hydroxydiphenylmethane-4'-azonaphthionate*, not melting below 340°.



When 4:4'-diaminodiphenylmethane is nitrated according to the method of Montagne and Charante (A., 1913, i, 55), the product crystallised from dilute sulphuric acid yields 2:2'-dinitro-4:4'-diaminodiphenylmethane hydrogen sulphate, m. p. 229°, but if this salt be crystallised from alcohol the normal sulphate, m. p. 235°, is obtained, and this salt is the supposed second isomeride of 2:2'-dinitro-4:4'-diaminodiphenylmethane of the earlier workers (*loc. cit.*). Both salts on treatment with ammonium hydroxide yield the free base, m. p. 211°, no isomeride being obtained. Nitration of 4:4'-diphthalimidodiphenylmethane (cf. Kaufler and Borel, *loc. cit.*) yields mainly *p*-nitrophthalimidobenzene, m. p. 271—272° (Pawlewski, A., 1895, i, 414, gives 262°), together with a small quantity of 3:3'-dinitro-4:4'-diphthalimidodiphenyl-



*methane*, m. p.  $311^{\circ}$ , which on hydrolysis yields 3 : 3'-dinitro-4 : 4'-diaminodiphenylmethane, m. p.  $232-233^{\circ}$  (Meyer and Rohmer, A., 1900, i, 222, give  $228^{\circ}$ ). Nitration of 4 : 4'-diacetamidodiphenylmethane, m. p.  $236-237^{\circ}$  (Staedel and Hause, A., 1890, 1422, give  $228^{\circ}$ ), yields mainly 3 : 3'-dinitro-4 : 4'-diacetamidodiphenylmethane (cf. Meyer and Rohmer, *loc. cit.*) and *p*-nitroacetanilide. The *brucine* salts of diphenylmethane-2 : 2'-dicarboxylic acid, its 4 : 4'-dinitro derivative, and 2 : 2'-dinitrodiphenylmethane-4 : 4'-dicarboxylic acid [m. p.  $180-182^{\circ}$  (decomp.), decomp.  $210^{\circ}$ , and decomp.  $136-141^{\circ}$ , respectively;  $[\alpha]_D$  in chloroform,  $-27.30^{\circ}$ ,  $-6.5^{\circ}$ , and  $-2.47^{\circ}$ , respectively] were prepared but could not be resolved. Nitration of diphenylmethane-2 : 2'-dicarboxylic acid with nitric acid, *d* 1.50, and concentrated sulphuric acid yields only 4-nitrodiphenylmethane-2 : 2'-dicarboxylic acid, m. p.  $284-285^{\circ}$ .

J. W. B.

### Coloured Salts of the Di- and Tri-phenylmethane Series.

W. MADELUNG (*J. pr. Chem.*, 1925, [ii], **111**, 100—146).—A theoretical paper in which the various theories of coloured salts of the di- and tri-phenylmethane series are reviewed. The work of Kauffmann, Hantzsch, Brand, Dilthey, and others indicates that Baeyer's "carbonium" theory as applied to these salts may be regarded as a special case of a general theory of organic complex positive ions.

The mono-, di-, and tri-acetyl derivatives of pararosaniline are prepared and their perchlorates described. C. H.

**Products of the Condensation of 2-Aminopyridine with Fatty-aromatic Ketones.** I. L. SCHMID and B. BANGLER (*Ber.*, 1925, **58**, [B], 1971—1973).—Skraup's quinoline synthesis does not appear to be applicable to 2-aminopyridine, which, also, does not yield with acetophenone anils which are susceptible to ring closure. With acetophenonedietiethylacetal, however, it yields 2- $\alpha$ -methylbenzylideneaminopyridine,  $C_5H_4N \cdot N : CMePh$ , b. p.  $174-175^{\circ}/11.5$  mm., which is unstable towards acids and alkalis and is slowly decomposed by moist air; the corresponding *methiodide*, m. p.  $162^{\circ}$ , and *methosulphate* are described. Hydrogen chloride at  $180^{\circ}$  does not effect ring closure of 2- $\alpha$ -methylbenzylideneaminopyridine to the corresponding naphthyridine derivative, but gives exclusively the *dypnone* derivative,  $CMePh \cdot CH \cdot CPh \cdot N \cdot C_5H_4N$ , m. p.  $118.5^{\circ}$  (*hydrochloride*, m. p.  $235^{\circ}$ ; *methiodide*, m. p.  $201-202^{\circ}$ ). H. W.

**Action of Phenylsemicarbazide on Acetylacetone.** A. S. WHEELER and F. P. BROOKS (*J. Elisha Mitchell Sci. Soc.*, 1924, **40**, 110—111).—The product obtained by interaction of phenylsemicarbazide and acetylacetone consists chiefly (85%) of 1-phenylcarbamyl-3 : 5-dimethylpyrazole, m. p.  $68-70^{\circ}$ .

CHEMICAL ABSTRACTS.

**Formation and Transformation of Pyrazolecarboxylamides.** K. VON AUWERS and B. OTTENS (*Ber.*, 1925, **58**, [B], 2072—2080; cf. von Auwers and Daniel, this vol., i, 1180). *Benzoylacetalddehyde*- $\alpha$ -semicarbazone,  $CH_2Bz \cdot CH \cdot N \cdot NH \cdot CO \cdot NH_2$ ,

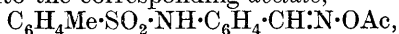
m. p. 175—176°, is prepared by the action of semicarbazide in neutral, faintly acid, or alkaline solution of hydroxymethyleneacetophenone, its benzoate, or ethyl ether. It is readily transformed into the corresponding *disemicarbazone*, m. p. 238°. The constitution of the monosemicarbazone is established by the observation that it is transformed by hydroxylamine into *γ-oximino-benzoylacetalddehyde-α-semicarbazone*, m. p. 189—190°, which differs from the *α-oximinobenzoylacetalddehyde-γ-semicarbazone*, m. p. 154°, obtained from Claisen's benzoylacetaldoxime, the constitution of which is regarded as established. The latter compound is converted by concentrated hydrochloric acid into 3-phenylpyrazole-1-carboxylamide, m. p. 142—143°, and 3(5)-phenylpyrazole, whereas the former compound gives 3-phenylisooxazole, b. p. 145°/30 mm., 131—132°/16 mm.,  $d_4^{18.7}$  1.1406,  $n_{\text{He}}^{18.7}$  1.56916. (1-Phenylisooxazole, prepared for purposes of comparison, has b. p. 128°/15 mm., m. p. 22°,  $d_4^{18.8}$  1.1399,  $n_{\text{He}}^{18.8}$  1.58693). The *dioxime* of benzoylacetalddehyde has m. p. 109—110°.

3-Phenylpyrazolecarboxylamide (*v.s.*) is also prepared by the action of a little sulphuric acid on a suspension of the monosemicarbazone in alcohol, by the successive action of carbonyl chloride and ammonia on 3(5)-phenylpyrazole, and by the action of potassium cyanate on phenylpyrazole hydrochloride dissolved in glacial acetic acid. The corresponding *picrate*, m. p. 165—166°, is described. The carboxylamide is transformed by silver nitrate into the *silver* salt of 3(5)-phenylpyrazole, m. p. 85°, and by bromine in chloroform at -15° into 4-bromo-3-phenylpyrazole-1-carboxylamide, m. p. 161—163° after softening, which is also obtained from 4-bromo-3-phenylpyrazole, glacial acetic acid, and potassium cyanate. 5-Phenylpyrazole-1-carboxylamide, m. p. 133—134°, is prepared directly from hydroxymethyleneacetophenone and semicarbazide hydrochloride in aqueous solution if the latter is allowed to become warm, whereas at -15° the semicarbazone, m. p. 175—176°, is produced, and this is converted by alcohol and concentrated hydrochloric acid into the carboxylamide. The latter is converted by picric acid in warm alcoholic solution into 3(5)-phenylpyrazole *picrate*, by silver nitrate into the silver salt of phenylpyrazole, and by bromine in chloroform at -15° into 4-bromo-3(5)-phenylpyrazole *hydrobromide*, m. p. 186—187° after softening. H. W.

**Constitution of Labile and Stable Acylindazoles.** K. von AUWERS (*Ber.*, 1925, **58**, [B], 2081—2088).—It is shown in the case of the toluenesulphonylindazoles that the labile 2-derivatives readily pass into the stable 1-derivatives by migration of the acyl group, and it therefore appears probable that many of the compounds described previously as "stable 2-acylindazoles" are actually the corresponding 1-derivatives. The number of actual isomerides is thus reduced from three to two, and the assumption of stereoisomerism is no longer necessary. The spectrochemical behaviour of the labile and stable acylindazoles is in agreement with the conception that they are structural isomerides. The action of an acyl chloride on indazole at low temperature or on its

silver salt proceeds according to the scheme  $C_6H_4\langle\begin{smallmatrix} CH \\ NH \end{smallmatrix}\rangle N \rightarrow C_6H_4\langle\begin{smallmatrix} CH \\ NH \end{smallmatrix}\rangle N\langle\begin{smallmatrix} CO\cdot R \\ Cl \end{smallmatrix}\rangle \rightarrow C_6H_4\langle\begin{smallmatrix} CH \\ N- \end{smallmatrix}\rangle N\cdot COR$ , thus yielding a 2-acylindazole. With the sodium salts, on the other hand, the strongly electro-positive metallic atom reacts directly with the chlorine of the acyl chloride so that 1-acyl compounds are directly produced.

*o*-2'-Toluenesulphonamidobenzaldoxime, m. p. 130—131°, is prepared in relatively poor yield by the action of *o*-toluenesulphonyl chloride on *o*-aminobenzaldoxime in the presence of pyridine or by oximation of *o*-2'-toluenesulphonamidobenzaldehyde. It is transformed by glacial acetic acid, acetic anhydride, and hydrogen chloride at 0° into the corresponding *acetate*,



which appears to exist in two isomeric forms, m. p. 151—153° and 129—131°, respectively. Either variety is converted at 180—190° into *o*-2-toluenesulphonamidobenzonitrile, m. p. 125—126°, which is also prepared from *o*-aminobenzonitrile and *o*-toluenesulphonyl chloride. Ring closure is effected by treatment of the acetate with alkali hydroxide, which at elevated temperatures yields mainly the original oxime, but at low temperatures affords 1-*o*-toluenesulphonylindazole, m. p. 108°, which is obtained directly from indazole and *o*-toluenesulphonyl chloride at 100°. On the other hand, the acid chloride converts the base in the presence of pyridine at 0° into 2-*o*-toluenesulphonylindazole, m. p. 81—84°, which passes into the isomeride, m. p. 108°, when heated for some time in solvents of high b. p. The 2-derivative is immediately hydrolysed by ethereal hydrogen chloride, whereas the 1-derivative remains unaffected. Exposure to moist air causes the transformation of the 2-compound into *indazole o*-toluenesulphonate, m. p. 167—169°.

*o*-4'-Toluenesulphonamidobenzaldoxime, m. p. 136—136·5°, is converted by Beckmann's mixture into an isomeride, m. p. 123—125°, which has not been investigated fully. Treatment of the oxime with boiling acetic anhydride affords the corresponding *acetate*, m. p. 101—102·5°, which is transformed by trituration with cold sodium hydroxide or treatment with acetone and sodium carbonate into 1-*p*-toluenesulphonylindazole, m. p. 104—105°.

H. W.

***o*-Aminophenylhydrazine and Some Interesting Heterocyclic Compounds Derived from It.** P. C. GUHA and S. K. RAY (*J. Indian Chem. Soc.*, 1925, 2, 83—94).—Reduction of *o*-nitrophenylhydrazine with stannous chloride and hydrochloric acid yields *o*-aminophenylhydrazine hydrochloride, m. p. 263—265° (decomp.), it being necessary to exclude air during the concentration of the hydrochloride solution. The free base has m. p. 295—302° (decomp.). It condenses with phenylthiocarbimide and *o*-tolylthiocarbimide to yield respectively 4-phenyl-1-*o*-phenylthiocarbamidophenylthiosemicarbazide and 4-*o*-tolyl-1-*o*-tolylthiocarb-

*amidophenylthiosemicarbazide*, m. p. 80° and 282°, respectively, and with benzaldehyde yields a *dibenzylidene* derivative (*hydrochloride* described). With potassium ethyl xanthate, *o*-aminophenylhydrazine yields 3-*thion*-1:2:3:4-*tetrahydro*-1:2:4-*benztriazine*, m. p. 298—300° (*benzoyl* derivative, m. p. 174°), which on treatment with iodine yields the corresponding *disulphide*, showing the presence of the thiol group. Condensation of aminophenylhydrazine with carbamide yields 3-*keto*-1:2:3:4-*tetrahydro*-1:2:4-*benztriazine*, m. p. 310—312° (sublimes at a higher temperature), and with glyoxal yields a *benzheptatriazine* compound,  $C_6H_4 \begin{smallmatrix} <N:CH \\ NH \cdot N \end{smallmatrix} > CH$ , m. p. 212—214° (decomp.). Reduction of *o*-nitrophenylthiosemicarbazide with tin and hydrochloric acid occurs in two stages, the nitro group being first reduced to amino followed by the loss of 1 mol. of ammonia to yield a benzthiadiazine derivative, and thus are obtained, 4-*phenyl*-1-*o*-aminophenylthiosemicarbazide, m. p. 253—255° (decomp.); and 2-*phenylimino*-1:2:3:4-*tetrahydro*-1:3:4-*benztriazine*, m. p. 150—151° (this product also resulting from the action of acetic anhydride on the amino compound, m. p. 253°). Condensation of *o*-nitrophenylhydrazine with allylthiocarbimide yields 1-*o*-nitrophenyl-4-allylthiosemicarbazide, m. p. 164—165°. Reduction of the benzylidene derivative of *o*-nitrophenylhydrazine yields 2-*phenyl*-1:3-*benz-diazole*, m. p. 288—289° (*hydrochloride*, m. p. above 306°). With salicylaldehyde, *o*-nitrophenylhydrazine yields a *salicylidene* derivative, m. p. 110° (*benzoyl* derivative, m. p. 180°). J. W. B.

**Oxidation of Uric Acid with Iodine.** W. E. FÜRTH (*Biochem. Z.*, 1925, 159, 130—140).—One mol. of uric acid in alkaline solution reacts as a maximum with  $3\frac{1}{2}$  atoms of iodine; 70% of the nitrogen appears as carbamide, about 15% as allantoin, which is not further oxidised by iodine, and is therefore produced by a side reaction. Alloxan is not formed, and ammonia and carbon dioxide only in traces. Oxalic acid as such is not formed, but substances are present in quantity which yield oxalic acid on hydrolysis.

E. C. S.

**3-Ethyluric Acid and 3-Ethylxanthine.** H. BILTZ and E. PEUKERT (*Ber.*, 1925, 58, [B], 2190—2199).—By customary methods, 3-methyluric acid can be converted only into a surprisingly small number of derivatives (cf. Biltz and Heyn, A., 1917, i, 291; 1919, i, 292); this is also the case with 3-ethyluric acid.

Ethylcarbamide is converted by cyanoacetic acid and acetic anhydride at 75° into *ω*-cyanoacetyl-*ω'*-ethylcarbamide, m. p. 167°, which is transformed by warm dilute ammonia into 6-*amino*-1-*ethyluracil*, decomp. 282°, which yields successively 5-*nitroso*-6-*amino*-1-*ethyluracil*, decomp. 249° (*ammonium* salt, decomp. 255°), and 5:6-*diamino*-1-*ethyluracil*, decomp. 270° after darkening at 250°. The latter compound is converted by ethyl chloroformate and sodium hydroxide into 6-*amino*-1-*ethyluracil*-5-*ethylurethane*, which, at 230—240°, affords 3-ethyluric acid. Diazomethane

converts 3-ethyluric acid smoothly into 1 : 7 : 9-trimethyl-3-ethyluric acid, m. p.  $240^{\circ}$ , identical with the product obtained by Biltz and Max (A., 1921, i, 131) from 1 : 7 : 9-trimethyluric acid and diazoethane. 5(4)-*Chloro-3-ethylisouric acid*, decomp. above  $150^{\circ}$ , is prepared by the action of chlorine on dehydrated 3-ethyluric acid dissolved in a mixture of acetic anhydride and glacial acetic acid; it is unusually sensitive to moisture, by which it is converted into carbamide and ethylalloxan. Reduction with potassium iodide converts it into 3-ethyluric acid. It is transformed by cold methyl alcohol into 4-hydroxy-5-methoxy-3-ethyl-4 : 5-dihydrouric acid,  $C_8H_{12}O_5N_4$ , decomp.  $195^{\circ}$ , which is reduced by fuming hydriodic acid and phosphonium iodide to hydantoin. 4-Hydroxy-5-ethoxy-3-ethyl-4 : 5-dihydrouric acid decomposes at  $189^{\circ}$  after darkening at  $160^{\circ}$ .

3-Ethyluric acid is transformed by phosphoryl chloride at  $130$ — $135^{\circ}$  into 8-chloro-3-ethylxanthine, decomp.  $295^{\circ}$ , from which 3-ethyluric acid is regenerated by dilute alkali hydroxide solution. The chloroethylxanthine is reduced by hydriodic acid and phosphonium iodide at  $100^{\circ}$  to 3-ethylxanthine, decomp.  $299^{\circ}$  after darkening at  $275^{\circ}$ , and converted by potassium hydrogen sulphide into 8-thio-3-ethyluric acid, decomp.  $365$ — $370^{\circ}$ . 8-Chloro-1 : 7-dimethyl-3-ethylxanthine, m. p.  $112^{\circ}$ , is prepared from 8-chloro-3-ethylxanthine, methyl sulphate, and sodium hydroxide; it is reduced by hydriodic acid to 1 : 7-dimethyl-3-ethylxanthine, m. p.  $128^{\circ}$  (the hydriodide and the perchlorate, explosive, decomp.  $300^{\circ}$ , are described). 8-Thio-1 : 7-dimethyl-3-ethyluric acid has m. p.  $272^{\circ}$ . Ethylation of 8-chloro-3-ethylxanthine with ethyl bromide and potassium hydroxide at  $100^{\circ}$  yields only 8-chloro-3 : 7-diethylxanthine, m. p.  $238^{\circ}$ , in which the position of the second ethyl group is established by its conversion into 3 : 7-diethyluric acid. 3 : 7-Diethylxanthine has m. p.  $183^{\circ}$ .

H. W.

**Synthetic Nucleosides. I. Theophylline Pentosides. II. Substituted Uracil Xylosides.** P. A. LEVENE and H. SOBOTKA (*J. Biol. Chem.*, 1925, **65**, 463—468, 469—477).—I. By the method of Fischer and Helferich (A., 1914, i, 333) there was prepared, from the silver salt of theophylline and acetobromoxylose, *theophylline triacetylxyloside*,  $[\alpha]_D^{25} -21.9^{\circ}$  in methyl alcohol, which with methyl-alcoholic ammonia gave *theophylline xyloside*, m. p.  $229^{\circ}$ ,  $[\alpha]_D^{25} -28.5^{\circ}$  in methyl alcohol. *Theophylline triacetylriboside* had  $[\alpha]_D^{25} -4.25^{\circ}$  in methyl alcohol and gave *theophylline riboside*, m. p.  $234^{\circ}$ ,  $[\alpha]_D^{25} -21^{\circ}$  in ethyl alcohol; the latter substance agreed in its optical rotation and rate of hydrolysis with dimethylxanthosine (cf. Levene, A., 1923, i, 611) and the synthesis is therefore direct evidence that in purine nucleosides the carbohydrate is attached in the 7-position.

II. The synthesis from silver salts of uracil derivatives and acetobromoxylose of various substituted uracil xylosides led only to the formation of compounds with the pentose attached in the 2- or 6-position which were unstable substances, reducing Fehling's solution and differing therein from natural uridine and cytidine.

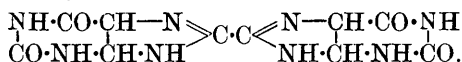
This is additional evidence in favour of the author's view of the structure of uridine (this vol., i, 979). 2-Ethylthiouracil triacetylxyloside has m. p. 104—105°,  $[\alpha]_D^{25} + 28.4^\circ$ , and when hydrolysed by methyl-alcoholic ammonia gave 2-ethylthiouracil xyloside, m. p. 114—115°,  $[\alpha]_D^{25} + 21.5^\circ$  in methyl alcohol; it was completely hydrolysed by heating at 100° for 2 hrs. with 0.2*N*-hydrochloric acid. 1-Methyluracil triacetylxyloside, which was optically inactive, gave 1-methyluracil xyloside,  $[\alpha]_D^{25} + 27.3^\circ$  in methyl alcohol; this required 3 hrs.' heating at 100° with *N*-hydrochloric acid for hydrolysis. The xyloside of 5-nitrouracil could not be obtained pure, and cytosine did not react with acetobromoxylene. No satisfactory results were obtained by substituting sodium or potassium salts of the uracil derivatives for the silver salts in the condensation except in the case of the potassium salt of 1-methylnitrouracil, which gave 1-methylnitrouracil triacetylxyloside, m. p. 243°,  $[\alpha]_D^{25} - 45.5^\circ$  in pyridine and methyl alcohol. C. R. H.

**5-Amino-2-phenyl-1 : 2 : 3 : 4-tetrazole.** R. STOLLÉ and O. ORTH (*Ber.*, 1925, 58, [B], 2100—2105).—5-Amino-2-phenyl-1 : 2 : 3 : 4-tetrazole is a still weaker base than 5-amino-1-phenyl-1 : 2 : 3 : 4-tetrazole, which it resembles in not yielding a diazonium salt, whereas 5-amino-1 : 2 : 3 : 4-tetrazole gives an unstable derivative; the substitution of the imino hydrogen atom of the tetrazole ring therefore diminishes the aromatic character of the compounds.

Methyl 2-phenyl-1 : 2 : 3 : 4-tetrazole-5-carboxylate is converted by excess of hydrazine hydrate at 110—120° into 2-phenyl-1 : 2 : 3 : 4-tetrazole-5-carboxylic hydrazide, m. p. 200° (decomp.) [the hydrochloride, m. p. 182° (decomp.), benzylidene derivative, m. p. 164° (decomp.), and isopropylidene compound, m. p. 117° after softening, are described]. The hydrazide is converted by nitrous acid into the corresponding azide, m. p. 100° (decomp.), and, apparently, a salt-like compound, m. p. 167° (decomp.), of 2-phenyl-1 : 2 : 3 : 4-tetrazole-5-carboxylic acid and 2-phenyl-1 : 2 : 3 : 4-tetrazole-5-carboxylamide. The azide is transformed in boiling xylene solution into *s*-di-2-phenyl-1 : 2 : 3 : 4-tetrazolyl-5-carbamide, m. p. 216° (decomp.), and by boiling ethyl alcohol into the ethylurethane, m. p. 106°. 5-Amino-2-phenyl-1 : 2 : 3 : 4-tetrazole, m. p. 142°, is prepared from the urethane and concentrated hydrochloric acid at 200° or concentrated sulphuric acid at 105—110°, or from the carbamide derivative (*v.s.*) and glacial acetic and hydrochloric acids; the corresponding benzylidene derivative, m. p. 123° (decomp.), and acetyl compound, m. p. 177° (decomp.) after softening, are described. Bleaching powder converts 5-amino-2-phenyl-1 : 2 : 3 : 4-tetrazole into azo-5 : 5'-di-2-phenyl-1 : 2 : 3 : 4-tetrazole, m. p. 148° after darkening, which is reduced by zinc dust and acetic acid at 100° to the corresponding hydrazo compound, m. p. 184° (decomp.). H. W.

**The Yellow Dye of the Wing of the Lemon Butterfly (*Gonepteryx rhamni*).** H. WIELAND and C. SCHÖPF (*Ber.*, 1925, 58, [B], 2178—2183).—The air-dried wings of *Gonepteryx rhamni* (male)

are freed from fat and wax by extraction with ether, and subsequently extracted with dilute ammonia, which dissolves the yellow dye. On evaporation of the solution in a vacuum over potassium hydroxide and sulphuric acid, the ammonium salt is hydrolysed, leaving the crude dye, which is further purified by repeated solution in dilute hydrochloric acid and precipitation by sodium acetate. The dye, for which the name *xanthopterin* is proposed, is thus obtained amorphous, but can be caused to crystallise if its *barium* salt,  $C_5H_5O_2N_4Ba \cdot 3H_2O$ , is dissolved in very dilute hydrochloric acid and the solution treated with sodium acetate. The relative proportions of amorphous and crystalline material thus obtained suggest that an isomeric dye may also be present in amorphous xanthopterin. The crystalline compound has the composition,  $C_5H_5O_2N_4$ , but owing to its very sparing solubility, determinations of mol. wt. could not be effected. When heated, it decomposes slowly at about  $360^\circ$  after darkening at  $270^\circ$ . This observation, considered in conjunction with its analytical composition and its ability to give the murexide reaction when evaporated with nitric acid, suggest the constitution



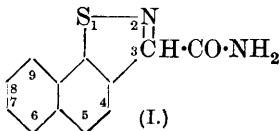
H. W.

**Thiodiazines. II. Condensation of  $\omega$ -Bromoacetophenone, with 4-Substituted Thiosemicarbazides. Constitution of Thiosemicarbazides.** P. K. BOSE (*J. Indian Chem. Soc.*, 1925, 2, 95—114; cf. this vol., i, 167).—The condensation of methyl-, ethyl-, allyl-, phenyl-, *o*- and *p*-tolyl-, and  $\beta$ -naphthyl-thiosemicarbazides with  $\omega$ -bromoacetophenone has been studied quantitatively, the results showing that the hypothesis that the formation of the thiazole derivative depends on the relative basicity of the two amino groups is inadequate, and that the 4-substituted thiosemicarbazides and their acetyl derivatives probably react in the form  $\text{NHR} \cdot \text{C}(\text{SH}) \cdot \text{N} \cdot \text{NHR}$ . The thioazoles are more basic and more susceptible to oxidation than the thiodiazines, and replacement of the alkyl by aryl groups in position 4 increases the stability but decreases the reactivity of the hydrazine group. The following compounds are obtained by the condensation of 4-substituted thiosemicarbazides cited above: 2-*anilino-5-phenyl-1:3:4-thiodiazine*, m. p.  $175^\circ$  (*hydrobromide*, m. p.  $191^\circ$ ; *acetyl* derivative, m. p. about  $110^\circ$ ); 2-*keto-3:4-diphenyl-2:3-dihydro-1:3-thiazolehydrazone*, m. p.  $198^\circ$  (decomp.) [*hydrobromide*, m. p.  $224$ — $226^\circ$  (decomp.), with nitrous acid yields an orange substance, m. p.  $195$ — $198^\circ$  (decomp.)]; 1-*acetyl-4-phenylthiosemicarbazide*, m. p.  $173^\circ$ ; 2-*keto-3:4-diphenyl-2:3-dihydro-1:3-thiazoleacetylhydrazone* (*hydrobromide*, m. p.  $224^\circ$ ); *acetone-4-phenylthiosemicarbazone*, m. p.  $128^\circ$ ; 2-*keto-3:4-diphenyl-2:3-dihydro-1:3-thiazoleisopropylidenehydrazone*, m. p.  $165^\circ$ ; *anisylidene-4-phenylthiosemicarbazide*, m. p.  $180$ — $181^\circ$ ; 2-*keto-3:4-diphenyl-2:3-dihydro-1:3-thiazoleanisylidenehydrazone*, m. p.  $161^\circ$ ; corresponding *benzylidene* compound, m. p.  $191^\circ$ ; 4-*p-tolylamino-5-phenyl-1:3:4-thiodiazine*, m. p.  $179^\circ$

(hydrobromide, m. p. 195°, acetyl derivative, m. p. indefinite 115°); 2-o-tolylamino-5-phenyl-1:3:4-thiodiazine, m. p. 148° (hydrobromide, m. p. 185°; monobromo derivative, m. p. 155—156°); 2-keto-4-phenyl-3-o-tolyl-2:3-dihydro-1:3-thiazolehydrazone, m. p. 136° [hydrobromide, m. p. 206—208° (decomp.)]; 2-allylamino-5-phenyl-1:3:4-thiodiazine, m. p. 99° (hydrobromide, m. p. 165°); 2- $\alpha$ -naphthylamino-5-phenyl-1:3:4-thiodiazine, m. p. 166.7° [hydrobromide, m. p. 220° (decomp.), acetyl derivative described]; 2-keto-4-phenyl-3- $\alpha$ -naphthyl-2:3-dihydro-1:3-thiazolehydrazone, m. p. 179° [hydrobromide, m. p. 208° (decomp.)]; 2- $\beta$ -naphthylamino-5-phenyl-1:3:4-thiodiazine, m. p. 153°; 2-methylamino-5-phenyl-1:3:4-thiodiazine, m. p. 144—145°; acetone-4-methylthiosemicarbazone, m. p. 118°; 2-keto-4-phenyl-3-methyl-2:3-dihydro-1:3-thiazoleisopropylidenehydrazone, m. p. 92.5° (hydrobromide, m. p. 208—209°); anisylidene-4-methylthiosemicarbazone, m. p. 207°; 2-keto-4-phenyl-3-methyl-2:3-dihydro-1:3-thiazoleanisylidenehydrazone, m. p. 127—128° (hydrobromide, m. p. 235—236°); 2-ethylamino-5-phenyl-1:3:4-thiodiazine, m. p. 158°. J. W. B.

**Benzisothiazole.** R. STOLLÉ, W. GIESEL, and W. BADSTÜBNER (*Ber.*, 1925, **58**, [B], 2095—2100).—Thionaphthenquinone is converted by concentrated aqueous ammonia and hydrogen peroxide into benzisothiazole-2-carboxylamide,  $C_6H_4 \begin{smallmatrix} \text{C}(\text{CO}\cdot\text{NH}_2) \\ \text{S} \end{smallmatrix} \text{N}$ , m. p. 134°, and dithiosalicylic acid, m. p. 289°. The amide is converted by aqueous sodium hydroxide into benzisothiazole-2-carboxylic acid, m. p. 143° (ethyl ester, m. p. 44°; additive compound of ester and silver nitrate,  $C_{10}H_9O_2NS\cdot AgNO_3$ , m. p. 170°), which loses carbon dioxide at 175° and yields benzisothiazole, b. p. 220°/atm. pressure, m. p. 37° [additive compound with silver nitrate,  $(C_7H_5NS)_2\cdot AgNO_3$ , m. p. 105°]. An alcoholic solution of the amide is transformed by hydrazine hydrate into benzisothiazole-3-carboxylic hydrazide, m. p. 138° (benzylidene derivative, m. p. 231°), which yields the corresponding azide, m. p. 102° (decomp.), and thence the anilide, m. p. 126°, and ethylurethane, m. p. 107°. The latter compound is hydrolysed by concentrated hydrochloric acid at 105—110° to 2-aminobenzisothiazole, m. p. 115°. The amine does not appear to yield a diazonium compound, being apparently transformed by nitrous acid into (?) 2-hydroxybenzisothiazole, m. p. 151°.

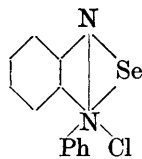
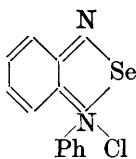
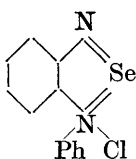
$\alpha\beta$ -Naphthisothiazole-3-carboxylamide (I), m. p. 245°, is prepared by the action of hydrogen peroxide or air on a solution of  $\alpha$ -benzthionaphthenquinone in concentrated aqueous ammonia. It is converted by ethyl alcohol and hydrogen chloride into ethyl  $\alpha\beta$ -naphthisothiazole-3-carboxylate, m. p. 131° (additive compound with silver nitrate, decomp. about 215°), which is hydrolysed to the corresponding acid, m. p. 212° (decomp.). H. W.



**Piaselenazonium Salts.** M. BATTEGAY and J. VÉCHOT (*Bull. Soc. chim.*, 1925, [iv], **37**, 1271—1291).—With the object of obtain-

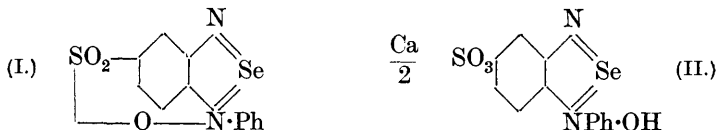


ing derivatives of piaselenole soluble in water without decomposition, the authors have condensed selenious acid in dilute hydrochloric acid with salts of *o*-aminodiphenylamine and obtained a series of well-defined piaselenazonium salts, which possess one of the following structures :

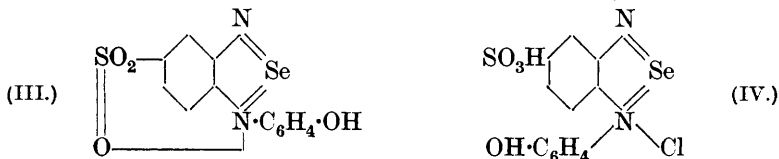


The reaction is accelerated by heating, and the products are slightly soluble in cold water, giving solutions the colour of which varies from yellow to red. The simplest compound, phenylpiaselenazonium chloride, dyes pale brown shades with a violet tinge on mordanted cotton, wool, and silk. The introduction of chlorine into the ring does not appreciably affect the shade; a nitro group gives yellower shades, whilst the sulphonic and hydroxyl groups have slight weakening and deepening effects on the shade, respectively. The absorption spectrum of piaselenole in alcoholic solution shows a band in the ultra-violet, analogous to that observed with phenazine. Phenylpiaselenazonium chloride shows an analogous band, but the band is more marked in aqueous solution, and varies with the  $p_H$ . Piaseleole (cf. Hinsberg, A., 1889, 785; 1890, 160) with perchloric acid at 50–60° yields a yellow *perchlorate*,  $C_6H_4N_2Se.HClO_4$ , which is immediately decomposed by water. *o*-Aminodiphenylamine hydrochloride and selenious acid yield *phenylpiaselenazonium chloride*, black, metallic crystals, decomp. at 215°, which are stable with water and mineral acid, but with dilute alkali yield a dark red, gelatinous precipitate, probably the azonium *hydroxide*,  $C_6H_4\langle\overset{N}{\text{---}}\text{N}^+\text{Ph}\rangle\text{Se}\cdot\text{OH}$ , which rapidly turns white and crystalline, giving *o*-aminodiphenylamine and the alkali selenite. Both acid and alkaline reducing agents yield *o*-aminodiphenylamine and free selenium, but in the latter case the selenium is obtained in the colloidal form. Similarly, from 4-chloro-2-aminodiphenylamine is obtained *phenyl-4-chloropiaselenazonium chloride*, brown crystals; from 4-nitro-2-aminodiphenylamine, *phenyl-4-nitropiaselenazonium chloride*, orange-red needles, which could not be reduced to the corresponding amino compound. Attempts to prepare the latter from 2:4-diaminodiphenylamine gave indefinite results, although the solution showed the characteristic reaction of a piaselenazonium salt with dilute alkali, and the use of acyl derivatives of 2:4-diaminodiphenylamine was also unsuccessful, benzoylation yielding *4-amino-2-benzamidodiphenylamine*, m. p. 213–214°, which does not condense with selenious acid or phenanthraquinone. Similarly, 2-amino-4'-dimethylaminodiphenylamine-4-sulphonic acid, obtained by reduction of *sodium 2-nitro-4'-dimethylaminodiphenylamine-4-sulphonate*, orange-red plates, does not condense with selenious acid. 4-Nitro-2-amino-

phenyl- $\beta$ -naphthylamine in acetic acid yields  $\beta$ -naphthyl-4-nitropiaselenazonium chloride, greenish-brown (+1Ac $\cdot$ OH, lost at 130°); *op*-diaminophenyl- $\beta$ -naphthylamine behaves similarly to 2:4-diaminodiphenylamine. 4-Nitro-2-amino-4'-hydroxydiphenylamine yields *p*-hydroxyphenyl-4-nitropiaselenazonium chloride, orange-brown. All the above salts behave similarly to phenylpiaselenazonium chloride on reduction. Phenylpiaselenazonium-4-anhydrosulphonate (I), greenish-brown, obtained from 2-amino-4-sulphodiphenylamine



hydrochloride, however, behaves differently; with weak bases or dilute alkali, solution takes place at once with production of a stable blood-red coloration. Concentrated alkali produces rupture of the selenazole ring, whilst acids reprecipitate the anhydrosulphonate. With a suspension of calcium carbonate in water the anhydrosulphonate similarly gives a red solution, which probably contains the calcium salt of the azonium hydroxide (II), but on concentration the solution decomposes, yielding the calcium salt of the original diphenylamine derivative. 2-Nitro-4'-hydroxydiphenylamine-4-sulphonic acid, from *p*-aminophenol and 4-chloro-3-nitrobenzenesulphonic acid, on reduction with iron or zinc and hydrochloric acid, yields the readily oxidised 2-amino-4'-hydroxydiphenylamine-4-sulphonic acid. The orange-red *p*-hydroxyphenylpiaselenazonium-4-anhydrosulphonate obtained from this resembles the anhydrosulphonate just described, but the dark-red calcium salt of the azonium hydroxide has been isolated. Freshly prepared dilute solutions ( $p_H$  2) are yellow, but slowly become green, the change being accelerated by heating and exposure to ultra-violet light. It is suggested that the salt in the yellow and green solutions has structures (III) and (IV), respectively. At

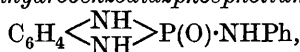


$p_H$  5—6 the colour changes to red with considerable alteration of the absorption spectrum. R. B.

**P-Oxodiazphospholes and Experiments with Trimethylenedisulphonyl Chloride.** W. AUTENRIETH and E. BÖLLI (*Ber.*, 1925, **58**, [B], 2144—2150; cf. Autenrieth and Meyer, this vol., i, 807).—Phenoxyphosphoryl dichloride, b. p. 138—140°/14 mm., is converted by *o*-phenylenediamine at 170° or, preferably, in the presence of benzene into “*phenoxy-P-oxodihydrobenzodiazphospholium*,”  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} \text{PO} \cdot \text{O} \cdot \text{Ph}$ , m. p. 185°, which is stable towards

boiling water and dilute acids, but is hydrolysed in alkaline solution. With hydrazine hydrate in aqueous solution, phenoxyphosphoryl dichloride gives *PP'-diphenoxy-PP'-dioxotetrahydrotetrazdiphosphinium*,  $\text{OPh}(\text{O})\text{P} \begin{smallmatrix} \text{NH} \cdot \text{NH} \\ \text{NH} \cdot \text{NH} \end{smallmatrix} \text{PO} \cdot \text{OPh}$ , m. p.  $132^\circ$ , the cyclic structure of which is established by its conversion by benzaldehyde into benzylideneazaine, phenol, and phosphoric acid. *Phenoxy-P-oxotetrahydrodiazphospholium*,  $\begin{smallmatrix} \text{CH}_2 \cdot \text{NH} \\ \text{CH}_2 \cdot \text{NH} \end{smallmatrix} \text{P}(\text{O}) \cdot \text{OPh}$ , m. p.  $196^\circ$ , is

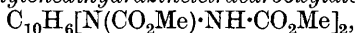
prepared similarly from ethylenediamine hydrate. In an analogous manner, *p*-tolylloxyphosphoryl dichloride gives *p*-tolylloxy-*P-oxodihydrobenzodiazphospholium*, m. p.  $158^\circ$ , *PP'-di-p-tolylloxy-PP'-dioxotetrahydrotetrazdiphosphinium*, m. p.  $168^\circ$ , and *p*-tolylloxy-*P-oxotetrahydrodiazphospholium*, m. p.  $204^\circ$ . Anilino-phosphoryl dichloride yields *anilino-P-oxodihydrobenzodiazphospholium*,



m. p.  $214^\circ$ , *PP'-dianilino-PP'-dioxotetrahydrotetrazdiphosphinium*, m. p.  $208\text{--}210^\circ$ , and *anilino-P-oxotetrahydrodiazphospholium*, m. p.  $232^\circ$ .

Trimethylenedisulphonyl chloride,  $\text{SO}_2\text{Cl} \cdot [\text{CH}_2]_3 \cdot \text{SO}_2\text{Cl}$ , m. p.  $48^\circ$ , is conveniently prepared by the successive action of saturated sodium sulphite solution and phosphorus pentachloride on trimethylene bromide. It is converted by the appropriate reagent into *trimethylenedisulphonamide*, m. p.  $165^\circ$ ; *trimethylenedisulphonhydrazide*, m. p.  $168^\circ$ ; *trimethylenedisulphonphenylhydrazide*, m. p.  $190^\circ$ , and *trimethylenedisulphon-o-aminoanilide*, m. p.  $152^\circ$ ; attempts to obtain cyclic compounds from it were unsuccessful. H W.

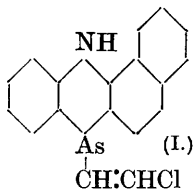
**Addition of Azodicarboxylic Esters to Aromatic Hydrocarbons.** R. STOLLÉ and G. ADAM (*J. pr. Chem.*, 1925, [ii], 111, 167—175; cf. Stollé and Leffler, A., 1924, i, 1002).—Methyl azodicarboxylate (2 mols.) reacts with naphthalene in dry ether saturated with hydrogen chloride in the presence of a little iodine, yielding *methyl 1 : 4-naphthylenedihydrazinetetracarboxylate*,



m. p.  $250^\circ$  (decomp.), which is reduced by hydriodic-acetic acid to 1 : 4-naphthylenediamine (dibenzoyl derivative, m. p.  $276^\circ$ ). The *ethyl* ester melts at  $234^\circ$  (decomp.). 4 : 4'-*Bis(dicarbomethoxyhydrazino)diphenyl*, m. p.  $246^\circ$  (decomp.), is similarly prepared from diphenyl, and may be reduced to benzidine (dibenzoyl derivative, m. p.  $356^\circ$ ; dibenzylidene derivative, m. p.  $231^\circ$ ); the *ethyl* ester has m. p.  $195^\circ$  (decomp.). 2 : 7-*Bis(dicarbomethoxyhydrazino)fluorene*, m. p.  $200^\circ$  (*ethyl* ester, m. p.  $152^\circ$ ), gives on reduction 2 : 7-diaminofluorene (sulphate, *dibenzoyl* derivative, m. p.  $324^\circ$ , and *dibenzylidene* derivative, m. p.  $248^\circ$ , are described). Anthracene combines with only 1 mol. of methyl azodicarboxylate to give  $\alpha$ -*dicarbomethoxyhydrazinoanthracene*, m. p.  $265^\circ$  (decomp.); the *ethyl* ester has m. p.  $241^\circ$  (decomp.). Reduction yields  $\alpha$ -anthrylamine (acetyl derivative, m. p.  $198^\circ$ ). Similarly, from phenanthrene are obtained 9-*dicarbomethoxyhydrazino*- and 9-*dicarb-*

*ethoxyhydrazino-phenanthrenes*, m. p.  $214^{\circ}$  and  $158^{\circ}$ , respectively, giving 9-aminophenanthrene, m. p.  $132^{\circ}$  (hydriodide, m. p.  $295^{\circ}$ ; benzoyl derivative, m. p.  $199^{\circ}$ ). C. H.

**$\beta$ -Chlorovinylarsines and their Derivatives.** W. L. LEWIS and H. W. STIEGLER (*J. Amer. Chem. Soc.*, 1925, **47**, 2546—2556).—The mechanism of the formation of  $\beta$ -chlorovinylarsines previously proposed (cf. Lewis and Perkins, *Ind. Eng. Chem.*, 1923, **15**, 290), viz., that an intermediate additive compound of 1 mol. each of arsenious chloride and aluminium chloride and 3 mols. of acetylene,  $\text{Al}(\text{CHCl}\cdot\text{CHCl})_3\text{As}$ , is first formed, is supported experimentally by the fact that the nature of the halogen in the final compound is determined only by the arsenious halide employed and is independent of the nature of the aluminium halide used as catalyst. The halogen atom becomes attached to the carbon atom in the  $\beta$ -position to the corresponding metal, and in no case were compounds containing mixed halogens obtained. Since in a fresh reaction mixture the yield of primary and secondary chlorovinylarsines is increased by warming with free arsenious chloride, these compounds must be formed through the intermediates,  $\text{Al}[(\text{CHCl}\cdot\text{CHCl}\cdot\text{AsCl}_2)(\text{CHCl}\cdot\text{CHCl})_2\text{AsCl}]$  and  $\text{Al}(\text{CHCl}\cdot\text{CHCl}\cdot\text{AsCl}_2)_3$ . A number of derivatives of these vinylarsines have been prepared and their physiological action examined, the following being new compounds. By the action of arsenious bromide on acetylene in the presence of aluminium chloride is obtained  $\beta$ -bromovinyl dibromoarsine,  $\text{CHBr}\cdot\text{CHAsBr}_2$ , b. p.  $140$ — $143^{\circ}/16$  mm., which, on oxidation with hydrogen peroxide, yields  $\beta$ -bromovinylarsinic acid, m. p.  $143^{\circ}$ , together with  $\beta\beta'$ -dibromodivinylbromoarsine, b. p.  $155$ — $165^{\circ}/16$  mm. Hydrolysis of  $\beta$ -chlorovinyl dichloroarsine with dilute ammonium hydroxide yields  $\beta$ -chlorovinylarsenious oxide, m. p.  $143^{\circ}$ ;  $\beta$ -chlorovinyl di-iodoarsine, m. p.  $37.5$ — $38.5^{\circ}$ ;  $\beta$ -chlorovinyl dibromoarsine, b. p.  $114$ — $116^{\circ}/15$  mm.; silver  $\beta$ -chlorovinylarsinate. By the condensation of  $\beta$ -chlorovinyl dichloroarsine with phenyl- $\alpha$ -naphthylamine is obtained 7- $\beta$ -chlorovinyl-7 : 12-dihydro-7-benzophenarsazine



(I), m. p.  $213^{\circ}$ , whilst if diphenylamine is employed the product is 6- $\beta$ -chlorovinylphenarsazine, m. p.  $186$ — $187^{\circ}$ . The following are also prepared:  $\beta$ -chlorovinylhydroxythiocyanoarsine, an unstable oil;  $\beta\beta$ -dichlorodivinylarsenious oxide, m. p.  $62$ — $63^{\circ}$ ;  $\beta\beta$ -dichlorodivinylarsenious sulphide, an oil (cyanide, a colourless oil);  $\beta\beta$ -dichlorodivinylethylarsine; methylethyl- $\beta\beta$ -dichlorodivinylarsonium iodide, sublimes at  $234^{\circ}$ ; methyl- $\beta\beta$ -dichlorodivinylarsine; dimethyl- $\beta\beta$ -dichlorodivinylarsonium iodide, decomp.  $243^{\circ}$ ;  $\beta\beta$ -dichlorodivinyl- $\alpha$ -naphthylarsine; methyl- $\beta\beta\beta$ -trichlorotrivinylarsonium mercuric iodide, m. p.  $150$ — $156^{\circ}$ ; corresponding phenylmercuriodide, m. p.  $147$ — $148^{\circ}$ ; double salt of  $\beta\beta\beta$ -trichlorotrivinylarsine and silver nitrate, m. p.  $144^{\circ}$ . J. W. B.

**New Pharmaceutical Products [Nitro- and Amino-3-chloro-4-hydroxyphenylarsinic Acid].** L. CASSELLA & Co. G.M.B.H. (Brit. Pat. 230487).—By nitrating 3-chloro-4-hydroxyphenylarsinic

acid in sulphuric acid at 5—12°, a new *3-chloro-2-nitro-4-hydroxyphenylarsinic acid* is formed, which can be reduced by customary methods to the corresponding *3-chloro-2-amino-4-hydroxyphenylarsinic acid*, crystallising in long needles, giving an *acetyl* derivative, fine, small, white needles from hot water. The acetyl compound has valuable therapeutic properties.

E. H. R.

**Arseno Compounds.** L. CASSELLA & Co., G.M.B.H. (Brit. Pat. 239951).—When *o*-aminohydroxy derivatives of arsenobenzene are treated with carbonyl chloride in alkaline solution, compounds are formed in which amino and hydroxyl groups can no longer be detected and which probably contain the benzoxazolone grouping,

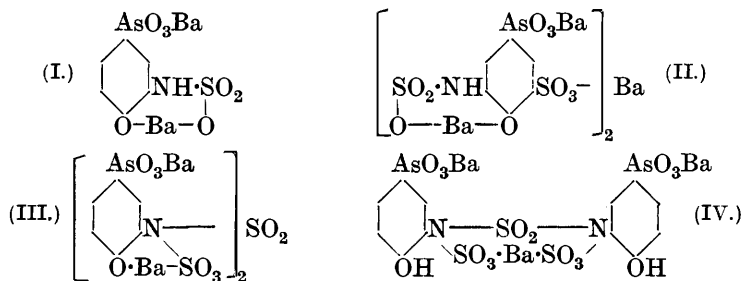
$\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix}\text{NH} \\ \text{O}\end{smallmatrix}\rangle\text{CO}$ . Thus, 4 : 4'-diamino-3 : 3'-dihydroxyarsenobenzene gives a yellow compound sparingly soluble in sodium hydroxide solution, and the isomeric 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene gives a more soluble compound. The same compounds can be obtained from the corresponding aminohydroxyphenylarsinic acids by first treating them with carbonyl chloride and then reducing the products to arseno compounds (cf. Brit. Pat. 214628).

E. H. R.

**Sulphur Content of Arsphenamine [Salvarsan] and its Relation to the Mode of Synthesis and the Toxicity.** V.

W. G. CHRISTIANSEN, A. J. NORTON, and J. B. SHOAN (*J. Amer. Chem. Soc.*, 1925, **47**, 2712—2724; cf. A., 1923, i, 723).—The rapidity of reduction of 3-nitro-4-hydroxyphenylarsinic acid by hyposulphite renders the reaction difficult to control. Reduction with sodium hydrogen sulphite is less vigorous, and the reaction proceeds in three different directions, depending on the conditions employed. When the acid or its sodium salt is boiled in aqueous solution with the sodium hydrogen sulphite, the arsenic is eliminated and *o*-nitrophenol obtained (cf. King, T., 1921, **119**, 1115). When the monosodium salt is treated with sodium hydrogen sulphite in cold aqueous solution, 3-nitro-4-hydroxyphenylarsenious oxide, a yellow, sternutatory powder, is obtained, the mother-liquor from which gives a positive test for a sulphamic acid. The trisodium salt yields similarly, in six days, a mixture of sulphamates from which, after removal of sulphite and sulphate by means of barium hydroxide, removal of barium by means of sodium carbonate, evaporation, extraction with alcohol, and treatment of the residual sodium salts with barium bromide, the following barium salts were obtained by fractional precipitation with alcoholic barium bromide solution: *dibarium 2-hydroxy-5-arsinobenzenesulphamate* (I), a yellow, flocculent precipitate; *tribarium 2-hydroxy-3-sulpho-5-arsinobenzenesulphamate* (II), white needles; and *tetrabarium 2 : 2' - dihydroxy - 5 : 5' - diarsinosulphonanilide - N : N' - disulphonate* (III), a dense, yellow powder. Hydrolysis of (I) and (III) with boiling 20% sulphuric acid affords 3-amino-4-hydroxyphenylarsinic acid; (II) yields similarly 3-amino-2-hydroxy-5-arsinobenzenesulphonic acid. When carbon dioxide is passed through an aqueous solution of (III), the corresponding *tribarium* salt (IV),

yellow, is obtained. The action of sodium hydrogen sulphite on 3-nitro-4-methoxyphenylarsinic acid also produces sulphamic acids.



Addition of solid sodium hyposulphite to a cold alkaline solution of 3-nitro-4-hydroxyphenylarsinic acid in cold alkaline solution affords 3-amino-4-phenylarsinic acid (yield, 65%), which is completely precipitated by the addition of oxalic acid. From the mother-liquor, a *barium* salt, isomeric, but not identical, with (IV) was obtained, together with an impure salt of a sulphoarsinic acid.

When 3-amino-4-hydroxyphenylarsinic acid is reduced with sodium hyposulphite in presence of the above sulphamic acids obtained by the action of sodium hydrogen sulphite on 3-nitro-4-hydroxyphenylarsinic acid, the rate of formation of insoluble reduction products is much less than when the amino-acid is reduced to arsphenamine base in the usual way. The insoluble products separate in such a finely divided state as to render filtration very difficult, and the resulting arsphenamine is considerably more toxic, and has a higher sulphur content, than when prepared from the pure amino-acid. A like effect is observed when 3-amino-4-hydroxyphenylarsinic acid is reduced similarly in presence of the above by-products isolated from the reduction of 3-nitro-4-hydroxyphenylarsinic acid with hyposulphite.

Attention is directed to the suitability of barium bromide for use in the preparation of barium salts from sodium salts in alcoholic media, owing to the solubility of sodium bromide in alcohol.

F. G. W.

**Organic Compounds of Antimony. I. Reaction between Magnesium  $\alpha$ -Naphthyl Bromide and Inorganic Antimony Compounds. Tri- $\alpha$ -naphthylstibine and Some of its Derivatives.** K. MATSUMIYA (*Mem. Coll. Sci. Kyōtō*, 1925, 8, [A], 11—18).—Antimony trichloride and amorphous antimony trisulphide both react with magnesium  $\alpha$ -naphthyl bromide to form *tri- $\alpha$ -naphthylstibine*, m. p. 216—217°. A benzene solution of this compound, treated with chlorine or bromine, yields *tri- $\alpha$ -naphthylstibine dichloride*, m. p. 256°, and *tri- $\alpha$ -naphthylstibine dibromide*, m. p. 232°, respectively. After long boiling with alcoholic potassium hydroxide and benzene, the dihalides yield *tri- $\alpha$ -naphthylstibine oxide*, m. p. 219—220°, which crystallises with 1 mol. of benzene, readily removed by gentle heating.

B. W. A.

**Benzene Derivatives of Bismuth.** J. SUPNIEWSKI (*Rocz. Chem.*, 1925, 5, 298—307).—Some aryl bismuth derivatives have been prepared by the usual methods. Triphenylbismuthine dibromide with silver nitrate affords the corresponding *nitrate*, explosive white crystals. The latter substance is converted by fuming nitric acid into *trinitrotriphenylbismuthine dinitrate*, explosive white crystals, from which by the action of concentrated hydrochloric acid is prepared the corresponding *dichloride*, white crystals, m. p. 132°, and this reacts with sodium hyposulphite, yielding *trinitrotriphenylbismuthine*, yellow crystals, m. p. 121°. In an analogous manner are prepared tri-*p*-tolylbismuthine, its *dichloride*, m. p. 147°, *dibromide*, m. p. 111°, and *dinitrate*, explosive powder, tri-2-nitro-*p*-tolylbismuthine, yellow powder, m. p. 125°, its *dinitrate*, explosive powder, and *dichloride*, m. p. 156°. From tritolylbismuthine dichloride is prepared by oxidation tri-*p*-carboxyphenylbismuthine dichloride, m. p. 130°. Diazobenzene (?) bismuth chloride, an explosive white powder, is obtained by the addition of bismuth trichloride and tartaric acid to diazobenzene. R. T.

**Ether Derivatives of Ring-substituted Mercury Aromatic Hydroxy-acids.** FARBENFABRIKEN VORM. F. BAYER & CO. (D.R.-P. 413835, additional to D.R.-P. 407669; from *Chem. Zentr.*, 1925, ii, 611).—*Hydroxymercuri-p-benzoyloxybenzoic anhydride* is obtained by mercurisation of sodium *p*-benzoyloxybenzoate or of *ethyl p*-benzoyloxybenzoate, m. p. 49°, followed by hydrolysis with water. *Hydroxymercuri-o-phenoxybenzoic anhydride* is similarly obtained from methyl *o*-phenoxybenzoate. R. B.

**Diketonates of Metalloids. VI. Action of Tin and Zirconium Tetrachlorides on  $\beta$ -Diketones.** W. DILTHEY (*J. pr. Chem.*, 1925, [ii], 111, 147—152; cf. A., 1903, i, 290, 405, 591; 1904, i, 132; 1906, i, 342).—It has already been shown that when three of the chlorine atoms of silicon tetrachloride, or two in the case of boron trichloride, are replaced by  $\beta$ -diketone residues, the remaining halogen atom is ionised, and Werner's co-ordination theory offers a simple explanation of the structure of the siliconium and boronium salts so formed. Titanium analogues show the same property in much smaller degree.

Zirconium tetrachloride and benzoylacetone (3 mols.) react in dry ether to give a compound,  $(\text{CHAcBz})_3\text{ZrCl}_2$ , m. p. 232—234°, or in boiling benzene to form Morgan and Bowden's  $(\text{CHAcBz})_3\text{ZrCl}$ , m. p. 128—129° (J., 1924, 125, 1252); neither substance shows salt-like properties. With dibenzoylmethane in ether or benzene, the product is  $(\text{CHBz}_2)_3\text{ZrCl}$ , m. p. 260°, which is feebly salt-like and forms a ferrichloride (Morgan and Bowden, *loc. cit.*). Zirconium oxychloride gives only an additive compound with acetylacetone.

Antimony pentachloride reacts with benzoylacetone (1.5—2 mols.) in boiling chloroform, and with dibenzoylmethane in boiling chlorobenzene; the products,  $(\text{CHAcBz})\text{SbCl}_4$ , m. p. 184°, and  $(\text{CHBz}_2)\text{SbCl}_4$ , m. p. 232—234°, have no salt-like properties.

From stannic chloride with benzoylacetone and dibenzoylmethane,

respectively, in boiling chloroform are obtained *compounds*,  $(\text{CHAcBz})_2\text{SnCl}_2$ , m. p.  $220^\circ$ , and  $(\text{CHBz}_2)_2\text{SnCl}_2$ , m. p.  $243\text{--}244^\circ$  (or  $258\text{--}259^\circ$  when prepared in chlorobenzene). C. H.

**Compounds of High Molecular Weight.** H. BERGMANN.  
**II. "High-molecular" Amino-acid Anhydrides of the Piperazine Type.** M. BERGMANN, A. MIEKELEY, and E. KANN (*Annalen*, 1925, **445**, 17—34; cf. this vol., i, 1134).—If amino-acid anhydrides (diketopiperazines) play any part in adding to the weight of the protein molecule, it should be possible to demonstrate a tendency in these compounds to be converted, without change in chemical composition, into high-molecular complexes. This is found to be the case with anhydroglycyl- and anhydroalanyl-serine anhydrides (*loc. cit.*). These substances have a normal mol. wt. in phenol. Acidification of their sodium derivatives, however, gives compounds which are much less soluble and have in phenol double the normal mol. wt., although by acetylation or reduction these give products with the original simple mol. wt.

2 : 5-Diketo-6-methyl-3-methylenepiperazine (anhydroalanyl-serine anhydride, *loc. cit.*), dissolved in 20% sodium hydroxide, separates after a few mins. as the *disodium* salt,  $\text{C}_6\text{H}_6\text{O}_2\text{N}_2\text{Na}_2 \cdot 6\cdot5\text{H}_2\text{O}$ , which loses  $6\text{H}_2\text{O}$  when dried in a vacuum below  $100^\circ$ . When treated with acetic anhydride in carbon tetrachloride, this salt is converted into "diacetate B,"  $\text{C}_{10}\text{H}_{12}\text{O}_4\text{N}_2$ , m. p.  $144\text{--}145^\circ$  (corr.), which has a normal mol. wt. in benzene. It readily loses one acetyl group, *e.g.*, by warming with glacial acetic acid or even by refluxing for a short time with acetic anhydride in carbon tetrachloride, giving the easily soluble *monoacetate*, m. p.  $225^\circ$ , becoming solid again at  $260^\circ$  and darkening above  $280^\circ$ . The monoacetate when hydrolysed with ammonia or dilute acids yields the "high-molecular" diketomethylisomethylenepiperazine, from which the same disodium salt and "diacetate B" may be prepared. When 2 : 5-diketo-6-methyl-3-methylenepiperazine is treated with acetic anhydride, "diacetate A," m. p.  $110\text{--}111^\circ$  (corr.), is formed; this has a sharp, burning taste, whilst "diacetate B" tastes slightly bitter. Catalytic hydrogenation of diketomethylisomethylenepiperazine or of its "diacetate B" yields alanine anhydride, m. p.  $282^\circ$ . A *tetrapeptide hydrochloride*,  $\text{C}_{10}\text{H}_{15}\text{O}_5\text{N}_4\text{Cl} \cdot \text{HCl}$  (*methyl ester hydrochloride*, decomp.  $280^\circ$ , forms an oily *picrate*), in which only one of the two chlorine atoms is ionisable, is obtained by prolonged hydrolysis of diketoisomethylenepiperazine with 5N-hydrochloric acid at  $70^\circ$ . Similar hydrolysis of diketomethylisomethylenepiperazine gives a *tetrapeptide hydrochloride* containing an additional mol. of water. The corresponding *methyl ester hydrochloride*,  $\text{C}_{13}\text{H}_{23}\text{O}_6\text{N}_4 \cdot \text{HCl}$ , sinters at  $232^\circ$  and decomposes at  $238^\circ$ . C. H.

**Action of Alkalis on Peptides and on Ketopiperazines.** P. A. LEVENE and M. H. PFALTZ (*J. Gen. Physiol.*, 1925, **8**, 183—188; cf. this vol., i, 795).—Neither glycyl-*l*-alanylglycine nor *l*-alanylglycine is racemised by dilute sodium hydroxide solutions, but, on the other hand, the piperazine derivatives



*l*-alanylglycine anhydride and *l*-prolylglycine anhydride are partly racemised by dilute sodium hydroxide solutions under similar conditions.  
W. O. K.

**Structure of Proteins.** E. ABDERHALDEN and E. KOMM (*Z. physiol. Chem.*, 1925, **145**, 308—315).—By the action of trypsin on edestin, a crystalline substance, m. p. 180—183°,  $[\alpha]_D^{20} = -202^\circ$ , probably glycylproline anhydride, was obtained after extraction with ether. Hydrolysis of dog's hair in the autoclave gave a crystalline substance, m. p. 235—237°, probably alanylglycine anhydride (after extraction with chloroform). Hydrolysis of pig's bristles in the autoclave gave alanyl-leucine anhydride, m. p. 235—238°,  $[\alpha]_D^{20} = -4.0^\circ$  (extraction with ether), and alanyl-leucine anhydride and alanylphenylalanine anhydride, m. p. 220—225° (extraction with ethyl acetate and fractional crystallisation from alcohol).

Various peptones have been oxidised with zinc permanganate, and the ratio of oxamide to deamination products determined. For silk-, keratin-, and elastin-peptones, ratios of 1:0.84—1.2, 1:1.44—1.5, and 1:3.7—5.6, were respectively obtained.

H. P. M.

[**Degradation of Proteins by Hypobromite.**] E. ABDERHALDEN (*Ber.*, 1925, **58**, [B], 1821—1822).—In reply to Goldschmidt and Steigerwald (this vol., i, 1109), it is pointed out that diketopiperazines have been previously isolated from proteins. H. W.

**Identity of Hæmatoidin and Bilirubin.** A. R. RICH and J. H. BUMSTEAD (*Bull. Johns Hopkins Hosp.*, 1925, **36**, 225—232).—Experimental evidence is offered in support of the view that hæmatoidin and bilirubin are identical, and not isomeric.

CHEMICAL ABSTRACTS.

**Formation of Sulphæmoglobin.** A. A. H. VAN DEN BERGH and H. WIERINGA (*J. Physiol.*, 1925, **59**, 407—412).—The combination of hydrogen sulphide with hæmoglobin or reduced hæmoglobin, and the accelerating action of phenylhydrazine on the formation of sulphæmoglobin are observed only in the presence of oxygen.

CHEMICAL ABSTRACTS.

**Combination of Nitric Oxide with Hæmoglobin.** M. L. ANSON and A. E. MIRSKY (*J. Physiol.*, 1925, **60**, 100—102).—In the formation of nitric oxide-methæmoglobin from nitric oxide and oxyhæmoglobin, methæmoglobin is formed immediately. Nitric oxide-methæmoglobin has amphoteric properties.

CHEMICAL ABSTRACTS.

**Hæmochromogen and the Relation of Protein to the Properties of the Hæmoglobin Molecule.** M. L. ANSON and A. E. MIRSKY (*J. Physiol.*, 1925, **60**, 50—68).—The non-protein portion of hæmoglobin, containing pyrrole nuclei and iron, is named "hem"; it may combine with a protein or an amine to form a hæmochromogen, an equilibrium being produced. Hæmoglobin

and alkali yield a hæmochromogen containing globin. Comparative data are given regarding the solubility and combination with oxygen and carbon monoxide of hæmochromogens and hæmoglobin, together with a method for determining the dissociation curve for carbon monoxide-hæmochromogen or carbon monoxide-hæmoglobin.

CHEMICAL ABSTRACTS.

[Non-protein Component of Hæmoglobin.] M. L. ANSON and A. E. MIRSKY (*J. Physiol.*, 1925, 60, 161—174).—"Hem," the iron-pyrrole component of hæmoglobin, is universal in nature.

CHEMICAL ABSTRACTS.

**Helicorubin and its Relation to Hæmoglobin.** M. L. ANSON and A. E. MIRSKY (*J. Physiol.*, 1925, 60, 221—228).—The iron-pyrrole components of hæmoglobin and helicorubin (from pulmonate molluscs) are identical. Helicorubin combines loosely with oxygen, the affinity increasing with the acidity of the medium.

CHEMICAL ABSTRACTS.

**Hydroxyhæmin.** A. HANSIK (*Z. physiol. Chem.*, 1925, 148, 99—110).—Crude hydroxyhæmin anhydride,  $\alpha$ -chlorohæmin, hydroxyhæmin, acetylhæmin, and oxalylhæmin are prepared by a modification of the author's method (A., 1924, i, 571) and purification is attempted. The  $\alpha$ -modification of the pigments obtained in the blood is converted by means of acids and alkalis into a mixture of  $\alpha$ -,  $\psi$ -,  $\beta$ -, and other modifications. It is not changed, however, by treatment with alcoholic potassium hydroxide for a short time, but is converted partly into the  $\beta$ -modification on treatment for a long time. The  $\alpha$ -modification can be separated from a mixture of  $\alpha$ -,  $\psi$ -,  $\beta$ -, etc. modifications by means of alcoholic potassium hydroxide, in which it is more soluble. The modification present in the blood of animals does not depend on their age. Slight putrefaction of the blood does not cause any change in the modification obtained therefrom.

P. W. C.

**Formation of Methæmoglobin. VI. Ferricyanide and *p*-Benzoquinone.** R. MEIER (*Arch. exp. Path. Pharm.*, 1925, 108, 280—294).—Oxyhæmoglobin is almost quantitatively converted into methæmoglobin by ferricyanide in acid, neutral, or alkaline solution; but with *p*-benzoquinone in alkaline solution the reaction stops considerably short of completion. Under different conditions, Conant found the reaction to be incomplete in acid solution (see this vol., i, 455). Some improvements in the gasometric method employed are described.

H. P. M.

**Iodine Absorption of Caseinogen.** F. LIEBEN and D. LÁSZLO (*Biochem. Z.*, 1925, 159, 110—125).—The amount of iodine absorbed by caseinogen cannot be correlated with the amount of any one amino-acid present, although after repeated treatment with iodine the absorption tends to approach the value of 2 atoms of iodine to 1 mol. of tyrosine. Quantitative determination of tyrosine and tryptophan during the process of absorption gives no indication of combination with either of these components. Treat-

ment with 5% sodium sulphite causes no loss of iodine; hence this is not a case of adsorption. On hydrolysis, the iodine appears partly as the free form, partly as soluble iodide, but there is no evidence of two types of combination in the intact protein.

E. C. S.

**Halogenated Proteins. V. Bromocasein.** A. J. J. VANDELDELDE (*Rec. trav. chim.*, 1925, **44**, 900—906; cf. this vol., i, 707).—The action of bromine in carbon tetrachloride solution on casein produces a *bromocasein* (N = 9—10%, Br = 32—35%) without liberation of hydrogen bromide. The action of water and alkalis yields substances of lower bromine content, the variations in composition according to varied conditions having been determined in detail. Heated at 100°, bromocasein loses bromine with production of a *substance* (N = 11.5%, Br = 24.2%). The action of water and alkalis upon this product has also been examined.

G. M. B.

**Liberation of Carbon Dioxide, Ammonia, and Amino-nitrogen from Casein by Acid Hydrolysis.** M. S. DUNN (*J. Amer. Chem. Soc.*, 1925, **47**, 2564—2568).—The quantities of amino nitrogen, carbon dioxide, and ammonia liberated from casein by hydrolysis with sulphuric acid during intervals varying from 5 to 30 hrs. have been determined. The amino nitrogen increased from 0.8% of the casein to 10.1%, becoming constant after 20 hrs., whilst the ammonia increased from 1.10% to 1.52% (cf. Van Slyke, A., 1911, ii, 779; 1912, i, 735), and the carbon dioxide from 0.31% to 0.81% over the period studied. At the beginning, the total ammonia liberated was in excess of the carbon dioxide, but after 5 hrs. these two substances were evolved at approximately the same rates, suggesting that they are produced simultaneously by the decomposition of some complex structure in the protein molecule, the uramino-acid and hydantoin structures being suggested.

J. W. B.

**Groups Responsible for the Nucleal Reaction and Nucleal Coloration. II. Preparation of Hydroxymethylfurfuraldehyde.** R. FEULGEN and K. VOIT (*Z. physiol. Chem.*, 1925, **148**, 1—16).—The authors' conclusion that the nucleal reaction is not caused by furfuraldehyde, but is specific for partly hydrolysed thymonucleic acid (A., 1924, i, 905, 1132), is maintained in opposition to the views of Steudel and Peiser (A., 1924, i, 438, 1362).

P. W. C.

**Anomalies of Salts of Nucleic Acids.** E. PEISER (*Ber.*, 1925, **58**, [B], 2051—2054).—The following salts are described: *brucine hydrogen guanylate*, *distrychnine guanylate*, *dibrucine adenylate*, *distrychnine adenylate*, *brucine inosinate*, *dibrucine cytosylate*, *dibrucine uracylate*. These salts may be crystallised unchanged from water. Extraction of the normal brucine salts of guanylic, inosinic, and adenylic acid with chloroform at the atmospheric temperature affords brucine hydrogen guanylate and inosinic and adenylic acids. The normal strychnine salt of adenylic acid

exhibits the same behaviour, whereas guanylic acid retains both molecules of strychnine under these conditions. The normal brucine salts of cytosylic and uracylic acids are stable towards warm chloroform. H. W.

**Dissociation Constants of Plant Nucleotides and Nucleosides and their Relation to Nucleic Acid Structure.** P. A. LEVENE and H. S. SIMMS (*J. Biol. Chem.*, 1925, **65**, 519—534).—A possible means of discrimination between the alternative structures which have been proposed for the nucleic acids exists in the fact that the different theories demand a different number of ionisable hydrogen atoms in the nucleotide molecule; the various dissociation constants of four nucleosides and the corresponding nucleotides have therefore been determined by electrometric titration. The results are in harmony with the structure proposed by Levene (A., 1920, i, 193) in so far as they indicate that the nucleotides possess only one (secondary phosphoric acid) group which is dissociated about  $p_H$  6.0, whereas the theory of Jones (A., 1920, i, 687) requires two ionisable hydrogen atoms in this region. It is further claimed that support is given to the theory of Levene by the results of Thomas and Dox (this vol., i, 873), whose own interpretation is fallacious owing to neglect of the dissociation of the hydroxyl groups, which is shown, by the present work, to occur in the alkaline solutions studied by these workers. The following values of  $p_K$  (not corrected for activity) were obtained: for adenosine, amino group 3.45; guanosine, amino group 1.6, hydroxyl group 9.16; cytidine, amino group 4.22, hydroxyl group 12.3; uridine, primary hydroxyl group 9.17, secondary 12.52; adenylic acid, primary phosphoric acid 0.89, secondary 6.01, amino group 3.70; guanylic acid, primary phosphoric acid 0.7, secondary 5.92, amino group 2.3, hydroxyl group 9.36; cytidine phosphoric acid, primary phosphoric acid 0.8, secondary 5.97, amino group 4.24; uridine phosphoric acid, primary phosphoric acid 1.02, secondary 5.88, primary hydroxyl group 9.43. C. R. H.

**Preparation, Solubility, and Specific Rotation of Wheat Gliadin.** D. B. DILL and C. L. ALSBERG (*J. Biol. Chem.*, 1925, **65**, 279—304).—By vigorous shaking during precipitation and by substituting lithium chloride for sodium chloride as the precipitating salt, preparations of gliadin were obtained with an average of 17.54% N and an ash content of less than 0.1%. Prolonged contact with 70% or more concentrated alcohol altered the gliadin in such a way that it was no longer soluble in 70% alcohol. For concentrations of gliadin between 2.5% and 25%, the temperature at which turbidity appeared on cooling an aqueous alcoholic solution of the protein varied with the concentration of alcohol but not with that of the protein; the condition of the protein in such solutions is therefore characterised as peptisation rather than true solution. Curves illustrating the relationship between the turbidity temperature and the proportion of alcohol in the solvent are given for solutions of gliadin in mixtures of methyl, ethyl, and *n*-propyl alcohols with water; above the turbidity temperature, no upper

limit was observed to the solubility of gliadin in any given aqueous alcoholic mixture. Gliadin was further found to be soluble in aqueous solutions of ammonium and potassium thiocyanate, potassium iodide, carbamide, and chloral hydrate; also in glycerol, ethylene and propylene glycols, and in mixtures of these and of methyl ethyl ketone with water. The specific rotation of gliadin in aqueous ethyl alcohol was at a maximum ( $[\alpha]_D^{20} - 91.0^\circ$ ) at a concentration of 60% alcohol; in aqueous propyl alcohol  $[\alpha]_D^{20} - 98.2^\circ$  and in 30% aqueous carbamide solution  $[\alpha]_D - 116.5^\circ$ ; the absence of any alteration in the last figure on keeping the solution at  $37^\circ$  for 7 days is taken as evidence against the formation of an alkali albuminate with the carbamide (cf. Spiro, A., 1900, i, 615).  
C. R. H.

**Preservative Principles of Hops.** T. K. WALKER (*J. Inst. Brew.*, 1925, **31**, 562—575).—The relative antiseptic values of the soft resin constituents are compared. Of the constituents, lupulon has the highest antiseptic power, being twice as powerful as humulon and four to five times more powerful than any other single constituent. The neutral or adventitious matter, which is always present in the resin, is devoid of preservative value. It is not a true soft resin, although soluble in light petroleum. The manner in which the constituents of the resin are prepared for biological trial may modify or seriously diminish its preservative value, unless carried out at the lowest possible temperature. The majority of tests were made with *Bacterium X*. [Cf. *B.*, Dec. 24th.]  
C. R.

**Nomenclature of the Hop Resin Constituents.** T. K. WALKER (*J. Inst. Brew.*, 1925, **31**, 576—577).—The soft resins are subdivided into  $\alpha$ - and  $\beta$ -fractions according as the lead salts are insoluble or soluble in methyl alcohol. Humulon and its derivative  $\alpha$ -resin form the  $\alpha$ -fraction, whilst the  $\beta$ -fraction consists of lupulon, its derivative  $\beta$ -resin, and the transformation product from  $\alpha$ -resin termed " $\alpha$ -resin transformation product." In addition, it contains 40% of a neutral material. The  $\gamma$ -resin (hard resin), insoluble in light petroleum, is a mixture consisting of the ultimate transition products of humulon, lupulon, their derivatives, and also the neutral material. [Cf. *B.*, Dec. 24th.]  
C. R.

**Proteins. I. Prolamines—their Chemical Composition in Relation to Acid and Alkali Binding.** W. F. HOFFMAN and A. R. GORTNER (*2nd Colloid Symposium Monograph*, 1925, 209—368).—The alcohol-soluble proteins from wheat, spelt, rye, maize, and kafir show no striking differences in nitrogen and sulphur content from those from durum, emmer, einkorn, teosinte, and sorghum, or from casein and fibrin, the various cereal proteins differing in nitrogen distribution, carboxyl groups, etc. Between  $p_H$  2.5 and  $p_H$  10.5, 1 g. of any protein binds approximately the same amount of acid or alkali, equivalent amounts of hydrochloric, phosphoric, and sulphuric acids being bound by a unit amount of protein. Contrary to Loeb, at the same equilibrium  $p_H$  much

more phosphoric acid was bound than hydrochloric. Between  $p_H$  2.5 and  $p_H$  10.5, the amounts of hydrochloric acid or sodium hydroxide bound at 15°, 25°, and 35°, respectively, were in the ratio 1:2:3. When the logarithms of the equivalents of acid or alkali bound are plotted against those of that added, the curves for a particular protein pass through a common point, at about  $p_H$  2.5 and  $p_H$  10.5 for acids and alkalis, respectively, the amount bound depending between these limits on the chemical composition of the protein. Two types of combination are suggested: (a) chemical, at  $p_H$  2.5—10.5, (b) adsorption, at other  $p_H$  values. Acid binding is correlated with the free amino-nitrogen, but the alkali binding could not be correlated with existing data regarding amino-acid content. The isoelectric point is probably an isoelectric range. The calculated isoelectric points are not related to the chemical composition of the protein.

## CHEMICAL ABSTRACTS.

**Decomposition Products of the Proteins.** N. IVANOV (*Bull. Acad. Sci. St. Pétersbourg*, 1916, [6], 971—972; from *Chem. Zentr.*, 1925, i, 2702).—Addition of dipotassium hydrogen phosphate or sodium hydroxide to autolytic yeast juice results in a decrease of amino nitrogen. The decrease is not due to lactam formation in an alkaline medium because the carboxyl content is unaltered. As in many instances there is an increase in ammonia, it is probable that there is a coupling of amino groups with formation of ammonia and imino groups. Addition of dextrose greatly increases the loss in amino nitrogen, due to the deamination of amino-acids, the ammonia of which reacts with the dextrose. Neither lactose, glycerol, nor Seignette salt can replace dextrose. With gliadin and taka-diastrase, the same effects are obtained as with yeast.

G. W. R.

**Sulphur in Proteins. II. Effect of Mild Alkaline Hydrolysis on Hair.** W. F. HOFFMAN (*J. Biol. Chem.*, 1925, 65, 251—254).—Heating on a steam-bath for periods of 1 hr. or more with 1—4% sodium carbonate solution removes considerable amounts of sulphur from hair, although determinations of nitrogen in the filtrate indicate a very small degree of hydrolysis. Removal in this manner of as little as 25% of the total sulphur renders impossible the subsequent isolation of cystine from the hair.

C. R. H.

**Scleroproteins.** Z. STARY and I. ANDRATSCHKE (*Z. physiol. Chem.*, 1925, 148, 83—98).—A study of the properties of several less accessible scleroproteins, gorgonin, conchiolin, byssus, spongin, and ovokeratin, and of their nitrogen distribution, leads to the acceptance of the view that the resistance to hydrolysis of these substances is due not to the presence of particular amino-acids but to the type of structure, probably the anhydride structure of Abderhalden.

P. W. C.

## Biochemistry.

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**Iron, the Oxygen-carrier of Respiration-ferment.** O. WARBURG (*Science*, 1925, **61**, 575—582).—A detailed argument is presented in support of the view that in respiring cells there is a cycle in which molecular oxygen reacts with an appropriate form of bivalent iron, the more highly oxidised iron thus formed reacting with the organic substance, with consequent reduction to the bivalent condition; molecular oxygen never reacts directly with the organic substance. Life without iron is thus considered to be impossible. A. A. E.

**Oxygen Exchange, Blood, and the Circulation. Factors Involved in Oxygen Supply.** C. D. MURRAY and W. O. P. MORGAN (*J. Biol. Chem.*, 1925, **65**, 419—444).—A further mathematical treatment of the arguments of Henderson and Murray (cf. this vol., i, 1483) leads to the equation: specific diffusing capacity =  $DC/(BF \times Hgb)$ , where DC is the diffusing capacity of a capillary region through which pass in 1 min. BF litres of blood of oxygen capacity Hgb; the reciprocal of the specific diffusing capacity as defined by this equation is termed the specific hæmoglobin flow. The process of oxygen exchange is considered as a system involving six variables: (1) metabolic rate (*i.e.*, rate of utilisation of oxygen); (2) oxygen capacity of the blood; (3) and (4) oxygen saturations of arterial and venous blood; (5)  $p_H$  of the serum; (6) tension of oxygen in alveolar air or tissues. Curves have been constructed from known data indicating the relationships between the first four variables which result from certain combinations of the last two. C. R. H.

**Dissociation of Oxyhæmoglobin in the Tissues.** J. A. CAMPBELL (*J. Physiol.*, 1925, **59**, 395—406).—Gas injected under the skin of an animal and allowed to remain until equilibrium is established undergoes changes as a result of muscular exercise. Changes in carbon dioxide content parallel the changes in the alveolar air. The oxygen tension is increased by muscular exercise by about 25%, probably due to the action of lactic acid on the dissociation of oxyhæmoglobin. Insulin injections have the same effect as muscular work. Conditions that produce tetany, forced artificial respiration, sodium hydrogen carbonate, injection of guanidine, greatly reduce the oxygen tension in the gas under the skin. This fall may be due, in part, to alkalosis.

CHEMICAL ABSTRACTS.

**Colorimetric Method for Studying the Dissociation of Oxyhæmocyanin suitable for Class Work.** C. F. A. PANTIN and L. T. HOGGEN (*J. Marine Biol. Assoc. U.K.*, 1925, **13**, 970—980).—The colourless nature of reduced hæmocyanin makes possible the direct colorimetric determination of oxyhæmocyanin in the partly

oxygenated serum of *Palinurus*, *Homarus*, *Cancer*, etc. Very dilute solutions of orange-G with a trace of logwood and Indian ink are used for diluting the reduced serum in making the colour standards (water should not be used owing to the faint orange tint of the reduced serum). The experimental serum, contained in a test-tube, is exposed to various pressures of air by first completely evacuating the tube and then shaking it when the pressure has been adjusted to the appropriate value. The effects of  $p_H$ , temperature, and the presence of certain salts on the dissociation curves of the hæmocyansins from *Palinurus* and *Helix* are recorded. The hæmocyanin from *Palinurus* is very sensitive to changes in  $p_H$ , whilst that from *Helix* is quite insensitive. The error of the method does not exceed 5%. P. E.

**Metabolism of Iron. I. Behaviour of Blood Pigment in Artificial Digestion.** W. LINTZEL (*Z. Biol.*, 1925, **83**, 289—296).—A small amount of iron is set free on digestion of blood pigment with trypsin and pepsin, but it is not due to the action of these enzymes. The iron in the ash was converted into the sulphide with ammonium sulphide, dissolved in hydrochloric acid, oxidised, and determined colorimetrically with ammonium thiocyanate. The free iron was determined by shaking the substance with air, treating with hydrochloric and trichloroacetic acids, and determining the iron either in the filtrate or in the precipitate. S. S. Z.

**Studies of Iron. I. Action of Digestive Ferments on the Iron of Hæmoglobin.** G. BARKAN (*Z. physiol. Chem.*, 1925, **148**, 124—154).—The digestive action of hydrochloric acid-pepsin and extract of pancreas on blood is studied by means of the thiocyanate method on the acid ultra-filtrate. These agencies are unable when acting either separately or successively to split off iron from hæmoglobin. The small amount of iron obtained amounts only to  $\frac{1}{18}$ — $\frac{1}{26}$  of the iron present in the hæmoglobin, and is not derived from the blood pigments. P. W. C.

**Alleged Power of Bacteria to Form Bile Pigment from Hæmoglobin.** A. R. RICH and J. H. BUMSTEAD (*Bull. Johns Hopkins Hosp.*, 1925, **36**, 376—380).—Bilirubin is not formed when whole or laked blood or solutions of hæmoglobin are subjected to the action of *Pneumococcus*, *Staphylococcus aureus*, *Streptococcus viridans*, and air bacteria. CHEMICAL ABSTRACTS.

**[Non]-Formation of Bile Pigment from Hæmoglobin by the Action of Enzymes.** A. R. RICH and J. H. BUMSTEAD (*Bull. Johns Hopkins Hosp.*, 1925, **36**, 437—445).—Attempts to convert hæmoglobin into bile pigment by means of an enzyme in the plasma or spleen failed. CHEMICAL ABSTRACTS.

**Connexion between the Reaction and the Total Ionic Equilibrium of the Blood.** K. GOLLWITZER-MEIER (*Biochem. Z.*, 1925, **160**, 433—441; cf. this vol., i, 177).—Determinations of hydrogen carbonate, chloride, phosphate, sodium, potassium, and calcium concentration in, and carbon dioxide tension of, the blood



after administration *per os* of sodium hydrogen carbonate, ammonium chloride, calcium chloride, and after periods of over-ventilation and carbon dioxide-breathing, have been made. The means by which the change of  $p_H$  of the blood is brought about, rather than the direction of the change, is the determining factor in the disturbance of the ionic equilibrium. E. C. S.

**Blood as a Physicochemical System. III. Deductions concerning the Capillary Exchange.** L. J. HENDERSON and C. D. MURRAY (*J. Biol. Chem.*, 1925, **65**, 407—417).—On the three assumptions that the gaseous interchange between alveolar air and blood and between blood and tissues is a process of simple diffusion, that the determinant of the rate of diffusion of oxygen is the difference in the tension of the latter in the two regions (*e.g.*, the alveoli and the blood), and that the tension of oxygen in the tissues is zero, curves are constructed from known data which give the specific diffusing capacities of the capillaries of the greater and lesser circulations at different points of the arterio-venous cycle. From the values so obtained, and the changes in blood flow and in oxygen saturation of the blood known to take place, it is calculated that during moderate work the number of patent capillaries in the lung is increased at least five-fold and that in the tissues to a greater extent. C. R. H.

**Hydrogen-ion Equilibrium in the Blood. I. Influence of Temperature on the  $p_H$  of Blood. II. Influence of Dilution on the  $p_H$  of the Blood and Serum.** C. L. HOU (*J. Biophysics*, 1925, **1**, 163—171, 172—176).—I. The variation of the blood  $p_H$  with the temperature is independent of the carbon dioxide tension. It is not constant for different individuals, or even for the same individual under different body conditions. Calculation of the  $p_H$  at 37° by subtraction of a constant from the value at 18° may involve an error of 0.1. The effect of temperature on the  $p_H$  is less for serum than for defibrinated blood from the same source.

II. When blood is diluted with physiological saline solution at 18°, the  $p_H$  varies only very slightly. This is due to two opposite effects, the reduction of concentration of the red corpuscles, which increases the  $p_H$ , and the dilution of the serum, which decreases it. At 37°, the  $p_H$  of the blood increases markedly with dilution. The difference between the  $p_H$  at 37° and that at 18° decreases with dilution. C. P. S.

**Measurement of Hydrogen-ion Concentration by Means of Quinhydrone. A New Double Electrode in Beaker Form.** E. MISLOWITZER (*Biochem. Z.*, 1925, **159**, 72—76).—A convenient modification of Bilmann's quinhydrone electrode (*A.*, 1921, ii, 372). E. C. S.

**Measurement of Hydrogen-ion Concentration of Blood. The Syringe as Electrode.** E. MISLOWITZER (*Biochem. Z.*, 1925, **159**, 77—79).—One to 2 c.c. of blood are drawn into a syringe containing 0.5 c.c. of a quinhydrone-Ringer solution, and into which a gold electrode is fused. The measurement is completed

before clotting occurs. For other body fluids than blood, a platinum electrode is more suitable.

E. C. S.

**Presence of Glutathione in the Corpuscles of Mammalian Blood.** H. F. HOLDEN (*Biochem. J.*, 1925, **19**, 727—728).—Glutathione is present in the corpuscles of the blood of sheep, goats, rabbits, and rats in the reduced form. It was isolated and identified from deproteinised sheep's blood. As it is the chief optically-active constituent in this medium, other than glucose, it is responsible for the results obtained by Winter and Smith (A., 1923, i, 513), which the latter attributed to the behaviour of an unstable modification of dextrose in the blood.

S. S. Z.

**Chemical Constituents of the Blood of the Dog.** R. L. HADEN and T. G. ORR (*J. Biol. Chem.*, 1925, **65**, 479—481).—Analysis of the whole blood of 200 normal dogs led to the following average results: non-protein nitrogen 30.8, urea nitrogen 11.7, creatinine 1.5, amino-acid nitrogen 6.7, dextrose 82, chlorides (as sodium chloride) 468 mg. per 100 c.c.; carbon dioxide combining power of the plasma 34.8 vols.%.  
C. R. H.

**Ammonia-content and Formation in Blood. III. Origin of Blood Ammonia.** J. K. PARNAS and M. TAUBENHAUS (*Biochem. Z.*, 1925, **159**, 298—310).—The ammonia of the blood does not arise from any of its colloidal constituents nor from the amino-acids, but is derived from some other substance present in the protein-free filtrate from blood. The limits of error in the colorimetric determination of small amounts of ammonia are discussed and a method for the determination of amino-acids in presence of ammonia is given.  
P. W. C.

**Amino-acid Content of Blood of Infants and Children.** G. N. HOFFEL and M. E. MORIARTY (*Amer. J. Dis. Children*, 1924, **27**, 64—66).—For infants (up to 22 months old) maximum, minimum, and average values were: amino-acid nitrogen, 6.93, 4.41, 5.57; non-protein nitrogen, 41.4, 15, 26.6; uric acid, 6.76, 1.28, 3.1 mg. %. Corresponding values for children (2 to 15 yrs. old) were, respectively, 7.14, 3.92, 5.28; 49.5, 22.7, 28.2; 5.88, 2.56, 3.8. For adults, the respective values were: 8.12, 6.38, 7.04; 34.2, 27.6, 30.5; 4.75, 3.28, 4.05. CHEMICAL ABSTRACTS.

**Proteins of the Blood. I.** H. HUECK (*Biochem. Z.*, 1925, **159**, 89—106).—An account of the differences existing between sera obtained from different sources under various conditions. Serum from defibrinated blood contains less protein than that separating spontaneously from the clot. Samples taken at intervals from the serum separating from a clot show a gradual increase in protein. No difference exists between serum from whole blood and from plasma. Considerable differences in protein content may be found in consecutive samples of serum from the same subject. The refractive index of serum increases on keeping under paraffin.  
E. C. S.

**Protein Determination in 0.1 c.c. of Serum.** S. HOLM and H. TÓMASSON (*Biochem. Z.*, 1925, **159**, 472—481).—A simple and clinically useful method for this determination consisting in a modification of Heller's nitric acid test for proteins is described. By means of a special apparatus, changes in the serum protein concentration of from 0.1% to 0.7% can be detected.

Normal values for serum proteins determined by this method agree with Kjeldahl analyses. The percentage of protein in the serum of normal adults varies between 5.55 and 8.77, average value being 7.08%. During menstruation, values outside these limits may be obtained.

H. D. K.

**New Potentiometer.** E. MISLOWITZER (*Biochem. Z.*, 1925, **159**, 68—71).—A simple form for use in electrometric titration is described.

E. C. S.

**Electrotitration in Physiological Liquids. I. Determination of Chlorides in Blood and Serum.** E. MISLOWITZER and M. VOGT (*Biochem. Z.*, 1925, **159**, 80—82).—One c.c. of blood is used. After freeing it from protein by heat coagulation, the titration is carried out with  $N/1000$ -silver nitrate. The results are in complete accordance with the Volhard and Bang methods.

E. C. S.

**Micro-method for the Determination of Chloride in Body Fluids.** A. NITSCHKE (*Biochem. Z.*, 1925, **159**, 489—490).—A useful micro-method, founded on Bang's principle of extraction of the chloride with alcohol. The results agree well with those given by the ordinary macro-technique.

H. D. K.

**Method for the Determination of Calcium and Phosphorus in Small Quantities of Blood.** K. MYRBÄCK (*Z. physiol. Chem.*, 1925, **148**, 197—206).—Calcium in 1 c.c. of blood is determined by a modification of the Kramer-Tisdall method (A., 1921, ii, 595) and phosphate by a combination of the strychnine-molybdate precipitation method of Embden (A., 1921, ii, 462) and the titration method of Neumann.

P. W. C.

**Colorimetric Method for the Determination of Bile Salts in Blood.** P. SZILÁRD (*Biochem. Z.*, 1925, **159**, 325—326).—A preliminary communication indicating how, after separation of oxycholesterol from blood serum, the bile salts remaining may be detected by the Lipschütz colour test.

P. W. C.

**Determination of Fat in Blood.** C. P. STEWART and A. C. WHITE (*Biochem. J.*, 1925, **19**, 840—844).—The blood is added to an alcohol-ether mixture. An aliquot portion of the extract is evaporated and saponified with  $N/10$ -alcoholic sodium hydroxide. To avoid a possible error produced by the formation of carbon dioxide, the residual sodium hydroxide is not titrated back at this stage, but a quantity of  $N/10$ -hydrochloric acid equivalent to that of the sodium hydroxide used in the saponification is added so that the free fatty acids are liberated. The concentrated

residue is taken up in alcohol and an aliquot portion is titrated with *N*/10-sodium hydroxide from a Rehberg burette, phenolphthalein being used as an indicator. The experimental error of this method is not greater than 5%. S. S. Z.

**A Simple Method for Taking Samples of Blood in the Hagedorn-Jensen Blood-sugar Determination.** G. FRITZ and B. PAUL (*Biochem. Z.*, 1925, **159**, 247—249).—A centrifuge tube provided with stopper and two tubes, one of which is a pipette, is employed for taking samples of blood. P. W. C.

**Distribution of Blood-sugar between Corpuscles and Plasma. Studies on Carbohydrate Metabolism.** E. FOCK and S. A. HOLBØLL (*Compt. rend. Soc. Biol.*, 1925, **92**, 1315—1317; from *Chem. Zentr.*, 1925, ii, 663).—The ratio corpuscle-sugar : plasma-sugar is 0.75 both in normal and in diabetic blood. Administration of sugar, after fasting, raises the ratio in some cases to more than unity. This occurs also in diabetics if a marked glycosuria takes place during the experiment, or after insulin treatment. The presence of different forms of dextrose ( $\alpha$ ,  $\beta$ , etc.) has no significance for the distribution of sugar in blood.

G. W. R.

**Determination of Dextrose in Blood.** J. A. MILROY (*Biochem. J.*, 1925, **19**, 746—749).—The method is based on the fact that 1:5-nitroanthraquinonesulphonic acid when heated with dextrose in alkaline solution produces a red tint the intensity of which corresponds with the quantity of dextrose present. The protein of the blood is removed by tungstic acid, and the coloration produced is compared with a series of controls containing graduated quantities of dextrose. At least 1 c.c. of blood is required for a determination. S. S. Z.

**Variations of the Phosphoric Acid during Glycolysis in Blood.** G. PIAZZA (*Arch. Farm. speriment. Sci. aff.*, 1925, **40**, 49—57).—In general, the inorganic phosphorus tends to increase during glycolysis of blood, but, contrary to the statement of Bierry and Moquet (this vol., i, 454), no parallelism exists between the amount of such increase and the intensity of the glycolysis. T. H. P.

**Thrombin of Alexander Schmidt. X. Blood-clotting.** E. WÖHLISCH (*Biochem. Z.*, 1925, **159**, 288—297).—The greater activity of Schmidt's thrombin solution depends on the coagulation activity of the material used in its preparation. Fresh serum gives a very active Schmidt's thrombin, whilst only traces are obtained from the plasma of the same animals. The author favours the views of Schmidt in opposition to those of Stuber (*A.*, 1923, i, 410; cf. *A.*, 1924, i, 681). P. W. C.

**Serological Differentiation of Lecithin and Cholesterol.** H. SACHS and A. KLOPSTOCK (*Biochem. Z.*, 1925, **159**, 491—501).—By previous injection of lecithin or cholesterol, each taken up in pig's serum, it is possible to obtain, from rabbits, anti-sera which

react characteristically with the original antigen *in vitro*, and thus permit of the serological differentiation of the two substances.

H. D. K.

**Precipitin Reactions of Fibrinogen.** L. HEKTOEN and W. H. WELKER (*J. Amer. Med. Assoc.*, 1925, **85**, 434—435).—The fibrinogens of ox, chicken, dog, horse, human, sheep, and swine blood are precipitinogenic. These and the fibrinogens of goat, guinea-pig, rabbit, and rat have antigenic elements more or less common to all of them. Fibrinogen is not necessarily wholly different for each species, as seems to be the case with serum proteins and hæmoglobin, but to a varying extent the same in different species, resembling in this respect caseinogen, lens protein, and to some extent thyroglobulin. The principle of strict species-specificity does not hold in the precipitin reaction of mammalian fibrinogen.

CHEMICAL ABSTRACTS.

**Protein Coagulation in Drops. VII. Study of the Precipitin Reaction by Means of the Drop Method.** V. MORÁŠKO (*Biochem. Z.*, 1925, **159**, 280—285).—Rabbits produce chemically different substances towards different antigens. The precipitin reaction towards human protein resembles precipitation with polyhydric phenols; towards the protein of dogs, with monohydric phenols; towards the protein of horse, with mineral acids; towards the protein of goats, with the combination of copper sulphate and phenol; towards the protein of sheep, with mercuric chloride; towards the protein of cows, with ferrous sulphate; towards the protein of hens, with weak organic acids.

P. W. C.

**Composition of Human Brain.** L. LEMATTE and L. BEAUCHAMP (*Compt. rend.*, 1925, **181**, 578—580).—The adult fresh human brain has the following average percentages of inorganic constituents: water, 80, total ash 1·2, phosphoric acid 1·0, sulphuric acid 0·45, sodium 0·25, potassium 0·21, hydrochloric acid 0·18, magnesia 0·022, iron 0·015, lime 0·005. In old age, the water content is decreased slightly, and the amount of sodium and phosphorus slightly increased.

L. F. H.

**Carbohydrate Content of the Brain.** K. TAKAHASHI (*Biochem. Z.*, 1925, **159**, 484—488).—Brain-tissue has been shown, by two methods of extraction, to contain glycogen in small quantities. Rabbit's brain contains from 14 to 28 mg. of glycogen per 100 g. of brain.

H. D. K.

**Micro-methods for the Determination of Brain Lipins.** H. GORODISSKY (*Biochem. Z.*, 1925, **159**, 379—393).—Micro-methods (which are, in the main, modifications of Fränkel's macro-methods) for the determination of cholesterol, unsaturated phosphatides, and saturated phosphatides+cerebrosides in brain are described in detail.

The determinations can be carried out on two portions of brain each of 40–60 mg., so that the lipin distribution in different parts of the same brain may be readily compared. H. D. K.

**Bile-acids. XXIII. Components of Human and Ox Bile. Constitution of Anthropodeoxycholic Acid.** H. WIELAND and R. JACOBI (*Z. physiol. Chem.*, 1925, **148**, 232–244).—Lithocholic acid, m. p. 184–185°, is isolated from human bile and anthropodeoxycholic acid, m. p. 108°, from ox bile. The latter is oxidised by chromic acid to dehydroanthropodeoxycholic acid, m. p. 154–155° (ethyl ester, 133°), identical with chenodehydrodeoxycholic acid (cf. this vol., i, 181, 405). The semicarbazone, m. p. 200° (not sharp), is converted by heating with sodium ethoxide into lithocholic acid. Anthropoloidanic acid, m. p. 213°, is obtained either by treatment of dehydroanthropodeoxycholic acid with fuming nitric acid or of anthropodeoxycholic acid with diluted nitric acid. A tetracarboxylic acid,  $C_{23}H_{36}O_8$ , is obtained by heating anthropoloidanic acid in an atmosphere of nitrogen; yield 30%, m. p. 219–220°. Anthropoloidanic acid on distillation in a high vacuum gives an acid,  $C_{22}H_{32}O_4$ , m. p. 142°. P. W. C.

**Bile-acids. XIV. Occurrence of Deoxycholic (Choleic) Acid in the Hydrolysed Bile of the Sheep.** M. SCHENCK (*Z. physiol. Chem.*, 1925, **148**, 218–224).—From the mixture of bile-acids resulting from the alkaline hydrolysis of the bile of the sheep was obtained about 4% of cholic acid and 0.4% of choleic acid, the latter being isolated as the acetic acid derivative (cf. this vol., i, 854). P. W. C.

**Isoelectric Points of Muscle Proteins.** E. WÖHLISCH and H. SCHRIEVER (*Z. Biol.*, 1925, **83**, 265–282).—The following are the isoelectric points of muscle proteins: “ammonium sulphate-myosin”  $p_H$  5.4 (approx.), “dialysed myosin”  $p_H$  4.8 (approx.), myogen  $p_H$  4.4 ± 0.2, myoprotein  $p_H$  3.3. These figures are discussed in connexion with theories of muscle contraction. S. S. Z.

**Collagen.** R. O. HERZOG and H. W. GOWELL (*Ber.*, 1925, **58**, [B], 2228–2230).—Röntgen spectrographic investigation establishes the identity of the collagen obtained from fish scales, tendons of rats' tails, neck ligament of the ox, and cartilage of the shark, whereas cartilage from calf and shark embryo gives Debye-Scherrer rings. H. W.

**Iodine. I. Avidity of the Thyroid Gland for Various Iodine Compounds *in vitro*.** I. M. RABINOWITCH [with A. B. FRITH] (*J. Clin. Invest.*, 1925, **1**, 473–481).—Normal thyroid glands, when exposed to various dilute iodine solutions, absorb considerably more iodine than other tissues. Pathological thyroids absorb much more iodine than normal thyroids. The quantity of iodine absorbed varies with the nature of the iodine solution.

The iodine taken up by the thyroid tissue does not combine with the lipid material because extraction with chloroform has no significant effect on the iodine content. Adsorption cannot explain the phenomenon.

CHEMICAL ABSTRACTS.

**Distribution of Iodine in the Hydrolytic Products of the Thyroid Gland.** N. ABELLES and H. POPPER (*Biochem. Z.*, 1925, **159**, 126—129).—A comparison of the distribution of iodine in the products of acid and alkaline hydrolysis of thyroid gland substance. The iodothyryn of Baumann and the first fractions obtained by Kendall's method contain only one-third of the total iodine of the gland. The melanoidin remaining after acid hydrolysis contains about one-fifth of the total iodine.

E. C. S.

**Determination of Iodine in Thyroid Gland.** F. A. PICKWORTH (*Biochem. J.*, 1925, **19**, 768—772).—The finely powdered dry thyroid is ground with sodium hydroxide and fused. The resulting iodide is oxidised to iodate with potassium permanganate solution. After removing the excess of the latter with animal charcoal, potassium iodide is added and the liberated iodine titrated with sodium thiosulphate.

S. S. Z.

**Recovery of Small Amounts of Zinc from Biological Material Ashed by Incineration.** P. K. THOMPSON (*J. Ind. Hygiene*, 1925, **7**, 358—370; cf. Mehurin, A., 1923, ii, 891; Severy, A., 1923, i, 415; Pfyl and Samter, A., 1924, ii, 276).—No appreciable amount of zinc is lost on incineration at 450° of various organic materials containing a small amount of the metal, its oxide, chloride, sulphate, or acetate. Methods are described for the determination of zinc in starch, flour, filter-paper, faeces, blood, muscle, urine, and vinegar, by nephelometric comparison of the ferrocyanide.

L. F. H.

**Comparative Determination of Phosphate-, Calcium-, and Magnesium-content of the Tibia of Rats and Guinea-pigs.** H. VON EULER and R. JOHANSSON (*Z. physiol. Chem.*, 1925, **148**, 207—210).—The Ca : PO<sub>4</sub> ratio for the dried bone substance of young rats (tibia) which had been fed on a mixed diet is 0.714 and of guinea-pigs (tibia and fibula) 0.66.

P. W. C.

**Placental Transmission. III. Amino-acids, Non-protein Nitrogen, Urea, and Uric Acid in Foetal and Maternal Whole Blood, Plasma, and Corpuscles.** E. D. PLASS and C. W. MATTHEW (*Bull. Johns Hopkins Hosp.*, 1925, **36**, 393—402).—The amino-acids, total non-protein nitrogen, and occasionally uric acid, but not urea, are higher in normal foetal than in maternal whole blood and plasma. The amino-acids do not pass the placenta by simple diffusion.

CHEMICAL ABSTRACTS.

**Hydrogen-ion Concentration in the Gut of certain Lamellibranchs and Gastropods.** C. M. YONGE (*J. Marine Biol. Assoc.*, 1925, **13**, 938—952).—In the Lamellibranchs and in certain Gastropods (*e.g.*, *Crepidula*) the acidity of the gut has its origin in the style, which is soluble at a  $p_H$  of 5 or more. Normally the

style is regenerated by the style-bearing tissues, but in abnormal conditions the style may be completely dissolved away. The average  $p_H$  range is given for different parts of the gut of *Pecten maximus*, *Mya arenaria*, *Ensis siliqua*, and five representative Gastropods. The stomach and digestive gland are usually the most acid ( $p_H$  4–5). P. E.

**Colostrum.** J. HÖLLEN (*Deut. tierärztl. Woch.*, 1925, **33**, 386–387; from *Chem. Zentr.*, 1925, ii, 665–666).—The colour, odour, and taste of the milk were abnormal only during the first 2 days after calving. The first day's colostrum coagulated after 3 mins.' heating at 70°; that of the second day did not coagulate even on long heating. The density fell to normal after 4 days. The ash of the colostrum differed considerably from that of normal milk, particularly in its high phosphorus content, which had not returned to normal on the sixth day, when the calcium and potassium contents had already increased, whilst that of sodium had decreased. G. W. R.

**Value of the Sodium Nitroprusside Test for the Detection and Determination of the Total Acetone in Urine and certain other Body Fluids.** N. O. ENGFELDT (*Biochem. Z.*, 1925, **159**, 257–275).—The limiting concentrations in Legal's test are for acetoacetic acid 6 mg. per litre and for acetone 100 mg. per litre. The limiting concentrations in Rothera's test are for acetoacetic acid 1 mg. per litre and for acetone 100 mg. per litre. Both tests may be carried out directly on urine. Rothera's test is applicable, within certain limits, to the detection of abnormal acetone contents of the blood. The limiting values are for acetoacetic acid 10 mg. and for total acetone 20 mg. per litre. An approximate method is outlined for the colorimetric determination of the total acetone of urine. P. W. C.

**Acidosis. XXI. Colorimetric Determination of  $p_H$  of Urine.** A. B. HASTINGS, J. SENDROY, jun., and W. ROBSON (*J. Biol. Chem.*, 1925, **65**, 381–392).—The apparent dissociation constants of phenol-red, bromocresol-purple, and bromocresol-green have been determined colorimetrically, the values agreeing with those found by previous workers; chlorophenol-red has  $pK_1$  6.02 at 20° and 5.93 at 38°. Using one or other of these indicators, the bicolour method of Hastings and Sendroy (A., 1924, ii, 869) has been applied to the determination of the  $p_H$  of urine. The error of the method is 0.1  $p_H$ . C. R. H.

**Determination of Iodides in Urine.** R. VON BODÓ (*Biochem. Z.*, 1925, **160**, 386–389).—The halides are precipitated with silver nitrate and the iodide is converted into iodic acid by Winkler's method. E. C. S.

**New Oxalate from Human Urine.** W. O. MOOR (*Biochem. Z.*, 1925, **159**, 245–246).—A simplification of the author's method of obtaining a new oxalate from urine (cf. A., 1924, i, 1134). P. W. C.



**Reagent for Determination of Sugar in Urine.** J. B. SUMNER (*J. Biol. Chem.*, 1925, **65**, 393—395).—The author's dinitrosalicylic acid reagent (this vol., i, 186) has been modified by the addition to it of phenol and sodium hydrogen sulphite, which, it is claimed, make it more specific for reducing sugars. C. R. H.

**Urinary Calculus.** E. G. RANDALL (*Hahnemannian Monthly*, 1925, **60**, 420—427).—The calculi contained practically no organic matter, being composed of iron, calcium, phosphates, silicates, and a trace of sulphates. Triple phosphate and oxalates were absent.

CHEMICAL ABSTRACTS.

**Plasma Proteins in Relation to Blood Hydration. I.** J. P. PETERS, A. J. EISENMAN, and H. A. BULGER (*J. Clin. Invest.*, 1925, **1**, 435—450).—Changes in plasma volume, as produced by oxalating the blood, varying the carbon dioxide and oxygen tension, venous stasis, exercise, hydræmia, etc., are reflected fairly closely in the concentration of plasma proteins. When blood is drawn under standard conditions in a normal individual, the plasma protein level is quite constant over a period of 2 years. Normal plasma proteins were found in patients with arteriosclerosis and hypertension, severe acute infections, disease of the liver, and in some cases of severe anæmia.

CHEMICAL ABSTRACTS.

**High Blood-sugar with Absence of Sugar in the Urine in Diabetes treated with Insulin.** R. H. MAJOR and R. C. DAVIS (*J. Amer. Med. Assoc.*, 1925, **84**, 1798).—The sugar in the blood ranged from 196 to 425 mg. per 100 c.c., usually above 300 mg.; sugar was absent from the urine.

CHEMICAL ABSTRACTS.

**Excretion of certain Nitrogenous Substances in the Urine in the Course of Experimental Nephritis.** J. MOSONYI (*Magyar Orvosi Archivum*, 1925, **26**, 244—247).—A dog poisoned with uranium showed a diminution in the excretion of carbamide, preformed ammonia, and creatinine. After regeneration of the kidney the excretion of creatinine reaches its normal amount much later than the other substances. The increase of nitrogen excretion, elsewhere stated to occur in the course of uranium-nephritis, could not be confirmed.

CHEMICAL ABSTRACTS.

**Excretion of Organic Acids after Pneumonia.** S. W. CLAUSEN (*Arch. Int. Med.*, 1925, **35**, 571—575).—During the period of resolution after pneumonia in children, large amounts of organic acids, most of which were insoluble in ethyl ether, were excreted in the urine.

CHEMICAL ABSTRACTS.

**Thyroxin and Tryptophan Content of the Diseased Thyroid Gland, and the Iodine Compounds in Desiccated Thyroid.** J. F. WEIR (*Amer. J. Med. Sci.*, 1925, **169**, 860—865).—In the normal gland, the iodine stable towards sodium hydroxide (thyroxin) is about 50% of the total iodine; in exophthalmic goitre, the total is subnormal and the thyroxin much reduced. Clinical improvement on administration of Lugol's solution is paralleled by increase

in both total iodine and thyroxin. The iodine which is soluble in acid after the gland has been digested with sodium hydroxide is organically combined. Tryptophan is present in the thyroid (average 3%).

CHEMICAL ABSTRACTS.

**Toxæmias of Pregnancy.** H. J. STANDER, E. E. DUNCAN, and W. E. SISSON (*Bull. Johns Hopkins Hosp.*, 1925, **36**, 411—427).—In normal pregnancy there is a slight decrease in the non-protein and urea nitrogen of the blood, and the carbon dioxide combining power is lower. Variations from the normal values associated with nephritic and pre-eclamptic toxæmia and with eclampsia are described. Results obtained with eclampsia suggest an association between carbohydrate and phosphorus metabolism.

CHEMICAL ABSTRACTS.

**Calcium Content of Blood of Normal and Tuberculous Subjects.** P. P. MATZ (*Amer. Rev. Tuberculosis*, 1925, **11**, 250—274).—The serum of normal subjects contains 9—12 mg. (average 10.28 mg.) of calcium per 100 c.c., and there is little variation in all stages of pulmonary tuberculosis. Calcium metabolism and the concentration of calcium in the blood are normally increased by simultaneous ingestion of cod-liver oil. Experiments on the relation between calcium ingestion, blood calcium concentration, and coagulation time are described.

CHEMICAL ABSTRACTS.

**Metabolic Differences, following X-Radiation, between Normal Rats and Rats Immune to Jensen's Rat Sarcoma.** E. C. DODDS, W. LAWSON, and J. C. MOTTRAM (*Biochem. J.*, 1925, **19**, 750—752).—The exposure of rats, previously inoculated with Jensen's rat sarcoma and in which no tumour results, to X-radiation causes an immediate fall in the blood-urea content from a normal value of about 35 mg. per 100 cc. to about 14 mg. per 100 c.c.

S. S. Z.

**Carbohydrate Metabolism of Tumours. II. Changes in Sugar, Lactic Acid, and Carbon Dioxide Combining Power of Blood Passing through a Tumour.** C. F. CORI and G. T. CORI (*J. Biol. Chem.*, 1925, **65**, 397—405).—In cases of chicken sarcoma and one case of human sarcoma the venous blood leaving the tumour tissue contained less dextrose, more lactic acid, and had a lower combining power for carbon dioxide than the blood from the normal tissues.

C. R. H.

**Lactic Acid Formation in Growths.** O. WARBURG (*Biochem. Z.*, 1925, **160**, 307—311).—Jensen rat sarcoma yielded 15.4% of its dry weight of lactic acid under anaërobic conditions. Peyton Rous chicken sarcoma yielded 12% anaërobically, 8% aërobically. The metabolism of these growths is therefore identical with spontaneous human carcinomata and sarcomata and the Jobling rat carcinoma (cf. *Biochem. Z.*, 1924, **152**, 51, 309).

E. C. S.

**Electrical Charges of Living Cells.** L. V. HEILBRUNN (*Science*, 1925, **61**, 236—237).—The observation that aluminium

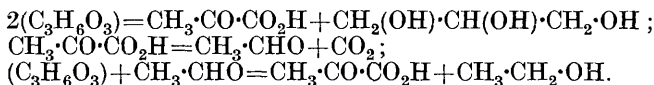
and cerium ions have a greater effect than calcium or magnesium ions in liquefying the protoplasm in the interior of a cell supports the conclusion (Heilbrunn, *Amer. J. Physiol.*, 1923, **64**, 481) that the particles in the interior of living cells bear a positive charge, whereas those on the surface bear a negative charge. The negative surface charge of living cells is ascribed to the assumed more ready diffusion of hydrogen carbonate and carbonate ions than of hydrogen ions through the surface membranes. A. A. E.

**Natural Synthesis of Amino-acids and its Experimental Reproduction.** F. KNOOP and H. OESTERLIN (*Z. physiol. Chem.*, 1925, **148**, 294—315).—A new type of synthesis of amino-acids claimed to be similar to that *in vivo* is carried out by catalytic hydrogenation of a mixture of keto-acid and ammonia, the yield being 66% of theory. The following compounds were used:  $\alpha$ -keto-butyric, trimethylpyruvic, oxalacetic,  $\alpha$ -ketoglutaric, lævulic, phenylglyoxylic, phenylpyruvic, phenyl- $\alpha$ -ketobutyric, benzoyl-acetic, benzoylpropionic acids and ethyl acetoacetate. Since the fixation of nitrogen is only brought about by ammonia and methylamine, but not by dimethylamine, the mixture probably reacts as an imino-acid, hydrogen being added at the double linking.  $\beta$ - and  $\gamma$ -Keto-acids form little or no amino-acid, and in several cases where amino-acid formation was difficult, hydroxy-acids were formed instead. The great ease of reaction of  $\alpha$ -keto-acids suggests that this may be the course of the biological synthesis. Since the reaction is reversible, even though the amino-acid synthesis *in vivo* be only slight, the removal of the ammonium ion is necessary before the combustion of the products of protein breakdown can proceed; this is accomplished by its conversion into carbamide. P. W. C.

**Carbohydrate Utilisation by the Cell and Variations in the Nucleus and Nucleolus.** A. MAIGE (*Cellule*, 1925, **35**, 325—340).—Sucrose, maltose, lactose, dextrose, lævulose, galactose, mannose, and glycerol are foodstuffs for the cells of the bean, whilst mannitol is probably not assimilable. The physiological utilisation, or non-utilisation of a carbohydrate is revealed by the changes which take place in nuclear and nucleolar material. In plants which form starch readily the changes can be most readily followed by variations in the nucleolus; where it is formed with difficulty changes in the nucleus are most readily detected. The changes which take place occur immediately after the penetration of the foodstuff; thus the cytophysiological method is quicker and more direct than the ordinary physiological method of determining the influence of foodstuffs on cellular changes. CHEMICAL ABSTRACTS.

**Mechanism of Carbohydrate Utilisation.** A. L. RAYMOND (*Proc. Nat. Acad. Sci.*, 1925, **11**, 622—624).—A mechanism of the process of alcoholic fermentation as carried out by enzymes is suggested. It is assumed that as a first step the hexose reacts with inorganic phosphate to form a hexose monophosphate, which facilitates the cleavage of the hexose molecule into two triose groups, one of which contains all the phosphorus. Then the phos-

phorus-containing portion is condensed to a hexose diphosphate, whilst the other, which is assumed to be a reactive triose not identical with any of the known triose isomerides, is transformed to alcohol and carbon dioxide. Finally, hydrolysis of the diphosphate regenerates the hexose and phosphate. The mechanism of the transformation of the reactive triose is assumed to follow the course :



The mechanism of the animal metabolism of carbohydrates is suggested as following the same steps as the above up to the cleavage of the hexose monophosphate, when in the presence of sufficient oxygen the reactive triose is oxidised. In a deficient oxygen supply, lactic acid is produced by isomerisation. It follows that lactacidogen is the hexose monophosphate, and not the diphosphate. The triose phosphate is not available to the organism until it is reconverted into the phosphorus-free hexose. It is suggested that glycogen is an intermediate in this process and that this is the main source of that material in the animal body.

A. E. M.

**Carbohydrate Metabolism. II. Mutarotation of  $\beta$ -Glucose.**  
**III. Nature of the Dextrose of the Blood of Normal Individuals.** **IV. Nature of the Dextrose of the Blood of Patients with Diabetes Mellitus and with Benign Glycosuria.** **V. Form of Dextrose in Body Fluids.** C. LUNDGAARD and S. A. HOLBØLL (*J. Biol. Chem.*, 1925, **65**, 305—322, 323—342, 343—362, 363—369).—II. In neutral aqueous solution the mutarotation of  $\beta$ -glucose is complete within 3 hrs.; the process is unaffected by changes in reaction between  $p_{\text{H}}$  4.0 and 7.0, is more rapid at  $p_{\text{H}}$  4.0 or less, and is practically instantaneous at  $p_{\text{H}}$  9.0 and above. A comparison of the very slow rate of mutarotation of the altered form of dextrose produced by the action of insulin and muscle-tissue (cf. this vol. i, 208) with that determined for  $\beta$ -glucose indicates that the two substances cannot be identical; the possibility of a stabilising effect on  $\beta$ -glucose by insulin and inactivated muscle is excluded by the fact that addition of these substances to solutions of  $\beta$ -glucose is without effect on the mutarotation of the latter. It is therefore concluded that the action of insulin and muscle-tissue on dextrose is to produce a more reactive form, designated "new-glucose," and it is suggested that this may be the aldehydic form of dextrose rather than the  $\gamma$ -glucose suggested by Winter and Smith (A., 1923, i, 513).

III. Comparisons were made of the optical rotation of the dialysate from normal blood with the concentration of dextrose as determined by a reduction method. The values of  $[\alpha]_{\text{D}}$  found were from  $15.9^\circ$  to  $42.2^\circ$ ; on long keeping, the normal specific rotation of dextrose was regained; normal blood therefore contains "new-glucose," and the observation of values for  $[\alpha]_{\text{D}}$  below  $19^\circ$  is further direct evidence that "new-glucose" is not identical with  $\beta$ -glucose.

IV. Extension of the above observations to diabetic patients

showed that the specific rotation of the dextrose of the blood was in close agreement with that of ordinary dextrose, but that the value of  $[\alpha]_D$  fell after administration of insulin; "new-glucose" is therefore absent from, or reduced in amount in, the blood of diabetics; patients with benign glycosuria showed similar results to those obtained in normal cases. In all cases where "new-glucose" could be demonstrated, the concentration of sugar was less in the venous than in the arterial blood; this was not so in those cases where there was no "new-glucose," which indicates that it is the latter form of dextrose which is utilised by the tissues.

V. Direct polarimetric examination of cerebrospinal fluid, œdema fluid, and pleural fluid from patients with normal carbohydrate metabolism indicates the presence in all cases of "new-glucose"; the concentrations observed were somewhat greater than in the blood, which is probably due to partial mutarotation having taken place during the dialysis of the latter. C. R. H.

**Glycogen and Cerebroside Metabolism of the Central Nervous System.** H. WINTERSTEIN and E. HIRSCHBERG (*Biochem. Z.*, 1925, **159**, 351—369).—The glycogen and cerebroside sugar content of the central nervous system of the frog reaches its maximum in the winter months and falls to a minimum in summer. The total carbohydrate compounds rapidly diminish when the isolated organ is kept in oxygenated physiological saline, but lack of oxygen, or narcosis with urethane, checks this decrease. Electrical stimulation of the brain also hinders the decrease in glycogen content. Insulin in large quantities diminishes the glycogen and cerebroside, but in smaller concentrations, particularly when the brain is at the same time electrically stimulated in presence of added dextrose, increases markedly the amount of both glycogen and cerebroside sugar.

These effects are due to a disturbance of the normal equilibrium in the brain between synthesis and hydrolysis of glycogen and cerebroside. H. D. K.

**Brain Metabolism. II. Carbohydrate Metabolism.** E. G. HOLMES and B. E. HOLMES (*Biochem. J.*, 1925, **19**, 836—839).—The lactic acid content of the brain does not begin to fall until the blood-sugar has dropped considerably after the administration of insulin. At the convulsive or pre-convulsive stage, the lactic acid content is very small. It is assumed that this fall is due to fall in the blood-sugar level and the consequent shortage of dextrose in the brain. S. S. Z.

**Relation between the Pancreas and the Carbohydrate Metabolism of Muscle. II. Antiglyoxalase and Glyoxalase.** D. L. FOSTER (*Biochem. J.*, 1925, **19**, 757—767).—The factor found in the pancreas (A., 1924, i, 897) which inhibits the production of lactic acid by chopped muscle *in vitro* is not antiglyoxalase. The "antiglyoxalase" action of pancreatic preparations is not due to its inhibitory action on the enzyme, but to the fact that the preparations contain something capable of changing phenylglyoxal into a highly coloured substance which cannot give rise to mandelic acid. Rabbit muscle does not contain glyoxalase. S. S. Z.

**Hexoses Taking Part in Carbohydrate Metabolism.** H. VON EULER and R. NILSSON (*Z. physiol. Chem.*, 1925, **148**, 211—217).—The hexose obtained by treating a solution of glycogen with malt amylase in presence of top yeast, ferments more rapidly than either dextrose or  $\alpha$ - or  $\beta$ -glucose. It is suggested that glycogen is synthesised from the stable forms,  $\alpha$ - and  $\beta$ -glucose (via zymophosphate), but on hydrolysis it breaks down into the more labile form,  $\alpha$ - and  $\beta$ -bioglucose ( $\gamma$ -glucose). P. W. C.

**Physiology of the Liver. X. Uric Acid following Total Removal of the Liver.** J. L. BOLLMANN, F. C. MANN, and T. B. MAGATH (*Amer. J. Physiol.*, 1925, **72**, 629—646).—Hepatectomy causes an increase in the uric acid content of the blood, and the appearance of large quantities of uric acid in the urine of dogs. The uric acid accumulated in the body of hepatectomised nephrectomised dogs is of the same magnitude as that excreted by the kidneys of hepatectomised dogs, so that the destruction of uric acid is a function of the liver. A. A. E.

**Calorific Value and Elementary Analysis of Animal Fats.** W. KRZYWANIEK (*Biochem. Z.*, 1925, **159**, 507—509).—Using the bomb calorimeter, the calorific value of the body fat of the following animals has been redetermined: horse, ox, sheep, pig, dog. Although the values found do not vary very appreciably from one animal to another, it is considered advisable that these differences should be taken into account in metabolism experiments.

H. D. K.

**Reciprocal Conversion of Creatine and Creatinine.** A. HAHN and H. FASOLD (*Z. Biol.*, 1925, **83**, 283—288).—When creatine is injected subcutaneously into rabbits, by far the greater part of it is utilised metabolically, since it can only be accounted for in its unchanged form in very small quantities. The amount of creatinine excreted is not increased by such injections. S. S. Z.

**Biological Relationship of Arginine to Agmatine.** H. MÜLLER (*Z. Biol.*, 1925, **83**, 320—324).—Neither by putrefaction nor by parenteral injection of arginine into rabbits was this substance converted into agmatine; 7.5% of the arginine carbonate injected was found unchanged in the urine a short time after the injection. S. S. Z.

**Mercapturic Acid Synthesis in the Dog.** H. I. COOMBS and T. S. HELE (*J. Physiol.*, 1925, **60**, Proc. xii.).—In the formation of *p*-chlorophenylmercapturic acid, which is produced in the dog after administering chlorobenzene, *p*-chlorophenol is not an intermediate compound, since the latter does not lead to mercapturic acid synthesis in the dog. CHEMICAL ABSTRACTS.

**Biochemistry of the Alkaline Earths.** E. HODEL (*Helv. Chim. Acta*, 1925, **8**, 514—518).—After intravenous injection into a rabbit of a solution of calcium and strontium salts in equimolecular proportions, with sodium and potassium chlorides to diminish the

toxic effect, analyses were made to determine the proportion of calcium to strontium in the blood, the urine, and various organs. Calcium was found to be in excess in the blood, the kidneys, and the spleen, there being no strontium in the latter organ. The two metals were in unaltered proportions in the liver, whilst strontium was in excess in the urine and the skin. The body thus gets rid of the more poisonous element as quickly as possible. G. M. B.

**Transformation of Calcium Oxalate into Calcium Carbonate in Animal Tissues.** M. LOEPER, R. SCHULMANN, and J. TOUNET (*Compt. rend. Soc. Biol.*, 1925, **92**, 1024—1025; from *Chem. Zentr.*, 1925, ii, 741).—Small collodion sacs containing calcium oxalate were introduced into the peritoneum and muscles of guinea-pigs and rabbits. After 11—60 days, they were removed and the content of calcium oxalate and calcium carbonate was determined. In the peritoneum 11.8—12.7%, in the muscles 7%, and in the skin 0% of the calcium oxalate had been converted into calcium carbonate. G. W. R.

**Phosphorus and Calcium Metabolism in an Adult Male.** H. HEINELT (*Z. ges. exp. Med.*, 1925, **45**, 616—627; from *Chem. Zentr.*, 1925, ii, 740).—During an experimental period of 1 year, an adult male had a positive phosphorus and calcium balance corresponding with more than 10 g. of calcium phosphate and 6 g. of calcium carbonate. Large daily and appreciable monthly fluctuations occurred. From 52.4% to 61.1% of the total excretion was in the urine. G. W. R.

**Effect of a Calcium Carbonate Supplement in the Diet of Hens on the Weight, Protein Content, and Calcium Content of the White and Yolk of their Eggs.** G. D. BUCKNER, J. H. MARTIN, and A. M. PETER (*Amer. J. Physiol.*, 1925, **72**, 458—463).—The eggs of hens given calcium carbonate in addition to a maize-wheat-buttermilk diet, with green food and siliceous gravel, were greater in number or had a greater total content than when calcium carbonate was not given, but the calcium and protein concentration in the white and yolk was not affected. A. A. E.

**Mode of Transference of Calcium from the Shell of the Hen's Egg to the Embryo during Incubation.** G. D. BUCKNER, J. H. MARTIN, and A. M. PETER (*Amer. J. Physiol.*, 1925, **72**, 253—255).—An aqueous solution of carbon dioxide can pass through egg-shell membranes and dissolve calcium, calcium hydrogen carbonate subsequently diffusing back through the membranes. It is inferred that during the first 9 days of incubation such a solution is produced and calcium thus made available for the metabolism of the embryo; after the ninth day the shell presumably gives up calcium hydrogen carbonate to the blood-stream as it discharges carbon dioxide. A. A. E.

**Phosphate Metabolism. I. Hexosephosphatases in Human Organs and Body Fluids.** F. DEMUTH (*Biochem. Z.*, 1925, **159**, 415—423).—The action of body-fluids and pulps of

various organs made 12 hrs. after death on sodium hexosediphosphate solution at varying  $p_H$  has been followed. All the organs and body-fluids investigated, with the exception of gastric juice, have a definite phosphatase activity. The optimum  $p_H$  for this action varies from one organ to another. Cerebrospinal fluid in meningitis contains phosphatase in much greater quantity than the normal fluid, whilst the blood-serum of children with florid rickets is much more active than that of healthy children, having a very sharp optimum of phosphatase activity at  $p_H$  7.9. H. D. K.

**Mineral Metabolism of Dairy Cows as Affected by Distilled Water and Previous Feeding.** C. F. MONROE and A. E. PERKINS (*J. Dairy Sci.*, 1925, 8, 293—311).—Cows fed continually on a winter ration showed a negative calcium balance less than half of that shown by cows which had previously been allowed pasture in the summer; similar results were obtained with nitrogen (in the first group a negative balance of an average of 3 g., and in the second group a positive balance of 8 g., and with phosphorus 1 g. positive balance compared with 4 g. positive balance), whilst no difference was found between the two groups in respect to the magnesium metabolism. The type of water used had no apparent effect on the balances of any of the minerals studied. CHEMICAL ABSTRACTS.

**Feeding of Goats on Ammonium Acetate, Urea, and Horn Meal as Protein Substitute.** E. PAASCH (*Biochem. Z.*, 1925, 160, 333—385).—The utilisation of urea, ammonium acetate, and horn meal ("ovagsolan") nitrogen compared with that of protein (dried yeast) nitrogen is 96.6%, 98.6%, and 113.1%, respectively. Ammonium acetate causes an increase in total milk output, without affecting its composition. Horn meal increases output but diminishes the fat content. Urea diminishes fat content without altering the volume. Ammonium acetate and, possibly, horn meal stimulate the mammary gland, the former causing a lowering of the positive nitrogen balance compared with the control periods, whereas urea causes an increase in the positive nitrogen balance, and has no specific action on the mammary gland. E. C. S.

**Mineral Metabolism with Dairy Cattle. Mineral Equilibrium after Prolonged Lactation.** H. G. MILLER, W. W. YATES, R. C. JONES, and P. M. BRANDT (*Amer. J. Physiol.*, 1925, 72, 647—654).—The nitrogen, sulphur, phosphorus, chlorine, calcium, magnesium, potassium, and sodium balances were determined. Supplementing the basal ration with bone meal caused increased storage of calcium and phosphorus, a marked increase in inorganic phosphate content, and a slight increase in the calcium content of the blood plasma; kale caused an increased calcium, but not phosphorus, storage, and increased calcium in the plasma. A. A. E.

**Carbohydrates. I. Relative Sweetness of Pure Sugars.** A. BIESTER, M. W. WOOD, and C. S. WAHLIN (*Amer. J. Physiol.*, 1925, 73, 387—396).—The relative sweetness of sugars is expressed



numerically as follows: sucrose, 100; lævulose, 173.3; dextrose, 74.3; xylose, 40.0; maltose, 32.5 (?); rhamnose, 32.5; galactose, 32.1; raffinose, 22.6; lactose, 16.0. A. A. E.

**Carbohydrates. II. Relative Sweetness of Invert-sugar.** J. J. WILLAMAN, C. S. WAHLIN, and A. BIESTER (*Amer. J. Physiol.*, 1925, **73**, 397—400).—The relative sweetness of invert-sugar compared with sucrose (100) is 127.4 when prepared by the use of invertase, and 130.0 when prepared synthetically. A. A. E.

**Kinetics of Colloidal Processes in the Stimulation of Tissues.** P. LASAREV (*Bull. Acad. Sci. St. Pétersbourg*, 1919, [6], 1035—1038; from *Chem. Zentr.*, 1925, ii, 658).—The author suggests that stimuli are always accompanied by changes in ionic concentration which effect the flocculation of protoplasmic colloids.

G. W. R.

**Glutathione. Its Influence in Oxidation of Fats and Proteins.** F. G. HOPKINS (*Biochem. J.*, 1925, **19**, 787—819).—In acid systems ( $p_H$  3.0—4.5) reduced glutathione (G·SH) promotes the oxidation of emulsions of fatty acids (linolenic and linoleic) and of lecithin. When the reaction is on the alkaline side ( $p_H$  7.4—7.6), oxidation of the thiol group and of the fatty acids takes place simultaneously with equipartition of oxygen. This oxidation is not brought about by the minute traces of iron which glutathione contains. The uptake of oxygen by the glycerides differs from that of the fatty acids. In acid systems ( $p_H$  3.5—4.0), there is a lag, during which period the system is practically inert, before the oxygen uptake becomes manifest. At  $p_H$  7.4—7.6, there is no lag period and the high initial velocity falls off rapidly. During the first stage of oxygen uptake, the thiol group of glutathione is oxidised without oxidising the fat. The longer the induction period an oil at  $p_H$  3—4 shows, the higher concentration of thiol is required to establish an active system at  $p_H$  7.6.

Glutathione also promotes oxidation of certain pure proteins in neutral and faintly alkaline but not in acid ( $p_H$  3.0—4.5) media. Oxidation proceeds when the protein is in solid phase, and only when it shows the presence of the thiol group (nitroprusside reaction). This group, although resistant to oxidation by molecular oxygen, is oxidised when in contact with a solution of the disulphide form of glutathione, which in its turn is reduced. Other thiol compounds can replace glutathione and the oxidation can also be effected under anaërobic conditions. The mutual oxidation and reduction occur as reversible processes, and equilibria are established between sulphur groupings in the solid phase and sulphur groups in solution. Evidence is produced that it is not a reversible adsorption process. When the protein thiol groups are oxidised, the total oxygen uptake is ten times the oxygen equivalent of the thiol group. On reducing the thiol group of the protein by means of the disulphide again, oxygen in excess of the oxygen equivalent of the thiol group is once more taken up, and this can be repeated successively until the protein finally takes up

at least 10 c.c. per g. Certain proteins, of which blood-serum is an example, will not undergo oxidation in their native state, but will do so after denaturation.

S. S. Z.

**Clinical Experiments with Phloridzin.** L. DÜNNER and M. MECKLENBURG (*Z. ges. exp. Med.*, 1925, **45**, 518—525; from *Chem. Zentr.*, 1925, ii, 665).—Both pituitary and thyroid extracts in subliminal doses produced glycosuria. Injection of sodium dihydrogen phosphate or of sodium monohydrogen phosphate decreased phloridzin glycosuria.

G. W. R.

**Action of Sodium and Calcium Ions on Frog's Heart.** E. HOLZLÖHNER (*Z. Biol.*, 1925, **83**, 107—119).—The observations of Sakai (*Z. Biol.*, 1913, **62**, 295; 1914, **64**, 505), demonstrating the uncompensated action of calcium ions in perfusing solutions poor in sodium salts, are confirmed. The action is largely independent of the  $p_H$ .

H. P. M.

**Action of Bismuth on the Red Blood-corpuscle.** A. SIMON (*Biochem. Z.*, 1925, **159**, 424—431).—In very small quantities, bismuth (potassium bismuth tartrate or ammonium bismuth citrate) has no effect on the red blood-corpuscle. In slightly higher concentrations, it brings about increased resistance of the corpuscle to hæmolytic agents. If the concentration of bismuth is raised still further, there is a diminution in the resistance of the corpuscle. Bismuth may be of value in the treatment of pernicious anæmia.

H. D. K.

**Determination of Small Quantities of Arsenic in Animal Organs.** E. PRIBYL (*Biochem. Z.*, 1925, **159**, 276—279).—The Marsh test may be replaced by the Reinsch test if a standard scale of arsenic coatings on copper strips is first prepared. The separated arsenic may be dissolved in *N*/10-iodine, decolorised with thiosulphate, and used directly for the Marsh test.

P. W. C.

**Antiseptic Action of Cupric Chloride in Solvents of Different Dielectric Constants.** N. KLISSIUNIS (*Biochem. Z.*, 1925, **159**, 107—109).—Cupric chloride has no antiseptic action when dissolved in isoamyl, propyl, and isopropyl alcohols, and acetone, but in ethyl and methyl alcohols, glycol, and water antiseptic action is manifested.

E. C. S.

**Adsorption of Poisons by Charcoal. II.** E. DINGEMANSE and E. LAQUEUR (*Biochem. Z.*, 1925, **160**, 407—416; cf. this vol., i, 736).—The authors have compared the efficiency of a number of commercial charcoals with respect to the adsorption of mercuric chloride, morphine, strychnine, oxalic acid, and methylene-blue. [Cf. *B.*, Dec. 24th.] The methylene-blue method of determining the efficiency of a charcoal is more accurate in the Joachimoglu modification (A., 1917, ii, 42) than the Wiechowski (*Ther. Gegenw.*, 1922, **24**, 129). Acidification with dry hydrogen chloride increases the adsorption of morphine hydrochloride. The adsorption of sodium oxalate and potassium cyanide by the most efficient charcoal was very slight.

E. C. S.

**Action of Santonin on Blood-sugar.** A. STASIAK (*Biochem. Z.*, 1925, **160**, 298—306).—Repeated administration to rabbits *per os* of "Natrium santoniticum cryst." in doses of 0.20—0.40 g. results in hypoglycæmia, hypotonia, and slight paresis of the hind limbs, followed by fall of body temperature and clonic convulsions. Temporary recovery is effected by application of heat and injection of dextrose, but death finally ensues. The liver histologically shows degenerative changes. The primary action of santonin is directed against the liver, the nervous effects being subsidiary. E. C. S.

**Toxicity of Saponins and Detoxication by Cholesterol.** L. KOFER and W. SCHRUTKA (*Biochem. Z.*, 1925, **159**, 327—336).—Eleven saponins were administered to white mice either orally or by intravenous or subcutaneous injection. White mice appear to tolerate higher doses per kg. body-weight than other mammals previously investigated. Profuse perspiration and inflammation of the eyes occur and death usually several days after administration. The lethal dose by oral administration is 3—300 times the intravenous dose. The three saponins which, *in vitro*, are most powerfully hæmolytic, viz., digitonin, primulic acid, and gypsophila saponin, are also most poisonous when injected intravenously, whereas guaiacum and horse-chestnut saponins, which are only faintly hæmolytic *in vitro*, are also only slightly toxic. The amount of cholesterol (in acetone solution) necessary to render the saponins inactive is ascertained quantitatively. Sapotoxin requires most cholesterol, primulic acids and digitonin less, and the horse-chestnut and guaiacum saponins least. A direct proportionality between the action of cholesterol and the toxicity of the saponin does not seem to exist. P. W. C.

**Standardisation of certain Glucosides which Affect the Heart, by Oral Administration to Frogs.** L. LENDLE (*Arch. exp. Path. Pharm.*, 1925, **109**, 35—49).—Different values were found for the lethal doses of digitalin and allied substances, according as the drug was given subcutaneously or *per os*. The difference was considerable for strophanthin and digitalin (lethal dose 20—40 times greater *per os*), but much smaller for digitoxin, scillitoxin, and the gitalin fraction ("verodigen") (1—3 times greater). Convallamarin appeared to be intermediate (13 times greater). The lethal doses *per os* were: strophanthin, 0.04; scillitoxin, 0.15; digitalin (in water), 0.45; digitoxin (in 40% alcohol), 0.01; "verodigen" (in 5% alcohol), 0.015; convallamarin, 0.18 (expressed in mg. per g. of frog). It made no appreciable difference whether the drug was given as an infusion or in powdered form. P. E.

**Salicylates. XV. Liberation of Salicyl from and Excretion of Salicyl Salicylate. XVI. Liberation of Salicyl from and Excretion of Methyl Salicylate, with a Note on the Irregular Toxicity of the Ester in Man.** P. J. HANZLIK and N. E. PRESKO (*J. Pharm. Exp. Ther.*, 1925, **26**, 61—70, 71—81).—Salicyl salicylate and methyl salicylate are relatively stable in presence of buffer mixtures ranging from  $p_H$  4.0 to 8.4 with or without the addition of

"pancreatin" or bile. When administered by mouth, 63% of the salicyl salicylate taken is excreted in the urine, and of this 10% is present as salicyl salicylate and the rest as sodium salicylate. The excretion of methyl salicylate is variable; on the average 50% of that taken is found in the urine as sodium salicylate and approximately 0.1% as unchanged methyl salicylate. Hydrolysis of those esters appears to take place in the tissues. W. O. K.

**Pharmacology of Proteinogenous Cholines.** T. GORDONOV (*Biochem. Z.*, 1925, **160**, 451—463).—Alanine-, leucine-, phenylalanine-, tyrosine-, and methyltyrosine-acetylcholine exhibit the same action as choline on isolated frog's heart, small intestine (rabbit), uterus (guinea-pig), and nerve-muscle preparation (frog). The non-acetylated choline derivatives phenylalanine-, tyrosine-, and methyltyrosine-choline iodides slightly increase the amplitude of beat of the frog's heart, and stimulate only transitorily, and in large doses, the intestine and uterus, the contractions being then myotropic. In the intact animal, none of the characteristic acetylcholine effects are shown by any of the above derivatives.

E. C. S.

**Relationship between Chemical Structure and Physiological Action. Effect of *l*-Adrenaline and Derivatives on Blood-sugar.** H. E. DUBIN, H. B. CORBITT, and L. FREEDMAN (*J. Pharm. Exp. Ther.*, 1925, **26**, 233—241).—The effects of the following adrenaline derivatives in raising the blood-sugar of normal rabbits decrease in the order named: *l*-adrenaline, *dl*-adrenaline, *dl*-adrenaline methyl ether, *d*-adrenaline, epinine, *dl*-adrenaline ethyl ether, methylaminoacetopyrocatechol, adrenaline anhydride, tyramine, and pyrocatechol. This indicates the importance, for physiological action, of the integrity of the secondary alcohol group, and its orientation. H. P. M.

**Influence of Histamine and Tyramine on the Nitrogen Metabolism of the Rabbit.** R. IWATSURU (*Bull. Soc. Chim. biol.*, 1925, **7**, 946—954).—Subcutaneous injections of histamine and tyramine into rabbits receiving a vegetable diet cause respectively a decrease and an increase in the total urinary nitrogen. Similar results are obtained when the diet of the animals contains a high percentage of fat or carbohydrate. H. J. C.

**Inhibition by Atropine and the Action of Organic Acids on the Intestine.** L. JENDRASSIK and H. TANGL (*Biochem. Z.*, 1925, **159**, 337—350).—That the contraction of the intestine is inhibited by atropine does not prove that it is similar to the pilocarpine contraction. Atropine appears to bring about a lowering of tonus and can completely inhibit the smaller barium and potassium contractions. The intestine appears to retain atropine and it is only after repeated washing out that it regains its sensitivity to atropine. The action of sodium acetate, propionate, and pyruvate is not conditioned by the liberation of choline esters, since their reaction occurs in presence of atropine, whereas under these conditions acetylcholine has no effect. Free acetic and propionic acids

are more active than their salts, and their action is not inhibited by atropine. P. W. C.

**Glycogen Content of Liver. I. Behaviour of the Blood-sugar and Liver Glycogen after Administration of Morphine.** N. FRANK and J. FÖRSTER (*Biochem. Z.*, 1925, **159**, 48—52).—Simultaneous determinations of blood-sugar and liver glycogen have been made in rabbits during a period following the injection of morphine. The blood-sugar concentration reaches a maximum in  $2\frac{1}{2}$  hrs., then falls gradually to the normal level. The rise synchronises with the mobilisation of the liver glycogen, the commencement of the fall with its exhaustion. E. C. S.

**Alcohol Tolerance in Man.** K. HANSEN (*Biochem. Z.*, 1925, **160**, 291—297).—After receiving 0.5 g. of ethyl alcohol per kg. per diem for 3—4 weeks, the rate of removal of alcohol from the blood increased in one subject, in a second subject it remained unaltered; the two subjects had not previously taken alcohol in any form. E. C. S.

**Effect of Alcohol, under Varying Conditions of Diet, on Man and Animals, with Some Observations on the Fate of Alcohol in the Body.** H. W. SOUTHGATE (*Biochem. J.*, 1925, **19**, 737—745).—Once the maximum concentration of alcohol in the blood has been reached, provided the subject be at rest and external conditions are maintained constant, the subsequent rate of its disappearance from the blood is independent of the concentration. There is no increased rate of absorption of alcohol in man when water is previously taken. A previous draught of milk, on the other hand, lowers the alcohol blood-concentration curve. A meal of bread has a similar effect, whilst a meal of bread and boiled milk has an even greater effect in lowering the concentration curve. The fat of milk or of bread and milk is not responsible for this depression. The concentration of alcohol in the urine exceeds that of the blood over a period of 1—6 hrs. after ingestion by about 40—50%. The amount of alcohol excreted in the urine varies from 3% to 5% of that ingested. Experiments are recorded of attempts made to discover the fate of the fraction of alcohol which cannot be traced. S. S. Z.

**Intoxication. III. Action of Ethylene. IV. Action of Propylene. V. Action of Ethyl Chloride. VI. Action of Methyl Ether.** B. M. DAVIDSON (*J. Pharm. Exp. Ther.*, 1925, **26**, 27—32, 33—36, 37—42, 43—48).—The subjective and objective effects of the inhalation by the human subject of various concentrations of ethylene, propylene, ethyl chloride, and methyl ether are described. Unconsciousness is produced by approximately 60% of ethylene, 20% of propylene, 3.6% of ethyl chloride, and 20% of methyl ether. Methyl ether gives rise to more depressant after-effects than any other of the gases investigated. W. O. K.

**Experiments with the Local Anæsthetics Psicaine and Tutocaine.** W. WAGNER (*Arch. exp. Path. Pharm.*, 1925, **109**, 64—73).—For both infiltration and surface anæsthesia, the minimal  
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effective concentration of tutocaine is one quarter that of cocaine or psicaine (about 0.013% for cocaine). The minimum lethal doses for guinea-pigs were 0.05 for cocaine, 0.10 for psicaine, and 0.20 for tutocaine (expressed in g. per kg. body-weight). The efficiencies, calculated as the ratio of the lethal dose to the minimal effective dose, were 4.0, 6.3, and 64.5, respectively. The anæsthesia is lengthened by the addition of adrenaline to the solution of the anæsthetic. The addition of phenol in small amounts increases the potency in surface anæsthesia. Psicaine produces a local irritant action, tutocaine does not.

P. E.

#### Localisation and Excretion of Alkylated Barbituric Acids.

R. FABRE and P. FREDET (*J. Pharm. Chim.*, 1925, [viii], 2, 321—334).—After intravenous injection of diethylbarbituric acid (veronal) and allylisopropylbarbituric acid into dogs, the drugs are found principally in the nervous centres and in the blood (mainly in the red cells); other organs excepting the spleen contain practically none of the anæsthetic. The excretion of these drugs is very slow and is not accelerated by diuretics. Methods for the determination of the drugs in the body (by proteolysis and ether extraction) and urine are described. It is noteworthy that even the unsaturated allylisopropylbarbituric acid is excreted unchanged.

L. F. H.

#### Influence of Method of Dissolving Amylase on Saccharification of Starch.

P. PETIT and RICHARD (*Compt. rend.*, 1925, 181, 575—577).—It is found that when allowed to act at the optimum hydrogen-ion concentration ( $p_H$  4.2; cf. Fernbach, A., 1906, i, 327), amylase dissolved in boiled water is the most potent; the same holds in more acid media, but in alkaline media amylase dissolved in water through which hydrogen is passed is the most active; in each case, amylase dissolved in aerated water is the least active. An algebraic relationship between the hydrogen-ion concentration of the medium and the amount of maltose produced has been observed, different equations being necessary on either side of an inflexion point, at  $p_H$  5.5—6.4. Saccharification of starch does not proceed in acid media, whilst production of maltose is retarded but not completely stopped in alkaline media.

L. F. H.

#### Hydrolysis of Natural and Synthetic Amylophosphates by Enzymes.

SAMEC (*Compt. rend.*, 1925, 181, 532—533; cf. A., 1913, i, 1155).—By the action of extracts of the seeds of *Glycine hispida*, of porpoise muscle, and of calf's femur on potato starch and synthetic amylophosphates, a certain amount of hydrolysis of the organic phosphates has been obtained, the reaction products being separable by dialysis and electro-dialysis.

L. F. H.

**Pringsheim's "Amylase Complement."** K. SJÖBERG (*Biochem. Z.*, 1925, 159, 468—471).—Confirming Pringsheim's work, it is shown that in certain kinds of yeast, a fairly thermostable substance (stable for 1 hr. at 80°) occurs, in presence of which "complement" malt extract is able to bring about complete hydrolysis of starch into maltose.

H. D. K.

**Arginase. II. Quantitative Determination of Arginase in Animal Organs. III. Arginine Exchange and Sexuality.** S. EDLBACHER and H. RÖTHLER (*Z. physiol. Chem.*, 1925, **148**, 264—272, 273—282).—II. An arginase unit is defined as that amount of arginase which, acting for 60 mins. at 38° on a solution containing 10 c.c. of a 1% arginine carbonate solution and 5 c.c. of a glycine, sodium hydroxide, and chloride buffer solution to bring the  $p_H$  to 9.5 (optimal, cf. this vol., i, 863), causes the formation of an amount of urea which on treatment with urease yields 0.34 mg. of ammonia, i.e., is equivalent to a titre (Folin's method) of 1 c.c. of *N*/50-sulphuric acid. For an extract of calf's liver, a table and typical curve are given indicating the titre of *N*/50-acid corresponding with 1—83 units of arginase. The curve is typical for the extracts of organs of a number of animals, but an exception is seen in the case of extract of hen's kidney, in which the titre of acid is directly proportional to the units of arginase used (cf. this vol., i, 104).

III. The mean arginase value (units of arginase per g. body-weight) of the liver, testes, and kidney of ten cocks is 0.363 unit and of the liver and kidney of ten hens 0.227 unit. Similar relations are obtained for ducks and pigeons, and also for dogs, cats, guinea-pigs, rabbits, and rats. The arginase value of mammals is about 500 times that of fowls, but if the female value is expressed as a percentage of the male value, about the same figure is obtained for all animals, viz., 60—70%. Attainment of puberty appears to be associated with increased arginine metabolism. The spleen, thyroid, mucous membrane of the gut, muscle, and heart in all animals are devoid of arginase, but the placenta and thymus contain a small amount. The authors conclude that higher arginine metabolism is a specific characteristic of the male sex. P. W. C.

**Bacterial Arginase.** A. KOSSEL and F. CURTIUS (*Z. physiol. Chem.*, 1925, **148**, 283—289).—Sterile emulsions of *Bacillus pyocyaneus* and liver arginase, in media containing *dl*-arginine, attack the *d*-form only (cf. A., 1924, i, 474). Living, arginase-free cultures of the bacillus attack both the *l*- and *d*-forms, probably by oxidation. This agrees with the results of Felix and Morinaka (A., 1924, i, 450), that *dl*-arginine completely disappears when perfused through the surviving liver, whereas liver arginase attacks only the *d*-form. The disappearance of arginine is followed throughout by precipitation of the unattacked base with flavianic acid, with subsequent re-liberation and examination of the rotation of the arginine. P. W. C.

**Liver and Blood Catalase. II.** P. RONA, A. FIEGEL, and Y. NAKAHARA (*Biochem. Z.*, 1925, **160**, 272—284; cf. A., 1923, i, 405).—The length of time taken for the recovery of liver and blood catalase from potassium cyanide poisoning depends on the concentration of cyanide. Recovery is brought about by destruction of the cyanide by hydrogen peroxide. The resulting oxidation product exerts a slightly inhibitory action on the catalase owing to partial destruction of the enzyme. Sulphate, chloride, and nitrate ions are strongly inhibitory from  $p_H$  3 to 5, but from  $p_H$  7.3 to 8 their inhibitory action is scarcely detectable. E. C. S.

**Purification and Properties of Hydroxynitrilase.** E. NORDE-FELDT (*Biochem. Z.*, 1925, **159**, 1—35; cf. *A.*, 1922, i, 66, 1077; 1923, i, 722).—Dry almond powder, preferably fat-free, is extracted with dilute alkali and precipitated with acetone, giving "crude emulsin." The purification is carried out by successive dialysis, acid precipitation, sorption on aluminium hydroxide, and elution in potassium dihydrogen arsenate or phosphate, and finally two successive precipitations with lead acetate. The product obtained is one hundred times more active in cyanohydrin synthesis than "crude emulsin." It is protein-free, almost carbohydrate-free, and the mol. wt. is estimated to be lower than 5000. The specific rotation falls during the purification process. The enzyme is very stable at the ordinary temperature, but heating at 75° for 1 hr. causes a loss of half its activity. The optimum  $p_H$  for cyanohydrin synthesis is 5.2—5.4. E. C. S.

**Rôle of Accompanying Substances in Immunisation with Invertase Preparations.** A. BACH, W. ENGELHARDT, and A. SAMYSSLOV (*Biochem. Z.*, 1925, **160**, 261—268).—Injection of beer-yeast invertase into rabbits causes the production of an immune serum. After adsorption on kaolin or ammonium phosphomolybdate, the immune serum, but not the normal serum, will remove invertase from solution. The enzyme retains its activity after precipitation. Purified invertase preparations give weaker immune sera than crude invertase of the same activity. Enzyme preparations inactivated by heat will cause the production of anti-enzyme sera, hence the accompanying proteins, and not the enzyme molecule, act as antigens. E. C. S.

**Factors Influencing the Action of Pancreatic Lipase.** B. S. PLATT and E. R. DAWSON (*Biochem. J.*, 1925, **19**, 860—874).—The optimum  $p_H$  for the action of pancreatic lipase is determined by the substances present in the reacting mixture. Even when the optimum reaction is ensured, the enzyme will not hydrolyse ethyl butyrate in the complete absence of activators. The effect of increasing concentrations of phosphates and of bile salts on the activity of the enzyme is the same. Two phases in which there is a rise of activity occur in both cases. The ester-hydrolysing properties of the enzyme are definitely altered by changing the accompanying protein. The apparent destruction of lipase by trypsin is due in part to the hydrolysis of the protein which activates the lipase. Formaldehyde has no appreciable effect on the activity of pancreatic lipase in concentrations less than 0.2%. S. S. Z.

**Separation of the Schardinger Enzyme from Milk.** F. G. HOPKINS and M. DIXON (*Biochem. Z.*, 1925, **159**, 482—483).—A reply to Sbarsky and Michlin's (this vol., i, 472) criticism of the method employed by Dixon and Thurlow (*A.*, 1924, i, 1380) for the separation of this enzyme. The Russian authors, in repeating Dixon and Thurlow's work, criticise a statement which the latter workers did not make. H. D. K.



**Methylglyoxalase.** O. MEYERHOF (*Biochem. Z.*, 1925, **159**, 432—443).—The production of lactic acid from methylglyoxal, unlike glycolysis, is not hindered by simultaneous uptake of oxygen, but resembles typical metabolic processes in its physico-chemical characteristics. In the cell and in cell extracts narcotics interfere with the process in varying degrees. The activity of a methylglyoxalase preparation is bound up with the protein content of the extract. Boiled tissue extracts considerably increase this enzymic activity, but there appears to be no ultra-filterable co-enzyme. The conversion of methylglyoxal into lactic acid in neutral solutions is catalysed by the presence of very small quantities ( $2 \times 10^{-5}$  to  $1 \times 10^{-4}$  *M*) of potassium cyanide. H. D. K.

**Constitution and Mode of Action of Proteolytic Enzymes.** E. HUGOUNENQ and J. LOISELEUR (*Bull. Soc. Chim. biol.*, 1925, **7**, 955—973).—From a consideration of results already reported (this vol., i, 1198), the enzyme system is regarded as consisting of an electrolyte, one ion of which has been adsorbed on a colloid, leaving the other ion in an active form; the chemical action of the enzyme is carried out by this "active" ion. The nature of the ion adsorbed depends on the electrical charge of the protein in colloidal solution. H. J. C.

**Action of Hydrochloric Acid and of Pepsin and Hydrochloric Acid on Dissolved Proteins.** H. W. VAN URK (*Biochem. Z.*, 1925, **160**, 448—450).—The observation of Abderhalden and Steinbeck (*A.*, 1910, i, 795) that, if the action of hydrochloric acid and pepsin on dissolved protein is followed polarimetrically, no difference can be observed from the action of hydrochloric acid alone, is shown to be due to the fact that the products of peptic digestion of acid metaprotein from egg-albumin have the same optical rotation as the original metaprotein. E. C. S.

**Nephelometric Investigation of Enzymic Proteolysis. IV. Kinetics of Peptic Hydrolysis of Serum-albumin.** P. RONA and H. KLEINMANN (*Biochem. Z.*, 1925, **159**, 146—174; cf. *A.*, 1923, i, 1145; this vol., i, 103, 473).—The course of the hydrolysis can be very well represented by the formula for a bimolecular reaction, either at the optimum  $p_H$  or on the alkaline side of neutrality, but on the acid side the reaction constant falls rapidly owing to the destruction of the enzyme. Between  $[H^+] = 4.17 \times 10^{-3}$  and  $1.7 \times 10^{-3}$  the velocity of hydrolysis is very nearly proportional to  $[H^+]$ . The presence of hydrolytic products (either from enzymic or acid hydrolysis) does not affect the course of the reaction. The temperature coefficient of the reaction between 30° and 40° is 1.9. E. C. S.

**Action of Bile on the Digestion of Proteins by Pancreatic Juice.** L. P. ROSENOV (*Biochem. Z.*, 1925, **159**, 240—244).—Bile, even when boiled, protects active trypsin against self-destruction. It also prevents the activation of trypsinogen. Digestion *in vitro* by means of inactivated pancreatic juice proceeds there-

fore more slowly in presence of bile, but digestion by means of activated juice is increased many times by the addition of bile.

P. W. C.

**Presence of Trehalose in Yeast.** E. M. KOCH and F. C. KOCH (*Science*, 1925, **61**, 570—572).—Air-dried pressed yeast was extracted first with ether and then with alcohol; the combined alcoholic extracts were seeded with crystals of a hexose accidentally obtained in a similar manner. The crystals which slowly deposited were dissolved in hot glacial acetic acid, and the cold solution was precipitated with acetone. An aqueous solution of the precipitate was then decolorised, concentrated, diluted with alcohol, and allowed to crystallise after careful addition of acetone. After several recrystallisations, a substance was obtained which was identified with trehalose, m. p.  $102.5^{\circ}$ , resolidifying at  $125$ — $135^{\circ}$  and melting again at  $208$ — $209^{\circ}$ ,  $[\alpha]_D^{20} +183.98^{\circ}$  (hydrated), or  $203.34^{\circ}$  (anhydrous).

A. A. E.

**Effect of Ammonium Salts on the Swelling of Colloids and the Growth of Yeast at Various Temperatures.** E. I. FULMER (*2nd Colloid Symposium Monograph*, 1925, 204—208).—Ammonium chloride, sulphate, nitrate, and tartrate promote at  $30^{\circ}$  a maximum crop of yeast at  $0.0353N$ , the phenomenon apparently being a function of the ammonium-ion concentration. At a higher temperature, a linearly higher concentration of the salt is required, the optimum being identical with that in which wheat gluten is least swollen. Temperature may thus affect the lyotropic series and the Donnan equilibrium. The temperature coefficient of reaction in heterogeneous systems varies with the concentration of the materials in the solution, and the effect of temperature alone cannot be determined unless the concentrations are appropriately varied.

CHEMICAL ABSTRACTS.

**Dependence of the Reduction Processes of Yeast on Fermentation.** S. L'vov (*J. Russian Botan. Congress*, 1921, **1**, 61).—The action of the reductase of yeast increases with the addition of sugar, phosphates, and co-enzyme, but phosphates in the absence of sugar do not accelerate reduction processes; that is, strengthening of the action of reductase requires organic phosphoric compounds which arise in the beginning of fermentation. It is possible to separate the process of fermentation from the action of the reductase; when diluted with water the former process is arrested, whilst the latter continues. The hydrogen which is derived by the reductase in the absence of fermentation is intimately connected with the process of fermentation, apparently with the synthetical substances of fermentation.

CHEMICAL ABSTRACTS.

**Phosphorylation of Sugar.** C. NEUBERG and M. KOBEL (*Biochem. Z.*, 1925, **160**, 464—466; cf. this vol., i, 476).—The presence of salts of pyrophosphoric acid, which inhibit the ionisation of iron, has no effect on the formation of lævulose phosphoric esters by yeast. The pyrophosphoric acid itself is not used in the synthesis.

E. C. S.

**Fermentation of Mannitol by Yeasts.** S. L'VOV (*J. Russian Botan. Congress*, 1921, **1**, 62).—Mannitol is not fermented by yeast immediately, but fermentation begins as soon as methylene-blue is added in substitution of a chromogen. Methylene-blue is reduced proportionally to the quantity of fermented mannitol. Fermentation proceeds similarly to the normal alcoholic type.

CHEMICAL ABSTRACTS.

**Action of Electric Current on Micro-organisms.** M. KLEIBER (*Biochem. Z.*, 1925, **160**, 312—324).—The temperature of inactivation of yeast in apple juice or beer wort is the same whether heat is applied externally, or internally by means of a direct or alternating current of potential difference 16 volts per cm. The fermentation of beer wort is somewhat inhibited by the passage of a direct current of 3—4 volts per cm. potential difference, but is unaltered by an alternating current of the same strength. This effect is due to electrolytic alteration of the wort, and not to a specific action of the current on the yeast-cell. The preservative effect in the electrosilo is not due to sterilisation. E. C. S.

**Conductivity Method as Applied to Studies of Bacterial Metabolism.** L. B. PARSONS and W. S. STURGES (*Abstr. Bact.*, 1925, **9**, 10).—Conductivity changes were correlated with formol titration and ammonia changes in the case of *Clostridium sporogenes* and *C. flabelliferum*. The conductivity and ammonia changes agreed to within 10%, and the formol titration also followed the conductivity changes fairly closely. The ammonia change (found by Folin's method) was more than sufficient to account for the observed changes in conductivity. A. A. E.

**Error Due to Ammonia and Ammonium Salts in Van Slyke's Procedure for Amino-nitrogen Determination as Applied in Studies of Bacterial Metabolism.** L. B. PARSONS and W. S. STURGES (*Abstr. Bact.*, 1925, **9**, 11).—A physico-chemical investigation of the decomposition of ammonium salts in Van Slyke's procedure. The reaction is of the first order, so that the relative amounts of ammonia nitrogen evolved are independent of the initial concentrations of the ammonium salts. The temperature coefficient of the reaction between 20° and 30° is 3.0. A. A. E.

**Oxydase Activity and Isolation of Pure Cultures of Bacteria.** L. D. FELTON (*J. Infect. Dis.*, 1924, **34**, 407—413).—*p*-Aminoleucomalachite-green (1 in 5000) in 0.5—1.0% dextrose-whole blood-meat infusion-agar with  $p_H$  7—7.6 shows the presence of oxydase in bacteria by the production of faint blue colonies. The medium is therefore suitable for the isolation of pure cultures of pneumococci and streptococci. CHEMICAL ABSTRACTS.

**Indicator for Testing the Reducing Power of Bacteria.** L. D. FELTON (*J. Infect. Dis.*, 1924, **34**, 414—419).—The reaction consists in the conversion of (green) *p*-nitromalachite-green into (red) *p*-aminomalachite-green. CHEMICAL ABSTRACTS.

**Fermentation Characteristics of Mannitol-forming Bacteria.**

W. H. PETERSON, E. B. FRED, and H. R. STILES (*Abstr. Bact.*, 1925, 9, 30).—Five groups of mannitol-forming bacteria have been isolated from soil, manure, water, silage, sauerkraut, yeast, and cereal infusions, and differentiated by their fermenting action on various sugars, alcohols, and acids. Pentoses yielded chiefly acetic and lactic acids; aldohexoses yielded chiefly ethyl alcohol, lactic acid, and carbon dioxide; lævulose gave chiefly acetic acid, lactic acid, carbon dioxide, and mannitol, this sugar having entirely disappeared within 3—4 days after inoculation, 50—60% of it being converted into mannitol. The lactic acid was mainly inactive, but a slight excess of one or other form was invariably present.

A. A. E.

**Oxalic Acid Test for Indole.**

S. A. KOSER and R. H. GALT (*Abstr. Bact.*, 1925, 9, 6).—Paper impregnated with oxalic acid and held in the mouth of a culture tube by the cotton plug becomes pink in the presence of indole, the delicacy of the test being influenced by the reaction of the medium.

A. A. E.

**Metabolism of *Bacillus botulinus*. XXVI.**

E. WAGNER, K. F. MEYER, and C. C. DOZIER (*J. Bact.*, 1925, 10, 321—412).—In 2% peptone solution, *Bacillus botulinus* causes a slow evolution of gas, and accumulation of ammonia, amino- and volatile acids, dextrose increasing its metabolic activity. The addition of gelatin to peptone solution increases its nutritional but not its buffer value; albumoses and proteoses are not necessary for growth or toxin formation. The volatile acids in a 10 days-old meat culture were valeric (3), butyric (7), and acetic (2). *Vibrio septique* causes only a slight degradation of nitrogenous substances. The products of *B. botulinus* and *B. tetani* are compared.

CHEMICAL ABSTRACTS.

**Bacterial Decomposition of Starch.**

A. S. SIEDICH (*Russ. Health Resort Service*, 1923, No. 1, 11—17).—A spore-forming rod and a coccus have been isolated from the soil, the former of which converts starch into dextrin, and the latter into the sugars, which are decomposed after all the starch has been used. The rod does not grow on ethyl alcohol, glycerol, or mannitol.

CHEMICAL ABSTRACTS.

**Production of Hydrogen Sulphide by Members of the Colon Group of Bacteria.**

MULSOW and PAINE (*Proc. Iowa Acad. Sci.*, 1924).—Lead acetate agar is prepared by adding the lead acetate solution before tubing and sterilising the medium. There are only a few strains of *Bacillus coli* which give hydrogen sulphide from peptone, and only a very few strains fail to give the gas from cystine or sodium sulphite.

CHEMICAL ABSTRACTS.

**Use of the Milk-agar of Freudenreich in the Investigation of Lactic Acid Bacteria.**

N. SLOBODSKA-ZAYKOVSKA (*Biochem. Z.*, 1925, 159, 216—220).—Milk agar (Freudenreich) cannot be used for proteolytic enzyme investigation of cheese, for lactic acid streptococcus, or for diagnosis. The medium is of value when the

bacteria are strongly proteolytic and is not injured when proteolysis leads to lactic acid formation.

P. W. C.

**Production of Gelatinase by *Proteus*.** W. M. CLARK and A. T. MERRILL (*Abstr. Bact.*, 1925, 9, 37).—Clark's method for the determination of gelatinase is sufficiently exact for determining the influence of various conditions on gelatinase formation. Surface exposure of cultures of *Proteus* considerably increases the rate of formation of gelatinase.

A. A. E.

**Preparation of Acetone and Alcohol by the Fermentation of Carbohydrates with *Bacillus macerans*.** N. MOSKOVITS (Austrian Pats. 99641 and 99642; from *Chem. Zentr.*, 1925, ii, 762).—The carbohydrate mash is first submitted to a proteolytic fermentation by the action of the lactic or butyric acid bacilli, hay bacillus, or *Tyrophthrix tenuis*, on yeast extract or autolysate. The mash is then sterilised by heating to 150°, and the *Bacillus macerans* culture is then added. The yield of acetone is improved by allowing proteolytic bacteria to act simultaneously with those forming acetone. Lupin and vetch are suitable raw materials. If anaërobic bacteria are used for the protein hydrolysis, air is blown through the fermenting mash to prevent excessive multiplication of these bacteria.

R. B.

**Amino-acid Content of the Tubercle Bacillus.** L. K. CAMPBELL (*Amer. Rev. Tuberculosis*, 1925, 11, 452—457; cf. Johnson and Brown, A., 1923, i, 160).—Of the total nitrogen, that as hexone bases is 32.99%, comprising arginine nitrogen 27.87%, histidine nitrogen 3.41%, and lysine nitrogen 1.71%. Glutamic acid nitrogen constituted 3.05%, and tyrosine nitrogen 0.73% of the total nitrogen of the fat-free bacilli.

CHEMICAL ABSTRACTS.

**Alanine and Histidine Metabolism of the Tubercle Bacillus.** L. K. CAMPBELL (*Amer. Rev. Tuberculosis*, 1925, 11, 458—470).—The metabolism of alanine yields appreciable quantities of volatile acids, predominantly acetic, but not volatile aldehydes. If ammonium phosphate was the only source of nitrogen, only small quantities of acids were produced; acetic acid was not formed. In the metabolism of histidine, glyoxalineacetic acid was probably formed, but not histamine.

CHEMICAL ABSTRACTS.

**Nitrogen Content in Volumetrically Standardised Bacterial Vaccines.** R. KAUTSKY, F. LEINEWEBER, and L. W. FAMULENER (*Abstr. Bact.*, 1925, 9, 6).—The nitrogen content of vaccines of members of the same species (*Bacillus coli communis*, *Staphylococcus aureus*, and *Streptococcus viridans*) correspond fairly closely.

A. A. E.

**Moulds and Bacteria which Utilise Quinic Acid.** W. BUTKEVITSCH (*Biochem. Z.*, 1925, 159, 395—413).—Certain moulds are able to utilise quinic acid as sole source of carbon, with intermediate formation of phenolic substances. The phenols are also able to act as the sole source of carbon for the same moulds. The utilisation of polyphenols by moulds depends, not only on the number

of hydroxyl groups, but also on their distribution in the benzene ring. Pyrocatechol is the most poisonous of the polyphenols in higher concentrations for *Aspergillus niger* and *Citromyces glaber*, but in lower concentrations acts as the best source of carbon. In dilute solutions, *A. niger* grows equally well on pyrocatechol, quinic acid, or dextrose.

The power of growing on quinic acid and phenols is associated, in a series of moulds, with the ability to produce acids such as gluconic and citric from dextrose.

Bacteria show similar relationships; many of those capable of growing on quinic acid and producing phenolic substances also give rise to gluconic acid in fairly large quantities when grown in presence of calcium carbonate.

H. D. K.

**Production of Acid by Cytolysis.** A. DRZEWINA and G. BOHN (*Compt. rend.*, 1925, **181**, 692—694).—On treatment with potassium chloride or even in fresh water, *Convoluta* undergo cytolysis, and the higher the concentration of organisms the more rapid is the cytolysis; this phenomenon is due to the production of acid on cytolysis. Cytolysis of a tentacle of *Anthea cereus* or of eggs of *Strongylocentrotus lividus* also produces acid, but to a smaller extent.

L. F. H.

**Insulin. I. Is Insulin an Unstable Sulphur Compound?** J. J. ABEL, E. M. K. GEILING, G. ALLES, and A. RAYMOND (*Science*, 1925, **62**, 169—171).—The authors have separated from commercial insulin crystalline amino-acids and protein-like fractions of varying sulphur and phosphorus contents. Alteration of an insulin fraction of high unitage takes place on boiling with 0.1N-sodium carbonate solution, whereby ammonia is not evolved, but dilute acids then liberate hydrogen sulphide from the material; the resulting physiological inactivation is thus associated with an alteration in the linking of at least part of the sulphur. The inert fractions contain very little labile sulphur. The labile sulphur content appears to be directly proportional to the degree of hypoglycæmic activity.

A. A. E.

**Reaction given by Insulin Solutions *in Vitro*.** S. R. BENEDICT (*Proc. Soc. Exp. Biol. Med.*, 1924, **21**, 529).—Solutions of insulin (iletin, Lilly) markedly accelerate the digestion of starch by various diastases. The reaction does not seem to be due to the  $p_H$  or to the protein content of the solutions.

CHEMICAL ABSTRACTS.

**Action of Insulin.** G. S. EADIE, J. J. R. MACLEOD, and E. C. NOBLE (*Amer. J. Physiol.*, 1925, **72**, 614—628).—For muscle or liver, the free and combined sugar which is soluble in hot ethyl alcohol is reduced by addition of insulin; a larger quantity, slightly increased by the presence of insulin, is extracted at 0°. Inconclusive results suggest, however, the presence of highly labile substances. Following the injection of insulin, although the fall in the blood phosphate value is practically coincident with that of the

blood-sugar, the phosphate commences to increase and attains its normal value first. "Lactacidogen" is slightly decreased by insulin.

A. A. E.

**Hormonal Regulation of Intermediary Carbohydrate Metabolism. II. Insulin-Adrenaline Antagonism in the Frog.** A. GOTTSCHALK (*Biochem. Z.*, 1925, **159**, 502—506).—Insulin convulsions in the frog may be rapidly relieved by injections of adrenaline. Injections of adrenaline previous to the administration of insulin also antagonise the action of the latter. Adrenaline alone produces motor paralysis, relieved somewhat by subsequent insulin injections.

H. D. K.

**Two-phase Action of Hormones. Antagonistic Endocrine Action.** H. ZONDEK and H. UCKO (*Z. physiol. Chem.*, 1925, **148**, 111—123).—Insulin administered to rabbits in small doses causes a fall in blood-sugar (first phase), followed by a rise above the previous level (second phase). When calcium or magnesium chloride accompanies the insulin, the phases are reversed. The facts are correlated with similar effects of adrenaline on blood-sugar and of pituitary extract on diuresis, and it is concluded that the hormones may act in one of two opposed directions, dependent on the condition of the cell.

P. W. C.

**Action of Pepsin on Insulin.** A. A. EPSTEIN (*Proc. Soc. Exp. Biol. Med.*, 1924, **22**, 9—11).—Pepsin inactivates insulin in solutions below  $p_H$  3.0. Reactivation takes place when the solution is made neutral or alkaline.

CHEMICAL ABSTRACTS.

**Preparation and Standardisation of the Ovarian Hormone.** F. DICKENS, E. C. DODDS, and S. WRIGHT (*Biochem. J.*, 1925, **19**, 853—859).—The physiologically active principle extracted from the ovary by means of alcohol is an oil soluble in ether, acetone, and olive oil, and can be obtained free from cholesterol. It can be heated to 200° without loss of activity, but withstands saponification only to a limited extent. By means of a series of injections, an ovariectomised rat can be kept in a state of continuous oestrus for a period of 14 days. Administration by the mouth is ineffective. The extract has a marked depressor action and it inhibits the blood-sugar reducing action of insulin.

S. S. Z.

**Sexual Glands and Metabolism. IV. Influence of Injections of Emulsions of Testes and Prostate and of Insulin-like Testicular Extracts on the Nitrogen Metabolism of Normal, Castrated, and Thyroidectomised Rabbits.** V. KORENCHESKY and M. CARR (*Biochem. J.*, 1925, **19**, 773—782).—An homologous emulsion of testes decreased the nitrogen metabolism of thyroidectomised rabbits much more than that of normal or castrated animals. It also decreased the urinary flow to about the same degree in rabbits both with and without thyroid glands. Insulin-like substances isolated from testes by Dudley's method also decreased the nitrogen metabolism in thyroidectomised rabbits

more than in rabbits with thyroids. These substances decreased the excretion of urine in both thyroidectomised and non-thyroidectomised animals during the periods following the period of injection. It is suggested that the action of the testicular emulsion is in part due to the presence in it of insulin-like substances. As these substances have been also isolated from kidneys, the same explanation might apply also to the action of kidney emulsions. Prostate emulsion appears to increase nitrogen metabolism of rabbits by stimulating the activity of the thyroid and also increases the flow of urine in both thyroidectomised and normal rabbits. S. S. Z.

**Vitamins. IV. Influence of Avitaminosis on Gastric Digestion of White Mice.** F. GROEBBELS and F. SPERFELD (*Z. physiol. Chem.*, 1925, **148**, 290—293).—If white mice be fed on a vitamin-free diet, the formation of pepsinogen is not inhibited, but the secretion of pepsin does not take place, the stomach wall becoming laden with pepsinogen. In the fasting condition, the formation of pepsinogen is disturbed only if the animal has been previously fed on a vitamin-free diet. P. W. C.

**Avitaminosis. VI. Influence of a Maize Diet on the Creatinine- and Creatine-nitrogen Excretion of Rabbits and on the Weight Curves of Guinea-pigs.** A. PALLADIN and K. KRATINOWA (*Biochem. Z.*, 1925, **159**, 179—191).—Rabbits fed on a maize diet lose appetite and their body-weight decreases, at first slowly, then rapidly, until, at death, it has fallen to about 50%. The daily total urinary nitrogen at first rises slightly, then falls until 2—4 days before death, when a large increase occurs. Creatine begins to appear on the sixth to eighth day and increases about 4 days before death. Creatinine excretion remains constant for some time, then slowly falls, but shows a slight rise before death. The results are compared with those obtained on feeding with vitamin-free oats. The daily weight curves of guinea-pigs fed on oats and turnips are either horizontal or slightly rising; on maize with turnips, gradually sinking; on maize, very much more rapidly sinking, and on maize heated at 130° for 3 hrs., still more rapidly sinking. The insufficiency of maize as the diet of rabbits and guinea-pigs is due, not merely to its lack of vitamins-A and -C, but also to the low biological value of its proteins. On a maize diet, the nitrogen and creatine metabolism in rabbits is characteristic of the fasting condition. Nitrogen equilibrium is not attained either in these experiments or in those of experimental scurvy, and it is suggested that the low biological value of the proteins plays a rôle also in the ætiology of pellagra (cf. this vol., i, 461). P. W. C.

**Improved Technique for Use with Synthetic Diets.** G. A. HARTWELL (*Biochem. J.*, 1925, **19**, 729—732).—Details for the preparation of a synthetic diet which approximates in composition and texture to ordinary foods are given. Rats thrive on this diet better than on the ordinary synthetic diet. S. S. Z.



**Vitamins. V. Storage of Vitamin-A by Young White Rats after Administration of Horseflesh to the Mother during Pregnancy.** A. SCHEUNERT and A. J. CANDELIN (*Biochem. Z.*, 1925, **159**, 83—88; cf. this vol., i, 617).—Horseflesh causes a considerable storage of vitamin-A in pregnant rats and their litters. E. C. S.

**Phosphate and Calcium Content of Blood of Guinea-pigs and Rats with Varying Vitamin-C and -A Administration.** H. VON EULER and K. MYRBÄCK (*Z. physiol. Chem.*, 1925, **148**, 180—196).—Lowering of phosphate content of blood may possibly be taken as an index of vitamin-C deficiency. Figures are given for normal values in whole blood, serum, and corpuscles. P. W. C.

**Effect of High Temperatures on the Accessory Food Factor Content of Cod-liver Oil.** H. W. SOUTHGATE (*Biochem. J.*, 1925, **19**, 733—736).—The antirachitic and growth-promoting factors of cod-liver oil are completely destroyed when the oil is heated slowly out of contact with air to 300°. When it is slowly heated and maintained for a few hours at 200° under the same conditions, the two factors disappear slowly. S. S. Z.

**Delicate Colour Reaction for the Presence of Vitamin-A.** O. ROSENHEIM and J. C. DRUMMOND (*Biochem. J.*, 1925, **19**, 753—756).—Arsenic chloride, methyl sulphate, trichloroacetic acid, acetyl chloride, and benzoyl chloride give a blue colour with substances containing vitamin-A such as cod-liver oil. The reaction is very sensitive and persists sufficiently long to allow a colorimetric comparison with a suitable standard. The reaction is obtained with the unsaponifiable fraction of cod-liver oil and with the distillate obtained by distilling this fraction in a nitrogen atmosphere or in a high vacuum. The reaction gradually disappears with the vitamin activity when a current of air is passed through cod-liver oil at 100°. A definite parallelism between the intensity of the coloration and the growth-promoting property of a number of oils and fats was observed. Cholesterol which was made antirachitic by irradiation failed to react with arsenic chloride. Both fat-soluble vitamins diffuse through a rubber membrane into petroleum. Cod-liver oil contains a reducing substance. S. S. Z.

**Association of Copper with Substances containing the Fat-soluble Vitamin-A.** J. S. MCHARGUE (*Amer. J. Physiol.*, 1925, **72**, 583—594).—Attention is directed to the wide distribution of copper in plant and animal tissues, particularly in vital organs. It is believed that copper is a necessary constituent of the blood in all animal life, and probably takes part in the respiratory process. Possibly the fat-soluble vitamin-A is a colloidal copper compound. A. A. E.

**Fats and Lipoids in Blood. II. Distribution of Fats and Lipoids in the Blood of Rabbits on a Vitamin-B-free Diet.** R. IWATSURU (*Pflüger's Archiv*, 1925, **208**, 41—48; from *Chem. Zentr.*, 1925, ii, 663; cf. A., 1924, i, 1126).—An increase occurs in

the fat content of the blood of rabbits, and of pigeons receiving food free from vitamin-*B*. The fat and lipin content of the blood-corpuscles does not vary appreciably from the normal. The same holds for the individual fractions of the lipins of the blood-corpuscles. The fat and lipin content of the serum is appreciably increased. The ester fraction of the cholesterol of the serum is increased relatively to the total cholesterol. G. W. R.

**Vitamin-*B* in the Excreta of Rats on a Diet Low in this Factor.** W. D. SALMON (*J. Biol. Chem.*, 1925, **65**, 457—462).—Rats kept on a diet deficient in vitamin-*B* may not show a normal response to this deficiency if they have access to their faeces; the apparent vitamin-*B* content of the latter is increased if the diet contains much indigestible matter; this is probably due to increased growth of the intestinal flora; the growth of moulds on the excreta does not increase the vitamin content of the latter. C. R. H.

**Concentration of Vitamin-*B*. II.** P. A. LEVENE and B. J. C. VAN DER HOEVEN (*J. Biol. Chem.*, 1925, **65**, 483—489).—The addition of a precipitation with basic lead acetate and recovery from the precipitate with sulphuric acid as a preliminary step to the precipitation with barium hydroxide previously described (A., 1924, i, 1272) led to a preparation containing 5.2% of nitrogen (calculated on the ash-free substance), which was physiologically active in amounts of 2—4 mg. per diem. Extraction of this preparation with silica gel yielded a product containing 80% of ash, 15% of nitrogen (on the ash-free substance); it gave negative reactions for protein and positive for pentoses; on hydrolysis it reduced Fehling's solution; it was active in daily doses of 0.1 mg. The product of the barium hydroxide precipitation could be largely freed from ash by precipitation with alcohol from strongly acid solution; such a preparation had C 40.0%, H 5.8%, N 4.1%, and was active in daily doses of 2.5 mg.; such ash-free preparations could not, however, be further purified so successfully by the silica method. C. R. H.

**Antineuritic Yeast Concentrates. I.** H. W. KINNERSLEY and R. A. PETERS (*Biochem. J.*, 1925, **19**, 820—826).—The acidified 50% alcoholic extract of "norit"-adsorbed vitamin from yeast (A., 1924, i, 1388) is successively precipitated with lead acetate, methyl and ethyl alcohols, and dialysed ferric hydroxide, and worked up with higher concentrations of alcohol until the active principle is dissolved in practically absolute alcohol. This fraction is precipitated with ether, and the ether fraction is treated with silver sulphate to remove further inactive material. The centrifugate, after being treated with silver nitrite in the presence of hydrochloric acid, is precipitated with ammoniacal silver hydroxide, which is extracted with hydrochloric acid and alcohol, yielding a preparation which cures and protects pigeons in doses of 0.084 mg. per day, but does not cause any increase in weight of the birds after the polyneuritic symptoms are cured. The authors use the expression "torulin" for this principle, and put forward a formula for estimating "torulin" activity. S. S. Z.

**Pellagra-preventive Action of Dried Beans, Caseinogen, Dried Milk, and Brewer's Yeast.** J. GOLDBERGER and W. F. TANNER (*U.S. Pub. Health Service Rep.*, 1925, **40**, 54—80).—The prevention and causation of pellagra involve a new factor, named *P—P*, which is present in brewer's yeast, milk, and lean meat, but scarcely, if at all, in dry soya beans, dry cow peas, butter, cod liver oil, or canned tomatoes. It may or may not be effective without the protein factor. CHEMICAL ABSTRACTS.

**Laboratory Apparatus for the Wet Grinding of Plant Tissues out of Contact with Air.** W. A. ROACH (*Biochem. J.*, 1925, **19**, 783—786).

**Energy Balance in Development of Various Vegetable Organisms and Oxygen Content of Medium.** E. F. TERROINE, R. BONNET, and A. HEE (*Compt. rend.*, 1925, **181**, 685—687; cf. this vol., i, 1117).—Addition of oxygen to the air above cultures of *Sterigmatocystis nigra*, and above seeds of lentil and black soya bean germinating in the dark does not affect the intensity of combustion in the organisms. L. F. H.

**Green Respiration Pigment of *Helianthus annuus*.** A. OPARIN (*Bull. Acad. Sci. St. Pétersbourg*, 1922, [6], 535—546; from *Chem. Zentr.*, 1925, ii, 728; cf. this vol., i, 1518).—Chlorogenic acid neutralised with ammonia absorbs 2 atoms of oxygen from the air and becomes green; neutralised with sodium hydroxide, it absorbs 3 atoms of oxygen and becomes brown. The calcium salt of the acid obtained after the oxidation of ammonium chlorogenate has the formula  $C_{32}H_{32}O_{19}Ca$  and thus contains 4 hydrogen atoms less than calcium chlorogenate. The oxidation is catalysed by phenolase or laccase. The oxidation of amino-acids in the presence of chlorogenic acid follows the equation  $R \cdot CH(NH_2) \cdot CO_2H + O \rightarrow R \cdot CHO + CO_2 + NH_3$ . In 2—4 days, 10—20% of the amino-acid nitrogen of glycine, alanine, leucine, arginine, aspartic acid, glutamic acid, tyrosine, phenylalanine, histidine, lysine, and proline are changed into ammoniacal nitrogen. Glycylglycine and alanylalanine are only oxidised slowly in the presence of chlorogenic acid. Oxalylaminoacetic acid and pyruvic acid are apparently among the products of oxidation. Peptone and globulin are oxidised even more slowly. G. W. R.

**Effect of Light on the Growth of Isolated Etiolated Bean Leaves.** W. PALLADIN (*Bull. Acad. Sci. St. Pétersbourg*, 1919, [6], 647—656, 959—990; from *Chem. Zentr.*, 1925, ii, 729—730; cf. this vol., i, 1518).—Data are given for the increase in weight of isolated bean leaves, in light and darkness respectively, floated on the surface of solutions of sucrose of varying concentration. In general, the increase in total weight is proportional to the increase in dry weight. It is concluded that there is a proportionality between increase in total weight and increase in protein both in light and in darkness, and that light affects protein synthesis only in so far as it affects growth generally. G. W. R.

**Effect of Light on the Growth and Formation of Chlorophyll in Isolated Etiolated and Green Leaves.** W. PALLADIN (*Bull. Acad. Sci. St. Pétersbourg*, 1922, [6], 547—568; from *Chem. Zentr.*, 1925, ii, 728—729).—Leaves of pumpkin, isolated at different stages in the growth of seedling plants, were placed in a dilute solution of sucrose in tap water. One series was kept in darkness and the other exposed to light. It was found that increase in weight was correlated with development of chlorophyll. The water content of the leaves increased rapidly after the first stages of their growth.

G. W. R.

**Variation of Protein Content of Maize. III.** H. B. ARBUCKLE and O. J. THIES, jun. (*J. Elisha Mitchell Sci. Soc.*, 1924, 40, 176—180).—Maize from N. Carolina, containing 6.82% of protein, when grown in W. Virginia contained in consecutive seasons 8.22% and 10.36%, respectively. Treatment with complete fertiliser or sodium nitrate raises the protein content, but not to an economic extent. The tip, middle, and butt of the ear of white cap maize contained, respectively, 9.29%, 9.46%, and 8.76% of protein.

CHEMICAL ABSTRACTS.

**Retrogressive Metamorphosis of Proteins in Germinating Seeds.** A. OPARIN (*Bull. Acad. Sci. St. Pétersbourg*, 1922, [6], 525—534; from *Chem. Zentr.*, 1925, ii, 727—728; cf. Oparin and Bach, A., 1924, i, 1276).—The oxidation of amino-acids according to the equation  $R\cdot CH(NH_2)\cdot CO_2H + O \rightarrow R\cdot CHO + CO_2 + NH_3$  was studied in the autolysis and germination of seeds. Oxidation was promoted by addition of "chlorogenic acid," and inhibited by exclusion of atmospheric oxygen. Crystalline globulin, after the action of the proteolytic ferment from sunflower seeds, yielded much more ammoniacal nitrogen in the presence than in the absence of chlorogenic acid. Sunflower seeds killed by chloroform and toluene yielded more ammoniacal nitrogen in the presence of chlorogenic acid and oxygen than in the absence of either of these. There was an increase in the amount of compounds of the type of oxalylaminoacetic acid in the presence of oxygen and chlorogenic acid. The formation of ammoniacal nitrogen and oxalylaminoacetic acid was greater in an atmosphere of oxygen than in an atmosphere of carbon dioxide.

G. W. R.

**Influence of Different External Factors on the Ash-content of Plants.** R. SEIDEN (*Landw. Versuchs-Stat.*, 1925, 104, 1—50).—A detailed study of the dry weight and ash-content of various parts of plants, in relation to such factors as light intensity, soil type, soil moisture, temperature, manurial treatment, etc. For a given plant, the ash-content of the leaves decreases with the distance from the base. In general, the ash-content is higher in dilute solutions than in stronger solutions of nutrient salts. Over a period of growth the ash-content of plants examined was at a maximum in August. The ash of plants grown in various soil types is largely influenced by the amount of nutrient salts in the

soil. Immersion of a plant in water decreases the ash-content and increases the percentage of silica, the variations in these two quantities being dependent on the length of time during which the plant is immersed. The significance of this fact in relation to irrigation and leaching and crops is discussed. O. O.

**Yield and Mineral Content of Crop Plants as Influenced by those Preceding.** P. S. BURGESS (*Rhode Island Agric. Exp. Sta. Bull.*, 1925, **198**, 4—25).—There is a correlation between the decrease in yield of mangolds and the increase in the acidity and active aluminium content of soils; mangolds from the more acid soils contain more aluminium and less phosphorus. Mangolds also remove much calcium and magnesium from the soil. Maize following mangolds absorbs more iron, aluminium, and acid constituents than when following maize, and the yield is less. The ash content of onions is greater when following mangolds than when following maize. CHEMICAL ABSTRACTS.

**Zymase Formation in Plants.** W. PALLADIN and W. ILLJUVIJEV (*Bull. Acad. Sci. St. Pétersbourg*, 1918, [6], 195—198).—*Aspergillus niger* was grown in a solution of quinic acid (3%) together with ammonium and potassium phosphates, magnesium, iron, and zinc sulphates. The mycelium and the juice from it evolved more carbon dioxide in the presence of sucrose, but only traces of alcohol. The *Aspergillus* contained none or only a trace of zymase. The edible pine mushroom was unable to ferment dextrose. In this case, the presence of chromogens may have an inhibitory effect. A. C.

**Fermentation of Dried Tobacco. I. Methods for Separating Nicotine and Ammonia. II. Enzymic Production of Volatile Products from Nicotine under the Influence of Tobacco-leaf Extracts.** A. FODOR and A. REIFENBERG (*Biochem. J.*, 1925, **19**, 827—829, 830—835).—I. The nicotine in the mixture of ammonia and nicotine obtained from tobacco leaves by direct distillation is precipitated by the addition of a solution of mercuric iodide in potassium iodide to the faintly acidified distillate. The filtrate is then treated with excess of potassium iodide, made alkaline, and the ammonia is distilled over and received into standard acid. The nicotine-nitrogen can be determined directly by the Kjeldahl method in the precipitate or indirectly by subtracting the ammonia-nitrogen from the total nitrogen of the mixture. This method does not eliminate any error that may accrue from distilling over from the tobacco volatile bases other than nicotine or ammonia.

II. Expressed juice and macerates of the tobacco leaf in various conditions produce by their enzymic activity on nicotine volatile nitrogen-containing bases. Expressed juice also possesses peptolytic activity. The nicotine probably decomposes with the production of pyridine, methylamine, and carbon dioxide. There is no evidence of the production of acid. S. S. Z.

**Behaviour of Saponins on Dialysis.** L. KOFLER and A. WOLKENBERG (*Biochem. Z.*, 1925, **160**, 398—406).—The following saponins were investigated and are placed in order of decreasing

rate of dialysis through parchment thimbles: digitonin, primulic acid, horse-chestnut saponin, sapotoxin, "saponin pur. albiss.," Sthamer saponin, powdered saponin, *Gypsophila* saponin, senegrin. The last two show no sign of dialysis after 8 days. This order corresponds approximately, but not completely, with their rate of absorption from the intestine (cf. Kofler and Schrutka, this vol., i, 1501). Saponins may be freed from mineral substances without loss of hæmolytic activity by electrodialysis. In the case of Sthamer saponin, "saponin pur. albiss.," and sapotoxin an increase of activity occurs. Electrodialysis is applied to the determination of saponins in lemonade. E. C. S.

**Galegine.** H. MÜLLER (*Z. Biol.*, 1925, **83**, 239—263).—An improved method of extracting galegine quantitatively based on its precipitation as the picrate is described. On methylating galegine trimethylethylguanidine results. The seed of *Galega officinalis*, the source of galegine, does not contain any free arginine. The *chloroaurate*,  $C_6H_{13}N_3HAuCl_3$ , m. p.  $156^\circ$ , and the *picrolonate*, which decomposed at  $254^\circ$ , were prepared. A new base, the constitution of which was not established, was also isolated from the seed. Galegine is present in the leaves of *G. officinalis*. When galegine is submitted to putrefaction, hydroxydihydrogalegine is produced. The pharmacological action of the hydroxy compound is the same as that of the base, but weaker. Yeast does not act on galegine. The base was recovered in the urine after a subcutaneous injection in goats. The stomach and milk of the animals showed the presence of questionable traces of galegine. Three other substances, possibly chemically related to galegine, were also isolated in pure condition from the urine in very small quantities. The presence of choline in the milk of the goats was established.

S. S. Z.

**Bromolecithins. I. Fractionation of Brominated Soya-bean Lecithins.** P. A. LEVENE and I. P. ROLF (*J. Biol. Chem.*, 1925, **65**, 545—549).—From the products of bromination of the lecithins of the soya bean were obtained a tetra- and a hexa-bromo derivative which, on hydrolysis with hydrochloric acid, gave tetra- and hexa-bromostearic acids, respectively. The result favours the hypothesis that ordinary lecithins are mixtures of several individual compounds. C. R. H.

**Occurrence of Dihydroxyquinolinecarboxylic Acid (the  $\beta$ -Acid of Suzuki) in Rice Husks.** Y. SAHASHI (*Biochem. Z.*, 1925, **159**, 221—234).—The  $\beta$ -acid of Suzuki (cf. A., 1912, ii, 980), obtained by acid hydrolysis of crude oryzanin, is shown to have the empirical formula  $C_{10}H_7O_4N$ , (mol. wt. from analysis of salts, 205), and by the preparation of salts, esters, acetyl, benzoyl, and bromo derivatives the presence of two hydroxyl and one carboxyl groups is deduced. Oxidation with nitric acid, gives juglonic acid (4:6-dinitro-3-hydroxy-*o*-phthalic acid) and oxalic acid. Heating with zinc dust in a sealed tube gives quinoline (identified as the picrate).

The  $\beta$ -acid is therefore formulated as either 3:6- or 2:6-dihydroxyquinoline-5-carboxylic acid.

P. W. C.

**Presence of  $\beta$ -Methylglucoside in the Leaves of *Scabiosa succisa*, L. (Dipsacæ).** N. WATTIEZ (*Bull. Soc. Chim. biol.*, 1925, 7, 917—924).—The leaves of *Scabiosa succisa*, L., contain scabioside and  $\beta$ -methylglucoside which has been isolated in the crystalline state.

H. J. C.

**Constituents of *Myoporum laetum*, Forst. (the "Ngaio").** I. F. H. McDOWALL (*J. Chem. Soc.*, 1925, 127, 2200—2207).—*Myoporum laetum*, Forst. (New Zealand), contains mannitol in the leaves (0.2%), wood (0.25%), and berries (which also contain formic acid). The leaves and terminal branchlets yield on distillation with superheated steam 0.12—0.3% of an oil, containing 0.01% of a paraffin hydrocarbon,  $C_{32}H_{66}$  or  $C_{34}H_{70}$ , m. p. 62—63°, the residual oil, after removal of stearoptene, having  $d_{20}^{20}$  1.0203,  $[\alpha]_D -26.54^\circ$ ,  $n_D^{20}$  1.4823, saponification value 17.9, and containing 86% of an oxygenated sesquiterpene ketone, *ngaione*,  $C_{15}H_{22}O_3$ , lemon-yellow oil, b. p. 188°/29 mm. (corr.),  $d_{20}^{20}$  1.0273,  $[\alpha]_D -26.20^\circ$ ,  $n_D^{20}$  1.4794, probably an open-chain diolefinic ketone having two separate oxide rings [*p*-nitrophenylhydrazones, m. p. 103°; *semicarbazone*, m. p. 120—122° (decomp.); *oxime*, lemon-yellow oil, b. p. 201°/27 mm.,  $d_{20}^{20}$  1.0640,  $[\alpha]_D -13.51^\circ$ ,  $n_D^{20}$  1.5008; the *thiosemicarbazone* and other derivatives are liquid]. Reduction of *ngaione* with sodium and alcohol yields the corresponding secondary alcohol, *ngaiol*, a lemon-yellow oil, b. p. 195—196°/29 mm. (corr.),  $d_{20}^{20}$  1.0163,  $[\alpha]_D -25.00^\circ$ ,  $n_D^{20}$  1.4784 [*acetate*, b. p. 190—192°/29 mm.,  $d_{20}^{20}$  1.0337,  $n_D^{20}$  1.4720; *monomethyl ether*, b. p. 182°/29 mm. (corr.),  $d_{20}^{20}$  0.9913,  $[\alpha]_D -16.82^\circ$ ,  $n_D^{20}$  1.4701; *methyl xanthate*; all these derivatives are liquid].

B. F.

**Volatile Constituents of Valencia Orange Juice.** J. A. HALL and C. P. WILSON (*J. Amer. Chem. Soc.*, 1925, 47, 2575—2584).—After several fractional distillations under 120 mm. and finally in steam, the product was extracted with ether. The aqueous solution contained formic acid, acetone, acetaldehyde, and ethyl alcohol. The ether extract from 39,085 litres of juice yielded 182 g. of oil,  $\alpha_D^{20}$  (1-dm. tube) +25.76°,  $n_D^{20}$  1.4691,  $d_{20}^{20}$  0.8866, ester value (aldehyde-free oil) 8.4, ester content 2.71%. From this oil citronellal (0.5%) was isolated. The residual oil was hydrolysed and steam-distilled and in the distillate *iso*(?)amyl alcohol, phenylethyl alcohol, an *alcohol*,  $C_{10}H_{18}O$  (of unknown constitution and forming 90% of the water-insoluble constituents), and possibly terpineol and geraniol were detected. The potassium salts of the acids were acidified and distilled, and *n*-octoic, formic, and acetic acids detected in the product, these acids being present as esters in the original juice.

J. W. B.

**Composition of Palestine Olives and their Oil.** F. MENCHIKOWSKY (*Zionist Organ. Inst. Agric. Exp. Sta. Bull.*, 1924, 2, 3—17).—For the flesh of olives, the following minimum, maximum, and

average values were obtained: moisture, 19.1, 55.55, 37.51; fat, 23.82, 51.14, 38.19; protein, 1.37, 2.72, 1.8; ash, 1.02, 2.35, 1.92%. The oil gave the following minimum and maximum values:  $d^{15}_{20}$  0.916, 0.918; saponification number, 187.5, 191.9; Reichert-Meissl number, 0.46, 1.84; iodine number, 81.75, 88.41; iodine number of liquid acids, 93.42, 106.6; percentage of liquid acids, 85.56, 94.23; percentage of solid acids, 5.77, 13.42. CHEMICAL ABSTRACTS.

**Insecticidal Principle of *Chrysanthemum cinerariaefolium*.** R. YAMAMOTO (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1925, **3**, 193—222; cf. Fujitani, A., 1909, ii, 825; Staudinger and Ruzicka, A., 1924, i, 510, 700, 758).—An account of work previously described (cf. A., 1919, i, 465; 1923, i, 1010; 1924, i, 1151). L. F. H.

**Plant Phosphatides.** V. GRAFE (*Biochem. Z.*, 1925, **159**, 444—448).—A short survey of some recent work. The author is of opinion that the phosphatides and cerebrosides of the plant cell are the mother substances of vitamins. H. D. K.

**Water-soluble Phosphatides from the Root of the Sugar Beet.** I. V. GRAFE and V. HORVAT (*Biochem. Z.*, 1925, **159**, 449—467).—A phosphatide may be separated from sugar beet by allowing the sliced root to remain in distilled water for 24 hrs., evaporating this extract in a vacuum, and finally precipitating with excess of lead acetate solution. Analyses have been carried out on the lead salt. From the phosphatide, oleic acid, palmitic acid, choline, and glycerophosphoric acid have been separated and identified. The N:P ratio is 1:2. The molecule appears therefore to be a double one, with a total mol. wt. of 2243.

From the solution which remains after filtering off the lead precipitate, a second phosphatide may be separated by removing the lead, evaporating the filtrate, and precipitating with a large excess of alcohol. This yields a less pure substance, which has been shown to contain a fatty acid, glycerophosphoric acid, and choline. It is possibly the same phosphatide as that precipitated by lead acetate, slightly "denatured" by the preliminary operations.

H. D. K.

**Composition of Potato Tubers.** J. J. WILLAMAN and R. M. WEST (*Minnesota Studies Plant Sci.*, 1924, No. 5, 211—227).—A statistical study. Environmental effects predominate, but early and late maturing varieties differ in that the former are low in dry matter and high in ether extract, mineral substances, and nitrogen. At the same stage of maturity the size of the tuber has no influence on the composition. The nitrogen content is correlated with values for the carbohydrate, ash, and ether extract.

CHEMICAL ABSTRACTS.

**Plant Diseases. VI. *Fusarium lini*, Bolley.** A. K. ANDERSON (*Minnesota Studies Plant Sci.*, 1924, No. 5, 237—280).—The  $p_H$  range for good growth is 3.5—9.5, acidity developing during growth due



chiefly to the production of carbon dioxide. The dry matter produced on media with potassium nitrate, aspartic acid, urea, asparagine, and ammonium sulphate as the only sources of nitrogen decreases in that order. Growth is good with dextrose, lævulose, galactose, mannose, xylose, sucrose, maltose, lactose, soluble starch, or inulin as the only source of carbon, the products of metabolism on dextrose being mainly carbon dioxide and ethyl alcohol, with traces of succinic acid and glycerol. The ratio of carbon dioxide to ethyl alcohol is nearly that of a typical yeast fermentation, but usually high on account of the utilisation of the latter as a source of carbon. The same substances are the main products of metabolism when (slower) growth takes place on xylose, but the proportions differ. *Fusarium lini* grows on ethyl alcohol as the only source of carbon, carbon dioxide being the main by-product, the  $p_H$  reaching 2.57. Succinic acid also serves as a source of carbon. On dextrose, the carbon in the mycelium increases, and the nitrogen decreases with age, but on xylose there is scarcely any change. On ethyl alcohol, the percentage of nitrogen in the mycelium is greater than when dextrose or xylose is the sole source of carbon. CHEMICAL ABSTRACTS.

**Silage, its Composition and Value as a Farm Food.** G. N. BLACKSHAW (*Rhodesia Agric. J.*, 1925, **22**, 191—201).—Values are tabulated of the water (64.7—87.5%), fat (0.2—3.3%), crude protein (1.4—6.6%), true protein (0.86—3.71%), carbohydrate (6.2—17.0%), fibre (1.8—11.5%), and ash (1.7—3.5%) content of the silage prepared from twenty different materials. CHEMICAL ABSTRACTS.

**Soil Potassium as Affected by Fertiliser Treatment and Cropping.** J. W. AMES and R. H. SIMON (*Ohio Agric. Exp. Sta. Bull.*, 1924, **379**, 185—212).—The supply of active potassium is gradually depleted where large yields have been produced by addition of lime and acid phosphate; addition of sodium nitrate slightly increases the amount of water-soluble potassium. Potassium chloride, but not potassium in stable manure, increases the amount of potassium in the subsoil. Calcium sulphate, sodium nitrate, ammonium sulphate, and monocalcium phosphate in 2% solutions increased the solubility of potassium in silt loam, clay loam, and clay soils which were unfertilised or fertilised with potassium. CHEMICAL ABSTRACTS.

**Effect of Cropping on the Active Potash of the Soil.** G. S. FRAPS (*Texas Agric. Exp. Sta. Bull.*, 1924, **325**).—The active potassium (that dissolved by 0.2N-nitric acid) is decreased when crops are grown on the soil. About 40.9% of the potassium is removed by crops grown with addition of dicalcium phosphate and ammonium nitrate. The correlation factor between the potassium removed by the crops and the active potassium lost from the soil is  $0.722 \pm 0.016$ . CHEMICAL ABSTRACTS.

**Physiological Reactions of Manuring Salts.** H. KAPPEN and M. LUKACS (*Z. Pflanz. Düng.*, 1925, **5 A**, 249—270).—From experiments on seedlings in water- and sand-cultures the facts

that inorganic nitrates are physiologically alkaline and ammonium salts physiologically acid are confirmed. For the seedlings used, the residual acidity was highest for maize, lowest for mustard, and intermediate for buckwheat. In a physiologically alkaline solution in which maize is growing, the acidity gradually decreases up to the 15th day, after which a slight increase sets in. In a physiologically acid solution, the acidity increases up to about the 18th day. Ammonium nitrate may be either acid or alkaline in this respect. The methods by which plant roots take up nutrients to produce such changes in reaction are discussed from the point of view of the electrolytic dissociation theory. O. O.

**Nitrogen Fixation in the Punjab.** P. E. LAUDER and B. ALI (*Mem. Dept. Agric. India, Bacter. Series*, 1925, 2, 1—28).—Punjab soils can fix large quantities of atmospheric nitrogen without the addition of carbohydrate. Under certain conditions, considerable losses of nitrogen may occur. The conditions which favour losses of nitrogen are not exactly known, but heavy soils show greater losses than light soils: light soils have the greater power of nitrogen fixation. Under ordinary cultural conditions, rapid depletion of soil nitrogen is unlikely. G. W. R.

**Determination of the Phosphorus Requirements of Soils.** M. J. VAN DER SPIJ (Z. Pflanz. Düng., 1925, 5A, 281—325).—The author has attempted to correlate response to phosphatic fertilisers in pot experiments, using oats and rye, with the total phosphorus, and phosphorus soluble in different solvents for a number of soils. Neither the total phosphorus content of soils nor the content of phosphorus soluble in 10% hydrochloric acid can be correlated with their requirements for phosphatic fertilisers. The ratio of phosphorus soluble in 0.5% citric acid to total phosphorus or to phosphorus soluble in 10% hydrochloric acid gives the best correlation with the phosphorus requirements of the soils examined. Good results are also obtained when 1% citric acid or 0.2N-nitric acid is used as extracting solvent. No satisfactory correlation was observed between response to phosphatic dressings and increase in the phosphorus content of plants consequent on such dressings. G. W. R.

**Availability of Phosphorus in Calcareous and Non-calcareous Soils.** J. W. AMES and C. J. SCHOLLENBERGER (*Ohio Agric. Exp. Sta. Bull.*, 1924, [380], 215—242).—Lime has little effect on the availability of either native or added phosphorus. With oats, the differences in phosphorus content attributable to fertilisation become less as the age of the plant increases. After 8 yrs. in cylinders, the soils became much more acid; the organic phosphorus was higher in unlimed soil than in the original soil.

CHEMICAL ABSTRACTS.

**Hydrogen Peroxide Catalase of Marsh Soils.** L. SMOLÍK (*Proc. Intern. Soc. Soil Sci.*, 1925, [ii], 1, 6—12).—In the subsoils

examined, the hydrogen peroxide catalase, the hygroscopicity, and the constant and variable hydrogen-ion concentration increased with the depth; soils having the greatest catalytic power showed a higher constant  $p_H$  value and a higher calcium carbonate content. The loss of catalytic power on heating at various temperatures was studied, the results showing irregularities. CHEMICAL ABSTRACTS.

**Acidity of Soils.** D. J. HISSINK and J. VAN DER SPEK (*Chem. Weekblad*, 1925, **22**, 500—501).—The acidity of soils is ascribed to hydrogen ions present in electrical double layers which exist round colloidal particles of clay acids and humus acids in the presence of water. The clay acids are weak acids, but the humus acids include some of considerable strength. S. I. L.

**Exchangeable Acidity of the Soil and the Relation between Actual and Titratable Acidity.** H. NIKLAS and A. HOCK (*Z. Pflanz. Düng.*, 1925, **5A**, 370—392).—The rôle of aluminium in soil acidity is discussed in detail. Exchangeable acidity is associated with the concentration of aluminium salts. From analysis of curves already described (this vol., i, 768) the  $p_H$  of soils is calculated, and this value, for a large number of soils, agrees with the value found by electrometric and colorimetric methods. Forest soils do not show such good agreement. O. O.

**Influence of Individual Factors on the Reaction of the Soil Solution.** E. W. BOBKO and D. W. DRUSCHININ (*Z. Pflanz. Düng.*, 1925, **5A**, 345—369).—In the preparation of aqueous soil extracts for  $p_H$  determinations the relative amounts of soil and water used have but little effect on the  $p_H$  up to a soil : water ratio of 1 : 25. In unlimed soils increase in the amount of water used caused slight diminution in  $p_H$ . In limed soils, the reverse holds. The soil solution of limed soils has a higher  $p_H$  than has an aqueous extract, and in unlimed soils the reverse occurs. The titratable alkalinity of a soil extract is directly proportional to the  $p_H$  of the extract. Assuming that titratable acidity = free  $\text{CO}_2$ , and titratable alkalinity =  $[\text{HCO}_3']$ , then  $p_H$  values calculated from the formula  $p_H = \log [\text{HCO}_3'] - \log [\text{CO}_2] + 6.52$  agree with those found experimentally for most limed soils. For unlimed soils and those rich in humus, the  $p_H$  values calculated in this way were higher than the experimental values.

In extracts of limed soils only does removal of free carbon dioxide increase the  $p_H$ . The buffer system  $\text{CO}_2 + \text{HCO}_3'$  changes to the system  $\text{HCO}_3' + \text{CO}_3''$ . In this case  $p_H$  calculated from the formula  $[\text{H}'] = [\text{HCO}_3'] \times 0.10^{-11} / [\text{CO}_3'']$  is in good agreement with the observed values.

These facts are explained on the assumption that the buffer system of the soil solution contains acids with higher dissociation constants than that of carbon dioxide. Such acids can only be organic acids. O. O.

**Influence of Neutral Salts on Soil Reaction.** O. ARRHENIUS (*Proc. Intern. Soc. Soil Sci.*, 1925, [ii], **1**, 24—33).—With increasing

concentration of neutral salt solutions in contact with an acid loam, an alkaline loam, a sandy soil, and a peat an increase of the hydrogen-ion concentration and titratable acidity of the extracts was observed, but not as a direct function of the concentration. Hence "potential acidity" is not a function of adsorption. The determination of the hydrogen-ion concentration of soils by the use of potassium chloride solution instead of water for the measurement of potential acidity, lime requirement, and the effect of fertiliser is untrustworthy as a measure of the acidity of the soil.

CHEMICAL ABSTRACTS.

**Hydrogen-ion Concentration of Soils as Affected by Carbon Dioxide and by the Soil : Water Ratio, and the Nature of Soil Acidity.** W. H. PIERRE (*Soil Sci.*, 1925, **20**, 285—305).—Neither the presence of the roots of actively growing plants nor the passage of carbon dioxide through the soil affects the  $p_H$  value of the displaced soil solution, soils being strongly buffered to carbon dioxide. The  $p_H$  of some soils, especially very acid ones, varies with the soil : water ratio used in making the suspensions; others show no variation. When soils which exhibit this difference are thoroughly leached and most of the soluble salts and acids removed, they no longer show any such variation. These observations support the mineral acid theory of soil acidity, since the solution will be saturated with respect to the relatively insoluble soil acids even at widely varying soil : water ratios. Data are recorded indicating that the hydrogen-ion concentration of a filtered soil extract or displaced soil solution determined by the colorimetric method agrees well (provided certain conditions are observed) with the figure obtained electrometrically with a suspension of the same soil.

C. T. G.

**Significance of the Carbon Dioxide of the Soil and of the Atmosphere in Agriculture.** E. H. REINAU (*Z. Pflanz. Düng.*, 1925, **5A**, 393—395).—A reply to various criticisms of the author's earlier work.

O. O.

**Comparison of Methods for the Determination of Hydrogen-ion Concentration in Soils.** H. NIKLAS and A. HOCK (*Landw. Versuchs.-Stat.*, 1925, **104**, 87—91).—The  $p_H$  values of soils as found by using nitrophenols as indicators and by Clark and Lubs' technique show reasonable agreement with each other and also with electrometric measurements.

O. O.

**Significance of Electrometric Titration in the Estimation of the Lime Requirements of Soils.** H. NIKLAS and A. HOCK (*Landw. Versuchs.-Stat.*, 1925, **104**, 93—102).—Further discussion of curves already described (this vol., i, 768).

O. O.

**Composition of the Soil Solution as Indicated by the Displacement Method.** J. C. MARTIN and J. S. BURD (*Calif. Sta. Rept.*, 1923, 174—176).—A modification of the Parker displacement method, using an apparatus which is illustrated, produced soil

solutions for analytical purposes apparently in the same condition in which they existed in the soil. CHEMICAL ABSTRACTS.

**Concentration of Phosphate in the Soil Solution according to the Displacement Method.** J. C. MARTIN and J. S. BURD (*Calif. Sta. Rept.*, 1923, 173).—Soil solutions, displaced after the initial displacement solutions ceased to give uniform concentrations, showed a rise in concentration of phosphate when the concentration of certain other electrolytes was lowered. CHEMICAL ABSTRACTS.

**Percolation of Water through Soils.** E. V. WINTERER (*Calif. Sta. Rept.*, 1923, 234—236).—The amount of colloidal material leached from soil varies directly with the rate of percolation of water. Treatment with dilute solutions of copper sulphate and formaldehyde increased the rate of percolation. The rate through gravel was twelve times greater than through loam. CHEMICAL ABSTRACTS.

**Moisture Relationships of Soils.** M. M. MCCOOL and A. W. WEIDEMANN (*Soil Sci.*, 1925, 20, 243—247).—When a solution of sucrose is brought into contact with different soils and soil fractions, the concentration of the solution is increased as measured by freezing-point determinations, indicating that water is removed from the solution. A soil dried at 55° or 100° removes considerably more water than the same soil kept at the ordinary temperature. This is considered to be additional evidence that soils are capable of holding appreciable amounts of water in an "unfree" condition (cf. Bouyoucos, *Mich. Agric. Exp. Sta.*, 1916—1918, *Tech. Bulls.*, 31, 36, 42). C. T. G.

**Relation of Biological Processes to Concentration of Cations in Soils.** J. S. BURD (*Soil Sci.*, 1925, 20, 269—283).—Studies are reported on the effect of time and various treatments on the concentration and composition of the liquid phase of soil from which the original soil solution has been removed by displacement with water (cf. Burd and Martin, A., 1924, i, 1396). After initial displacement of an amount of liquid equivalent to the total water in the sample of soil used, a second (and in some cases a third and fourth) displacement was carried out. Examination of successive portions of the displaced solutions showed that, when the soils were kept undisturbed and saturated with water, *i.e.*, under conditions such that biological activities were absent or reduced to a minimum, there was a definite increase of concentration due to the inherent solubility of the solid material. The total concentration of the liquid phase of such depleted soils remained, however, very low. On the other hand, when the soils were removed from the tubes after the initial displacement and kept under aërobic conditions, the total concentration of the liquid from later displacements was very greatly increased. Further, it is shown that biological oxidations resulting in substantial increases in the concentration of nitrates and sulphates tend in general to increase the total con-

centration of the soil solution and, in effect, determine the concentration of cations as well as of anions. Under anaërobic conditions (favouring reduction processes), there is a great decrease of nitrates without an equivalent decrease in concentration of cations, the loss being compensated for by increase of hydrogen carbonate ion. These changes are very similar to those occurring in cropped soils.

C. T. G.

**Influence of the Amount and Nature of the Replaceable Base on the Heat of Wetting of Soils and Soil Colloids.** W. W. PATE (*Soil Sci.*, 1925, **20**, 329—335).—Saturation of a soil, or of colloidal material extracted from it, with a univalent base lowered the heat of wetting. Saturation with a bivalent base had no very marked effect. Comparing the extracted colloids from different soils, it is shown that the heat of wetting can be positively correlated with the amount of replaceable base in the colloid (cf. Bouyoucos, this vol., i, 1228).

C. T. G.

**What is Humus?** S. A. WAKSMAN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 463—468).—On adding excess of hydrochloric acid to a 5% sodium hydroxide extract of soil, a precipitate, nearly ash-free and containing 2.5—3.5% of nitrogen, is obtained: this fraction is soluble in alkalis and reprecipitated by acids. The filtrate from this fraction, on neutralisation with sodium hydroxide, yields a precipitate soluble in acids and alkalis, and quantitatively precipitated from solution at  $p_H$  4.8. It contains 30—50% of ash and about 1% of nitrogen, and to it the buffering properties of the soil are due.

H. J. C.

**"Hager" Soils.** E. KNICKMANN and M. HELBIG (*Z. Pflanz. Düng.*, 1925, **5 A**, 209—248).—The term "hager" is applied to a forest humus soil of low fertility and in which humification is retarded by the action of wind and sun. The results of a comprehensive physical and (inorganic) chemical examination of such a soil are given as compared with a normal forest soil. The "hager" soil is richer in humus and has a higher water capacity than the normal soil. The texture of the "hager" soil is more uniform than that of the normal soil in which the subsoil is richer in the finer soil particles. The solubility in hydrochloric acid and the nitrogen content are both lower for the "hager" soil than for the normal soil. In both cases, the humus is acid, the acidity being highest in the "hager" soil and lowest in the normal subsoil.

O. O.

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# ABSTRACTS

ISSUED BY THE

## BUREAU OF CHEMICAL ABSTRACTS.

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### A. PURE CHEMISTRY.

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#### PART II.

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#### [General, Physical, and Inorganic Chemistry.]

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**Experimental Test of the Theory of Bohr, Kramers, and Slater.** W. BOTHE and H. GEIGER (*Z. Physik*, 1924, 26, 44).—An experimental test of the theory of Bohr, Kramers, and Slater (cf. A., 1924, ii, 433, 509) is suggested. On the basis of the Compton theory of X-ray scattering, the simultaneous production of scattered radiation and of the electron associated with it is necessitated. According to the proposed theory, no such simultaneity should be observed. As the scattered radiation and the electron have not the same direction, it should be possible to record their production by two Geiger counters, and to detect any statistical connexion between the two events. S. B.

**Extension of Bohr's Correspondence Principle to Small Quantum Numbers.** P. W. KETCHUM (*Physical Rev.*, 1924, 24, 463—465).—When an electron falls spirally from an orbit of quantum number  $n_2$  to one of  $n_1$ , the frequency of the radiation emitted is an integral ( $n_2 - n_1$ ) multiple of the mean frequency of rotation in its orbit during the spiral motion, assuming that the number of rotations made for a change of quantum level  $dn$  is proportional to  $dn$ . A. A. E.

**Simultaneous Jumping of Two Electrons in Bohr's Model.** P. S. EPSTEIN (*Proc. Nat. Acad. Sci.*, 1924, 10, 337—342).—A theoretical discussion of the abnormal triplet series in calcium discovered by Russell and Saunders. The series is  $1p - mp'$ , and the frequencies of the third and of all successive members of the series are greater than the frequency of the normal series limit for the return of an electron to the  $1p$  orbit. The excess energy required for the emission of these lines is supposed to be derived from orbital changes of a second electron. The author shows by

consideration of a simplified model that such series are compatible with the principle of correspondence, and are due to the coupling of the electrons within the atom. Such coupling is shown to modify the selection rules so that the azimuthal quantum number of an electron may change by two, or the quantum number of two electrons may simultaneously change by unity. S. B.

**Constants of the Rydberg-Ritz Equation.** J. H. JONES and J. C. BOYCE (*Proc. Roy. Soc.*, 1924, A, 106, 773—784).

**Atomic Force Fields.** F. S. BRACKETT (*J. Opt. Soc. Amer.*, 1924, 9, 237—249).—Regularities have been traced in the variation with atomic number of the energies of inner virtual orbits. These are correlated with changes in the quantum defects for the same elements. The assignment of quantum numbers due to Brackett and Birge is confirmed. S. B.

**Relations between the Optical Spectra of Different Atoms of the Same Electron Structure. I. Lithium-like and Sodium-like Atoms.** D. R. HARTREE (*Proc. Roy. Soc.*, 1924, A, 106, 552—580).—General theoretical relations of a quantitative nature are given based on the Bohr atom.

Comparison with experimental results on the line spectra of a number of elements is effected by a computation of a quantity known as the "term excess" which is given by the difference between the wave number corresponding with the energy term of the orbit under consideration and the wave number of the corresponding term of the hydrogen-like atom of the same core charge.

The observed values of the "term excess" for sodium-like and lithium-like atoms which remain entirely outside the core agree very closely with a relation of the type indicated by the theory. For orbits which penetrate the core values are found which agree roughly with the values deduced from observed spectra. R. W. L.

**Spectra of some Lithium-like and Sodium-like Atoms.** D. R. HARTREE (*Proc. Camb. Phil. Soc.*, 1924, 22, 409—425).—The argument on the interpretation of the experimental results (cf. preceding abstract) is treated in considerable detail. R. W. L.

**Optical Constants of Matter.** C. G. DARWIN (*Trans. Camb. Phil. Soc.*, 1924, 23, 137—167).—An analysis of the refraction, reflection, and absorption of light in their relation to the simple phenomenon of scattering without having recourse to any atomic theory, thereby obviating the difficulties that are inherent in the application of the laws of classical thermodynamics to electrons. The results, it is claimed, of this analysis are not to be construed in any sense as in opposition to the classical electron theory; they merely represent an extraction from that theory of the parts which may be regarded without any distrust.

A number of typical results of the application of the analysis now advanced is appended to the paper. R. W. L.

**Optical Separations and Atomic Numbers.** A. C. MENZIES (*Nature*, 1924, 114, 861).—The relativity X-ray formula  $d\nu = K(Z-s)^4$



(cf. Millikan and Bowen, A., 1924, ii, 710) has been applied to doublets and triplets generally, and the values of  $s$  have been tabulated. The values within the same group are directly proportional to the atomic number, and the slopes of the graphs are very nearly the same for all groups. A. A. E.

**Controlled Orbital Transfers of Electrons in Optically Excited Mercury Atoms.** R. W. WOOD (*Proc. Roy. Soc.*, 1924, A, 106, 679—694).—The fluorescence of mercury vapour has been studied. The exciting radiation was from a water-cooled mercury arc. The atoms are primarily excited by absorption of the line at 2536 Å., and an electron is thereby raised to the  $2p_2$  orbit. It is raised to higher levels by subsequent absorption of other lines, and the fluorescent light indicates the return path of the electron to the  $1S$  orbit. Addition of nitrogen and other gases has remarkable effects on the phenomena. Nitrogen causes the excited vapour to absorb 4046 ( $2p_3-2S$ ) strongly, and an intense emission of 5461 ( $2S-2p_1$ ), and also other changes. Many other effects of mixtures are recorded. S. B.

**Anomalous Zeeman Effects.** W. HEISENBERG (*Z. Physik*, 1924, 26, 291—307).—To explain the phenomena of the complex Zeeman effects and other phenomena due to the coupling of several electrons, it is necessary to introduce a further quantum restriction on the value of the coupling energy. S. B.

**Spectral Theory and the Origin of the "Nebulium" Lines.** S. ROSSELAND (*Nature*, 1924, 114, 859—860).—A theoretical consideration of the possibility that the nebulium spectrum may be due to helium. The assumption of a metastable state of hydrogen would harmonise with observations on nebulae, but the nebular lines can scarcely be ascribed to a molecular compound of hydrogen and helium. A. A. E.

**Sommerfeld's and Landé's Rules for Classification of Terms and Zeeman Patterns in Spectra.** W. M. HICKS (*Phil. Mag.*, 1924, [vi], 48, 1036—1048).—Contains a suggested change in form of the enumeration of species of term types and the rules for predetermination of Zeeman patterns, and the discussion of the evidence for and against a rule, accepted by Landé, supposed to give the ratios of the separations in multiplets. C. W. B.

**Doppler Effect in Canal Rays from Hydrogen, Oxygen, and Nitrogen.** H. KREFFT (*Ann. Physik*, 1924, [iv], 75, 75—107).—Canal rays generated in one chamber were passed into another containing gas at a lower pressure than the first, as in the method of Wien (*Physikal. Z.*, 1910, 11, 377), producing light by collision, and the Doppler effect of this was studied in relation to the potential difference across the discharge tube. Contrary to previous reports, no limiting velocity was found. The relation of the velocities of the extinction maxima are discussed and also the effect of changing the gases in the chambers. By the use of an electromagnetic field, it is shown that the spark lines of oxygen and nitrogen are

produced from singly positively charged atoms, whilst the arc and series lines probably originate from neutral atoms. With the highest velocities, indications of doubly charged oxygen atoms are obtained.

L. J. H.

**Series Regularities in the Spark Spectrum of Nitrogen.**

C. C. KIESS (*Science*, 1924, 60, 249).—Lines in the red and infra-red regions of the arc spectra of metals in air have been identified as spark lines of nitrogen. The sensitive lines result from combinations of a triple *P* term with an *S* term, another triple *P* term, and a five-fold *D* term. The series regularities given in a table are of odd multiplicity (quintet system) and therefore belong to the spark spectrum of nitrogen.

A. A. E.

**Fine Structure of the Helium Line 5876 Å.**

L. S. ORNSTEIN and H. C. BURGER (*Z. Physik*, 1924, 26, 57—58).—The relative intensities of the two components of the yellow helium line 5876 Å. are 1 : 6. If the line is a normal doublet of the type  $2\pi-3\delta$ , the relation should be 1 : 2. It is concluded that the line is probably either an intercombination of two singlet terms or a multiplet of a new type.

S. B.

**Structure of the Iron Spectrum. II.**

O. LAPORTE (*Z. Physik*, 1924, 26, 1—22).—A continuation of previous work (*A.*, 1924, ii, 364). Septet terms have been identified, and their inter-combinations with the fundamental *d*-term of the iron spectrum. Additional triplet and quintet terms have been found. Complete tables are given. A quarter of the total number of iron lines have now been assigned orbital transitions.

S. B.

**Pole Lines occurring in the Interrupted Arc Spectra of Silver, Gold, and Copper.**

H. LOWERY (*Phil. Mag.*, 1924, [vi], 48, 1122—1131).—Spectroscopic observations have been made of the silver, gold, and copper arcs produced under conditions similar to those of Hemsalech and the Comte de Gramont (*A.*, 1922, ii, 176, 410). In the regions studied, 5220 to 3380 Å., a number of lines have been found in the neighbourhood of the fixed pole which readily fall into two classes according as they cease abruptly at the end of the initial stages of the arc flash or tend to pass on into the intermediate and final stages. Most of the lines have been identified with previously observed arc and spark lines, but a number of them do not seem to have been previously recorded. Lists of the "new" lines occurring in the region 5220 to 3380 Å. are given.

C. W. B.

**Spark Spectrum of Cæsium.**

L. A. SOMMER (*Ann. Physik*, 1924, [iv], 75, 163—181).—The spark spectrum of cæsium has been carefully measured from 3268—7280 Å. The series lines of the arc spectrum were measured at the same time:  $2p_2-2p_1=554.038\text{ cm.}^{-1}$ , in good agreement with Meissner's value (*A.*, 1921, ii, 565). The series lines of the spark spectrum ( $\text{Cs}^+$ ) are evidently too widely spaced for three or more members of the same series to be included in the region studied. Two groups of lines (51) have

been analysed for constant differences and can be arranged into a scheme similar to that of Landé for neon (A., 1921, ii, 669) and to that obtained from an analysis of the lines of xenon. These analogies afford qualitative confirmation of the Sommerfeld-Kossel displacement law.

L. J. H.

**M-Series of Tungsten.** R. THORAEUS (*Z. Physik*, 1924, 26, 396—399).—The wave-lengths of the *M*-series of tungsten have been measured. The measurement of such long wave-lengths was made possible by the substitution of a red celluloid window in the X-ray tube, in the place of a metal foil.

S. B.

**Series Limit Absorption in Sodium Vapour.** G. R. HARRISON (*Physical Rev.*, 1924, 24, 466—477).—As the wave-length decreases, the transmission of sodium vapour rises to a maximum at 2465 Å., decreases regularly to a minimum at the series limit 2414 Å., and returns to its former value at 2200 Å. Eighteen similar curves were obtained for different vapour densities. The results, however, do not permit determination of the precise variation of atomic absorption with wave-length.

A. A. E.

**Absorption and Dispersion of Thallium Vapour.** A. L. NARAYAN, D. GUNNAIYA, and K. R. RAO (*Proc. Roy. Soc.*, 1924, A, 106, 596—601).—Thallium vapour in the non-luminous state absorbs lines of the sharp and diffuse series and the  $1, \pi_2$  orbit is the ground-orbit of the valency electron. At about  $900^\circ$ , a large number of bands of diffuse and complex structure make their appearance, which are attributed to  $Tl_2$  molecules. The infra-red absorption shows no selectivity in the region  $0.9 \mu$  to  $1.35 \mu$ , and therefore  $1, \pi_2 - 1, \pi_1$  is not the single-line spectrum of the metal. The work of Geisler and of McLennan on the anomalous dispersion exhibited at 5350.6 Å. has been confirmed. Anomalous dispersion is, however, more prominent at 3775.7 Å.

R. W. L.

**Relative Absorbing Powers of the *L*-Levels for Radiation of Varying Wave-length.** H. W. B. SKINNER (*Proc. Camb. Phil. Soc.*, 1924, 22, 379).—Measurements of the absorbing power were made by a new method, which consists in recording photographically by a Secman spectrograph the relative intensities of the fluorescent *L*-spectrum of cerium excited by the *K*-radiations of copper, molybdenum, and silver.

The results are held to confirm the work of Robinson (cf. A., 1923, ii, 818) on the relative absorbing powers of the *L*-levels, and to indicate that the  $\lambda^3$  ( $\lambda = X$ -ray wave-length) law is invalid when applied to individual *L*-levels.

R. W. L.

**Methods of Estimating the Successive Ionisation Potentials of any Element.** D. R. HARTREE (*Proc. Camb. Phil. Soc.*, 1924, 22, 464—474).—By assuming that for different elements the quantum numbers of the normal orbit of each of the first 18 electrons captured by a bare nucleus are independent of the atomic number, an analysis is advanced of the corresponding terms representing the energies of the normal orbit for different atoms of the same

electronic structure. It is shown that, assuming the quantum numbers of the term corresponding with the normal orbit, there are four methods which may be used to estimate the value of this term from which the ionisation potential may be evaluated. Approximate values of the successive ionisation potentials of oxygen, iron, and silver are given in tabular form, together with detailed illustrations of the method of calculation. R. W. L.

**Negative and Doubly-charged Positive Ions in Argon.** H. A. BARTON (*Nature*, 1924, **114**, 826—827).—Singly-charged, positive, atomic argon ions are first detected when an accelerating potential of about 17 volts (uncorr.) is applied to electrons striking the atoms, and doubly-charged positive atomic ions at 45 volts. The result is contrary to the assumption that the critical potential of 34 volts at which the first part of the blue spectrum appears corresponds with the production of doubly-charged ions. Since negative ions originate in that part of the tube where impacting electrons have just sufficient energy to excite the atoms, it would appear that for argon it is a necessary and sufficient condition for the capture of an electron that the atom should first be in an excited state. A. A. E.

**Nature of the Ions in Air and in Carbon Dioxide.** H. A. ERIKSON (*Physical Rev.*, 1924, **24**, 502—509).—The mobility curves obtained are explained by assuming that ionisation involves the detachment of an electron from a molecule, leaving a positive, unimolecular ion which soon attaches itself to a neutral molecule forming the final, unstable, bimolecular, positive ion, whilst the electron almost immediately joins a neutral molecule forming a stable, negative, unimolecular ion. Dissociation is considered to play only a small part. It is concluded that single molecules singly charged, positively or negatively, all have about the same mobility which is independent of mass and molecular volume, and that a singly-charged cluster of two or more molecules, not forming a single molecule, has a smaller mobility. A. A. E.

**Measurement of Critical Potentials of Gases.** E. G. DYMOND (*Proc. Camb. Phil. Soc.*, 1924, **22**, 405—408).—It is suggested that these potentials will be more accurately obtained if, instead of plotting the current-voltage curve, as is the usual practice, the differential of this curve be plotted. An experimental method of directly obtaining this value is outlined, and has been tested with helium. The results obtained are essentially preliminary, but much greater sensitivity than with the usual method is promised. L. F. G.

**Conditions for Statistical Equilibrium between Atoms, Electrons, and Radiation.** P. A. M. DIRAC (*Proc. Roy. Soc.*, 1924, **A.**, **106**, 581—596).—The principle that every process occurring in an assembly in thermodynamic equilibrium is exactly balanced by the reverse process occurring to the same extent is applied to the general case of  $n$ -body encounters, both radiative and non-radiative processes being considered. Reaction equilibrium con-

ditions are obtained involving the probabilities of the direct and reverse processes. It is shown that the van't Hoff isochore is of universal validity even for radiative processes and with relativity mechanics.

From Planck's law of radiation it is deduced that every process by which radiation is emitted is stimulated by external radiation of the same frequency, the ratio of stimulated to spontaneous emission being independent of the nature of the process, and inversely proportional to the cube of the frequency. The analysis is extended to the deduction of formulæ for the degree of ionisation of a gas which differs but slightly from those advanced by Saha and Fowler. R. W. L.

**Statistical Theory of Dissociation and Ionisation by Collision, with Applications to the Capture and Loss of Electrons by  $\alpha$ -Particles.** R. H. FOWLER (*Proc. Camb. Phil. Soc.*, 1924, **22**, 253—272).—In a previous analysis (cf. A., 1924, ii, 221) on the basis of the classical Bohr-Thomson theory of ionisation by collision, the author ignored the interactions in the core of any atom entered by an  $\alpha$ -particle. The limitations inherent to these premises are obviated in the analysis now advanced.

Formulæ are given for the frequency relations between the general 2- and 3-body collision processes of dissociation and recombination in a perfect gas. For ionisation and its reverse, the formulæ take a simple form. The results are applied to an investigation of the theory of the capture and loss of an electron by swift  $\alpha$ -particles in which the effects of the general field of the atom are included. Rutherford's  $V^5$ -law for the equilibrium ratio  $[H^{++}]/[He^+]$  is a necessary consequence simply of the classical formulæ for the distribution in velocity of the  $\delta$ -particles ejected by  $\alpha$ - or  $\beta$ -particles of given velocity. R. W. L.

**Photoelectric Thresholds of Elements.** R. HAMER (*J. Opt. Soc. Amer.*, 1924, **9**, 251—257).—The maximum wave-lengths able to stimulate the photoelectric activity of a number of common elements have been measured. The metallic surfaces were only roughly prepared, and the values are regarded as preliminary estimates. S. B.

**Calculation of the Fall of Potential in the Ion and Electron Gas Emitted from Glowing Metals.** M. VON LAUE and N. SEN (*Ann. Physik*, 1924, [iv], **75**, 182—188).—Mathematical. L. J. H.

**Ionic Mobilities in Gaseous Mixtures.** L. B. LOEB and M. F. ASHLEY (*Proc. Nat. Acad. Sci.*, 1924, **10**, 351—355).—The mobilities of ions have been measured in mixtures of air and ammonia in varying proportions, with the intention of testing the view that a gaseous ion is surrounded by a cluster of neutral molecules. The results were indecisive. S. B.

**Slow Corpuscular Radiations from Salts.** T. VOLMER (*Z. Physik*, 1924, **26**, 285—290).—A number of salts have been found to emit positively charged particles at comparatively low temper-

atures (about  $450^\circ$ ). Determinations of  $e/m$  have now shown that these particles consist of atoms of the metal which is a constituent of the salt. The salts studied were halides of cadmium, copper, zinc, lead, and calcium. S. B.

**Soft X-Rays and Secondary Electrons.** J. A. BECKER (*Physical Rev.*, 1924, **24**, 478—485).—The velocity distribution of photo-electrons excited by soft X-rays has been analysed by a method similar to that used for  $\beta$ -rays. The following critical potentials were obtained: aluminium,  $L_3$ , 70 volts;  $L_1$ , 80 volts; silver,  $N_1$ , 134 volts;  $M_6$ , 365—370 volts. The following characteristic lines in the  $N$  spectrum of tungsten were observed:  $N_3-O_5$ , 410 volts;  $N_2-O_4$ , 482 volts;  $N_1-O_3$ , 560 volts;  $N_5-O_3$ , 305 volts;  $N_4-O_2$ , 312 volts. The results are in agreement with Bohr's theory. A. A. E.

**Electron Emission Excited by  $\alpha$ -Rays.** A. BECKER (*Ann. Physik*, 1924, [iv], **75**, 217—275).—Aluminium, silver, and gold were bombarded with  $\alpha$ -rays in a vacuum. Ten electrons per  $\alpha$ -particle are emitted if the velocity of the latter is  $1.5 \times 10^9$  cm./sec., and more, up to 20 per  $\alpha$ -particle, for higher velocities, independently of the nature of the metal and the direction of the bombardment, i.e., whether perpendicular or oblique. The average velocity with which the electrons leave the surface is independent of the metal, the direction, and the velocity of the exciting  $\alpha$ -rays. The distribution of the velocity follows the Maxwell law of random distribution about the value 2 volts, but it is not possible to say whether there is a definite upper limit. The direction of emission is also distributed at random according to the same law. These results are compared with those obtained in the related phenomena of thermionic and  $\delta$ -ray emission, the laws of which are similar, but not identical. All three are probably due to the same fundamental mechanism. L. J. H.

**Radioactive Constant of Niton.** I. CURIE and C. CHAMIE (*J. Phys. Radium*, 1924, vi, **5**, 238—248).—The life constant of radium emanation has been determined by a new method. In principle, equal quantities of emanation are sealed into two bulbs, and the activity of one bulb is immediately noted. The time is then taken during which the combined activity of the two bulbs falls to the same value. The period of half-life is thus obtained directly. The corrections required in practice are described. The activity measured was the  $\gamma$ -ray activity of the emanation, filtered through 12 cm. of lead. Preliminary experiments showed that this activity obeyed the simple logarithmic decay law, and that, therefore, no radiation from the active deposit was interfering. The half-life period of niton is given as 3.823 days ( $\lambda = 7.554 \times 10^{-3}$  per hour) with a probable error of 0.05%. S. B.

**Number of  $\beta$ -Particles from Radium-*E*.** K. G. EMELÉUS (*Proc. Camb. Phil. Soc.*, 1924, **22**, 400—404).—By means of an electrical counter, the numbers were measured of  $\alpha$ - and of  $\beta$ -particles from a source of radium-*D*, -*E*, and -*F*, of which the quantities of

the last two were nearly in their equilibrium ratio. After correcting for reflection of  $\beta$ -particles at the source, the numbers were approximately equal, although no great accuracy is claimed for this result. According to previous work on their absorption (Meitner, A., 1915, ii, 663), the  $\beta$ -particles from radium-*D* would not be recorded under the experimental conditions. The observed  $\beta$ -radiation was therefore due to disintegration of radium-*E*, and since this was in equilibrium with radium-*F*, of which one atom is assumed to give one  $\alpha$ -particle on disintegration, it follows that about one  $\beta$ -particle is emitted per disintegrating atom of radium-*E*. This result does not agree with that of Moseley (A., 1912, ii, 1024), who found that one atom of radium-*E* appeared to emit little more than half a  $\beta$ -particle.

L. F. G.

**Decay of Radium-*E*.** L. BASTINGS (*Phil. Mag.*, 1924, [vi], 48, 1075—1080).—No appreciable difference has been detected between the decay constant of those radium-*E* atoms ejecting fast  $\beta$ -particles and the average radium-*E* atom. A value of the decay constant of radium-*E*:  $\lambda = 0.139_0 \pm 0.000_1 \text{ day}^{-1}$  has been obtained corresponding with a half-period of 4.98<sub>5</sub> days.

C. W. B.

**Electron Emission from Adsorbed Films on Tungsten.** K. H. KINGDON (*Physical Rev.*, 1924, 24, 510—522).—Measurements were made of the electron emission from tungsten filaments covered more or less completely with films of oxygen, thorium, caesium, caesium and oxygen, and of thoria in the presence of nitrogen.

A. A. E.

**$\beta$ -Ray Spectrum of Radium.** O. HAHN and L. MEITNER (*Z. Physik*, 1924, 26, 161—168).—The  $\beta$ -ray spectrum of radium, carefully purified from disintegration products, has been examined. Three groups of rays have been identified with the disintegration of radium itself with the He-values 1037, 1508, and 1575. The differences between the energies of these correspond with the differences between the energies associated with the *K*, *L*, and *M* levels in the atom. It is concluded that their emission is caused by absorption of nuclear  $\gamma$ -radiation of wave-length  $6.6 \times 10^{-10} \text{ cm}$ .

S. B.

**High Energy Groups in the Magnetic Spectrum of the Radium-*C*  $\beta$ -Rays.** C. D. ELLIS (*Proc. Camb. Phil. Soc.*, 1924, 22, 369—378).—Recent determinations (Ellis and Skinner, A., 1924, ii, 85) having indicated that whilst the relative values of the energies of radium-*C*  $\beta$ -rays as determined by Rutherford and Robinson (A., 1913, ii, 899) are accurate, their absolute values are low. The absolute energies of the  $\beta$ -ray spectra have now been determined to an estimated accuracy of 1 in 300 and a probable accuracy of 1 in 1000, using the standardised technique of Ellis and Skinner (*loc. cit.*).

It is concluded that the greater portion of this spectrum is due to the conversion according to the quantum relation of certain high-frequency monochromatic  $\gamma$ -rays in the *K*, *L*, *M*, *N* . . . levels of the radium-*C* atom, and a good agreement is reached between the

values calculated for the energy of the  $\gamma$ -rays necessary to excite the radium-*C*  $\beta$ -rays, and those observed by Bohr and Coster (A., 1923, ii, 110).

Further analysis of the spectrum indicates that  $\gamma$ -rays of up to  $2 \times 10^6$  volts show no fresh absorption phenomena, which, it is held, indicates that the seat of the  $\gamma$ -ray emission lies in the nuclear electronic system but is distinct from the disintegration electron, and whilst neither the disintegration electron nor the  $\alpha$ -particle is actually concerned in the  $\gamma$ -ray emission, strong  $\gamma$ -ray emission is more likely to be followed by instability of the electronic system than of the  $\alpha$ -particle system.

A nuclear level system of radium-*C* is advanced provisionally.

R. W. L.

**$\beta$ -Ray Spectrum of Mesothorium. II.** D. H. BLACK (*Proc. Roy. Soc.*, 1924, A., 106, 632—640).—A repetition of the work of v. Baeyer, Hahn, and Meitner (*Physikal. Z.*, 1912, 264) using much more accurate methods of focussing the  $\beta$ -rays.

It is concluded that the electrons are emitted from the various energy levels in the atom by nuclear  $\gamma$ -rays, and that the  $\gamma$ -rays arise through energy transitions in the nucleus.

R. W. L.

**$\gamma$ -Rays and Atomic Disintegration.** L. MEITNER (*Z. Physik*, 1924, 26, 169—177).—Radioactinium and actinium-*X*, in undergoing an  $\alpha$ -ray change, emit a number of distinct, nuclear, monochromatic  $\gamma$ -rays. Radium only emits one type of  $\gamma$ -ray.  $\alpha$ - and  $\beta$ -ray changes may be divided into two classes, those accompanied by  $\gamma$ -ray emission, and those unaccompanied by radiation. The number of types of monochromatic  $\gamma$ -rays emitted, and their frequencies, increase with the magnitude of the nuclear disturbance causing them. The  $\alpha$ -ray changes of ionium, polonium, and thorium-*C*, and the  $\beta$ -ray changes of uranium-*X*<sub>1</sub>, radium-*E*, and thorium-*C* are free from  $\gamma$ -ray emission.

S. B.

**Large Quantum  $\gamma$ -Rays from the Active Elements of the Thorium Family.** J. THIBAUD (*Compt. rend.*, 1924, 179, 1052—1054; cf. A., 1924, ii, 717).—A study of the  $\beta$ -spectra excited photoelectrically by  $\gamma$ -rays from mesothorium. From lead, for example, are obtained  $\beta$ -corpuscles with energies 491.5, 571.3, 706, 819, 873.5 kilovolts. These are mostly from the *K* level of electrons, and are excited by  $\gamma$ -rays of 580.7, 795.2, 908.2, 962.7 kilovolts. The first of these is probably from thorium *C+C''*.

W. E. G.

**Experiments with an  $\alpha$ -Particle Counter.** E. V. APPLETON, K. G. EMELÉUS, and M. A. F. BARNETT (*Proc. Camb. Phil. Soc.*, 1924, 22, 434—453).—Experiments carried out with the aim of elucidating the action of an  $\alpha$ -particle counter of the Rutherford and Geiger type (cf. A., 1908, ii, 555 and *Proc. Roy. Soc.*, 1908, A., 81, 141) are described. The results are discussed, and some consequential points bearing on the accuracy of enumeration of the particles are considered.

L. F. G.



**Emission of Nitrogen and Hydrogen in the Infra-red.** A. H. PFUND (*J. Opt. Soc. Amer.*, 1924, 9, 193—196).—The infra-red emission spectrum of hydrogen has been studied with a vacuum tube 150 cm. in length. A preliminary experiment with nitrogen confirmed the observation of Coblenz of maxima in the band at about  $1\ \mu$  (maxima found at 0.59, 0.68, 0.78, 0.90, 1.06, and  $1.20\ \mu$ ). With hydrogen in the tube a maximum was detected, in spite of much continuous radiation from the walls of the tube, at  $7.40\ \mu$ , corresponding with the first number of a new infra-red series of hydrogen, expressed by  $\nu = N(1/5^2 - 1/m^2)$ . The Brackett series was well developed. S. B.

**Band Regularities in the Secondary Hydrogen Spectrum.** O. W. RICHARDSON and T. TANAKA (*Proc. Roy. Soc.*, 1924, A, 106, 663—678).—Selective intensity changes in the secondary hydrogen spectrum observed in thermionic tubes (see this vol., ii, 13) have led to the recognition of a *P*, *Q*, *R* associated system of bands in this spectrum. The initial and final moments of inertia of the molecule for the emission of the lines in question are found to be several times greater than the moments of the molecules emitting the Fulcher hydrogen bands, or the helium band spectrum. It is suggested that the molecule responsible is abnormal, and may possibly be  $H_3$ . S. B.

**Second Positive Nitrogen Bands.** E. HULTHÉN and G. JOHANSSON (*Z. Physik*, 1924, 26, 308—322).—The structure of the nitrogen bands at 3536, 3755, and  $3805\ \text{\AA}$ . has been studied. They fall into an "energy level" scheme in which there are five initial and twelve final levels. S. B.

**Structure of the Second Positive Group of Nitrogen Bands.** P. LINDAU (*Z. Physik*, 1924, 26, 343—370).—The lines of the second positive bands of nitrogen have been classified according to the modern theory of band spectra. S. B.

**Effect of Argon on the First Positive Band Spectrum of Nitrogen.** R. C. JOHNSON (*Phil. Mag.*, 1924, [vi], 48, 1069—1074).—Traces of nitrogen in high-pressure argon show the first positive band spectrum in a considerably modified form. This consists in a selection of a few only of the band heads of the various groups, and the general effect is that found in the afterglow spectrum. Quantitative investigations are described which indicate that there is an energy displacement towards the more refrangible end of each band group. This also is similar to the conditions of the afterglow. It is suggested that all the phenomena hitherto regarded as peculiar to the electrical conditions obtaining in the afterglow may be reproduced in high-pressure argon. The bearing of these facts on the nature of the afterglow spectrum is discussed. C. W. B.

**Origin of the Mercury Band Spectrum. A New Band of Mercury.** E. HULTÉN (*Compt. rend.*, 1924, 179, 528—530).—The feeble band spectrum exhibited by mercury in a Geissler tube is increased in intensity by passing a current of hydrogen at a pressure

of 1 mm. through the tube. Air, however, appears to have the opposite effect. If no current of gas is passed, the bands disappear as the intensity of the electric current increases. This is attributed to the evaporation of the moisture in the tube, and the author infers that his observations accord with the hypothesis of a compound of the metal with hydrogen. A new band composed of feeble lines between the more intense lines of the band  $4017 \text{ \AA}$ . was observed.

H. J. E.

#### Absorption Spectrum and Specific Heat of Chlorine Dioxide.

H. MAYER (*Z. physikal. Chem.*, 1924, **113**, 220—234).—The absorption spectrum of chlorine dioxide determined by Kåbitz (*Diss.*, Bonn, 1905) can be described in terms of five series. The ratio of the velocity of sound in chlorine dioxide to the velocity in air at  $20^\circ$  is  $0.6148$  at one atmosphere pressure and  $0.6214$  at  $0.1$  atmosphere. From these results,  $C_p$  for chlorine dioxide is calculated to be  $7.5 \pm 0.5$ .

M. B. D.

Influence of the Deformation of Ions on Optical and Chemical Constants. III. H. KORNFIELD (*Z. Physik*, 1924, **26**, 205—222; cf. this vol., ii, 16).—The theories developed by Bonn and Heisenberg have been applied to the calculation of the infra-red frequencies of the carbonate ion, with a double negative charge.

S. B.

Tesla-luminescence Spectra. IV. Hydrocarbons containing a Single Benzene Nucleus. W. H. McVICKER, J. K. MARSH, and A. W. STEWART (*J. Chem. Soc.*, 1924, **125**, 1743—1750).—In continuation of previous work (A., 1924, ii, 712) the spectra of thirteen further substances are described. These spectra are constitutional properties somewhat sensitive to minor changes, but showing broad resemblances between related compounds. No clear relationship can be traced between the nature of the substituents and the lengths of the spectra emitted or the distance towards the visible region to which they extend, but if attention be confined to substances having saturated side-chains, a rough relationship exists between the molecular weight and the wavelengths to which the spectra extend in the ultra-violet. Relative brightness also appears constitutive. Both increase in the mass of the substituents and in unsaturation of the side-chain appear to damp down the spectrum.

L. J. H.

Phosphorescent Properties of the Rare Earths in Alkaline-earth Phosphors. I. R. TOMASCHEK (*Ann. Physik*, 1924, [iv], **75**, 109—142).—A detailed description is given of the phosphorescence spectra of the oxides of the rare earths in diluents of the oxides, sulphides, etc. of the alkaline-earths. The spectrum studied is that of the after-glow, excitation being effected sometimes by the light from the iron arc, sometimes by that from the carbon arc, and sometimes by bombardment with cathode rays. Scandium, yttrium, lanthanum, gadolinium, and aldehydium give no "after-glow" in the visible region. Theoretical conclusions are deferred to a later paper.

L. J. H.

**Luminescence of Phosphors under Magnetic and Electric Fields.** E. RUPP (*Ann. Physik*, 1924, [iv], 75, 326—336).—If a phosphor ( $\text{ZnSCu}\alpha$  or  $\text{ZnSMn}\alpha$ ) has been excited by ultra-violet light and is exposed, whilst the luminescence is fading, to a very powerful magnetic field (more than 20,000 gauss), a temporary increase in the luminescence results, weaker, but analogous to the results with an electric field (cf. Schmidt, *ibid.*, 1923, [iv], 70, 161). The phenomenon is directly explicable on Schmidt's theory. Under the influence of the magnetic (only) field, the light is partly polarised perpendicularly to the lines of magnetic force. This shows that the emission process in the phosphor centre is directly influenced by the field. The atomic magnetism of the metallic atoms of the phosphor may influence the result. Apart from this, the influence of a magnetic field (switched on or off) is similar to that of the electric field, because this is created by the movement of the electrons in the changing (magnetic) field. Electric fields of 2000 and 4000 volts are equivalent to magnetic fields of 20,000 and 45,000 gauss, respectively, and the latter to a rise in temperature (after correcting for that due to the electric field itself) of  $4^\circ$ .  
L. J. H.

**Measurement of Fluorescence of Solids.** A. GYEMANT (*Z. Physik*, 1924, 26, 223—234).—A simple method for estimating the intensity of fluorescent light is described. The intensity is compared with a radioactively excited "standard." To measure the intensity of a source of ultra-violet light, the fluorescence it excites in screens containing different surface concentrations of the fluorescing substance are matched with the "standard." The hardness of the constituents of a beam of X-rays can be estimated similarly, by using absorbing screens of various thicknesses, to absorb successively the different wave-lengths.  
S. B.

**Polarisation of Fluorescence from Dye Solutions.** III. W. L. LEWSCHIN (*Z. Physik*, 1924, 26, 274—284).—It was shown by Weigert (*Verh. d. Phys. Ges.*, 1920, 23, 100) that the fluorescent light from solutions of dyes is partly polarised. The present paper considers the effects of temperature, wave-length of exciting light, and concentration of the dye. Increase of temperature decreases the degree of polarisation. The influence of wave-length is not the same for all dyes, but in some instances the degree of polarisation increases for longer wave-lengths. Increase of concentration of the solutions always decreases the polarisation.  
S. B.

**Striking and Breaking Potentials for Electron Discharges in Hydrogen.** O. W. RICHARDSON and T. TANAKA (*Proc. Roy. Soc.*, 1924, A, 106, 640—662).—A systematic study has been made of the discontinuous increments in the current passing through a thermionic tube filled with hydrogen when the exciting potential is gradually raised. With a pressure of less than 1 mm. of mercury and the electrodes about 2 cm. apart, three types of discharge have been observed as the potential is raised. These are accompanied by sudden increases in current and by characteristic luminosity

phenomena. The breaking potential is less than the striking potential and probably has a simpler physical significance. The potentials at which these changes occur depend on several factors. They fall to a constant value as the electron emission from the cathode is increased. They change with the gas pressure, having a minimum value for about 1 mm. pressure. The breaking potentials diminish with decreasing electrode separation, but the value is approximately constant for distances less than 1 cm. It is concluded that the value to which the minimum breaking potential converges for small electrode distances is the ionisation potential of the gas. Sources of error and corrections are indicated, and an approximate value of 14.5 volts is obtained for the first ionisation potential of hydrogen. This supports the estimates of Olmstead and of Horton and Davies against the higher value of 17.1 volts obtained by Franck. Oscillations in the exciting circuit decreased the striking potentials by 0.1 volt, but left the breaking potentials unchanged. The ionisation of hydrogen at exciting potentials of about 16 volts is probably expressed by  $H_2 \rightarrow H_2^+ + e$ . This view is supported by the weakness of the Balmer lines and the intense development of the secondary hydrogen spectrum in the luminosity. Contrary to the observation of Horton and Davies, the continuous spectrum of hydrogen could not be obtained at lower potentials than the secondary spectrum.

S. B.

### Dielectric Polarisation in Pure Compounds and Mixtures.

L. EBERT (*Z. physikal. Chem.*, 1924, **113**, 1—27).—The dielectric constant  $\epsilon$  of a substance is an indirect function of the polarisability, which is proportional to the moment produced per c.c. by the action of an electric field. The specific polarisation  $\pi$  is  $(\epsilon-1)/(\epsilon-2)$ , and the molecular polarisation  $P$  is equal to  $\pi.M/d$ , where  $M$  is the molecular weight and  $d$  the density. For large values of  $\epsilon$ ,  $P$  depends principally on the molecular volume. The molecular polarisation may be divided into components which depend on the structure of the molecule. The electron polarisation  $P_E$  within the atoms is, in general, identical with the molecular refraction, and is responsible for absorption in the extreme ultra-violet. The polarisation within the molecule is due to polarisation of the atoms  $P_A$ , of the ions  $P_I$ , or of the radicals  $P_R$ , the corresponding absorption region being the long-wave infra-red. Finally, there is the orientation polarisation of the whole molecule  $P_O$ , the absorption region extending from wave-lengths of a few mm. to those of several dm.  $P_A$ ,  $P_I$ , or  $P_R$  can only be determined indirectly from the difference between  $P$  and  $P_E$ , where  $P_O$  is very small, that is, in gases and liquids with symmetrical molecules.  $P_A$  is small for non-polar compounds, for example, paraffins, but large for typically polar compounds. Only the sum  $P_A+P_O$  can be exactly determined. A qualitative idea of the magnitude of  $P_O$ , and also of the manner and the extent of the association between the dipoles can, however, be obtained. Large values of  $P_O$ , and hence large moments, indicate a lack of symmetry in the molecule which may be made up of several dipolar groups. Large values, for

instance, are found in the case of derivatives of water and ammonia. In simple molecules, the magnitude of  $P_0$  is related to the value of the Kerr constant. In liquid mixtures, no uniform behaviour is to be expected, because of the different degrees of association between the components. The moments of dual ions and salt dipoles are relatively much greater than those of aliphatic dipoles or water. M. S. B.

**Kerr Effect in Gases.** G. SZIVESSY (*Z. Physik*, 1924, 26, 323—342).—The Kerr effect has been studied for sulphur dioxide, ammonia, and carbon dioxide. The magnitude of the electrical double refraction is proportional to the square of the electrical field imposed. The Kerr constant is proportional to the pressure of the gas, and inversely proportional to the wave-length of the light. Kerr constants are given for sulphur dioxide,  $1.67 \times 10^{-10}$  ( $17.3^\circ$ ); for ammonia,  $0.59 \times 10^{-10}$  ( $17.9^\circ$ ); and for carbon dioxide  $0.24 \times 10^{-10}$  ( $17.5^\circ$ ). S. B.

**Molecular Coefficients of Refraction.** F. EISENLOHR and L. SCHULZ.—(See i, 17.)

**Optical Activity. Copper Salts of Malic Acid.** E. DARMOIS (*J. Phys. Radium*, 1924, [vi], 5, 225—237).—The acidity and optical activity of solutions of copper oxide in malic acid have been studied. It is concluded that such solutions contain only an acid malate of copper and a basic malate. Mixed malates containing copper and alkali metals have also been prepared and are being investigated. S. B.

**Mutarotation. IV. Solution Volume and Refraction Constants of  $\alpha$ - and  $\beta$ -Methylglucoside.** C. N. RIBBER.—(See i, 8.)

**Determination of Constitution by Spectroscopic Methods. Constitution of Amino-acids. I.** H. LEY and F. H. ZSCHACKE.—(See A., 1924, i, 1341.)

**Colour and Constitution. IX.** F. KEHRMANN.—(See A., 1924, i, 1326.)

**Co-ordination Positions of the Oxygen Atom.** J. PICCARD (*Helv. Chim. Acta*, 1924, 7, 800—802).—From the nature of the additive products of ethers with triphenylmethyl, the view is put forward that the oxygen atom has a co-ordination number of four, and not three as previously suggested (A., 1922, ii, 212), and that the co-ordination positions are at the peaks of a regular tetrahedron. On this view, the angle between the atoms H—O—H in water is slightly greater than  $109^\circ 28'$ , the deviation from the value for the regular tetrahedron being due to the slight repulsion of the hydrogen atoms. This value is in agreement with Eucken's calculation (cf. *Jahr. Radioaktiv. Elektronik*, 1920, 16, 408). H. T.

**Electronic Theory of Valency. IV. Origin of Acidity.** T. M. LOWRY (*Trans. Faraday Soc.*, 1924, 20, 13—15).—A restatement of the author's views on acidity (cf. A., 1924, ii, 447). S. S.

**Suggestions for a Magnetic Theory of Valency.** A. P. LAURIE (*Trans. Faraday Soc.*, 1924, **20**, 1—10).—Electrons arranged in shells about the atom are each supposed to move in a small orbit, so that they may be regarded as small magnets termed magnetons. The interaction of the magnetic fields is used to account for the formation of polar and non-polar bands, and the structure of hydrates and of ice. The connexion between the Bohr and Langmuir atom models is discussed in terms of this hypothesis. S. S.

**Compressibility of Methyl Ether and Molecular Weight of the Gas.** T. BATUECAS (*Compt. rend.*, 1924, **179**, 565—567).—Corresponding values of pressure and volume of a known quantity of gaseous methyl ether were made, the results being represented by using the formula  $pv=a-bp$ . From these, the calculated value of  $1+\lambda$  was found to be 1.0270 and the molecular weight of the gas 46.044 (cf. Baume, A., 1908, ii, 372), which is in excellent agreement with modern physico-chemical determinations. H. J. E.

**Determination of Molecular Fields. III. From Crystal Measurements and Kinetic Theory Data.** J. E. JONES (*Proc. Roy. Soc.*, 1924, **A**, 106, 709—718; cf. *ibid.*, 441 and 463).—Calculation of the potential energy and interatomic distances in cubic crystals of argon, potassium chloride, and calcium sulphide. W. E. G.

**Influence of the Deformation of Ions on Optical and Chemical Constants. II.** W. HEISENBERG (*Z. Physik*, 1924, **26**, 196—204).—The methods developed in an earlier paper (A., 1924, ii, 434) have been applied to calculate the stability and heats of formation of triatomic ions and molecules. S. B.

**Secondary Electrons Produced by Hard X-Rays in Light Elements.** H. FRICKE and O. GLASSER (*Proc. Nat. Acad. Sci.*, 1924, **10**, 441—447).—A corollary of the theory of A. H. Compton (*Physical Rev.*, 1923, **21**, 483; 1924, **23**, 439) for the scattering of X-rays consists in the prediction and quantitative description of a type of secondary electrons, "recoil electrons," which result from the passage of X-rays through matter. The correctness of this prediction is tested by a determination of that fraction of the ionisation of X-rays in air for which the recoil electron emission is responsible. The actual experimental method consists in a comparison of the ionisation currents produced by X-rays, 0.180 Å. and 0.115 Å., in small ionisation chambers made of different light elements and their salts. A description of the details of the experimental technique has already appeared (Fricke and Glasser, *Amer. J. Roentgenol.*, 1924, **11**, 435). The experimental data furnish a direct determination of the ratio of two ionisation effects, one due to the photo-electric effect of the rays, and the other to the scattering process. The value of this ratio can also be calculated from Compton's theoretical coefficient and known experimental data. For carbon, the observed and calculated values are in fair agreement. J. S. C.

**Compton and Duane Effects.** J. A. BECKER (*Proc. Nat. Acad. Sci.*, 1924, **10**, 342—346).—According to Compton's quantum theory explanation of the scattering of X-rays, the wave-lengths of the scattered rays should be slightly longer than those of the incident rays by an amount varying with the scattering angle. The effect has been photographically verified by several observers. Duane, however, has been unable to detect the effect using an ionisation chamber method. He finds instead a shift of the lines dependent on the material of the scattering body, which he attributes to the emission of tertiary radiation. Experiments are described to test whether the incompatibility of these results is due to the differences of intensity in the incident X-rays used by the observers. The rays scattered by aluminium through  $100^\circ$  were photographed. The Compton effect was verified, and indications of a Duane effect were obtained at the lowest intensity of incident radiation that could be employed. S. B.

**Precision X-Ray Spectrometers.** J. C. HUDSON (*J. Opt. Soc. Amer.*, 1924, **9**, 259—301).—The technique of X-ray wave-length measurements is described. Both the photographic and the ionisation methods are included, with especial reference to the apparatus developed by Siegbahn and by Duane. X-Ray wave-length tables are appended. S. B.

**Structure of Graphite.** J. D. BERNAL (*Proc. Roy. Soc.*, 1924, **A**, **106**, 749—773).—Measurements by the method of the rotating single crystal, by the ionisation spectrometer, and from Laue photographs give results agreeing with the hexagonal lattice proposed by Hull (*Physical Rev.*, 1917, **10**, 661), but disagreeing with the lattice proposed by Debye and Scherrer (*A.*, 1917, ii, 437). The unit cell contains four carbon atoms; their probable positions are considered, and it is deduced that the atoms of carbon in graphite lie in planes of successive nets of hexagons superposed so that half the atoms in one net lie normally above half the atoms in the net beneath, whilst the other half lie normally above the centres of the hexagons in this net. Alternate nets lie atom for atom normally above the others. The complete structure is thus essentially that of Hull, but with all the carbon atoms lying in the cleavage plane, as in the Debye and Scherrer model. This agrees well with the more recent views of Bohr on the structure of the carbon atom. Artificial and natural graphite are identical in structure. L. F. G.

**Precision Crystal Measurements on Alkali and Ammonium Halides.** R. J. HAVIGHURST, E. MACK, and F. C. BLAKE (*J. Amer. Chem. Soc.*, 1924, **46**, 2368—2374).—The film on which the crystal powder is mounted is calibrated by mixing the latter with a standard substance with which it is not miscible at the ordinary temperature (*e.g.*, sodium chloride); the position of the lines for the latter can then be calculated and compared with the observed. The presence of small amounts of isomorphous impurities has only a negligible effect on the length of the side of the crystal unit, the observed values for which were: ammonium chloride  $3.866 \pm 0.002$ ,

bromide  $4.047 \pm 0.002$ , and iodide  $7.244 \pm 0.003$ ; potassium chloride  $6.280 \pm 0.003$ , bromide  $6.578 \pm 0.003$ , and iodide  $7.052 \pm 0.003$ ; rubidium chloride,  $6.571 \pm 0.004$ , bromide,  $6.868 \pm 0.004$ , and iodide,  $7.325 \pm 0.004$ ; caesium chloride,  $4.110 \pm 0.002$  Å. S. K. T.

**Crystal Structure of Tetragonal Lead Monoxide.** R. G. DICKINSON and J. B. FRIAUF (*J. Amer. Chem. Soc.*, 1924, **46**, 2457—2463).—The unit cell of red (tetragonal) lead monoxide contains 2 molecules; its dimensions are  $a=5.01$  Å.,  $b=c=3.99$  Å. The oxygen atoms are at (0, 0, 0),  $(\frac{1}{2}, \frac{1}{2}, 0)$ , and the lead atoms at  $(0, \frac{1}{2}, 0.24)$ ,  $(\frac{1}{2}, 0, 0.24)$ . S. K. T.

**Optical Properties of Calamine.** P. SÈVE (*J. Phys. Radium*, 1924, [vi], **5**, 249—256).—The dispersion of the optic axes and the double refraction of calamine have been studied photographically in the visible and the near ultra-violet. The plane of the optic axes crosses at  $3270$  Å., for which wave-length the crystal is pseudo-uniaxial. The order of the interference produced by the passage of parallel light through a plate of calamine in the direction of the acute bisectrix has a maximum at  $5200$  Å. As the order of interference is almost constant over a wide range in the visible, the use of calamine as a material for half-wave plates etc. is suggested. S. B.

**Structure of Chromium.** H. COLLINS (*Chem. News*, 1924, **129**, 331—334).—Speculative. A. R. P.

**Reflection of X-Rays by Barytes.** S. K. ALLISON (*Amer. J. Sci.*, 1924, **8**, 261—276).—The axial ratios of barytes ( $\text{BaSO}_4$ ) have been remeasured by an X-ray ionisation spectrometer;  $a:b:c$  is given as  $0.8148:1:1.3131$ . The unit cell is a rectangular parallelepiped of dimensions  $4.449$ ,  $5.448$ , and  $7.170$  Å., containing 2 mols. of barium sulphate. The units of structure are arranged at the equivalent points of the space group  $V_h^{13}$ . S. B.

**Nitrogen and Uranium.** P. D. FOOTE (*Nature*, 1924, **114**, 789).—As a pure speculation regarding the origin of the nitrogen obtained by Hillebrand and by Ramsay from uraninite, it is suggested that the uranium nucleus may contain nitrogen nuclei, since the atomic weight of the former is almost exactly an integral multiple of that of the latter. A. A. E.

**Rarity of the Inert Gases on the Earth.** F. W. ASTON (*Nature*, 1924, **114**, 786).—It is considered probable that the apparent rarity of the inert gases—as compared with the abundance predicted by their positions on the mass-number curves—is in fact real. In collisions of bodies resulting in the formation of a solar system, such atoms unconstrained by chemical combination would collide and rebound indefinitely, gravitating towards the larger masses, e.g., the sun. A. A. E.

**Applications of Röntgen Crystal Analysis to Questions of Structure of Organic Compounds.** H. MARK.—(See i, 1.)

**Electronic States of the CN Molecule.** R. S. MULLIKEN (*Nature*, 1924, **114**, 858—859).—A brief survey of recent work on



the CN bands. The substance which above  $2000^{\circ}$  can be excited thermally to the emission of the bands must be represented by CN; the red and violet bands respectively correspond with electronic resonance potentials of 1.78 and 3.18 volts. The equilibrium concentration of CN at low temperatures must be extremely small, very much smaller than that of  $(\text{CN})_2$ , but presumably increases with rise of temperature, probably more rapidly than that of  $(\text{CN})_2$ , until above  $2100^{\circ}$  it becomes sufficient for appreciable absorption and emission of the violet CN bands. At much higher temperatures, e.g., in the carbon arc, the CN bands are very intense. A. A. E.

**Absorption Spectra of Mixed Metallic Vapours.** S. BARRATT (*Nature*, 1924, **114**, 827).—Band spectra peculiar to mixtures of magnesium (and calcium) with alkali metals have been obtained, indicating the existence of molecules of volatile alloys in the vapours. Further, the development of lines of the series  $1S-md$  in the absorption spectra of rubidium and caesium vapours has been observed, although this is in contravention of the selection principle.

A. A. E.

**Absorption Spectrum and Constitution of Sulphur Vapour. Predissociation of Molecules.** V. HENRI and M. C. TEVES (*Nature*, 1924, **114**, 894—895).—The ultra-violet absorption spectrum of sulphur has been studied between  $100^{\circ}$  and  $1000^{\circ}$ , at 0.5—53 mm., the measurements being accurate to 0.02—0.1 Å. When only  $S_8$  and  $S_6$  molecules were present, there is general absorption between 2700 Å. and 2300 Å., no structure being observed. At higher temperatures, a band spectrum of  $S_2$  molecules is obtained, the intensity and number of the bands being determined by the partial pressure of the  $S_2$  molecules. This spectrum is divisible into three distinct portions: (a) 3700—2794.2 Å., bands with fine structure; the rotational movement of the molecule is quantised. The distance between the nuclei of the two sulphur atoms is computed to be 0.7 Å. in the normal, and 0.73 Å. in the activated  $S_2$  molecule. (b) 2794.2—2592 Å., narrow, continuous bands without fine structure. The change, involving the disappearance of the quantised rotation of the  $S_2$  molecule, is abrupt. (c) 2592—2475 Å., broad, continuous bands; again the change is abrupt, and the distance between the nuclei becomes greater than before. The second change involves an increase in internal energy corresponding with the resonance potential of sulphur vapour (4.78 volts). It would therefore appear that before that state is reached in which the valency electrons have jumped into higher orbits, a molecule can be modified internally in that the atoms are driven apart, the bonds weakened, and greater reactivity is displayed. It is proposed to denote this preliminary change by the term "predissociation." Thus for each molecule there may be distinguished the following states in which it can be activated: normal, predissociated, resonance, ionised, and dissociated. A. A. E.

**Constitution of Phosphoric Acid.** I. FRÖSCHL (*Rad. Acad. Sci. Zagreb*, 1923, **228**, 16—37).—The author determined the mol. weight

of orthophosphoric acid in aqueous solutions by measurements of boiling point elevation. The following values were found: for solutions containing 1—6.5% of phosphoric acid, 137.2; 7—12%, 125.9; 14—27%, 115.7. The curve representing the molecular weights shows discontinuities at 7 and 13% of phosphoric acid. In order to account for the different behaviour of the hydroxyl groups in phosphoric acid, the author supposes that in the acid  $\text{P}(\text{OH})_5$  ("protophosphoric acid"), three hydroxyl groups have an acid character, one is amphoteric, and one basic. In this case, compounds of the protophosphoric acid with other strong acids must be expected. Derivatives of such compound acids occur at natural minerals (apatite, wagnerite, dahlite) and have been obtained by Weinland and Alfa (A., 1898, ii, 217; 1899, ii, 594). Some new derivatives have been prepared by the author. Alcoholic solutions of phosphoric acid with solid sodium hydrogen carbonate yield a very hygroscopic substance with the empirical composition  $\text{Na}_2\text{CO}_3 \cdot \text{H}_3\text{PO}_4$ . It is decomposed readily by water, yielding carbon dioxide. When potassium sulphate is dissolved in concentrated phosphoric acid and the solution poured into alcohol, a crystalline precipitate,  $2\text{K}_2\text{SO}_4 \cdot \text{H}_3\text{PO}_4$ , is formed. If hot phosphoric acid is saturated with potassium sulphate until crystals appear on cooling, and then precipitated with alcohol, crystals with the composition  $\text{K}_2\text{SO}_4 \cdot \text{H}_3\text{PO}_4$  separate. Ammonium sulphate treated in a similar way yielded a substance corresponding with the formula  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{NH}_4\text{H}_2\text{PO}_4$ . The same behaviour as with phosphoric acid may well be expected with other hydroxides containing more than one hydroxyl group, as, for instance, aluminium, uranium, and osmium. The peculiarities of some organic substances (aldehydes, ketones) may be better understood if the different character of the hydroxyl groups present is assumed.

S. S. M.

**Distribution of Atoms in Mixed Crystals.** G. TAMMANN (*Ann. Physik*, 1924, [iv], 75, 212—216).—A reply to Borelius (*ibid.*, 1924, 74, 216) summarising the arguments for and against a "normal" distribution of the atoms in mixed crystals. The "normal" distribution of two kinds of atoms in mixed crystals is that for which, when mixed as completely as possible, the symmetry corresponds with that of the two end members of the series. The total lattice may be thought of as divided into two partial lattices, the first corresponding with one atomic species and the second with the other. Such an arrangement can be attained from random distribution only if the atoms are free to change places, which may not be the case at low temperatures. Hence there is often a difference between mixed crystals obtained from the molten state (by cooling) and those obtained from solution (by removal of solvent). Interference X-ray figures should be very sensitive to slight deviations from the "normal" distribution, whilst the limits (of concentration) of chemical action should not.

L. J. H.

**Experimental Investigation of the Lattice Structure of some Alloys.** S. HOLGERSSON and E. SEDSTRÖM (*Ann. Physik*, 1924, [iv], 75, 143—162).—The structure of palladium-gold and

palladium-copper alloys was studied by the röntgenographic method of Debye and Scherrer. The former series showed a face-centred cubic lattice. The variation of the lattice parameter with atomic concentration may be represented by a smooth curve convex to the concentration axis. In the latter series, a compound, PdCu, is indicated, this having a centred-cubic lattice ( $a=2.988 \times 10^{-8}$  cm.). Except in the immediate neighbourhood of the compound, where mixed lattice structure is found, the whole series has a face-centred cubic lattice.

L. J. H.

**Molecular Dimensions of "Celluloid."** V. P. BARTON and F. L. HUNT (*Nature*, 1924, **114**, 861).—Experiments on the thickness of films indicate that the diameter of the molecular complex of "celluloid" is not greater than  $10 \text{ \AA}$ .

A. A. E.

**Index of Refraction of Calcite for X-Rays.** C. C. HATLEY (*Physical Rev.*, 1924, **24**, 486—501).—By using the wedge method, the index of refraction of calcite for molybdenum  $K\alpha_1$  rays is  $\mu=1-(2.03 \pm 0.1) \times 10^{-6}$ , which agrees well with the value given by Lorentz's dispersion formula. The wave-length of the rays, after correction, is  $0.70772 \text{ \AA}$ .

A. A. E.

**Coloration of Rock Salt by Radium.** P. LUDEWIG and F. REUTHER (*Z. Physik*, 1924, **26**, 45—53; cf. *ibid.*, 1923, **18**, 183).—The coloration of rock-salt specimens by radium has been quantitatively examined. Colour changes were still slowly progressing after 137 days' exposure to 40 mg. of radium. Blue rock-salt passes into a colourless state after 1 day's exposure, and then becomes yellow.

S. B.

**Coloration of the Alkali Halides by X-Rays.** P. L. BAYLEY (*Physical Rev.*, 1924, **24**, 495—501).—Cæsium, rubidium, and calcium fluorides, cæsium, rubidium, potassium, sodium, lithium, silver, barium, beryllium, and calcium chlorides, cæsium, rubidium, and potassium bromides, potassium, sodium, cadmium, and mercury iodides, and potassium silicate assume a coloration when exposed to X-rays, but no correlation appears to exist between the colour and the position of the element in the chemical table. Halite, coloured amber, has an absorption band from  $0.3\mu$  to  $1.3\mu$ , with a maximum at  $0.46\mu$ . Sylvite, coloured purple, has a similar band with a maximum at  $0.55\mu$ . The conditions of fading of the colorations were investigated.

A. A. E.

**Optical Properties of Crystals of certain Cyanoplatinates.** I. A. POCHETTINO (*Atti R. Accad. Sci. Torino*, 1924, **59**, 133—141).—Crystals of magnesium, yttrium, and erbium cyanoplatinates exhibit double refraction which increases in absolute magnitude as the wave-length of the light diminishes from  $\lambda=0.660$  to  $\lambda=0.470$ , but decreases as the wave-length falls from  $0.440$  to  $0.410$ . With change in  $\lambda$  from  $0.455$  to  $0.445$ , the uniaxial magnesium cyanoplatinate crystals show a sudden change in the sign of the double refraction, whereas with the biaxial yttrium and erbium cyanoplatinate crystals the plane of the optical axes undergoes a rotation of  $90^\circ$ .

T. H. P.

**Photochemical Properties of Stannous Iodide.** P. FREUNDLER and Y. LAURENT (*Compt. rend.*, 1924, **179**, 1049—1051).—When prepared from solutions of stannous chloride and potassium iodide, the precipitated stannous iodide consists of a mixture of red and yellow modifications, excess of stannous chloride favouring the production of the red modification, and excess of potassium iodide that of the yellow. On exposure to sunlight, the yellow form is changed into the red modification, the reverse change taking place in the dark. When potassium iodide is used, the red form is at once produced if the mixture is heated on a water-bath. When, however, sodium iodide is used, excess of stannous chloride favours the production of the yellow form, which is the stable modification at 100°. The use of sodium iodide greatly reduces the oxidation of the mixture on exposure to air. The presence of traces of tin possibly influences the iodine content of marine plants. W. H.-R.

**Pseudo-complexes.** A. SCHLEICHER (*Z. anorg. Chem.*, 1924, **140**, 371—378).—A theoretical discussion, in which it is shown that, from a study of the crystal structure of compounds, a distinction must be drawn between true complex compounds having characteristic crystal properties and a high order of symmetry and pseudo-complexes having no characteristic crystal structure of their own and possessing a lower order of symmetry. The formation of both classes of complexes is, however, due to the co-ordination power of the atoms, but the crystal lattice of the pseudo-complexes can be regarded as a growth of the simple molecule of the compound by reason of a definite symmetry of the molecule of lower order and according to certain crystallographic laws analogous to those controlling the formation of twinned crystals. The crystal symmetry of sodium and caesium chlorides, calcium fluoride, cuprous oxide, zinc sulphide, graphite, and calcium carbonate is derived from the above considerations. A. R. P.

**Nature of the Martensitic Structure [of Steel].** F. SAUERWALD and G. JACKWIRTH (*Z. anorg. Chem.*, 1924, **140**, 391—398).—By the method already outlined (A., 1924, ii, 863) it is shown that the martensitic structure of steel is always oriented in the same way as the original  $\gamma$  grain boundaries and that the slip planes are similarly oriented. It would therefore appear that the needle-like structure of martensite is caused by slip phenomena induced by the hardening process (quenching) the steel has undergone and that martensite cannot be regarded as a distinctive phase in the structure of steel. [Cf. B., 1925, 42.] A. R. P.

**Metal Crystals. I.** E. GRÜNEISEN and E. GOENS (*Z. Physik*, 1924, **26**, 235—249).—The elastic constants of zinc and cadmium have been determined from extension experiments etc. carried out at different crystallographic orientations on large single crystals. Zinc and cadmium show, probably on account of their large axial ratios, an unusually large elastic anisotropy. S. B.

**Metal Crystals. II.** E. GRÜNEISEN and E. GOENS (*Z. Physik*, 1924, **26**, 250—273).—The velocities of sound in zinc and

cadmium crystals, determined from their elastic constants (see preceding abstract), have been used to calculate the specific heats of these metals by Debye's method. The specific resistances of the crystals at the temperature of liquid air have also been measured.

S. B.

**Relation between the Mechanical and Piezo-electrical Properties of a Rochelle Salt Crystal.** F. C. ISELY (*Physical Rev.*, 1924, **26**, 569—574).—Stress-strain curves have been obtained for 20°, 22.5°, and 30°, and curves showing the variation of charge with stress for 16—35°. The temperature of maximum piezo-electric response is 22.25°.

A. A. E.

**Dielectric Anomalies in Rochelle Salt Crystals.** J. VALASEK (*Physical Rev.*, 1924, **24**, 560—568).—Residual charge and fatigue effects for a Rochelle salt condenser have been studied; it is supposed that at -20° there is a loosening of the water ions sufficient to permit a slight motion with reference to the salt molecules, whilst above 25° there is further loosening. There is an apparent evolution of heat commencing at 24° and persisting to 54°, when a considerable absorption of heat takes place.

A. A. E.

**Metastability of Elements and Compounds as a Result of Enantiotropy and Monotropy.** VIII. E. COHEN and W. D. HELDERMAN (*Z. physikal. Chem.*, 1924, **113**, 145—156).—By means of the electrical adiabatic colorimeter (cf. *ibid.*, 1924, **112**, 141), measurements have been made of the intermediary heats of solution between various concentrations of the two forms of ammonium nitrate, III and IV, at the transition temperature 32.3°. The difference in these two values for the two modifications, between corresponding pairs of concentrations, gives the heat of transition, which is thus found to be 4.99 cal. per g. According to Bridgman (*Proc. Amer. Acad. Arts Sci.*, 1916, **51**, 581) it is 4.66. The latter value is attributed to the employment of a metastable mixture of the two modifications instead of the pure form. [Cf. A., 1924, ii, 449.]

M. S. B.

**Atomic Weight of Antimony.** P. F. WEATHERILL (*J. Amer. Chem. Soc.*, 1924, **46**, 2437—2445).—Antimony trichloride, prepared by the action of chlorine on pure antimony in a vacuum, was dissolved in an aqueous solution of pure tartaric acid and the resulting solution quantitatively precipitated with silver nitrate solution. From the ratio  $\text{SbCl}_3 : 3\text{Ag}$ , the atomic weight of antimony was found to be  $121.748 \pm 0.00086$ .

S. K. T.

**Variation of the Molecular Weight of Mercury with Temperature.** A. JOUNEAUX (*Bull. Soc. chim.*, 1924, [iv], **35**, 1293—1305).—The molecular weight of mercury through the temperature range -40° to 320° was calculated from previously known cryoscopic and surface tension data and from Clapeyron's law and Trouton's rule. The values obtained change regularly with the temperature, independently of the method of calculation, and range from 280 at low to 200 at the higher temperatures. From the Eötvös-Ramsay-

Shields formula, the critical temperature of mercury was found to be  $1552^{\circ}$ . H. T.

**Determination of Molecular Weight by Aid of the Gas-Interferometer of Haber and Löwe.** E. BERL and F. RAU (*Ber.*, 1924, 57, [B], 1829—1834).—A current of dry air, free from carbon dioxide, is saturated with (a) the vapour of the pure solvent and (b) the vapour from the solution of the substance under investigation in the same solvent, and the difference of the vapour tension in the two cases is measured by means of the Haber-Löwe gas-interferometer. The instrument is calibrated with the aid of solutions of azobenzene. Benzene is the most suitable solvent. H. W.

**Electrical Properties of Liquid Sulphur.** D. H. BLACK (*Proc. Camb. Phil. Soc.*, 1924, 22, 393—399).—The relative conductivities of liquid sulphur between  $130^{\circ}$  and  $200^{\circ}$  were determined and compared with changes in the viscosities over this range. Conductivity increases to a maximum at about  $160^{\circ}$ , then falls to a minimum at about  $185^{\circ}$ , and thereafter increases. This behaviour thus agrees approximately with the known viscosity changes, which exhibit a minimum and a maximum at  $150$ — $160^{\circ}$ , and at about  $200^{\circ}$ , respectively. The specific resistance at  $163^{\circ}$  was found to be  $7.5 \times 10^{10}$  ohms, approximately. Evidence is given that the conduction is electrolytic in nature. *E.M.F.s.* of polarisation were observed qualitatively (cf. Threlfall and Brearley, *Phil. Trans.*, 1896, A, 187, 57). L. F. G.

**Method for the Determination of the Specific Heat of Metals.** W. U. BEHRENS and C. DRUCKER (*Z. physikal. Chem.*, 1924, 113, 79—110).—A method similar to Pirani's (*A.*, 1913, ii, 102) has been employed for the determination of the specific heat of metals. A thin wire is heated to constant temperature in a vacuum and its resistance measured, by means of a Wheatstone's bridge arrangement, before and immediately after the addition of a definite quantity of electrical energy. Making use of the previously determined temperature coefficient of the resistance of the wire, the temperature, and thence the specific heat, may be calculated from the change in resistance. Values for the specific heat of zinc ranging from 0.0921 at  $5^{\circ}$  to 0.0992 at  $225^{\circ}$  have thus been found. The value of  $\alpha/c$ , the ratio of the relative temperature coefficient to the specific heat, has also been determined for different temperatures by allowing the heating current to pass through a similar wire kept at the ordinary temperature, and measuring only the difference of the relative change of resistance in the two wires at different temperatures of the experimental wire. By this means the dependence of specific heat on temperature and previous thermic treatment may be studied. Zinc, however, shows no anomalies in the value of  $\alpha/c$  between  $0^{\circ}$  and  $225^{\circ}$ , although the work of previous investigators shows that there is probably a transition point between  $100^{\circ}$  and  $200^{\circ}$ .

The advantages claimed for this method are : the smallness of the amount of material and of the energy additions necessary, the

rapidity of the operation, the possibility of measurement over small temperature intervals, and the great degree of exactitude attained.

M. S. B.

### Latent Heats of Fusion. II. Palmitic Acid and Benzene.

K. STRATTON and J. R. PARTINGTON (*Phil. Mag.*, 1924, [vi], 48, 1085—1089; cf. A., 1922, ii, 258).—The latent heats of fusion and the molecular depressions of freezing point (with mesitylene as solute) have been determined for carefully purified palmitic acid and benzene. For palmitic acid of setting point  $62.25^\circ$ ,  $L=51.03$  g.-cal. per g.;  $E$  for 100 g. solvent= $43.13$ . For benzene of setting point  $5.85^\circ$ ,  $L=29.92$  g.-cal. per g.;  $E$  for 100 g. solvent= $51.39$ . The results remove the larger discrepancies between the observed and calculated values of  $E$  in the case of palmitic acid which are given in the literature.

C. W. B.

### Density and Diffusion Measurement by Interferometry.

C. BARUS (*Proc. Nat. Acad. Sci.*, 1924, 10, 349—351).—A continuation of previous results (A., 1924, ii, 385).

S. B.

**Relation between the Volume of a Substance at Absolute Zero and its Critical Temperature.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, 140, 379—383).—From theoretical considerations the equation  $v_0 M/T_K = \text{constant}$  is deduced, where  $v_0 M$  is the molecular volume of a substance at the absolute zero and  $T_K$  is its critical temperature. The value of this constant has been determined for a large number of organic and inorganic compounds and for the gaseous elements from data already published. The figures obtained appear to show that the relationship holds approximately only for "ordinary" substances (cf. van Laar, *Z. anorg. Chem.*, 1918, 104, 57; 1922, 120, 203) and that the deviations vary in magnitude according to the extent that the substance differs from the "ordinary."

A. R. P.

**Density of Zirconium and Hafnium Oxides.** G. HEVESY and V. BERGLUND (*J. Chem. Soc.*, 1924, 125, 2372—2375).—Carefully purified zirconium dioxide and hafnium dioxide, prepared from the sulphates and ignited at  $1000^\circ$ , had  $d^{20}$  5.73 and 9.67, respectively. The determination of  $d$  for a mixture of the two oxides affords a ready and accurate means of determining the percentage of hafnium dioxide present, which is given by the formula  $x = (d - 5.73)/0.0394$ . It is necessary to prepare the mixture from the sulphates and by exactly the same methods. The values for  $d$  found for oxides otherwise prepared is lower and presumably less accurate.

C. I.

**Density of Gaseous Methyl Ether.** T. BATUECAS.—(See A., 1924, i, 1280.)

**Vapour Pressures of Monatomic Substances.** A. C. EGERTON (*Phil. Mag.*, 1924, [vi], 48, 1048—1054).—On the basis of the thermodynamic vapour pressure formula a linear equation  $\log p = -a/T + b$  closely represents the variation of vapour pressure with temperature of a solid with monatomic vapour, and a vapour

pressure determination at a single temperature should suffice to determine the course of the whole curve. C. W. B.

**Vapour Pressures of Rochelle Salt, the Hydrates of Sodium and Potassium Tartrates, and their Saturated Solutions.** H. H. LOWRY and S. O. MORGAN (*J. Amer. Chem. Soc.*, 1924, **46**, 2192—2196).—The vapour pressures of the hydrates of sodium and potassium tartrates and Rochelle salt, and of their saturated solutions, have been determined for the temperature interval 15—40° by a static method. The graphs of  $t_w$  against  $t$ , where  $t_w$  is the temperature at which the vapour pressure of water is equal to the vapour pressure of the substance, or its solution, at  $t$ , may be represented by the linear equation:  $t = at_w + b$ ,  $a$  and  $b$  being constants. The results of van Leeuwen (*A.*, 1897, ii, 397) are confirmed. Reproducible values for the vapour pressures of Rochelle salt, or its solution, cannot be obtained if the latter has been previously heated, at any time, above 40° (*cf. loc. cit.*). S. K. T.

**Kinetic Theory of Vaporisation.** S. C. BRADFORD (*Phil. Mag.*, 1924, [vii], **48**, 936—947).—The kinetic theory has been applied to obtain a quantitative expression for the vapour pressure of liquids in the form:  $p = 56.47 T e^{-3.806 \sigma V A^{1/3} / T \delta' d} / (\Phi_s d^{1/2} A)$ .  $\Phi_s$  is the co-volume,  $\delta' \times 10^8$  the nearest distance of approach of the centres of two molecules of the liquid,  $A$  is an arbitrary constant to allow for molecular association of the liquid. Vapour pressures calculated by means of the formula agree very well with the values observed at given temperatures and become equal to 1 atmosphere at the boiling points of the liquids. Edser's formula,  $\sigma = K\delta/4$ , may be used to calculate the cohesion of liquids with considerable accuracy. C. W. B.

**Corresponding Temperatures of Solids.** A. BRODSKY (*Compt. rend.*, 1924, **179**, 498—500).—The results obtained by Michaud from experiments on specific heat and entropy (*A.*, 1920, ii, 532) are susceptible of deduction from the theory of specific heats. From the simplest Einstein formula it can be shown that Michaud's "corresponding temperature" depends on the nature of the substance considered, and a further deduction shows that the values of the specific heat for similar values of the corresponding temperature are independent of the nature of the substance. Absolute zero being a corresponding temperature for all bodies, the additivity of the specific heats at this temperature is consistent with the consequences of the Nernst theorem. At higher temperatures than those dealt with, the deductions do not hold in the case of specific heats at constant volume. H. J. E.

**Corresponding Temperatures of Solids.** H. LAFUMA (*Compt. rend.*, 1924, **179**, 684—686).—A claim for priority against Brodsky (*cf. preceding abstract*). T. H. P.

**Dependence of Coefficient of Expansion of Liquids on Temperature and Chemical Structure.** J. J. SASLAWSKY (*Z. physikal. Chem.*, 1924, **113**, 111—130).—From the expression for



the density of liquids  $\delta_t = \delta_k(1 + 2.73\sqrt{T/T_0})$ , where  $T_0 = 1.05 T_k$  ( $T_k$  is the absolute critical temperature),  $T$  is the observation temperature, and  $\delta_t$  and  $\delta_k$  are the densities at the observation and critical temperatures, respectively (cf. A., 1924, ii, 452), a formula for the expansion coefficient has been deduced,  $\beta = 1.365/(\sqrt{T/T_0} + 2.73T)$ . This formula has been tested by the experimental data for a number of liquids at temperatures extending from  $-90^\circ$  to  $+200^\circ$ . The deviations of the experimental values of  $\beta$  from the calculated values are greatest in the case of the alcohols, and for these, contrary to the general behaviour, the experimental value is the smaller one. For other liquids, deviations are small and of approximately the same relative magnitude and may in part be due to inaccuracy in the experimental data. In general, therefore, the expansion coefficient does not depend on the nature of the liquid, but is a simple function of the critical and observation temperatures, and will be the larger the lower the value of the critical temperature. For an ideal liquid,  $\beta$  will reach a minimum value of  $1.365/3.73T_0$  at absolute zero, and will approach an infinite value at the critical temperature, owing to the passage from liquid to vapour. The deviations observed in the alcohols cannot be due to association, since other liquids considered to be associated do not exhibit the same behaviour.

M. S. B.

**Coefficient of Expansion at Low Temperatures.** G. BORELIUS and C. H. JOHANSSON (*Ann. Physik*, 1924, [iv], 75, 23—36).—Measurements have been made of the coefficients of expansion of copper, cadmium, and zinc between  $100^\circ$  and  $300^\circ$  Abs. by means of the double-mirror dilatometer.

W. E. G.

**Diffusion of Mercury and Iodine Vapours through Nitrogen.** J. M. MULLALY and H. JACQUES (*Phil. Mag.*, 1924, [vi], 48, 1105—1122).—The diffusion coefficients of the vapours of mercury and of iodine have been determined by placing the free elements at the opposite ends of a closed glass tube containing nitrogen. An iodide deposit appears as a narrow ring across the axis of the tube. The gradient can be calculated from the known vapour pressures of mercury and iodine, the distance of the deposit from the ends of the tube, and the partial pressures of mercury and of iodine over the mercury iodides formed. Further, weighing and analysing the deposits after a time interval enable absolute values for the diffusion coefficients to be calculated. Thus, in nitrogen at 9.78 mm. of mercury and  $19.4^\circ$ ,  $D_{IN} = 5.80 \text{ cm.}^2/\text{sec.}$  and in nitrogen at 5.65 mm.,  $D_{HgN} = 17.3 \text{ cm.}^2/\text{sec.}$  To compensate for the large difference in vapour pressure between iodine and mercury either the tube can be constricted or an iodine compound such as caesium tri-iodide can be used.

C. W. B.

**Diffusion of Hydrogen into Air, measured by the Interferometer U Gauge.** C. BARUS (*Proc. Nat. Acad. Sci.*, 1924, 10, 447—452; cf. A., 1924, ii, 385).—A modified form of the apparatus previously described has been employed to determine

the coefficient of diffusion of hydrogen into air. The equations for the calculation of this coefficient from the experimental data are given. The mean value of  $a$  (diffusion coefficient  $a^2$ ), obtained with tubes of different lengths and diameters is 1.014 cm./sec. This is considerably higher than the usually quoted value ( $a=0.81$ ).

J. S. C.

**Precision Method for the Determination of Diffusion Coefficients in any Solvent. II.** E. COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1924, **113**, 157—159).—The diffusimeter previously described (A., 1923, ii, 130) has been tested with reference to the exactness of the measurement of the height of the diffusion layer when the lubricants used for the plates have different viscosities. The influence of the viscosity is not appreciably greater than the errors of experiment.

M. S. B.

**Technique and Theory of Measuring the Diffusion of Coloured Substances.** R. AUERBACH (*Kolloid-Z.*, 1924, **35**, 202—215).—Diffusion in sufficiently dilute gelatin jellies proceeds parallel with free diffusion in water, and such jellies can be used for studying the degree of dispersion of solutions of the technical dyes. The diffusion of aqueous solutions containing 1 g. per litre of the colouring matter into solid jellies containing 4% of a "medium hard" gelatin has been measured at 20° for a period of 24 hours. The results are expressed in terms of the distance between the meniscus of the gelatin and the point where the colour of the diffused layer matches a solution of one-tenth the concentration of the original solution. By the use of Einstein's formula, the radius of the particles expressed in terms of  $\mu\mu$  is found to be  $0.127/D$ , where the diffusion coefficient  $D$  is expressed in terms of sq. cm. per day. Thus a connexion between the size of the particles of the dyes in solution and the value  $l_{1/10}$  defined above has been traced in the form of a graph. This graph intersects the vertical co-ordinate at the value  $\mu\mu=1.75$ , whence it is inferred that a 4% jelly is no longer permeable to particles having a diameter greater than 3.5  $\mu\mu$ . The method, however, is very useful for the study of colloidal solutions containing smaller particles, including the majority of dye solutions. Since the value  $l_{1/10}$  involves an aliquot ratio of the original concentration, it is independent of variations in the purity of the substance and many other sources of error are eliminated by adopting this method.

J. F. B.

**Stokes-Einstein Law for Diffusion in Solution.** (Miss) C. C. MILLER (*Proc. Roy. Soc.*, 1924, **A**, 106, 724—749).—The diffusion constants,  $D$ , of iodine in a number of organic solvents and in aqueous solutions of ammonium bromide and ammonium iodide were determined. The viscosity coefficients,  $Z$ , were also measured. If the Stokes-Einstein equation were applicable under the conditions obtaining,  $DZ$  should be constant for the various solvents; this, however, was not observed with organic solvents. The variability of  $DZ$  was apparently not connected in any simple way with the colours of the iodine solutions, nor with the following properties

of the solvents—molecular weight, molecular volume, density, viscosity, or dielectric constant.  $DZ$  was found to be fairly constant for bromide solutions, but for iodide solutions the product increased almost linearly with the concentration of the salt. For fifteen organic solvents and twenty-four aqueous solvents, the relative values of  $DZ$  lie between the limiting values derived from the Stokes-Einstein and the Sutherland (*Phil. Mag.*, 1905, [vi], 9, 781) equations, respectively. The temperature coefficient of diffusion increases rather irregularly as  $D$  decreases. On the average,  $DZ$  scarcely increases with rising temperature to the extent required by the Stokes-Einstein equation.

L. F. G.

**Experiment on Solid Diffusion and its possible Bearing on the Structure of Solid Solutions.** F. C. THOMPSON and W. H. DEARDEN (*Trans. Faraday Soc.*, 1924, 20, 84—85).—Copper diffuses into pure gold and silver at 650° more rapidly than into a solid solution of these two metals. With silver, well marked zones similar to Liesegang's rings are formed. These results support the view that in solid solutions the added atoms are accommodated in spaces in the original lattice and do not replace atoms in the lattice itself.

S. S.

**Binary Liquid Mixtures.** O. FAUST (*Z. physikal. Chem.*, 1924, 113, 482—489; cf. A., 1922, ii, 423).—The deviations from the simple mixture law of the vapour pressures recorded in the literature for 50% acetone-chloroform mixtures at temperatures of 20—90° show an approximately linear variation with temperature, and extrapolation shows that this deviation would vanish at about 150°, at which temperature complex formation must cease. The relation of this result to those obtained for the gaseous phase by Schultze (A., 1913, ii, 676) is discussed. The molecular heats of vaporisation of mixtures of acetone with chloroform and of ether with chloroform are found to be greater than the values required by a simple mixture law, combination of the molecules of the two being indicated. For mixtures of benzene with ethylene dichloride the simple mixture law is obeyed, but for mixtures of carbon disulphide with acetone the values lie below those calculated, this effect being due to depolymerisation of complex molecules. In the case of the system acetic anhydride-water, the latent heat of the (stable) complex, acetic acid, is far below that calculated from the values for its components.

G. M. B.

**Influence of Proximity to the Critical Solution Temperature on the Volume.** N. PERRAKIS (*Compt. rend.*, 1924, 178, 703—705).—The densities of mixtures of *o*-cresol with ethyl alcohol and of phenyl ether with ethyl alcohol have been studied, and curves are given showing the dependence of the volume on the composition. For the first pair, the curve is pseudo-parabolic, and similar to that for mixtures of acetic acid and benzene, the components of which are also completely miscible. For the second pair, the components of which are only completely miscible near the critical temperature, the curve is complex, with a well-marked rectilinear portion. This

behaviour is supposed to be entirely due to the proximity of the critical point, and not to the existence of definite chemical compounds.

L. L. B.

**Solubility of Benzoic Acid in Benzene and in Toluene.** J. CHIPMAN (*J. Amer. Chem. Soc.*, 1924, 46, 2445—2448).—The solubility of benzoic acid in benzene and in toluene has been determined at various temperatures. Graphic methods for the interpolation of the experimental data are described. The heats of solution calculated from Mortimer's expression (A., 1922, ii, 621) indicate a transition point near  $95^{\circ}$ , but no evidence of this is afforded by the cooling curves.

S. K. T.

**Determination of the Solubilities of Sparingly Soluble Substances. I. Solubility of Magnesium Oxide in Water.**

H. REMY and A. KUHLMANN (*Z. anal. Chem.*, 1924, 65, 1—24).—The solubility of magnesium oxide in water free from carbon dioxide has been determined by evaporating a volume of the saturated solution and weighing the residue, by conductometric titration with standard acid, and by Kohlrausch's conductivity method. The values obtained by these methods agree fairly well, being 0.40, 0.39, and 0.35 millimol. per litre.

A. R. P.

**The Salting-out Effect.** K. LINDERSTRØM-LANG (*Compt. rend. Trav. Lab. Carlsberg*, 1924, 15, 1—65).—The influence of salts on the solubility of neutral substances may be expressed by equations of the form  $\log s_0/s_n = k \cdot c_n$  or  $s_0/s_n - 1 = k'c_n$ , where  $s_0$  is the solubility in water,  $s_n$  is a salt solution of concentration  $c_n$ , and  $k$  (or  $k'$ ) is a constant independent of  $c_n$ , but varying with the temperature and the nature of the salt and of the neutral substance. The present work is an investigation of the causes of this variation. From the solubility, the activity coefficient,  $f$ , has been found for quinol, quinone, succinic acid, and boric acid in various salt solutions, and the equation  $\log f = k \cdot c$  is on the whole confirmed. From the solubility data at different temperatures, the heats of solution have been calculated.

The causes of the variation in  $k$  with the nature of the substances salted out and of the ions are discussed with reference to Debye's views (A., 1920, ii, 356) on the nature of the cohesive forces, the structure of the univalent alkali and halogen ions being brought into relation with the structure of the corresponding inactive gases. It is probable that  $k$  must decrease with increasing size and polarisability of the ions forming the salt, and that the variation from potassium chloride to caesium chloride will run parallel to that from potassium chloride to potassium iodide. This parallelism can be effaced by the influence of chemical affinity between the ions and the neutral substance, the sign of the ionic charges being determinative for this. The attraction of the water also affects the absolute value of  $k$ , and, owing to the great solvent power of water,  $k$ , which for gases is chiefly negative, will in solution be chiefly positive, answering to an increased activity of the neutral substance. The hydration of ions is touched on, and the view expressed that none

of the ions  $K^+$ ,  $Rb^+$ ,  $Cs^+$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$  is hydrated. Attention is directed to the effacing influence on the forces of cohesion involved by hydration of ion or neutral molecule, but the view that hydration plays the leading part in the salting-out process is rejected.

In agreement with deviations from the mentioned parallelism, as far as regards quinol and quinone it is shown how the reducing qualities of the former and the oxidising power of the latter cause an increased attraction of the former to positive ions and of the latter to negative ions, whereby the importance of chemical affinity for the determination of the activity in concentrated solution, even where no chemical action occurs, is made clear. A special interpretation is found for the salting-out effect in the case of boric acid. Directions are given for the practical application of solubility data to the correction of measurements with the quinhydrone electrode in salt solutions. L. L. B.

**Adsorption of the Two Stereoisomeric Hydrobenzoin on Charcoal.** P. H. HERMANS (*Z. physikal. Chem.*, 1924, **113**, 385—388).—The fact that *r*-hydrobenzoin is more easily adsorbed by charcoal from solution in water or alcohol than its stereoisomeride, notwithstanding its greater solubility, is explained by assuming that the planes of the benzene rings lie on the adsorbing surface whilst the hydroxyl groups are attracted by the solvent. The case is compared with that of the adsorption of fumaric and maleic acid from aqueous solutions. G. M. B.

**Absorption of Salts by Storage Tissues.** W. STILES (*Ann. Bot.*, 1924, **38**, 617—633).—From a study of the ions absorbed and excreted from tissue surrounded by salt solutions, it is inferred that the absorption of salts is not a simple process of diffusion through a cell membrane. Accordingly, all data obtained by plasmolytic methods are open to considerable doubt. O. O.

**Effect of Hydrogen-ion Concentration on Compound Formation and Adsorption of Dyes by Mordants.** R. E. MARKER and N. E. GORDON (*Ind. Eng. Chem.*, 1924, **16**, 1186—1188; cf. A., 1923, ii, 616).—The adsorption of dyes (methylene-blue, crystal-violet, orange-II, and metanil-yellow) by inorganic gels (ferric and aluminium hydroxides and silicic acid) depends on the  $p_H$  of the solution. The acid dyes are adsorbed from acid solutions (low  $p_H$ ), all three gels, but particularly the ferric and aluminium hydroxides, taking up orange-II and metanil-yellow very readily from solutions of  $p_H$  about 2.3. Basic dyes, on the other hand, are adsorbed from alkaline solutions (high  $p_H$ ). Crystal-violet is very readily adsorbed by ferric and aluminium hydroxides at  $p_H$  11, and methylene-blue by all three gels at  $p_H$  12, but only weakly by the silica. Both ferric and aluminium hydroxides yield crystalline salts with orange-II. W. A. S.

**Surface Tension of "Tetralin," "Decalin," and Lubricating Oil.** L. GRUNMACH and G. SCHWEIKERT (*Z. physikal. Chem.*, 1924, **113**, 432—440).—The surface tensions of a lubricating oil and two substitutes have been determined by a method involving measure-

ment of the capillary rise between two plates and by the capillary wave method. "Tetralin,"  $d_0$  0.9766,  $\gamma$  3.493 mg./mm. at 18.3°. "Decalin,"  $d_0$  0.9026,  $\gamma$  3.210 mg./mm. at 18.8°. Lubricating oil,  $d_0$  0.9327,  $\gamma$  3.171 mg./mm. at 19.8°. G. M. B.

**Molecular Structure of Thin Films. VI.** N. K. ADAM and J. W. W. DYER (*Proc. Roy. Soc.*, 1924, **A**, 106, 694—709); cf. A., 1921, ii, 488; 1922, ii, 687; 1923, ii, 539, and *Proc. Roy. Soc.*, 1922, **A**, 101, 452).—Five long-chain alcohols examined formed both condensed and expanded films. The area of cross-section of the chain is near that of long-chain acids, being about 20.4 sq. Å.; the area of the  $\text{CH}_2\cdot\text{OH}$  group is 21.6 sq. Å. Acetates of three long-chain alcohols gave condensed and expanded films; the area of the  $\text{Me}\cdot\text{CO}\cdot\text{OCH}_2\cdot$  group is 23 sq. Å. Two long-chain methyl ethers were prepared and formed very unstable films; the methyl group on the oxygen apparently weakens the attraction of the molecule for water. Linolenic and clupanodonic acids, containing 3 and 5 double bonds, respectively, behave similarly to oleic acid, previously examined. Arachidic acid and some derivatives were prepared; they gave results in harmony with those already found for other members of the same series. The transition between "allotropic" condensed films of carbamide derivatives is examined more closely than hitherto; transition temperatures increase with length of carbon chain. Condensed film allotropy is exhibited also by hexadecyl- and octadecyl-acetamides; here the closer packing is with the low-temperature films, the reverse of the behaviour of the carbamide derivatives. The typical properties of condensed films of very long-chain compounds, *i.e.*, more than 27 carbon atoms long, are not so marked as with shorter-chain compounds. In pentaerythrityl tetrapalmitate, the four chains attached to a common centre through polar groups should be normally directed to the corners of a tetrahedron, but when present in films are oriented perpendicular to the surface. The application of a comparatively large compressive force is necessary before close packing occurs; this is ascribed to the resistance of the valency linkings in the central group of carbon atoms to deviation from their normal directions. L. F. G.

**Micro Determination of Molecular Weights by the Method of K. Rast.** W. S. SSADIKOW and A. K. MICHAÏLOW (*Biochem. Z.*, 1924, 150, 368—371).—An examination of the applicability of Rast's micro camphor method of determining molecular weights (A., 1922, i, 421). Results are sometimes variable even when the substance is soluble in camphor. J. P.

**Cryoscopic Measurements with Nitrobenzene. II. Variation of Molecular Depression with Water Content.** F. S. BROWN and C. R. BURY (*J. Chem. Soc.*, 1924, 125, 2219—2226).—Cryoscopic measurements were made with the water content kept constant by the presence of salt hydrate pairs (T., 1923, 123, 2037). Washburn's equation, in which the depression is set proportional to the sum of the mol. fractions of the solutes,

fits the data accurately for benzil and some other solutes, whilst the equation of van't Hoff agrees less satisfactorily. L. J. H.

**Anomalous Rotatory Dispersion.** F. BÜRKI (*Helv. Chim. Acta*, 1924, 7, 759—762).—The criterion for anomalous dispersion put forward by the author (cf. A., 1924, ii, 218) shows that, contrary to the views of Lowry and Dickson (A., 1915, ii, 660), the menthyl  $\alpha$ -phenylcinnamate, 1 : 2 : 2 : 3-tetramethylcyclopentyl  $\beta$ -phenylethyl ketone, and menthyl  $\alpha$ -acetyl- $\beta$ -phenylbutyrate behave anomalously. H. T.

**Dimensions of Ions in Aqueous Solutions.** K. JABŁCZYŃSKI (*Rocz. Chem.*, 1923, 3, 362—376).—The limiting values for the volume occupied by a dissolved electrolyte, that is, the sum of the volumes of the anion and cation, have been calculated from measurements of densities of solution. It is shown that the values are practically identical in each case with the sum of the volumes of the ions in the solid state as calculated by W. L. Bragg (A., 1920, ii, 537) by his X-ray method. Measurements show that, in the case of the halogen acids and lithium bromide and iodide, the volume of the undissociated molecule is equal to the sum of the volumes of the component ions; in other cases, a difference is found. The volume of the bromine ion is twice and that of iodine three times as great as those deduced from Bragg's measurements. Those of hydrogen, lithium, sodium, and silver ions are almost identical. The volumes of some compound ions such as ammonium and hydrazine were found to be practically identical with those of methane and ethane, respectively; the volumes of methylamine and trimethylamine ions are also close to the calculated values, but the volumes of anions do not show additive properties.

The relation between the volume of an ion in solution and its mobility is expressed by the Stokes-Einstein equation  $lw^{1/3} = K_1$ , the theoretical value for  $K_1$  being 102.77. Experimentally, however, greater values are found, and this is attributed to the effects of hydration; thus a lithium ion carries 12, sodium 5, potassium 0.6 mol.  $H_2O$ ; rubidium, caesium, and ammonium are not hydrated. These figures are in good agreement with those obtained from cryoscopic and ebullioscopic measurements (Jabłczyński and Kon, T., 1923, 123, 2953). Taking hydration into account, the new value of  $K_1$  becomes 207.9, or twice the value calculated from Stokes' equation; it is suggested that for ions this should have the form  $3\pi\eta v$ .

G. A. R. K.

**Activity Coefficients of Dilute Aqueous Solutions of Hydrogen Chloride, Thallous Chloride, and Lead Nitrate.** M. RANDALL and A. P. VANSELOW (*J. Amer. Chem. Soc.*, 1924, 46, 2418—2437).—Accurate determinations of the freezing points of solutions have been made with a modified Adams' apparatus (A., 1915, ii, 222), all dissolved air and other gases being removed from the solutions by prolonged evacuation. The activity coefficients of hydrogen chloride, thallous chloride, and lead nitrate derived from the data agree with the values obtained by other methods,

but not with the values given by the equation of Debye and Hückel (A., 1923, ii, 724; cf. A., 1924, ii, 306). S. K. T.

**Physico-chemical Investigations on Uric Acid.** R. STERN (*Biochem. Z.*, 1924, 150, 535—541).—The spontaneous transformation of a solution of sodium monourate on keeping for 4 days into a colloidal sol showing opalescence, increased viscosity, and a tendency to double refraction is described. J. P.

**Dissolution of Substances in Mixed Liquids with Special Reference to Colloids.** E. W. J. MARDLES (*J. Chem. Soc.*, 1924, 125, 2244—2259).—The solvent action on colloidal substances, such as tannic acid and cellulose acetate, of various binary mixtures of liquids suspected of forming molecular complexes with each other has been investigated, together with some of the physical properties (viscosity, surface tension, etc.) of the sols produced. The presence of the colloid greatly exaggerates any abnormality of the composition-viscosity (etc.) curve. In general, molecular simplification increases the solvent action, but where the components are themselves associated, the effect of complex formation may be masked by the molecular dissociation of the component liquids. [Cf. B., 1925, 1.] L. J. H.

**Physical Differences between Sols and Gels of Agar.** E. HATSCHKE and R. H. HUMPHRY (*Trans. Faraday Soc.*, 1924, 20, 18—22).—Sols and gels containing 3% or more of agar show optical differences, the gel scattering light much more effectively. The electrical conductivity of agar solutions containing 2% of copper sulphate is 1—2% greater in the gel than in the sol at the same temperature; the same result was obtained by the use of direct and alternating currents. It is suggested that in the gel condition the segregation of a phase rich in agar leaves a less viscous phase which contains most of the electrolyte and has a greater conductivity than the viscous sol. S. S.

**Influence of Anions on the Coagulation of a Negative Colloidal Sol.** D. C. HENRY and V. A. MORRIS (*Trans. Faraday Soc.*, 1924, 20, 30—36).—From a study of the coagulation of a gold sol by a series of sodium salts, it is found that the anion exerts a definite stabilising effect. The order of the anions is oxalate  $> \text{HPO}_4'' > \text{CO}_3'' > \text{OH}' > \text{citrate} > \text{HCO}_3' > \text{Br}', \text{I}', \text{acetate}, \text{valerate} > \text{butyrate}, \text{CNS}' > \text{SO}_4'' > \text{Cl}', \text{benzoate}$ . The order is not that of the Hofmeister series nor that of the effectiveness of the anions in the coagulation of positive sols. S. S.

**Velocity of Coagulation of Colloids of the Second Order.** C. K. JABŁCZYŃSKI (*Bull. Soc. chim.*, 1924, [iv], 35, 1286—1292).—Smoluchowski's equation (A., 1917, ii, 297) has been derived and experimentally confirmed for the velocity of coagulation of colloids of the second order, although the processes taking place in the coagulation of colloids of the two types are essentially different. This relationship also holds in the presence of protective colloids. Vigorous stirring has no influence on the velocity of coagulation.

H. T.



**Slow Coagulation of Colloids of the First Order.** C. K. JABŁCZYŃSKI (*Bull. Soc. chim.*, 1924, [iv], 35, 1277—1286).—Smoluchowski's equations (A., 1917, ii, 297) for the coagulation of colloids of the first order have been confirmed by observations on the slow coagulation of ferric hydroxide and arsenious sulphide. The method used depends on the absorption of light by the hydrosol, the absorption being measured by passing the light through crossed Nicols and finding the angle through which one had to be rotated to give equal illumination with the standard. If  $\alpha$  denotes this angle then  $\log \tan \alpha - \log \tan \alpha_0 = Kt$ . This equation is shown to be identical with Smoluchowski's. Two new methods for the derivation of his equation are described. H. T.

**Ageing of Metal Hydroxides, and the System Chromium Hydroxide-Chromite-Sodium Hydroxide.** R. FRICKE and O. WINDHAUSEN (*Z. physikal. Chem.*, 1924, 113, 248—260).—Both amorphous chromium hydroxide and crystalline aluminium hydroxide (prepared by dilution of 5*N*-sodium aluminate to 3*N* and shaking in the absence of air) when added to a solution of sodium hydroxide, dissolve to an extent which depends on the amount of solid phase present. This agrees with the results obtained by Müller (A., 1923, ii, 71) and is attributed to the inhomogeneity of the hydroxides. The rate of solution of these hydroxides is extraordinarily slow in spite of the very large surfaces exposed. The possible causes for this behaviour are discussed, since the explanation given by Müller for amorphous chromium hydroxide cannot be applied to crystalline aluminium hydroxide. M. B. D.

**Protection and Precipitation of Gold by Proteins.** R. ZSIGMONDY and E. JOËL (*Z. physikal. Chem.*, 1924, 113, 299—312).—The influence of gelatin on the stability of a colloidal gold sol depends on the concentration of the protein. As the concentration diminishes, it shows a protective action, later a coagulating effect, and finally becomes indifferent. The colour changes characteristic of these stages with fine and coarse gold hydrosols, with and without sodium chloride, have been tabulated. The results are explained on the assumption that several protein molecules may be combined with a gold particle or that gold particles may be adsorbed on the surface of a particle of the protective colloid. M. B. D.

**Antagonism between Dyes and Inorganic Salts in their Absorption by Storage Tissue.** C. E. T. MANN (*Ann. Bot.*, 1924, 38, 753—777).—Using thin slices of mangold tissue, the absorption of methylene-blue, neutral-red, and orange-G, respectively, has been followed in simple solution and in solutions containing the chlorides of ammonium, magnesium, aluminium, and lanthanum. In simple solution, the dyes are absorbed in the order: neutral-red > methylene-blue > orange-G at a time when equilibrium is being approached. This absorption is explained on the ultra-filtration theory of the nature of the plasma-membrane. The chlorides of aluminium and ammonium in 0.1*N*-solution have nearly the same effect, which is greater than that of magnesium

chloride. The presence of a salt in the solution of the dye antagonises the intake of the dye by the living tissue, and the magnitude of this antagonism is a function of the valency of the cation and its concentration. The antagonistic action between electrolyte and methylene-blue is stronger than that between the same electrolyte and neutral-red. The results obtained support Kahho's colloid precipitation theory of the plasma membrane (A., 1922, i, 94).

O. O.

**Hydration of Molecules and Ions.** R. FRICKE (*Kolloid-Z.*, 1924, 35, 264—274).—A summary, with bibliography of recent work.

E. M. C.

**Water Fixation in Colloids.** A. KUHN (*Kolloid-Z.*, 1924, 35, 275—294).

E. M. C.

**The Colloid-chemical Theory of Water Fixation in the Organism.** M. H. FISCHER (*Kolloid-Z.*, 1924, 35, 294—302).

E. M. C.

**Water Fixation in Colloids, from the Medical Point of View.** H. SCHADE (*Kolloid-Z.*, 1924, 35, 302—309).

E. M. C.

**Water Metabolism and Pharmacological Action.** H. HANDOVSKY (*Kolloid-Z.*, 1924, 35, 309—313).

E. M. C.

**Retention of Water in Soils.** G. WIEGNER, R. GALLEY, and H. GESSNER (*Kolloid-Z.*, 1924, 35, 313—322).—The properties of clay suspensions are determined by the nature of the "stabilising" cations associated with the ionised surface molecules of silicic acid. Clays with a single stabilising ion show a gradation in properties through the series Li, Na, K, and  $\text{NH}_4$ , Rb, Cs, and H; the stability of the clay depends on the hydration of the cation. A lithium clay is lyophilic, bulky, viscous, and insensitive towards electrolytes, whilst a caesium clay is lyophobic, sensitive to electrolytes, and has a less viscous. The alkaline-earths show a similar series. The flocculating powers of salts follow the hydration of their cations. When more than one cation is present, base exchange plays an important part in the coagulation process and takes place the more readily the higher the hydration of the stabilising ion and the lower that of the coagulating ion.

E. M. C.

**Influence of Solvent on the Equilibrium of Isomerides.** O. DIMROTH (*Annalen*, 1924, 438, 58—67; cf. A., 1911, ii, 31; 1913, ii, 763).—A theoretical paper, polemical against Smits (A., 1915, ii, 750; 1917, ii, 232; "Die Theorie der Allotropie," Leipzig, 1921, pp. 80—100, 138, 368—473). The isomerism of benzoyl-formaldehyde hydrazone and of acetaldehyde phenylhydrazone is discussed.

C. H.

**Dynamics of the Malonic Ester Equilibrium.** A. SKRABAL and A. MATIEVIC (*Monatsh.*, 1924, 45, 39—41).—The velocity of hydrolysis of malonic esters has been measured in aqueous alcoholic solution at 25° with hydrochloric acid as catalyst. The ester equilibrium has been calculated from the data. For methyl

malonate,  $K=4.2$  (cf. Palomaa, A., 1918, ii, 435). For ethyl malonate,  $K=2.4$ . The results are compared with those for oxalic esters (A., 1919, ii, 57, 144). F. M. H.

**Equilibrium in the Alcohol-Ether Reaction at 130° and 275°.** R. N. PEASE and C. C. YUNG (*J. Amer. Chem. Soc.*, 1924, **46**, 2397—2405).—The equilibrium  $2\text{EtOH} \rightleftharpoons \text{Et}_2\text{O} + \text{H}_2\text{O}$  has been investigated at 275° with alumina as catalyst, and at 130° with sulphuric acid-ethyl alcohol mixture as catalyst. The value of  $K$  ( $=[\text{Et}_2\text{O}][\text{H}_2\text{O}]/[\text{EtOH}]^2$ ) is  $0.66 \pm 0.1$  at 275° and  $8.0 \pm 0.2$  at 130°, representing the conversion of 62% and 85% of alcohol, respectively. With the help of previously published data, the heat of the reaction is shown to be 7100 cals., the free energy change in the reaction and the free energy of formation of ether vapour at 25° are -3210 cals. and -35,900 cals., respectively (cf. A., 1924, i, 363). S. K. T.

**Dual Ions and Internal Salts.** A. THIEL (*Z. physikal. Chem.*, 1924, **113**, 53—54).—Polemical against Blüh (A., 1924, ii, 658). Blüh's view of the behaviour of helianthin has long ago been dis-

carded. The formula  $\text{NMe}_2 \cdot \text{R} \cdot \text{SO}_2\text{Na}$  for the internal salt is impossible from the chemical point of view. Dual ions and internal salts are always "charge isomerides," the charges in the former being free, whilst in the latter they are bound by internal compensation of valencies. M. S. B.

**Ionisation Constant of Hypochlorous Acid.** F. G. SOPER (*J. Chem. Soc.*, 1924, **125**, 2227—2231).—Dilute solutions ( $10^{-4}$  to  $4 \times 10^{-3}$ ) of hypochlorous acid have been distilled at 25° and the ratio of the concentration in the distillate to that in the original solution has been found to be constant = 2.69. In this connexion, the conclusions of Noyes and Wilson (A., 1922, ii, 692) are criticised. From the value of the ratio and the concentration of hypochlorous acid in the distillate obtained from solutions of sodium hypochlorite, the hydrolysis constant for the latter at 25° is  $1.0 \times 10^{-6}$  corresponding with the value  $1.0 \times 10^{-8}$  for the ionisation constant of the acid. L. J. H.

**Conditions of Maximum Solubility : Gypsum.** A. COLSON (*Compt. rend.*, 1924, **179**, 1041—1045).—Gypsum shows a maximal solubility at 35°, and, according to the thermochemical data of Berthelot, the heat of dissolution at this temperature is zero, a result which is said to be incompatible with theoretical conclusions. If the gypsum is previously dried at 140°, a supersaturated solution, when kept at 35°, deposits its excess of gypsum with the evolution of 8.8 cal. per g. of anhydrous salt. Nearly the same value is obtained by determining the heat of solution of the similarly dried powder and subtracting the heat of hydration. These values are in fair agreement with that calculated by means of the Clapeyron equation (7.7 cal. per g.). These results indicate that the heat of dissolution is positive at the point of maximum solubility.

W. H.-R.

**Measurement of Vapour Pressures of Aqueous Salt Solutions by Depression of the Freezing Point of Nitrobenzene.** N. V. SIDGWICK and E. K. EWBANK (*J. Chem. Soc.*, 1924, **125**, 2268—2273; cf. Roberts and Bury, T., 1923, **123**, 2037).—The freezing point of dry nitrobenzene is  $5.689^{\circ}$ . The lowering in contact with solutions of known vapour pressure was determined and the relation may be expressed by the equation  $d=0.672p+0.00148p^2$ . This is in harmony with the assumption that water exists in nitrobenzene as single and double molecules only, and that the relative proportions are determined by the mass-action law. From the data it may be calculated directly that  $[H_4O_2]/[H_2O]=2.26$ . The vapour pressures of other solutions are then determined from the freezing points of nitrobenzene in equilibrium with them.

L. J. H.

**Hydration of Salts and their Effect on the Vapour Pressure of Water.** N. V. SIDGWICK and E. K. EWBANK (*J. Chem. Soc.*, 1924, **125**, 2273—2275; cf. preceding abstract).—The vapour pressure of some inorganic salt solutions is compared with the water of crystallisation of the solid salt. Those which are hydrated in the crystalline state give greater depressions, pointing to the hydration persisting correspondingly in solution. Nitrates are exceptional and association of the anion is inferred. No similar regularity is shown by aqueous solutions of the alkali salts of weak organic acids.

L. J. H.

**Equilibria at High Temperatures by the Pyrometric Method.** N. A. PUSCHIN and J. V. GREBENSCHTSCHIKOW (*Z. physikal. Chem.*, 1924, **113**, 57—78).—An apparatus is described for determining the cooling curve of a substance at a constant high pressure. By means of this, cooling curves have been obtained, under pressures up to 4000 kg./sq. cm., for a number of compounds, namely, diphenylamine, urethane, *p*-toluidine, benzene, phenol, *p*-nitroanisole, and trimethylcarbinol dihydrate. In general, the experimental results are in good agreement with those of other investigators by the manometric method. From the time required for crystallisation, the latent heat of fusion of urethane has been determined. It diminishes from 40.7 cal./g. at a pressure of 25 kg./sq. cm. to 29.3 at 3050 kg./sq. cm., and the results agree well with those deduced by Bridgman (*Proc. Amer. Acad.*, 1915, **51**, 118) from theoretical considerations. The temperature of transition from one crystalline form of phenol to the other is  $64.4^{\circ}$  under a pressure of 2200 kg. per sq. cm. (cf. Tammann, A., 1910, ii, 1051; Bridgman, *loc. cit.*). The chief advantages of the pyrometric over the manometric method are: the greater rapidity in determination, the much smaller quantity of material necessary, the possibility of determining at the same time the change of heat of fusion with pressure, and also the possibility of employing the pyrometric method in the study of equilibrium in systems of more than one component (cf. A., 1912, ii, 331).

M. S. B.

**Heat of Solution of Alkali Halides.** J. WÜST and E. LANGE (*Z. Elektrochem.*, 1924, **30**, 523—528).—Heats of solution at  $25^{\circ}$

have been measured by adiabatic calorimetry, at the dilute end by dissolving solid salts, at the saturated end by measuring heats of dilution. The integral heats of solution for a series of concentrations up to saturation have been drawn up for chlorides, bromides, and iodides of potassium and sodium. For sodium salts, they lie throughout below those for the corresponding potassium salts, and in both series the integral heats are lowest for chlorides and highest for iodides. In the case of sodium halides, the curves show a maximum, which is especially well marked with sodium iodide, not far from the saturation point. W. A. C.

**Calorimetric Researches. VI. Determination of Heat of Combustion of Salicylic Acid. Proposed Adoption of this Substance as Secondary Standard in Calorimetry.** P. E. VERKADE and J. COOPS (*Rec. trav. chim.*, 1924, **43**, 561—581).—The desirability of introducing a secondary standard for determining the thermal capacity of the calorimetric system is advocated. As standard substance salicylic acid is proposed, because it fulfils the following necessary conditions: Its heat of combustion is accurately known, viz., 5242 cal.<sup>15</sup>/g. (air) or 5232 cal.<sup>15</sup>/g. (vac.). It is easily obtainable in the pure state, is quite stable and not hygroscopic. It is non-volatile and offers no difficulties in its combustion. W. E. E.

**Dependence of the Heat of Vaporisation and the Surface Tension of a Liquid on the Molecular Forces.** J. J. PLĂCINTEANU (*Z. physikal. Chem.*, 1924, **113**, 290—298).—The equation given by Hammick (A., 1919, ii, 389; 1920, ii, 85) showing the connexion between the molar latent heat of vaporisation and the surface tension of a liquid, viz.,  $Mr/6 = \gamma V/d$ , where  $M$  = molecular weight,  $r$  = heat of vaporisation per gram,  $\gamma$  = surface tension,  $V$  = molecular volume, and  $d$  = diameter of a molecule, has been derived by the author, who finds that the constant =  $3\pi$  instead of 6. Using this new constant, he shows that it gives a better agreement with experimental results. M. B. D.

**Solubility, Heat of Solution, and Lattice Energy of Salts.** J. A. V. BUTLER (*Z. physikal. Chem.*, 1924, **113**, 279—289).—A close parallelism exists between the heat of solution of salts and their solubility. The solubility can be estimated from the heat of solution, modified by the condition of the surface. Since the heat of solution of a salt is equal to the difference between the sum of the heats of solution of its gaseous ions and its lattice energy, these are the fundamental quantities from which to estimate the solubility. A comprehensive series of values of the heat of hydration of salts has been calculated from their lattice energies (cf. Grimm, A., 1923, ii, 16). These values confirm the addition rule of Fajans (A., 1920, ii, 12). M. B. D.

**Conductivity of Aqueous Perchloric Acid.** E. LINDE (*Z. Elektrochem.*, 1924, **30**, 255—259).—The conductivity of perchloric acid has been measured at 25° over a range 1.05—13.50*N* and at 50° from 4.25—14.04*N*. The conductivity reaches a

maximum at  $25^{\circ}$  in 4.7*N*-solution. The viscosity of these solutions has been measured over the same range of concentration and the values for the degree of dissociation, after correction for viscosity, show a maximum at  $\text{HClO}_4 \cdot 3\text{H}_2\text{O}$  (approx.) and a minimum at  $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ . The temperature coefficient of the specific conductivity of a 4.7*N*-solution is 0.0125. M. B. D.

**Conductivity of Chlorides in Fused Antimony Trichloride and Ghosh's Theory.** Z. KLEMENSIEWICZ (*Z. physikal. Chem.*, 1924, **113**, 28—34).—Determinations of the electrical conductivity of solutions of potassium, rubidium, ammonium, and thallium chlorides in fused antimony trichloride have been made at  $98.5^{\circ}$ . By plotting values of  $\log_e \mu$  as ordinates against values of  $100 \sqrt[3]{\eta}$  as abscissæ,  $\mu$  and  $\eta$  being the equivalent conductivity and concentration, respectively, straight-line graphs are obtained. The graphs for the first three chlorides are nearly parallel and the tangent of the inclination to the axis of abscissæ is in close agreement with that theoretically deduced by Ghosh for uni-univalent electrolytes. For thallium chloride, however, the tangent is much greater and approaches the value for bi-univalent salts, possibly on account of the subsidiary valencies due to trivalent thallium. With the help of Frycz and Tolloczko's determinations of the transport number of the chlorine ion in antimony trichloride ("Gedenkbuch der Lemberger Universität," 1912) an extraordinarily high value, 137.5, has been found for the average mobility of the chlorine ion. On the analogy of the behaviour of the hydroxyl ion in water, this might be due to the fact that the solvent and solute produce the same anion, but it is noteworthy that the correction applied by Ghosh in the case of the hydroxyl ion, in order to obtain the linear relation between  $\log_e \mu$  and  $100 \sqrt[3]{\eta}$ , is not necessary here. The mobilities of  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Rb}^+$ , and  $\text{Tl}^+$  are 25.5, 16.5, 22.5, and 21.5, respectively, considerably less than in water, namely, 64.7, 64, 67.6, and 66. This is not accounted for by the difference in viscosity of the two solvents. The conductivity of mercuric chloride is so small that it can only be accounted for by incomplete ionisation, and this suggests that the variations in the behaviour of the uni-univalent chlorides may also be due to the same cause, contrary to Ghosh's complete ionisation theory. The effect of temperature on conductivity corresponds qualitatively with Ghosh's views, but a quantitative study is not possible owing to lack of data on the dielectric constant.

M. S. B.

**Electrical Conductivity of Solid Salts at High Temperatures.** P. VAILLANT (*Compt. rend.*, 1924, **179**, 530—532; cf. A., 1922, ii, 418; 1924, ii, 456).—The conductivity of solid sodium chloride, measured over a wide temperature range, increases to a maximum at  $28.6^{\circ}$ , decreases up to  $56.5^{\circ}$ , and thence increases to a much greater value than that of the first maximum up to  $420^{\circ}$ , the highest temperature of experiment. On reheating immediately after the first experiment, the first maximum is practically absent whilst the conductivity values forming the second remain unchanged.

At the higher temperatures, the current passing is approximately proportional to the electrode surfaces, and the inference is drawn that the passage of electricity takes place over the whole cross-section of the solid. Potassium sulphate and chloride give similar results, but in the case of barium chloride maxima were observed at  $28.4^{\circ}$  and  $107.9^{\circ}$ . The second of these has a particularly high value, being much greater than the value at  $456^{\circ}$ , the highest temperature employed. On reheating, both these maxima are absent.

H. J. E.

**Migration of Ions in Solid Electrolytes.** LE BLANC and M. KRÖGER (*Z. Elektrochem.*, 1924, **30**, 253—255).—Tubandt's experiments (A., 1921, ii, 426) are explained by assuming that the mobile ion is the one the displacement of which causes the least disturbance and suggest replacing the electrodes of the first cell by reversible iodine electrodes in order to test this theory. The experiments of Tubandt and Reinhold (*Z. Elektrochem.*, 1923, **29**, 313) do not clear up the work of Ketzer (A., 1920, ii, 217) on the change in conductivity of lead chloride powder produced by adding small amounts of sodium chloride.

M. B. D.

**Influence of Gelatin on Transport Numbers.** G. SCATCHARD (*J. Amer. Chem. Soc.*, 1924, **46**, 2353—2357).—A criticism of recent work by France and his co-workers (A., 1922, ii, 114; 1924, ii, 148). The values obtained (*loc. cit.*) for the transport numbers are shown not to have the significance ascribed to them. The proof that the change in the liquid-junction potential cannot be due to a change in the concentration of the acids is independent of the experimental results; these afford no evidence either for or against the conclusions reached by the authors.

S. K. T.

**Introduction to a General Theory of Electromotive Force.** E. DENINA (*Gazzetta*, 1924, **54**, 750—765).—Theoretical.

T. H. P.

**Determination of the Decomposition Potential of Aluminium Bromide in Aqueous Solution.** W. D. TREADWELL and H. STERN (*Helv. Chim. Acta*, 1924, **7**, 627—637).—From observations on the cell  $\text{Al}|\text{AlBr}_3 \text{ KBr}|\text{Br}_2 \text{ Pt}$ , the decomposition potential of aluminium bromide has been derived for temperatures from  $60^{\circ}$  to  $100^{\circ}$ . The value for  $100^{\circ}$  is 1.76 volts. Since the heat capacities of the hydrated and anhydrous salts are nearly equal, there is practically no difference between the heat of hydration and the free energy of the process. Introducing this quantity a value of  $1.76 + 1.23 = 2.99$  volts is obtained for the decomposition potential of saturated aqueous aluminium bromide and  $2.99 - 1.07 = 1.92$  volts for the normal potential of aluminium. Corresponding numbers have been obtained for aluminium chloride and iodide.

H. T.

**Differences of Potential at the Boundaries of Solutions.** R. FRICKE and C. ROHMANN (*Z. Elektrochem.*, 1924, **30**, 537—544).—Measurements of *P.D.* in concentration cells connected by

capillary siphons are not trustworthy when the capillary bore is 0.3 mm. or less, or when the concentration is lower than 0.1*N*. At comparatively low normalities, the *P.D.* of sodium and potassium hydroxide solutions is slightly below the calculated *P.D.*, owing to incomplete dissociation. From 2—3*N* onward, however, the *P.D.* found progressively exceeds that calculated. W. A. C.

**Diffusion Potentials and Ionic Mobilities of Benzoates and Salicylates and their Modification by a Membrane of Parchment Paper.** E. B. R. PRIDEAUX and W. E. CROOKS (*Trans. Faraday Soc.*, 1924, 20, 37—44).—The transport numbers of the anion calculated from the limiting conductivity and from observations of diffusion potentials for solutions of potassium and sodium benzoate and potassium salicylate are in good agreement. The mean values at 18° are potassium benzoate, 0.396; sodium benzoate, 0.310; potassium salicylate, 0.325. When a parchment paper diaphragm is interposed between the two solutions, a higher diffusion potential is found which corresponds with transport numbers of 0.318, 0.248, and 0.242, respectively, for these three salts. This is ascribed to the retardation of the anion by the membrane, the retardation being approximately constant for the two benzoates and greater in the case of the salicylate. S. S.

**Barium and Strontium Amalgam Electrodes.** P. S. DANNER (*J. Amer. Chem. Soc.*, 1924, 46, 2385—2390).—Three types of electrodes for use with two-phase alkali and alkaline-earth amalgams are described. The *E.M.F.* of barium and of strontium two-phase amalgams against calomel in 0.1*N*-solutions of the chlorides of the respective earth metals are 2.0240 and 2.2472 volts. These results are said to afford further evidence of the salt-like character of the mercurides. S. K. T.

**Seat of the Electromotive Force in the Galvanic Cell.** J. A. V. BUTLER (*Phil. Mag.*, 1924, [vi], 48, 927—935).—An extension of a previous paper (cf. A., 1924, ii, 598). The existence of large metal contact *P.D.*'s is in no way inconsistent with the correspondence between the *E.M.F.* of a galvanic cell and the energy of the chemical reaction occurring therein. The cell  $M|M^+aq|[H^+aq|H_2]Pt$  is taken as an example, and statistical expressions for the different junctions  $M|Pt, M|M^+aq, H^+aq|H_2|Pt$ , are combined to give an expression for the total *E.M.F.* of the combination. Differentiation of this latter expression yields the Gibbs-Helmholtz equation. C. W. B.

**Zinc-Carbon Battery.** H. D. NYBERG (*Z. Elektrochem.*, 1924, 30, 549—552).—With a view to facilitate depolarisation of the carbon anode by means of atmospheric oxygen, the anode is made of porous carbon and is impregnated with paraffin, but in such a way that its outer surfaces are not prevented from being wetted by the electrolyte, which consists of 10% sodium hydroxide solution. The zinc cathode is converted into insoluble zinc hydroxide when current is produced. An initial *E.M.F.* closely approximating to the calculated value of 1.2 volts is obtained. W. A. C.



**Photovoltaic Phenomena.** R. AUDUBERT (*Compt. rend.*, 1924, **179**, 682—684; cf. A., 1923, ii, 827).—The effect of illumination is to render cupric oxide electropositive and cupric bromide electronegative. With silver chloride or sulphide, the sign of the effect depends on the mode of formation and thickness of the film; for very thin films, the effects of red and blue rays are of opposite sign, but with thick deposits, the chloride becomes electropositive and the sulphide electronegative. Polarisation of opposite sign to that of the deposit always increases the effect slightly, whilst polarisation of the same sign diminishes or even annuls, but never reverses, the effect. If other conditions are equal, blue rays are more active in this respect than red rays. These results are not in accord with Athanasius's conclusions (A., 1924, ii, 239). Thermal and photochemical effects may, indeed, be superposed on and may mask the photo-electric effect, but if precautions are taken to avoid the former and carefully cleaned electrodes are used, results attributable to a photo-electric mechanism are obtainable. T. H. P.

**Electrolysis at the Mercury Dropping Cathode.** J. HEYROVSKY (*Compt. rend.*, 1924, **179**, 1044—1046; cf. A., 1924, ii, 598, 599).—Theoretical. If  $\pi$  and  $\pi'$  are the potentials of the mercury dropping cathode in solutions of concentration  $c$  and  $c'$ , and if the current intensities are identical in the two cases,  $\pi - \pi' = RT/nF \log_e c/c'$ , where  $n$  is the valency of the metal and  $R$ ,  $T$ , and  $F$  are the usual energy symbols. The current-*E.M.F.* curves (cf. Heyrovsky, *loc. cit.*) in solutions of different concentrations are thus superposable, being simply moved a distance  $RT/nF \log_e c/c'$  along the axis of potentials. But if there are only traces of a metal of the order  $10^{-6}$  mol. per litre, the slight electrolysis changes the concentration of the ions that may be deposited, and the saturation current is soon attained, forming a wave in the current-*E.M.F.* curve, and the two curves are no longer superposable. W. H.-R.

**Electrolytic Polarisation. I. Cathodic Overvoltage of Lead.** S. GLASSTONE (*J. Chem. Soc.*, 1924, **125**, 2414—2423).—As long as bubble formation is taking place, the potential of an electrode at small current density measured by the direct method is almost identical with the instantaneous back *E.M.F.* The overvoltage may be calculated from a formula of the type  $E = a + b \log (I - c)$ , where  $c$  is a term which takes account of the loss of potentiometric material by diffusion and may become important at low current densities. At appreciable current densities, the cathodic potential of a lead electrode is influenced by the presence of alkali-metal ions, probably owing to alloy formation, but the minimum overvoltage is uninfluenced. Roughening the surface of the electrode affects the minimum overvoltage. L. J. H.

**Hydrogen Overvoltage at Arsenic Cathodes.** G. GRUBE (*Z. Elektrochem.*, 1924, **30**, 517—523).—The cathode potential at which hydrogen begins to be evolved from galvanically deposited crystalline arsenic is 0.358 volt in 2*N*- and 0.284 volt in *N*-sulphuric acid. In sodium hydroxide solutions, it approximates to 1.0 volt.

Further experiments show that the potential imparted by arsenic hydride when it decomposes at an arsenic electrode in presence of sodium hydroxide solution is also about 1.0 volt. Hence, whereas in acid solutions formation and decomposition of arsenic hydride play a minor part, in alkaline solutions electrolysis leads primarily to arsenic hydride, of which the hydrogen evolved is a decomposition product.

W. A. C.

**Hydrogen Overvoltage on Alloys.** P. FISCHER (*Z. physikal. Chem.*, 1924, **113**, 326—328).—The hydrogen overvoltage for various alloys of cadmium, zinc, lead, tin, silver, and copper has been measured by experiments in 0.1*N*-sodium hydroxide solutions. The solution was stirred and the alloys were carefully polished. The author finds that the overvoltage is independent of the percentage composition of the alloy and is determined by the constituent having the smallest overvoltage.

M. B. D.

**Passivity Phenomena and Cathodic Overvoltage.** E. LIEBREICH and W. WIEDERHOLT (*Z. Elektrochem.*, 1924, **30**, 263—279).—The anodic and cathodic behaviour of chromium, iron, and mercury in 1.02*N*-sulphuric acid is shown in a series of current-potential curves in which discontinuities divide them into several regions corresponding with different electrode processes. A chromium anode at high current densities dissolves as chromate, but at lower current densities and potentials below  $e_h = +1.3$  volts this process ceases, the metal being probably coated with a chromic chromate film and dissolving only slightly. At about  $e_h = +0.5$  volt and a very small current density, the potential shows slight abrupt rise with falling current density and the true passive condition, ascribed to the insolubility of a film of chromic hydroxide, is attained. At zero current density, the passive metal has a potential of about  $e_h = +0.45$  volt. This passive condition persists, when the metal is made a cathode, at small current densities. At  $e_h = -0.4$  volt, the curve rises steeply owing to the metal dissolving as  $\text{Cr}^{++}$  ions, which are partly oxidised near the electrode, giving secondary hydrogen evolution (*a*). At higher current densities, metal solution gives place entirely to direct hydrogen evolution at about  $e_h = -0.5$  volt (*b*). Reducing the current density at an electrode in the condition (*a*) results in the metal returning to the passive state, but from the condition (*b*), the metal remains active even when the current is reduced to zero ( $e_h = -0.48$  volt). This base potential is retained when the metal is made an anode, but at a certain current density the potential jumps to a positive value and the metal dissolves as chromate. The curves for iron show similar discontinuities, but they are less marked except in the case of the generally recognised passivation change. The passivity of iron differs from that of chromium chiefly in that it corresponds with the highest state of oxidation, and is explained by the existence of a transparent film of a higher oxide. The curves for mercury are also discontinuous and cathodic treatment is shown to cause the formation of visible oxide films before the potential for hydrogen evolution is reached. The authors conclude that on cathodic treatment of a

metal, the monatomic hydrogen, resulting from hydrogen-ion discharge, is at first used up in reducing any oxygen present and by being dissolved in or adsorbed on the metal. Hydroxyl ions thus accumulate at the metal surface and react to form hydroxides. After these processes have taken place, the evolution of hydrogen as gas is retarded by the performance of chemical work in reducing the hydroxide layer which has formed, as well as of surface work in detaching the gas bubbles from the electrode. Film formation may thus be an essential factor in cathodic overvoltage as well as in passivity phenomena.

M. B. D.

**Theory of Electrolytic Oxygen Evolution with Anodic Polarisation. I. Magnesium, Cadmium, Zinc, and Mercury Electrodes in Alkaline Solutions.** F. JIRSA and K. LORIS (*Z. physikal. Chem.*, 1924, **113**, 235—240).—The polarisation of magnesium, mercury, zinc, and cadmium anodes has been measured at 25° in *N*-sodium hydroxide for varying current densities. At low densities, the metals dissolve in the bivalent form;  $\text{Hg} = -0.15$  volt,  $\text{Cd} = -0.60$  volt, and  $\text{Zn} = -1.35$  volts. On increasing the current density, oxygen is evolved and the metal becomes passive. The higher oxides formed are unstable, since when the current is stopped the potentials gradually sink to the above values. Magnesium, in contrast to the other metals, gives a more negative potential with increasing current density.

M. B. D.

**Theory of Electrolytic Oxygen Evolution with Anodic Polarisation. II. Palladium in Alkaline Solution.** F. JIRSA (*Z. physikal. Chem.*, 1924, **113**, 241—247).—The relation between current density and the potential of a palladium anode (against the normal hydrogen electrode) has been studied in *N*-sodium hydroxide at 18°. The graphed results indicate that palladium may exist in at least two active states, in addition to the usual passive form. An electrode which has previously been heated in air is always passive. By comparing the potentials at which breaks occur in the current density-polarisation curves with those in the corresponding curves for the anodic and cathodic treatment of palladium coated with  $\text{PdO}$  and  $\text{PdO}_2$ , respectively, it is concluded that in alkaline solution a palladium anode is oxidised in the following steps; to  $\text{Pd}_2\text{O}$  (at +0.15 volt); to  $\text{PdO}$  (at +0.4 to 0.5 volt); to  $\text{PdO}_2$  (at +0.95 volt); and to unstable  $\text{PdO}_3$  at 1.22 volts. Oxygen evolution occurs at more positive potentials through the medium of  $\text{PdO}_3$ , which breaks down into  $\text{PdO}_2$  and oxygen.

M. B. D.

**Conditions of the Appearance of Anode Effect in the Electrolysis of Fused Chlorides.** T. A. HEPPENSTALL and W. J. SHUTT (*Trans. Faraday Soc.*, 1924, **20**, 97—105).—Fused potassium, zinc, and lead chlorides were electrolysed with a conical anode arranged to vary the area of immersion in the fused mass. At a given temperature, the anode effect (a sudden large increase in resistance when the fused salt ceases to wet the anode) set in at a definite current density. This limiting current density increased

with rising temperature; at a given temperature, the superposition of alternating current on the direct current lowered the current density at which the anode effect appeared. Sodium chloride gave irregular results owing to corrosion of the cathode and crucible used.  
S. S.

**Electrochemical Behaviour of Chromium.** N. BOUMAN (*Rec. trav. chim.*, 1924, **43**, 399—402).—From results previously obtained (A., 1924, ii, 150), the author calculates the ratio of chromic to chromous ions in the liquid boundary layer to be  $10^{-2} : 1$ , so that whilst the solution in which the chromium electrode is immersed consists of pure chromic sulphate, the boundary layer contains mainly chromous ions. In order to maintain chromium in an active condition, the hydrogen-ion concentration must be at least  $10^{-3}$ , and it would appear from previous reasoning that the boundary liquid is alkaline. This is attributed to an error in the value of the hydrogen solubility product, which is now shown to be abnormally large,  $10^{2 \times -42}$  in place of  $10^{2 \times -48}$ . The author now regards his measurements of the potential of a chromium electrode on which another metal has been deposited as values of the potential of the two metals, the chromium not being completely covered by the small quantity of separated metal.  
H. J. E.

**Influence of Light and X-Rays on Anodically Polarised Platinum Electrodes.** G. GRUBE and L. BAUMEISTER (*Z. Elektrochem.*, 1924, **30**, 322—332).—Platinised platinum electrodes which had been treated with gaseous oxygen or anodically polarised were dipped in 2*N*-sulphuric acid and exposed to the light of a quartz mercury vapour lamp. The nobler the initial potential, the greater was the fall in potential. This continued in the same direction for 15 minutes after the light had been turned off, after which it rose again. Smooth platinum, coated with a golden-yellow oxide by superposition of alternating current on direct current, also showed an initial reduction of potential on exposure to light. On continued illumination, the potential rose until it was higher than the initial value and after four successive illuminations the total rise in potential was 0.179 volt. An electrode which had been strongly oxidised and kept in the dark showed no decrease in potential on exposure to light, but only a positive effect. The sensitivity of the electrode to light is weak in potassium cyanide and still weaker in sodium hydroxide. The action of X-rays is similar to that of light. The results are explained on Baur's photolysis theory (A., 1919, ii, 264). The electrodes are assumed to be covered with a solid solution of  $\text{PtO}_3$ ,  $\text{PtO}_2$ , and  $\text{PtO}$ . In light,  $\text{PtO}_2$  is converted into  $\text{PtO}_3$  and  $\text{PtO}$ . The  $\text{PtO}_3$  can then either decompose into  $\text{PtO}_2$  and oxygen or recombine with  $\text{PtO}$  to form  $\text{PtO}_2$ . As to which of these reactions predominates depends on the relative concentrations of the oxides, *i.e.*, on the potential of the electrode. The effect of increasing the (alternating) current density on an oxygen electrode is to make its potential pass through a minimum.  
M. B. D.

**Studies in Electro-endosmosis.** I. F. FAIRBROTHER and H. MASTIN (*J. Chem. Soc.*, 1924, **125**, 2319—2330).—An experimental method of measuring electro-endosmosis through a diaphragm of powdered material, together with the potential gradient across the diaphragm (using reversible electrodes) is described. The effective cross-section of the diaphragm is measured electrically. With carborundum powder, the electro-kinetic potential varies with hydrogen-ion concentration reaching a maximum in dilute alkali, the carborundum being relatively negative. In distilled water, the value is  $-0.0698$  volt. Contrary to other observers, no reversal is observed up to  $N/50$ -hydrochloric acid. L. J. H.

**Magneto-chemical Phenomena.** A. SCHÜKAREW (*Z. physikal. Chem.*, 1924, **113**, 441—463).—Numerous observations are recorded of currents observed between two electrodes immersed in a solution in which a chemical reaction is occurring or has just occurred, and of the effect on these currents of a strong magnetic field; of the increase caused by a magnetic field in a current maintained between two plates in a space in which certain gaseous reactions are occurring, and of the current which arises between two electrodes when placed in a strong magnetic field and in the vicinity of one plate in an electrolytic cell carrying a small current. The last effect is similar to, but not identical with, the Hall effect. No explanation of these phenomena is suggested. G. M. B.

**Velocity of Bimolecular Reactions in Solutions.** J. A. CHRISTIANSEN (*Z. physikal. Chem.*, 1924, **113**, 35—52).—Theoretical. Expressions for the velocity of non-ionic and ionic bimolecular reactions in solution are deduced on the basis of the expression for the velocity of a bimolecular gas reaction,  $h = C_1 \cdot C_2 \cdot v_{12} \sqrt{T} e^{-Q_{12}/RT}$ , where  $h$  is the velocity,  $C_1$  and  $C_2$  are the molar concentrations of the reacting gases 1 and 2, and  $v_{12}$  and  $Q_{12}$  two characteristic constants. These equations are compared with Brönsted's formula (A., 1922, ii, 699; see also Bjerrum, A., 1924, ii, 240). M. S. B.

**Kinetics of Coupled Reactions.** R. WEGSCHEIDER (*Z. physikal. Chem.*, 1924, **113**, 55—56).—Polemical with Thiersch (A., 1924, ii, 666). M. S. B.

**Improvements in the Apparatus for Measuring the Velocity of Very Rapid Chemical Reactions.** H. HARTRIDGE and F. J. W. ROUGHTON (*Proc. Camb. Phil. Soc.*, 1924, **22**, 426—431).—A continuation of previous work (A., 1923, ii, 746). More rapid reactions can now be investigated, four new modified types of the apparatus being described. One of them should be capable of dealing with reactions half completed in  $1/1000$  second, and has been tested with bimolecular reactions half completed in  $1/700$  second. A thermal method has been devised for determining the stages reached by a reaction at different intervals of time from its commencement. The principle of this method is to measure the temperature of the mixed fluid at different cross-sections of an observation tube. The apparatus employed allows the first observation of the temperature

to be taken 1/5000 second after the commencement of mixture, and for five subsequent measurements to be made at intervals of 1/7000 second; it has been used with 0.1N-hydrochloric acid and 0.1N-sodium hydroxide, to confirm the authors' conclusions as to the rate of mixture attained in their previous experiments.

L. F. G.

**Temperature Coefficient and Mechanism of a Chemical Reaction.** F. O. RICE, C. F. FRYLING, and W. A. WESOŁOWSKI (*J. Amer. Chem. Soc.*, 1924, **46**, 2405—2418).—The temperature coefficient of a reaction is said to depend on certain "residual molecules" the concentration of which is very small and varies rapidly with the temperature. Thus acetone is probably largely hydrated in solution, and the non-hydrated molecules are "residual molecules." At least one reactant molecule must be a "residual molecule" if a reaction is to proceed with measurable speed; from this, the existence of slow unimolecular reactions is denied. Variation of the solvent has only a very slight influence on the temperature coefficient of a reaction. The name "protions" is suggested for unsolvated ions. The errors accompanying the determination of reaction velocities are discussed in detail.

S. K. T.

**Formation of Ammonia in the Oxyhydrogen Flame.** H. TOMINAGA (*Z. Elektrochem.*, 1924, **30**, 528—534).—It is pointed out that Maxted's (T., 1918, **113**, 168, 386; 1919, **114**, 113) extrapolation of Haber's formula for the equilibrium  $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  to temperatures approaching 4000° is unsafe, since it leads to values for the specific heat of hydrogen and nitrogen which are somewhat too high. Moreover, the oxyhydrogen flame cannot be regarded merely as a source of heat, because at the temperatures concerned there is dissociation of water vapour, with consequent formation of nitric oxide. In the author's apparatus, mixtures of nitrogen (1 part) and hydrogen (1.8 to 6.0 parts) were passed under pressures up to 30 atm. on to an oxyhydrogen flame burning at a porcelain jet. Temperatures of about 3000° Abs. were observed. Approximately equal parts of ammonia and nitric oxide are formed. In agreement with calculation, the yield is increased as the temperature is lowered, i.e., as the amount of water formed is diminished. Considerably larger yields were obtained than by Maxted's method. W. A. C.

**Limits for the Propagation of Flame in Inflammable Gas-Air Mixtures. I. Mixtures of Air and One Gas at Ordinary Temperature and Pressure.** A. G. WHITE (*J. Chem. Soc.*, 1924, **125**, 2387—2396).—A summary of previous data is given. Lower and upper limits of propagation upward, downward, and horizontally have been determined afresh for ten combustible gases. The relations previously found in the case of vapours (T., 1922, **121**, 1244) hold less well in these cases, but for carbon monoxide and all the hydrocarbons examined (except acetylene) the lower limits may be calculated with reasonable approximation from the calorific values. [Cf. B., 1925, 2.]

L. J. H.

**Mechanism of the Oxidation of the Iodine Ion by the Ferricyanide and Ferric Ion.** C. WAGNER (*Z. physikal. Chem.*, 1924, **113**, 261—274).—On the assumption of the formation of a di-iodide ion (an additive product of atomic iodine and an iodide ion) the author explains the oxidation of iodide ions by ferricyanide ions and the retarding effect of the ferrocyanide ion on the rate of the reaction (cf. Just, A., 1908, ii, 825). In accordance with Herzfeld's explanation (A., 1919, ii, 503) of the rate of formation of hydrogen bromide from its elements, it is assumed that there is a primary reaction resulting in the formation of a di-iodide ion, followed by two further concurrent reactions in which this ion is converted either into iodine or into two iodide ions. The same explanation applies in the case of oxidation of iodide ions by ferric ions.

M. B. D.

**Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. IX. Reduction of Permanganate Passing from Neutral to Alkaline Solution.** J. HOLLUTA (*Z. physikal. Chem.*, 1924, **113**, 464—481; cf. A., 1924, ii, 115, 187).—A continuation of previous work. The influence of the hydroxyl ions on the velocity of the reduction of permanganate by sodium formate in slightly alkaline solutions has been studied. The results are fully in accord with the theories previously developed. The effect of the hydroxyl ions increases gradually with increasing concentration of alkali, manganate appearing more and more as an intermediate product in the process. The two stages in the reaction (A., 1922, ii, 771) characteristic of strongly alkaline solutions can be detected at relatively low hydroxyl-ion concentrations, although not so clearly. A side reaction occurs when the concentration of alkali is very low, according to the equations  $\text{MnO}_4' + \text{HCO}_2' + \text{H}_2\text{O} = \text{H}_2\text{MnO}_4' + \text{HCO}_3'$  and  $2\text{MnO}_4' + 2\text{OH}' + \text{HCO}_2' = 2\text{MnO}_4'' + \text{HCO}_3' + \text{H}_2\text{O}$ . With slight alkalinity hydroxyl ions cause a diminution of the oxidising action of permanganate owing to a decomposition of the manganate first formed with regeneration of permanganate.

G. M. B.

**Velocity of Esterification of *n*-Butyric Acid in Glycerol.** A. KAILAN and R. OBOGI (*Rec. trav. chim.*, 1924, **43**, 512—525).—The velocity of esterification of *n*-butyric acid at 25° in absolute glycerol, or in glycerol + 1½ mol. of water per litre, is proportional to the concentration of the catalyst (hydrochloric acid). In glycerol, the retarding action of water is less than in alcohol. The velocity of esterification of butyric acid without a catalyst was measured in absolute and aqueous glycerol at 183° and the reaction was found to be "sesquimolecular" (so also for benzoic acid). The water had not a retarding, but a weakly accelerating action when its concentration was 1½ to 2 mol. per litre.

F. M. H.

**Mutarotation.** R. KUHN and P. JACOB (*Z. physikal. Chem.*, 1924, **113**, 389—431).—Measurements of the velocity of mutarotation of dextrose in aqueous solutions having  $p_{\text{H}}$  values from 0.77 to 8.64 show that the isomeric change occurs chiefly to un-ionised

molecules. Dextrose is found to have an acid dissociation constant of  $10.5 \times 10^{-13}$  at  $25^\circ$ , agreeing well with the value of Michaelis and Rona (A., 1913, ii, 379), whilst a basic dissociation constant is indirectly estimated to be  $7.8 \times 10^{-17}$  at  $25^\circ$ . The observations show that the velocities of change of undissociated molecules, cations, and anions are, respectively, 0.0104, 54.4, and 113.2, and the observed velocities of mutarotation are given by  $k=0.0104+0.334[H']+9345[OH']$  (cf. Hudson, A., 1907, ii, 942).

Observations of the influence of a number of alkali salts and also of acetate, phosphate, and citrate mixtures on the velocities of mutarotation are discussed in detail from the point of view of the activity theory, and the reaction velocity is shown to be proportional, not to the concentration (Brönsted, A., 1922, ii, 699), but to the activity of the reacting molecular species. The conclusion of Baker, Ingold, and Thorpe (T., 1923, **125**, 268) that water is not involved in the mutarotation of tetra-acetylglucose in methyl-alcoholic solution is confirmed for dextrose in aqueous solution by the fact that the velocity of the change does not vary, as the participation of the water in the reaction would require, when the activity of the water is varied in solutions of 2—50% concentration.

Measurements of the velocity of the Lobry de Bruyn change of dextrose in presence of alkalis show this to be an ionic phenomenon. The constitution of the ions is discussed and the conclusion is reached that the hydrogen ion separates from the terminal hydroxyl group, the spatial configuration of the groups attached to the second carbon atom being unaltered. The mechanism of the Lobry de Bruyn and the Fischer inversions is considered. The enolisation theory is supported by the behaviour of sugars in alkaline solution towards permanganate, but the conclusion of Armstrong and Hilditch (T., 1919, **115**, 1410), that there is no connexion between the alterations in structure revealed by their experiments and those involved in mutarotation, is disproved by a study of the permanganate reduction in phosphate buffer solutions of known  $p_H$  in which the minimum reducing effect coincides with the minimum of velocity of mutarotation (at  $p_H$  3.0—4.5). Corresponding results are obtained with lactose and arabinose. In the case of lævulose, a maximum reaction velocity with permanganate was found between two minima, and this is held to indicate the existence of a particularly reactive form of lævulose in phosphate solutions between  $p_H$  3 and 4.

G. M. B.

**Reaction of some Glycols with Acetone.** P. H. HERMANS (*Z. physikal. Chem.*, 1924, **113**, 337—384; cf. Böeseken and Hermans, A., 1924, i, 257).—The Böeseken boric acid method is trustworthy only where a comparison is made of molecules so closely related as to eliminate errors due to direct constitutive influences on conductivity. The degree of formation of cyclic acetals by reaction with acetone is now shown to give results qualitatively parallel with those obtained by the boric acid method in the cases of a number of glycols. Exact measurements are recorded for the equilibrium, and the velocity of the reaction at



two temperatures, between acetone and *cis*-hydrindene-1 : 2-diol, *cis*-tetrahydronaphthalene-1 : 2- and -2 : 3-diols, and the two stereoisomeric hydrobenzoin. The results in the case of the two hydrobenzoin are explained by the assumption that the two phenyl groups repel each other strongly and hinder free rotation. This conception and the suggested mechanism of the reaction are supported by a thermodynamic consideration of the data obtained. The critical increment in such a reaction may be of a complex nature, one portion being due to a "steric increment" involved in the preliminary passage of the molecule into the suitable orientation for reacting with acetone ("steric activation"). G. M. B.

**Reducibility of certain Metallic Halides by means of Hydrogen.** F. DE CARLI (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 94—97).—Measurements have been made of the proportions of the halides undergoing reduction at various temperatures when a definite quantity of hydrogen is passed over stannic, stannous, cupric, cuprous, lead, and cobalt halides. The chlorides are reduced in smaller proportion than the bromides and these in smaller proportion than the iodides, and the halogens are given up the more readily by the metal with the higher than by the same metal with lower valency. [Cf. *B.*, 1924, 941.] T. H. P.

**Oxidation of Hydrogen by Potassium Permanganate.** E. WILKE and H. KUHN (*Z. physikal. Chem.*, 1924, 113, 313—325).—Measurements of the amount of hydrogen oxidised when the gas is bubbled through a solution of potassium permanganate show that the reaction is not so simple as was assumed by Just and Kauko (*A.*, 1911, ii, 494). The anomalies are probably due to the separation of manganese dioxide. The velocity of oxidation is decreased by the addition of acid and alkalis or by the action of X-rays. M. B. D.

**Electromagnetic Nature of Colloidal, Enzyme, and Catalytic Action and its Significance.** N. E. DITMAN (*Science*, 1924, 60, 183—184).—If hydrogen peroxide solution and colloidal platinum suspension, in separate vessels, are connected by a platinum or other metallic wire, a well-marked evolution of gas occurs from the hydrogen peroxide. If the primary circuit of an induction coil forms part of the conductor, and one pole of the secondary circuit is connected with another quantity of hydrogen peroxide, evolution of oxygen occurs much more rapidly than from samples connected with the primary coil or directly with the colloidal suspension. It would appear that an interrupted or oscillating electrical effect must pass through the metallic conductor. A similar result is obtained with various colloidal substances and with small detached pieces of platinum, copper, or iron. Potassium permanganate appears to produce a similar effect, as also does pancreatin in sodium carbonate solution. The production was observed of peptone from albumin solutions connected in the above manner with a solution of pancreatin in sodium carbonate. A. A. E.

**Landolt's Reaction. IV.** J. EGGERT (*Z. Elektrochem.*, 1924, 30, 501—503; cf. A., 1921, ii, 686).—Sodium thiosulphate catalyses the second stage of Landolt's reaction, viz.,  $\text{IO}_3' + 5\text{I}' + 6\text{H}' = 3\text{I}_2 + 3\text{H}_2\text{O}$ . The experiments do not decide whether the true catalyst is thiosulphate ion or sulphur in colloidal suspension. When the reagents are present in 0.001*N*-solution, thiosulphate in *N*/10<sup>9</sup> concentration accelerates the reaction velocity by 7%. Similar effects are observed when a crystal of sulphur is momentarily dipped into the solution, and this provides a delicate test for traces of sulphur. The inference is drawn that iodine is acted on more rapidly by sulphite ion than by thiosulphate ion. W. A. C.

**Behaviour of Active Hydrogen.** K. F. BONHOEFFER (*Z. physikal. Chem.*, 1924, 113, 199—219).—Active hydrogen produced in long vacuum tubes (cf. Wood, A., 1920, ii, 569; 1921, ii, 665) is found to reduce certain metallic oxides, halides, and sulphides. Sulphur, arsenic, and phosphorus are converted into their corresponding hydrides, and oleic acid is hydrogenated. Molecular hydrogen is formed under the catalytic influence of thin layers of metals or metallic oxides. The amount thus formed was determined by smearing the bulb of a thermometer with the metal or its oxide and noting the rise in temperature. The catalytic activity of a metal depends on its previous treatment and corresponds with its hydrogen overvoltage value, metals with high overvoltage being poor catalysts. The results are best explained on the assumption that active hydrogen is monatomic hydrogen. M. B. D.

**Active Hydrogen.** K. F. BONHOEFFER (*Z. physikal. Chem.*, 1924, 113, 492; cf. preceding abstract).—Errata. G. M. B.

**Activation of Oxygen in the Slow Oxidation of Sodium Sulphite.** W. P. JORISSEN and C. VAN DEN POL (*Rec. trav. chim.*, 1924, 43, 582—585).—A study of the simultaneous oxidation of sodium sulphite and sodium antimonite, when mixed in aqueous solution in the presence of sodium hydrogen carbonate (Jorissen, *Z. physikal. Chem.*, 1897, 22, 34; A., 1900, ii, 720). (a) The mixture was titrated with iodine immediately after its preparation and then at intervals of some days until the value was constant. The difference between the initial and final titrations was double the titration corresponding with the sodium sulphite originally present. (b) A solution of sodium sulphite, sodium antimonite, and sodium hydrogen carbonate was allowed to oxidise at 30° in a closed vessel fitted with a manometer. At the same time, an equal quantity of sodium sulphite solution was diluted with water to the same total volume and allowed to oxidise at 30° in an identical apparatus. Although the sodium sulphite solution alone was completely oxidised after 2 days, the absorption of oxygen by the mixture continued for 6 days. At the end of that time, the fall of pressure caused by the mixture was double that caused by the sodium sulphite alone. Thus the quantity of oxygen activated by the sodium sulphite is equal to that which it absorbs itself. Potassium carbonate, potassium hydroxide, and to a small extent quinol, inhibit the activation of oxygen by sodium sulphite. W. E. E.

**Autocatalysis.** A. QUARTAROLI (*Gazzetta*, 1924, **54**, 713—750).—Results are given of a large number of experiments on the decomposition of hydrogen peroxide in presence of metallic oxides or hydroxides. In alkaline solution, the decomposition effected by hydroxides of the heavy metals is distinctly febrile, the velocity of the reaction sometimes increasing to one hundredfold its initial value, then remaining stationary for a time, and afterwards diminishing more or less rapidly. With certain oxides, such as mercuric oxide, the decomposition exhibits an ephemeral febrile period, owing to the formation of an active catalyst, which afterwards undergoes rapid decomposition. When cupric hydroxide is used, under certain conditions there are formed green oxides of enormous catalytic activity, which increases with dilution of the hydrogen peroxide and of the copper; thus the velocity increases continuously as the reaction proceeds and is approximately inversely proportional to the mass of the reagents. Of all the metals examined, silver, or better, its oxide catalyses the decomposition of hydrogen peroxide most actively; gold is slightly less effective.

The decomposition of hydrogen peroxide under the influence of colloidal metals is a unimolecular reaction, whilst in presence of powdered and presumably inert substances, such as amorphous carbon, the velocity diminishes continuously as the reaction proceeds.

T. H. P.

**Catalysis of Hydrogen Peroxide by Iron Salts.** E. SPITALSKY and N. PETIN (*Z. physikal. Chem.*, 1924, **113**, 161—198).—The existence of ferrous iron in the presence of hydrogen peroxide (Manchot and Wilhelms, A., 1901, ii, 658) indicated by the formation of a blue precipitate when potassium ferricyanide is added, may be due to reduction of the ferricyanide by hydrogen peroxide. The catalysis of hydrogen peroxide on the addition of ferrous sulphate has been studied in both acid and alkaline solutions. In acid solutions, the reaction velocity is accurately reproducible. Previous results which show that the reaction velocity is directly proportional to the iron concentration and inversely proportional to the hydrogen-ion concentration are confirmed. In slightly acid and neutral solutions, the catalysis is complicated by the formation of a yellow basic precipitate which is catalytically inactive. This precipitate has an indirect retarding action for which alternative explanations are suggested. The catalytic activity of the clear solution is determined by its content of ferric and hydroxyl ions. In slightly alkaline solutions a reddish-brown precipitate is formed which at first has a strong catalytic activity, but this disappears as the precipitate ages. The clear solution is inactive. In strongly alkaline solutions, the reaction is again homogeneous until near the end, when the reddish-brown precipitate again separates.

M. B. D.

**Influence of some Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Methane-Air Mixtures.** W. P. JORISSEN and J. C. MEUWISSEN (*Rec. trav. chim.*, 1924, **43**, 591—597; cf. A., 1924, i, 253).—The observed

limits of inflammability depend on the nature of both explosion vessel and spark. The limits for pure methane-air mixtures are found to be: at 20°, 3.7 and 11.55% (by vol.) of methane; at 11.5°, 4.9 and 12.6%; in a round-bottomed flask of 1120 c.c. capacity, at 20°, 5.15 and 13.65%. For technical methane, the limits are: at 20°, 5.15 and 10.15%; at 11.5°, 4.5 and 12.6%.

At 7.9°, in the presence of 7.2% (by vol.) of pure carbon tetrachloride vapour, the limits for pure methane are 6.4 and 8.95%; at 10.1°, with 7.5% of vapour, 7.4 and 8.15%; at 11.0° with 7.8% of vapour, the limits coincide at 7.8%.

With technical methane commercial carbon tetrachloride completely inhibits explosion under the following conditions: with 9.6% of vapour at 15.0° between the limits 8.65 and 10.0%; with 9.0% of vapour at 14.0° between 8.65 and 10.2%; with 8.5–8.7% of vapour at 13.0° between 8.6 and 9.8%.

Explosion is also inhibited by 8.5 to 8.6% of pure carbon tetrachloride vapour at 13.0° between 8.0 and 9.0%. With 7.5% of pure vapour at 10.0°, the limits of inflammability coincide at 8.5%; with 7.2% of vapour at 8.0° the limits are 7.9–9.7%.

With technical methane, trichloroethylene completely inhibits explosion under the following conditions: with 3.5–3.6% of vapour at 5.0°, between 7.7 and 9.5%; with 2.7% of the vapour at 0.2°, between 8.0 and 9.6%.

Using one particular burette, the limits of inflammability of pure methane-air mixtures in the presence of 5.8% of trichloroethylene vapour are 2.6 and 9.8%.

In the case of pure methane-air mixtures trichloroethylene depresses the lower limit of inflammability very considerably. This anomaly is thought to be due to the presence in the trichloroethylene of some lower-boiling inflammable constituent. W. E. E.

**Electrolytic Separation of Base Radioactive Elements.** F. TÖDT (*Z. physikal. Chem.*, 1924, **113**, 329–335).—Systematic study of the separation of radium and its isotopes (thorium-X and actinium-X), thorium and its isotope, and actinium or mesothorium-II (cf. A., 1912, ii, 10; 1913, ii, 821; 1914, ii, 607; 1915, ii, 126). Thorium-X is separated from calcium by depositing it electrolytically on a silver wire cathode covered with a layer of silver chromate. The chromate precipitate containing only 0.5 mg. of barium can now be redissolved in hydrochloric acid and electrolysed without difficulty. Thorium is deposited cathodically in 0.1N-hydrogen chloride, using a high current-density. Mesothorium-II is electrolysed in 0.1N-hydrogen chloride containing ferric chloride and barium chloride. The barium chloride increases the conductivity of the solution and mesothorium-II is deposited with the iron owing to the similarity of their hydroxides. M. B. D.

**Anodic Oxidation of Gold. III.** F. JIRSA and H. JELINEK (*Z. Elektrochem.*, 1924, **30**, 534–537; cf. A., 1924, ii, 692).—From electrolytically prepared solutions of auric nitrate, by hydrolysis, the solubility product  $[\text{Au}^{+++}] \times [\text{OH}']^3 = 5.5 \times 10^{-46}$  is deduced, in fair agreement with the result from auric sulphate. Hence the

solubility of auric hydroxide is  $2.4 \times 10^{-12}$  mol. per litre. The value of the potential  $\text{Au} - \text{Au}^{+++}$  is found to be +1.37 volts, confirming previous results. The affinity constant of auric hydroxide, allowing for the formation of  $\text{HAu}(\text{SO}_3)_2$  in sulphuric acid solutions, is calculated to be  $1.1 \times 10^{-6}$ , so that the basicity of the former is similar to that of hydrazine.

W. A. C.

**Rectifying Action of Contact Detectors.** I. STRANSKI (*Z. physikal. Chem.*, 1924, **113**, 131—144).—The possible mechanism of the process required by the electron theory (cf. Schottky, *Z. Physik*, 1923, **14**, 99) of the rectifying action of a contact detector, consisting of a conductor in the form of a point and a crystal of a metallic compound, is discussed. Every atom is subjected to stresses, due to the electric fields produced by neighbouring atoms, and these tend to bring about deformation. The extent of deformation increases with atomic volume, and is therefore much greater in the anion than in the cation. The deforming action of the cation on the anion increases with the charge on the former, and should be greatest in the heavy metals, especially as, in compounds containing heavy metals, the ions are nearer together than in compounds containing cations which have the atomic structure of the rare gases (Fajans and Herzfeld, *A.*, 1921, ii, 174). The deformation taking place may result in a tendency for the anion to lose an electron, either by electron emission from the molecule, or by transference to the cation whereby the molecule changes from a heteropolar to a homopolar condition. Either process would tend to a rectifying action on the passage of an alternating current. At high temperatures, alkalis and alkaline-earth oxides show high electron emission, and at the same time they may exert a rectifying action. The heavy metal cations have not the large repulsive power due to the inert gas structure, and, instead of electron emission, there is probably a tendency to the production of a homopolar state. Any heteropolar compound should be capable of becoming a detector, but those must be the most sensitive in which the anion is already so much deformed that only a very small increase of energy is necessary to cause the transference or emission of an electron. Oxides, sulphides, selenides, and tellurides are chiefly employed as detectors. The halides do not give such deformable anions and the nitrides are already more or less homopolar compounds. If the point rests on more cations than anions on the crystal lattice, the current will flow from the point to the crystal and *vice versa*, poor response being obtained if the numbers of the two types of ion are nearly equal. The direction will probably depend also on the amount of pressure brought to bear by the point on the crystal surface. With too large a current strength there may be transference or emission of the whole anion and a regrouping of the atoms, accompanied by an inversion of the current. By continued action the crystal may be ruined.

M. S. B.

**Fluorescence and the General Laws of Reaction Velocity.** J. PERRIN and (Mlle.) CHOUKROUN (*Compt. rend.*, 1924, **178**, 1401—1406).—An application of Arrhenius' conception of acti-

vated molecules and the quantum theory to certain photochemical reactions. The actinic destruction of methylene-blue and of eosin in glycerol has been studied. In this solvent, the concentration of molecules in the critical state is fixed by the temperature and is proportional to  $e^{(-h\nu_2/RT)}$ , where  $\nu_2$  is the frequency of the radiation effecting the conversion of the glycerol molecules into the critical state. This frequency corresponds with an infra-red absorption of  $3.3\mu$ . The fluorescence of these substances decreases with concentration. It follows from the theory developed that if the concentration of the critical molecules is decreased, the destruction in glycerol is diminished. For the same light intensity, the destruction of methylene-blue (1 in 5000) in glycerol was one-tenth as great as at a concentration of 1 in 50,000. Similar results were obtained with eosin. Methylene-blue was studied in varying concentrations of glycerol and it was found that the "pseudo" velocity constant decreases as the glycerol concentration increases. In the case of eosin, which has previously been shown to react directly with ordinary (not critical) molecules of glycerol, the velocity constant was found to be directly proportional to the concentration of the latter. A hypothesis is advanced to explain these results.

L. L. B.

**Oxidation of Hydrogen Iodide. II.** C. WINTHER (*Z. physikal. Chem.*, 1924, **113**, 275—278).—Polemical, in reply to Plotnikov (*A.*, 1924, ii, 668).

M. B. D.

**Photochemical Decomposition of Gaseous Sulphur Dioxide.** R. A. HILL (*Trans. Faraday Soc.*, 1924, **20**, 107—112).—The decomposition of sulphur dioxide by light of a small range of frequencies has been studied using the radiation from a mercury lamp passed through suitable filters. The line  $313\mu$  was found to be responsible for 94% of the decomposition under the conditions of the experiment; it is concluded, however, that any wave-length within the absorption band is capable of bringing about decomposition if it is of sufficient intensity. The thermal decomposition of sulphur dioxide is discussed in terms of the radiation quantum hypothesis.

S. S.

**Photo-electric Properties of Silver Halides and the Mechanism of the Formation of the Photographic Latent Image.** R. AUDUBERT (*Compt. rend.*, 1924, **179**, 1046—1049).—An explanation is given of the formation of the photographic latent image in terms of the photo-electric properties of the silver halides (Audubert, *ibid.*, 1924, **179**, 682). The silver halide micellæ are surrounded by a gel in the water of which the silver halide molecules can dissolve and ionise; a potential difference probably exists between the grain and the electrolyte. Under the influence of light, an electron leaves the halide grain, enters the electrolyte, and attaches itself to a silver ion, which thereby becomes a free atom. At the same time, a chlorine ion leaves the electrolyte and discharges on the surface of the granule. These two ions are then immediately replaced by the dissolution of a further molecule of

the halide. In this way, exposure to light produces a number of free metallic atoms which act as nuclei for further reduction under the influence of the developer. The number of nuclei formed will depend on the length of the exposure, and will be greater with rays of short wave-lengths, since these are specially active in producing photo-electric effects. Calculation shows that the expulsion of an electron is favoured by increase in size of the particles.

W. H.-R.

**Photochemical Decomposition of Silver Bromide.** E. J. HARTUNG (*J. Chem. Soc.*, 1924, 125, 2198—2207).—The decomposition of silver bromide was investigated by means of a Steele-Grant microbalance sensitive to  $2 \times 10^{-5}$  mg. A silver film was deposited on a flat silica support and freed from occluded matter by ignition at  $400^\circ$  in a silica flask. It was then brominated. The relative weights of silver and bromine were in all cases within 0.1% of the theoretical. A glass exposing vessel is described into which the film could be sealed. In a side tube through which the vessel was exhausted was placed a roll of copper gauze as bromine absorbent. After exposure, the film was weighed, exposed to bromine vapour, and weighed again. With the use of copper 95% of the bromine content of the film was removed by insolation; with less efficient absorbents, somewhat less. It is suggested that the 5% not removed is due to contamination of the reduced silver film by gases from the glass walls of the vessel or from the atmosphere. The rate of bromination of silver films was studied by exposing films for varying times to a definite concentration of bromine vapour in a large flask. No discontinuity which might indicate the formation of a sub-bromide could be detected. Insolated silver bromide films absorb bromine much more rapidly than freshly-prepared silver films, presumably on account of different surface conditions.

C. I.

**Mercury and Helium.** J. J. MANLEY (*Nature*, 1924, 114, 861).—Under certain conditions, and in the presence of an electric glow discharge, mercury and helium combine to form mercury helide. This is a stable substance, decomposed at a bright red heat, and is but slightly absorbed by charcoal cooled in liquid air; it has not yet, however, been analysed quantitatively. A. A. E.

**Active Hydrogen.** F. PANETH (*Z. Elektrochem.*, 1924, 30, 504—507).—Active hydrogen, supposed to have the composition  $H_3$ , has been obtained by two methods. Hydrogen may be passed over an incandescent Nernst filament, but within a short time the filament is partly reduced and becomes useless. Alternatively, hydrogen is passed under reduced pressure through a palladium capillary heated to redness. All the active hydrogen formed was retained by a U-tube dipping in liquid air, and was given off again when the refrigerant was removed. The active hydrogen, which at best was formed in traces only, was detected by its reactions with sulphur and with tungstic acid.

W. A. C.

**Polysulphides of the Alkali Metals. V. Lithium Monosulphide and Disulphide.** J. S. THOMAS and J. H. JONES (*J. Chem. Soc.*, 1924, **125**, 2207—2214).—Lithium hydrosulphide alcoholate was heated very rapidly in a vacuum at  $300^{\circ}$ , yielding a faintly yellowish-brown mixture of lithium monosulphide and lithium ethoxide. This was treated with a current of hydrogen, containing 10% of hydrogen sulphide, at  $120^{\circ}$ , the ethoxide being reconverted into hydrosulphide. It was then heated to  $300^{\circ}$  in presence of phosphoric oxide and solid potassium hydroxide, when nearly pure lithium monosulphide was obtained. Lithium disulphide was prepared by boiling alcoholic lithium hydrosulphide with sulphur and concentrating the solution obtained, both operations being performed in a current of dry hydrogen. No higher polysulphide was produced. The solubility of sulphur in 0.5*N*-alcoholic lithium hydrosulphide was found to be, at  $80^{\circ}$ , 7.99 parts of sulphur to 2 parts of metal; at  $25^{\circ}$ , 6.94 parts of sulphur, and at  $15^{\circ}$ , 6.52 parts of sulphur. The excess of sulphur in these solutions over that present in the disulphide is to be accounted for by residual valency. The constitution of the disulphide was demonstrated by treatment with allyl iodide, diallyl disulphide being formed.

C. I.

**Normal and Basic Copper Sulphate.** A. KRUGER (*J. pr. Chem.*, 1924, [ii], **108**, 278—296; cf. Casselmann, *Z. anal. Chem.*, 1865, **4**, 24).—By warming a dilute solution of copper sulphate (5 g. per litre) in presence of sodium acetate, a green precipitate, approx.  $8\text{CuO} \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , was produced. By the slow hydrolysis of copper sulphate in dilute solution, a small quantity of precipitate of variable composition is produced; solutions containing 10—40 g. of copper sulphate per litre give a precipitate having the formula  $6\text{CuO} \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$  (cf. Pickering, A., 1883, 853). The first compound is also produced by hydrolysis in the slightly alkaline solution obtained by the addition of potassium hydrogen carbonate. It corresponds very closely with the mineral langite,  $4\text{CuO} \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$ , which may be produced by the hydrolysis of copper sulphate in dilute solution in presence of sodium acetate, potassium hydrogen carbonate, or magnesium oxide under very definite conditions of temperature and concentration, as a pale blue, crystalline precipitate, insoluble in water. On addition of a little copper sulphate or acetic acid to the aqueous suspension, the green salt,  $8\text{CuO} \cdot 2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ , is produced. With alkalis or alkali carbonates, a dark brown, amorphous hydroxide is produced. By hydrolysis of a very dilute solution of copper sulphate with potassium hydroxide, an amorphous precipitate,  $4\text{CuO} \cdot \text{SO}_3 \cdot 5\text{H}_2\text{O}$ , is produced. The following formulæ are proposed for the basic copper sulphates described:

$$[\text{Cu}(\text{OH})_2]_3, \text{CuSO}_4 \cdot 2\text{H}_2\text{O}; \quad [\text{Cu}(\text{OH})_2]_3, \text{CuSO}_4, \text{H}_2\text{O};$$

$$2\frac{1}{2}[\text{Cu}(\text{OH})_2]_3, \text{CuSO}_4, \text{H}_2\text{O}.$$

Langite appears to be formed by digestion of the brown copper hydroxide in excess copper sulphate solution at  $30$ — $40^{\circ}$ , the precipitate becoming green, and being, apparently, an adsorption compound. Details are given for the preparation of the dark amor-



phous copper hydroxide,  $8\text{CuO}\cdot\text{H}_2\text{O}$ , and for the preparation of normal copper sulphate. A. E. C.

**Action of Chlorine on Mercury.** A. F. O. GETMAN (*J. Physical Chem.*, 1924, 28, 1218—1220).—Polemical against Venkataramaiah (A., 1923, ii, 149). M. B. D.

**Thallous Thallie Halides.** A. J. BERRY (*Proc. Camb. Phil. Soc.*, 1924, 22, 363—368).—Solutions of thallous and thallie chlorides containing the two halides in varying proportions were prepared, and the composition of the crystals deposited from such solutions determined. Whilst the composition of the liquid phase could be varied over a wide range, the composition of the solid phase deposited was practically constant and corresponded with the formula  $\text{TlCl}_3\cdot 3\text{TlCl}$ . That this substance is therefore a definite compound and not the end member of a series of mixed crystals as is considered by Meyer (A., 1900, ii, 655) was confirmed by the fact that it recrystallised unaltered from 0.01N-hydrochloric acid. The compound,  $\text{TlBr}_3\cdot 3\text{TlCl}$ , orange-red crystals, can be prepared by the action of thallous chloride on solutions of thallie bromide (cf. Thomas, A., 1907, ii, 547; Cushman, A., 1900, ii, 725; Meyer, *loc. cit.*). The analysis of these bromide-chloride mixtures was facilitated by the fact that the thallie constituents are soluble in methyl alcohol, whereas the thallous constituents are insoluble or only slightly soluble in this substance. A method of readily preparing the compound  $\text{TlBr}_3\cdot \text{TlBr}$  is described;  $\text{TlBr}_3\cdot 3\text{TlBr}$  is difficult to prepare in the pure state. The observations of previous investigators that these compounds are decomposed by water are confirmed. Thallous thallie halides in aqueous solution exhibit no evidence of the formation of any stable complex ions. In this connexion, the observations of Cushman (A., 1902, ii, 322) on the interaction of silver nitrate and thallium chloride in the presence of nitric acid are confirmed. In all cases, exposure to low temperatures causes a very marked temporary diminution in the intensity of the colour of thallous thallie halides. L. F. G.

**Preparation of Tin Hydride by Cathodic Reduction.** F. PANETH and E. RABINOVITSCH (*Ber.*, 1924, 57, [B], 1877—1890; cf. A., 1920, ii, 41; 1922, ii, 383).—Tin hydride is formed by the electrolysis of a solution of tin sulphate between tin or lead electrodes, but the yield is very small and subject to great fluctuation. The addition of a small proportion of colloids (dextrin, gelatin, gum arabic, or agar-agar) or of larger amounts of certain crystalloids (sugar) to the electrolyte, not only increases the yield very greatly, but also stabilises it. In general, dextrin to the amount of 0.5% is found to be suitable. The lead electrodes then require an induction period of about 15—30 minutes, after which the cathodes gradually become coated with a loose, black deposit of spongy lead. Uniformly high yields of tin hydride may be obtained from such cathodes for an indefinite period if the electrolyte is renewed every 6—8 hours. The yield appears to increase somewhat with increasing strength of current, but to be independent of current density

between the limits 0.5—7.5 amps./sq. cm. Under all conditions with respect to the material of the cathode and the nature of the organic addenda, it increases initially with increasing concentration of tin in the electrolyte, attains a maximum (below 0.02% Sn), and then decreases rapidly to zero. Temperature appears to have little influence on the yield. Lead, as cathode, may be replaced by tin, cadmium, or platinum, but not by zinc or mercury or by amalgamated zinc or lead. The theory of the reaction is discussed in detail, and the authors are led to the conclusion that the optimum conditions for the production of tin hydride are the greatest possible concentrations of "overvoltage hydrogen" and "overvoltage metal." The concentration of the hydride in the electrolytic hydrogen is 1:10,000 in the most favourable case; this ratio is approximately that of the tin and hydrogen ions in the solution.

Electrolysis is effected conveniently in a crystallising dish or beaker, in which the anode, made of lead rod, is placed in a small, porous cell. The cathode is formed by melting lead in a curved glass tube, through one end of which a copper wire is inserted into the metal while hot; the metal at the other end of the tube is affixed to a lead disc. The junction between metal and glass is rendered liquid-tight by gypsum or paraffin. The cathode is placed under a small bell, which is readily made from a Gooch adapter. This form of cathode has the advantage that it may be removed without disturbing the remainder of the apparatus.

H. W.

**Preparation and Properties of Pure Tin Hydride.** F. PANETH, W. HAKEN, and E. RABINOVITSCH (*Ber.*, 1924, 57, [B], 1891—1903).—Tin hydride, prepared by the electrolysis of tin sulphate between lead electrodes in a series of the cells described in the preceding abstract, is washed by water and alkaline lead acetate solution, dried by passage through tubes at  $-80^{\circ}$  or  $-100^{\circ}$ , and condensed by means of liquid air. It is purified by Stock's method of fractional distillation and fractional condensation, whereby considerable difficulties are found in the removal of propane, arsine, hydrogen sulphide, carbon dioxide, and ethane and other volatile hydrocarbons. A final, very slow fractional distillation yields tin hydride containing not more than 0.3% of impurities. The formula,  $\text{SnH}_4$ , is derived by the quantitative thermal decomposition of the gas into its elements. Indications of the formation of higher hydrides were not obtained, but their existence is not impossible. Tin hydride has m. p.  $-150^{\circ}(\pm 2^{\circ})$ ; the variation of vapour pressure with temperature is expressed by the formula  $\log p = -1000/T + 7.4$ ; the latent heat of evaporation is 4.55 Cal. The colour imparted by tin hydride (mixed with hydrogen) to the flame depends greatly on its concentration. Tin mirrors, obtained by thermal decomposition of the hydride, are generally pale grey, occasionally silvery. In Marsh's tube, the deposit is formed in front of or in the heated part; the brown mirrors obtained previously behind the heated part (*A.*, 1922, ii, 383) are due to tin sulphide. Tin hydride is relatively stable; in glass vessels, it decomposes spontaneously after several days, but the change is not

accelerated by light. It decomposes immediately at 145–150°. It is very sensitive to the nature of the surface with which it is in contact, being decomposed at ground glass joints and, particularly, at tin mirrors, even when the latter are invisible to the unassisted eye. The instability of the gas in contact with solid desiccating agents (calcium chloride, phosphoric oxide) is probably a manifestation of this phenomenon. It is unaffected by dilute alkali hydroxide solutions (up to 15%), dilute sulphuric acid, dilute and concentrated nitric acid, and most metallic salts (sodium carbonate, copper sulphate, lead acetate, ferric chloride); it is absorbed to some extent by concentrated alkali hydroxide solutions or by concentrated sulphuric acid, completely by solid alkali hydroxides and soda-lime. It is quantitatively absorbed by silver nitrate (or sulphate) solution, giving a black precipitate which contains silver and tin in varying proportions, whilst tin is also present in the solution. It appears to reduce mercuric chloride to mercurous chloride.

H. W.

**Action of Normal Sodium Arsenite on Azido Compounds.** A. GUTMANN.—(See i, 84.)

**Bismuth. II. Tendency of Bismuth to Form Complex Salts.** H. MÜLLER and L. KÜRTHY (*Biochem. Z.*, 1924, **147**, 385–389).—The relative amount of bismuth recoverable by precipitation with hydrogen sulphide, after the metal has been added in the form of the nitrate to normal urine, gradually diminishes with lapse of time. This is ascribed to the formation of complex salts—more especially in the presence of chlorides—in which the bismuth is present in a non-ionisable form. Such complexes are not formed in the presence of nitric acid, whilst in certain concentrations of glycine bismuth nitrate undergoes considerable hydrolysis, which is ascribed to the interaction of the amphoteric acid with both positively (simple) and negatively (complex) charged bismuth ions.

J. P.

**Compounds of Tervalent Molybdenum. II. Molybdenyl Monochloride.** W. WARDLAW and R. L. WORMELL (*J. Chem. Soc.*, 1924, **125**, 2370–2372).—A solution of molybdenum trioxide in hydrochloric acid was electrolytically reduced in a diaphragm cell, concentrated with exclusion of air, and again electrolysed until a sample of the cathode liquid gave a buff-coloured precipitate when poured into acetone. This precipitate, which contains only trivalent molybdenum and has the composition  $\text{MoOCl}_4 \cdot 4\text{H}_2\text{O}$  was washed with acetone, alcohol, and ether, with exclusion of air, and stored in a desiccator under carbon dioxide, which was then evacuated. This compound oxidises gradually in air, but does not deliquesce. It is soluble in water or hydrochloric acid and is a strong reducing agent. Addition of lead acetate and acetic acid to its solution does not cause precipitation of lead chloride.

C. I.

**Cobaltammines of the Nitrogen Sulphonic Acids and Sulphato Cobaltammines.** F. EPHRAIM and W. FLÜGEL (*Helv. Chim. Acta*, 1924, **7**, 724–740).—The solubilities of a number of

cobaltammines of the nitrogen sulphonic acids were determined in order to test Ephraim's theory (A., 1923, ii, 644). In the majority of cases, compact molecules, *i.e.*, those with equivalent cation and anion, were less soluble than those in which the anion and cation possessed different values. The luteo salts of imidodisulphonic acids are exceptions, in that they are less soluble than the bivalent xantho salts. The preparation of the following new cobalt compounds is described: nitrilosulphonic acid, *hexamine* and *aquopentamine*; imidosulphonic acid, *hexamine*, *aquopentamine*, and *nitritopentamine*; amidosulphonic acid, *hexamine*, *aquopentamine*, *diaquotetrammine*, *nitritopentamine*, *cis-* and *trans-dinitritotetrammine* and *carbonato-tetrammine*; hydroxylaminetrisulphonic acid, *hexamine*, *aquopentamine*, *cis-* and *trans-dinitritotetrammine*; hydroxylaminedisulphonic acid, *nitritopentamine*; hydroxylamineisodisulphonic acid, *hexamine*, *nitritopentamine*, *chloropentamine*, *cis-* and *trans-dinitritotetrammine*; hydroxylaminemonosulphonic acid, *hexamine*; sulphatoaquotetramminecobalt chloride, bromide, iodide, nitrate, perchlorate, picrate, and sulphate; sulphatopentaminecobalt chloride, iodide, picrate, chromate, dichromate, chlorate, perchlorate, and fluosilicate; *hexaminecobalt* iodide sulphate; *aquopentaminecobalt* nitrate sulphate, nitrate iodide, and iodide sulphate.

H. T.

**Electrolytic Preparation of Ozone with an Alternating Superposed on a Continuous Current.** G. MALQUORI (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 102—106).—Good yields of ozone are obtainable by the electrolysis of aqueous sulphuric acid of density 1.1—1.4 by means of superposed continuous and alternating currents, an internally cooled anode of either lead coated with lead peroxide or platinum being used. [Cf. B., 1924, 942.] T. H. P.

**Preparation of Very Pure Barium and Strontium.** P. S. DANNER (*J. Amer. Chem. Soc.*, 1924, 46, 2382—2385).—Very pure metallic strontium or barium (99.9%) was prepared as follows. The pure oxide of the metal was partly (10%) converted into the peroxide and reduced by mixing with coarse aluminium metal (free from volatile impurities) and striking an arc in the mass. The cold fused mass was then ground, the fine particles sifted off, and the remainder sealed up in a distillation apparatus of special design, which was evacuated as rapidly as possible. When the absorbed gases had been removed and the pressure had reached  $10^{-4}$  mm., the temperature was raised to 950°, and the alkaline-earth metal distilled off in the form of soft, silver-white, crystalline pellets. The barium was spontaneously inflammable in moist air and hydrogen and tarnished rapidly in pure, dry carbon dioxide. Strontium was slightly less reactive.

S. K. T.

**Separation of Zirconium and Hafnium.** NAAMLIOOZE VEN-NOOTSCHAP PHILIPS' GLOEILAMPENFABRIKEN (Fr. Pat. 568978; from *Chem. Zentr.*, 1924, ii, 541).—Solutions of the salts, *e.g.*, those obtained by fusing the raw materials with potassium hydrogen

fluoride or potassium hydrogen sulphate, after removal of other metals by known methods, are either treated with a base or a basic substance (such as ammonia, sodium acetate, or sodium thiosulphate) in quantity insufficient to precipitate both the metals, the resultant precipitate being richer in zirconium and poorer in hafnium than the original material, or both elements are precipitated as hydroxides by excess of base and the washed precipitate is then treated with a quantity of acid insufficient for complete dissolution, the residual precipitate being poorer in hafnium and the solution richer. By frequent repetition of the process and, if necessary, purification of the fractions, a hafnium-free precipitate of zirconium hydroxide is obtained, and a zirconium-free solution of a hafnium salt from which the metals may be obtained in the usual manner. F. A. M.

**Separation of Zirconium and Hafnium.** NAAMLooZE VEN-  
NOOTSCHAP PHILIPS' GLOEILAMPENFABRIKEN (Fr. Pat. 569016;  
from *Chem. Zentr.*, 1924, ii, 541).—Ores containing zirconium and  
hafnium are fused with potassium hydrogen fluoride, then dissolved  
in water or hydrofluoric acid, and the solution mixed with potassium  
hydrogen fluoride; alternatively, the ores are fused with other  
substances and the mass is dissolved and treated with hydrofluoric  
acid or potassium hydrogen fluoride etc. The resultant solution is  
then fractionally crystallised, the crystals being richer in zirconium  
and poorer in hafnium than the original substance. The mother-  
liquor is then evaporated, again allowed to crystallise until the  
solution is practically free from zirconium, and is then worked up  
in the usual way for hafnium. Alternatively, the solution of the  
double fluoride is treated with a quantity of disodium hydrogen  
phosphate insufficient for complete precipitation, the washed  
precipitate is dissolved in hydrofluoric acid, and again fractionally  
precipitated etc., the precipitates becoming gradually richer in  
hafnium (cf. preceding abstract). F. A. M.

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## Mineralogical Chemistry.

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**Composition of the Earth's Crust.** F. W. CLARKE and H. S. WASHINGTON (*U.S. Geol. Survey Prof. Paper*, 1924, **127**, 1—117).—The following new average composition for igneous rocks of the earth's crust is deduced from 5159 of the more trustworthy published analyses:  $\text{SiO}_2$ , 59.12;  $\text{Al}_2\text{O}_3$ , 15.34;  $\text{Fe}_2\text{O}_3$ , 3.08;  $\text{FeO}$ , 3.80;  $\text{MgO}$ , 3.49;  $\text{CaO}$ , 5.08;  $\text{Na}_2\text{O}$ , 3.84;  $\text{K}_2\text{O}$ , 3.13;  $\text{H}_2\text{O}$  (over  $110^\circ$ ), 1.15;  $\text{CO}_2$ , 0.102;  $\text{TiO}_2$ , 1.050;  $\text{ZrO}_2$ , 0.039;  $\text{P}_2\text{O}_5$ , 0.299;  $\text{Cl}$ , 0.048;  $\text{F}$ , 0.030;  $\text{S}$ , 0.052;  $(\text{Ce}, \text{Y})_2\text{O}_3$ , 0.020;  $\text{Cr}_2\text{O}_3$ , 0.055;  $\text{V}_2\text{O}_5$ , 0.026;  $\text{MnO}$ , 0.124;  $\text{NiO}$ , 0.025;  $\text{BaO}$ , 0.055;  $\text{SrO}$ , 0.022;  $\text{Li}_2\text{O}$ , 0.007;  $\text{Cu}$ , 0.010;  $\text{Zn}$ , 0.004;  $\text{Pb}$ , 0.002%, and other elements in still smaller amounts. Averages for different regions and continents are also deduced. Ninety-nine % is accounted for by ten

oxides, and by but few common minerals. Possible analytical errors are considered in detail for each element. Igneous rocks (including metamorphic rocks) form 95% of the solid crust (lithosphere), the remainder being the sedimentary rocks, shale (4%), sandstone (0.75%), and limestone (0.25%). An average composition is deduced for each of these rocks; and taking into account also the oceans and the atmosphere, an average composition is deduced for the whole of the earth's exterior (to a depth of 10 or 20 miles in the solid crust). For a 10-mile crust, hydrosphere, and atmosphere the average is: O, 49.52; Si, 25.75; Al, 7.51; Fe, 4.70; Ca, 3.39; Na, 2.64; K, 2.40; Mg, 1.94; H, 0.88; Ti, 0.58; Cl, 0.188; P, 0.12; C, 0.087; Mn, 0.08; S, 0.048; Ba, 0.047; Cr, 0.033; N, 0.030; F, 0.027; Zr, 0.023; Ni, 0.018; Sr, 0.017; V, 0.016; Ce, Y, 0.014; sum of remainder 0.042%. These elements are in vast preponderance and, with some others, are classed as "petrogenic" elements. "Metallogenic" elements are those falling below Cu, Zn, Ga, Ge, As, Se, Br in the periodic table. The compounds of these two "natural" groups of elements as represented in nature by minerals are compared in detail. Petrogenic elements form mostly oxides and oxygen salts, whilst metallogenic elements form mostly sulphides, arsenides, and sulpho-salts. General remarks are added on the evolution of the elements.

L. J. S.

**Dumontite, a new Radioactive Mineral.** A. SCHOEP (*Compt. rend.*, 1924, **179**, 693—695).—This mineral, which occurs in pockets of the compact torbernite of Chinkolobwe, in the Belgian Congo, forms translucent, ochre-yellow, biaxial, elongated prisms,  $n > 1.78$ . The chemical reactions of the mineral are the same as those of dewindtite (A., 1922, ii, 305) and parsonsite. The composition is:

H <sub>2</sub> O.	P <sub>2</sub> O <sub>5</sub> .	UO <sub>3</sub> .	PbO.	TeO <sub>3</sub> .	Total.
5.78	8.65	56.49	27.19	1.01	99.12

which, neglecting the tellurium, corresponds with the formula,  $2\text{PbO} \cdot 3\text{UO}_3 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$ . The whole of the water is expelled at about 300°, and oxygen is lost at above 500°. T. H. P.

**Alkali Granite and Nepheline Syenites, Canadite, and Foyaite, in the Vredefort Mountainland, South Africa.** G. A. MOLENGRAAFF and A. L. HALL (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 465—486).—Descriptive. L. J. H.

**Specific Gravities of Minerals and Crystallised Chemical Compounds.** U. PANICHI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 182—188).—Theoretical considerations. T. H. P.

### Analytical Chemistry.

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**Apparatus for the Determination of  $p_H$ .** M. TRÉNEL (*Z. Elektrochem.*, 1924, **30**, 544—548).—A platinum electrode is fixed in a porous cell which is impregnated with a saturated solution of



potassium chloride and filled with the standard solution. Surrounding this diaphragm is a glass tube carrying the annular second electrode, also of platinum. The whole is immersed in the solution to be tested, and the potential difference is measured by potentiometer. Arrangements for temperature-compensation and for direct reading of  $p_H$  are described. W. A. C.

**Determination of Carbon, Hydrogen, and Nitrogen in Organic Compounds.** J. HESLINGA (*Rec. trav. chim.*, 1924, **43**, 551—560).—The method depends on the quantitative conversion of carbon and hydrogen in organic compounds into carbon dioxide and water, respectively, by passing the vapour over manganese dioxide at 400° or above. When halogens are present, lead dioxide is added to the manganese dioxide, whilst temperature modifications are made for substances containing sulphur or nitrogen. Similarly, manganese dioxide may be used in a Dumas nitrogen determination. In the combustion of benzil, it is shown that two-thirds of the oxygen comes from the manganese dioxide and one-third from the air. It is said that, with halogen compounds, the halogen is the true catalyst. [Cf. *B.*, 1924, 970.] F. M. H.

**Critical Studies on Methods of Analysis. XIV. Chlorine.** L. A. CONGDON, W. B. CRABTREE, H. W. COLES, L. L. SMITH, and M. L. VEHALGO (*Chem. News*, 1924, **129**, 302—304, 317—320, 334—336).—A record of comparative results obtained in the determination of chlorine by several different methods. The indirect method of adding an excess of silver nitrate and determining the excess by titration with thiosulphate gave more accurate results when the silver chloride was first removed by filtration, but direct titration with silver nitrate, using chromate as indicator, gave better results than either indirect method except in the presence of ammonium salts, when high results were obtained. A. R. P.

**Potentiometric Determinations with Mercurous Salts.** C. MÜLLER and H. AARFLOT (*Rec. trav. chim.*, 1924, **43**, 874—878).—A solution of mercurous perchlorate, prepared by boiling mercuric oxide (1 mol.) with concentrated perchloric acid (2 mols.) and excess of mercury, gives better results than mercurous nitrate solution (Behrend, A., 1893, i, 387) in the potentiometric titration of chlorides or bromides with a mercury electrode. The decomposition potentials for chlorides (+0.32  $\epsilon$ ) and bromides (+0.29  $\epsilon$ ) are too close together to allow of determinations of two halogens in the presence of each other. Iodide, cyanide, and thiocyanate can be determined when solutions containing these are run into the mercurous perchlorate solution. If the procedure is reversed, results are obtained for the iodide and thiocyanate which are 0.5—0.8% too low, and in the case of the thiocyanate the differences are even greater. This is attributed to the greater tendency of mercuric as compared with mercurous ions to form complex ions, such as  $HgI_4^{2-}$ . In the case of the iodide, this is shown by the initial production of a dark coloured solution containing free mercury according to the reaction  $Hg_2^{2+} \rightarrow Hg + Hg^{2+}$ . Cyanides, thiocyanates,

and iodides can be determined more exactly by Kolthoff's method (A., 1923, ii, 873). Chlorides can also be determined by potentiometric titration with mercuric perchlorate solution, the decomposition potential being  $+0.41 \text{ v}$ , but the method cannot be used for the determination of mercurous and mercuric mercury in a mixture.

R. B.

**"Chloramine" as a Substitute for Iodine in Chemical Analysis.** A. NOLL (*Chem.-Ztg.*, 1924, **48**, 845—846).—"Chloramine T" (the sodium salt of *p*-toluenesulphochloroamide), behaves like an inorganic hypochlorite except that it is much more stable and can be purified by recrystallisation from water. A 0.1N-solution is suitable for most analytical processes in which the much more expensive iodine solution is used; a small amount of potassium iodide and starch solution is used as indicator and the solution is preferably standardised against arsenic trioxide.

A. R. P.

**Determination of Nitrogen in Organic Compounds by Catalytic Hydrogenation.** H. TER MEULEN (*Rec. trav. chim.*, 1924, **43**, 643—644).—The organic nitrogen compound is heated in a current of hydrogen and the mixture of gases passed over nickelised asbestos prepared by low-temperature reduction; all the nitrogen is reduced to ammonia, which is collected in acid and determined volumetrically.

If the substance contains sulphur or halogens, the hydrogen sulphide or halide formed is absorbed in soda-lime.

W. E. E.

**Determination of Nitrogen by Kjeldahl's Method and its Modifications.** II. P. FLEURY and H. LEVALTIER (*J. Pharm. Chim.*, 1924, [vii], **30**, 265—272).—The authors' method (cf. A., 1924, ii, 273) gives good results in most cases, including pyridine derivatives, if the mixture is heated for  $1\frac{1}{2}$  hours. Nitrates, nitriles, oximes, and azo compounds, however, require the addition of benzoic acid, and aromatic nitro derivatives and hydrazines and their derivatives require the addition of zinc. The benzoic acid method gave the best results (96% of the theoretical) for anti-pyrine and pyramidone. Semicarbazide and its derivatives require for their reduction the addition of both zinc and benzoic acid to the standard mixture of sulphuric acid, phosphoric acid, and potassium sulphate.

J. K.

**Application of the "Formol Titration" to the Kjeldahl Method of Nitrogen Determination.** W. S. SHAW (*Analyst*, 1924, **49**, 558—565).—The distillation of the colourless solution obtained after digestion with acid in the Kjeldahl method may be eliminated by titrating an aliquot portion of the neutralised, reacidified, boiled, and reneutralised solution to which a definite quantity of formaldehyde of known acidity has been added, with standard sodium hydroxide solution. [Cf. B., 1925, 30.]

D. G. H.

**Pemberton-Neumann Method for the Determination of Phosphorus.** M. B. RICHARDS and W. GODDEN (*Analyst*, 1924, **49**, 565—572).—The main sources of error were found to be

(1) variation in the volume of standard alkali used to dissolve the precipitate (1—2 c.c. excess gave the best results); (2) carbon dioxide absorbed by the alkali used to dissolve the ammonium phosphomolybdate precipitate may not all be expelled, and to effect this it is necessary to boil with excess of acid before the final titration; (3) the factor used. Assuming the formula of the precipitate to be  $(\text{NH}_4)_3\text{PO}_4 \cdot 2\text{MoO}_3$  the factor is 0.001365. [Cf. *B.*, 1925, 30.] D. G. H.

**Detection of Ortho-, Pyro-, and Meta-phosphate Occurring Together, and in Presence of Sodium Fluoride.** J. H. DE BOER (*Chem. Weekblad*, 1924, **21**, 561—566).—A 1% solution of luteocobalt chloride gives a distinct cloudiness with a 0.01% metaphosphate solution; with stronger solutions, an amorphous precipitate, which does not settle, and is not arrested by filter-paper, is obtained. Pyrophosphate gives no precipitate in dilute solutions, but a characteristic crystalline precipitate is obtained, after seeding, with a 0.05% solution; this, unlike the metaphosphate precipitate, dissolves in dilute acetic acid. Orthophosphate gives no precipitate, even in 5% solution. Small quantities of pyrophosphate may be detected by means of zinc or copper sulphate in presence of acetic acid; ortho- and meta-phosphates under these conditions give precipitates only when present in large quantities. Orthophosphate is detected by means of silver nitrate or ammonium molybdate; the latter test is extremely sensitive and specific.

In presence of fluorides, metaphosphate may be detected as before; the phosphates are then separated by means of silver nitrate, and zinc or copper sulphate is employed to test for pyrophosphate. Orthophosphate is detected as above, thorium nitrate being also added. S. I. L.

**Physico-chemical Analysis, by Conductivity, of Vegetable Ash. I. Determination of Phosphoric Acid.** L. DESHUSSES and J. DESHUSSES (*Helv. Chim. Acta*, 1924, **7**, 681—688).—Phosphoric acid in vegetable ash can be quickly determined with an accuracy of 1—2% by titrating the acid extract of the ash with uranyl nitrate solution in the presence of ammonium acetate, the end-point being determined by a conductivity method similar to that used by Dutoit et Duboux ("L'Analyse des Vins par Volumétrie phys. chim.," 1912). The amount of ammonium acetate added is regulated by the amount of acid present. H. T.

**Preparation of the Magnesium Ammonium Phosphate Precipitate for the Determination of Phosphoric Acid or of Magnesia.** B. SCHMITZ (*Z. anal. Chem.*, 1924, **65**, 46—53).—As a result of investigation into the best method of producing a precipitate of magnesium ammonium phosphate free from trimagnesium phosphate and from tetrammonium magnesium diphosphate, the following procedure is recommended for the determination of phosphoric acid. The slightly acid solution is treated with magnesia mixture, ammonium acetate, and a few drops of phenol-

phthalein. After heating to incipient boiling a 2.5% solution of ammonia is allowed to drop in slowly from a burette while the liquid is stirred until it becomes turbid; stirring is continued until the precipitate becomes crystalline, ammonia is added until the solution becomes pink, and the whole is allowed to cool. Concentrated ammonia solution equal to one-fifth the volume of the liquid is added and the mixture is stirred for a few minutes and filtered on a Neubauer crucible. The precipitate is washed with 2.5% ammonia, then with alcohol, ignited at  $1000^{\circ}$  for 30 minutes, cooled, and weighed. [Cf. *B.*, FEB.] A. R. P.

#### **Removal of Phosphates in Systematic Qualitative Analysis.**

L. J. CURTMAN, C. MARGULIES, and W. PLECHNER (*Chem. News*, 1924, **129**, 299—301, 315—317).—Instead of the usual procedure of precipitating the phosphoric acid as ferric phosphate, precipitation as zirconium phosphate is recommended. The solution is treated in succession with ammonium chloride, zirconium oxychloride, and ammonia until alkaline, boiled for 2 minutes, acidified with hydrochloric acid, and again boiled and filtered. If only small amounts of phosphoric acid are present a little fine asbestos added to the solution aids in filtering the zirconium phosphate. Excess of zirconium is found with the aluminium in the subsequent separation and may be removed by digestion of the mixed precipitate with sodium hydroxide. A. R. P.

#### **Separation of Arsenic and Antimony by Distillation.**

F. L. HAHN and H. WOLF (*Ber.*, 1924, **57**, [B], 1858—1860).—Complete separation of arsenic from antimony by distillation of solutions of the chlorides can be effected if the distilling flask is placed on an asbestos board pierced with a small hole and heated with a small flame which touches only that portion of the glass which is invariably covered by liquid. The operation is tedious and requires great care. A rapid and quantitative separation is obtained, however, if the flask is provided with a fractionating inset which is figured in the original. H. W.

#### **Invert-sugar as a Reagent for Boric Acid Determinations.**

G. VAN B. GILMOUR (*Analyst*, 1924, **49**, 576—577).—The reagent is prepared by inverting commercial granulated sugar with sulphuric rather than hydrochloric acid, since the small quantities of chloride present in the latter case would interfere with sodium chloride determinations which, in the case of butter and margarine, are frequently made on the same solution. [Cf. *B.*, 1925, 54.]

D. G. H.

#### **Qualitative and Quantitative Analysis of Sodium Dithionate.**

F. M. LITTERSCHEID and H. LÖWENHEIM (*Chem.-Ztg.*, 1924, **48**, 881—883).—The ordinary crystallised sodium dithionate contains  $2\text{H}_2\text{O}$ ; specimens with  $5\text{H}_2\text{O}$  are sometimes found and an unstable form with  $6\text{H}_2\text{O}$  undergoes efflorescence to the stable form with  $2\text{H}_2\text{O}$  at the ordinary temperature. Water of crystallisation is determined by drying at  $60^{\circ}$  for  $1\frac{1}{2}$  hours and finally at  $100^{\circ}$

for  $\frac{1}{2}$  hour. The pure salt should show no reaction for sulphate, sulphite, chloride, or carbonate. In testing for iron and other metallic bases care should be taken not to boil the salt with strong acids owing to liberation of sulphur dioxide. When heated at  $250^{\circ}$  or to low redness, the whole of the sulphur dioxide is expelled, leaving a residue of sodium sulphite. This residue should be examined for purity and freedom from sulphite and carbonate. If during heating a sublimate of sulphur is formed or if the salt turns brown or black, it is impure. A method is described whereby the sulphur dioxide is expelled in a current of carbon dioxide as when conducting a combustion analysis of organic materials. The sulphur dioxide is absorbed in standard iodine solution and determined by titration of the latter. J. F. B.

**Precipitation of Calcium Oxalate in the Presence of Ammonium Citrate.** W. F. JAKÓB (*Roczniki Chemji*, 1923, 3, 308—324).—The precipitation of calcium in the form of oxalate has been examined with special reference to the inhibiting action of citrates. It is found that the latter appreciably increase the solubility of calcium oxalate, more especially in the presence of free ammonia, this effect being attributed to the formation of complex calcio-citrate ions; the tribasic citrate ion is mainly responsible for complex formation. The complete precipitation of calcium is nevertheless possible if a sufficient excess of ammonium oxalate is used. The shape of the precipitation curve indicates that the process takes place in two phases corresponding with two hydrates of calcium oxalate; the principal constituent obtained at  $40^{\circ}$  is one containing  $2.5\text{H}_2\text{O}$ , whilst the remainder is the monohydrate which is precipitated towards the end of the reaction. The former of these is coarsely granular and easily filtered and is probably well adapted to the determination of calcium, as it will not tend to form isomorphous mixtures with magnesium oxalate.

G. A. R. K.

**Contradictions and Errors in Analytical Chemistry. V. Precipitation of Magnesium Ammonium Phosphate from Solutions containing Aluminium.** F. L. HAHN and S. SCHEIDERER (*Ber.*, 1924, 57, [B], 1854—1858).—The simultaneous presence of tartaric acid and aluminium can not only delay, but may also actually prevent the precipitation of magnesium as magnesium ammonium phosphate. Magnesium if present in small amount (about 1%) in aluminium alloys cannot therefore be determined in this manner. Separation of magnesium from aluminium and zinc is effected by the use of an excess of alkali hydroxide; the precipitate is contaminated with zinc and aluminium, but is so far enriched in magnesium that a quantitative separation is brought about by redissolution and subsequent precipitation by ammonium sulphide. H. W.

**Volumetric Determination of Zinc.** E. BEYNE (*Bull. Soc. chim. Belg.*, 1924, 33, 507—516).—Various modifications of Schaffner's method of titrating zinc in ammoniacal solution with sodium

sulphide are discussed. To obtain satisfactory results, a compensatory method is necessary. The amounts of ammoniacal salts are important, as is the density of the ammonia, which should be 0.92. Various passages in Olivier's pamphlet (1921) on the Vieille Montagne method are commented on. [Cf. *B.*, 1924, 1016.]

F. M. H.

**Volumetric Determination of Zinc.** K. KIEPER (*Chem.-Ztg.*, 1924, 48, 893).—An excess of standard sodium sulphide solution is added to the ammoniacal zinc solution, the mixture is heated and the precipitate filtered off. The filtrate is cooled, acidified with acetic acid, and titrated with iodine. [Cf. *B.*, 1925, 29.]

A. R. P.

**Co-ordination Studies on the Analytical Behaviour of Heavy Metal Sulphides.** F. FEIGL [in part with F. PAVELKA and R. SCHACHERL] (*Z. anal. Chem.*, 1924, 65, 25—46).—The chief characteristics of the heavy metal sulphides are their very pronounced colour, great insolubility, and ability under certain conditions to carry down with them sulphides of other metals which are normally soluble. The freshly-precipitated sulphides are much more soluble than those which have aged for some time and are capable of forming compounds with other metallic salts, such as  $(\text{HgS})_2$ ,  $\text{HgCl}_2$ , whilst some double sulphides of the types  $\text{FeS}, \text{NiS}$  and  $\text{Ti}_2\text{S}_3, 2\text{CuS}$  are known. These phenomena may be explained by assuming that the precipitates formed by addition of a soluble sulphide to a salt of a heavy metal are polymerides of the single sulphide and that on ageing the polymerides become more complex; in all cases, the formation of these complexes is due to the subsidiary valencies of sulphur. Further investigations on the nature of heteropolysulphides have led to the discovery of many new examples of which the following are the best defined: nickel sulphide co-precipitated with lead sulphide is appreciably soluble in 1:10-hydrochloric acid, but in the absence of lead sulphide absolutely insoluble; manganese sulphide is readily soluble in acetic acid, but digestion with acetic acid of a mixture of zinc and manganese sulphides that have been precipitated together leaves a residue of zinc sulphide that may contain up to 24% of manganese; cadmium and manganese sulphides precipitated together by ammonium sulphide yield the compound  $2\text{MnS}, 3\text{CdS}$ ; mercuric sulphide, precipitated from acid solutions containing zinc, usually contains 2—3% of zinc, or precipitated from very strongly acid chloride solutions containing cadmium, may contain as much as 60% of the total cadmium present. Precipitated together with manganese sulphide by means of ammonium sulphide, it gives the compound  $2\text{HgS}, \text{MnS}$ , which does not yield all its mercury to sodium sulphide or its manganese to acetic or 1:1-hydrochloric acid. A further type of co-ordination complex is exemplified by the polysulphides of the metals; molybdenum polysulphide is prepared by treating a boiling mixture of ammonium molybdate and yellow ammonium sulphide with sulphuric acid and extracting the free sulphur from the precipitate by means of bromocamphor which leaves a dark

brown residue of  $\text{MoS}_3 \cdots \text{S}_2$ . This sulphide is readily formed by passing hydrogen sulphide into a molybdenum solution containing free iodine, and this procedure obviates the necessity of heating the liquid under pressure to obtain complete precipitation.

The above facts show that under certain conditions the sodium sulphide procedure of qualitative analysis may fail to reveal the presence of some elements, whilst others may appear in the wrong place. Even the ordinary hydrogen sulphide method fails to effect a complete separation of, for example, mercury from zinc and cadmium and tin from cobalt.

A. R. P.

**Analytical Separation of Rare Earths from Uranium. Alkali Uranylsalicylates.** G. CANNERY and L. FERNANDES (*Gazzetta*, 1924, 54, 770—773).—Hauser's modification of the oxalate method for separating rare earths from uranium (A., 1908, ii, 987) yields inaccurate results, but a satisfactory separation may be effected by conversion of the uranium into uranylsalicylic acid.

The uranylsalicylates have the formula  $\text{UO}_2(\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{R})_2$ , and are moderately stable, the uranium not being detectable by the ordinary reagents, including concentrated alkali hydroxide solution. The *sodium* (+9H<sub>2</sub>O) and *potassium* (+10H<sub>2</sub>O) salts form orange-red needles; the *ammonium* salt (+13H<sub>2</sub>O) was also prepared. [Cf. B., 1925, 54.]

T. H. P.

**Separation of Gallium.** E. H. SWIFT (*J. Amer. Chem. Soc.*, 1924, 46, 2375—2381).—Gallium may be separated from many metals with which it occurs (*e.g.*, lead or indium, but not iron) by extraction with ether of a solution in 5—6*N*-hydrochloric acid. The most efficient extraction occurs when 5.5*N*-acid is used. Gallium does not volatilise when solutions of the chloride are evaporated. It may be separated from iron as follows. Sodium hydroxide, not less concentrated than 0.3*N*, is added in slight excess to the solution in hydrochloric acid, the mixture is boiled for 2 minutes, cooled, and the precipitated iron hydroxide filtered off. The filtrate is just acidified with 6*N*-hydrochloric acid, diluted to 100 c.c., and the gallium precipitated by boiling for 2 minutes with 5 c.c. of 3*N*-ammonium acetate. In a neutral or slightly acid solution, the metal is completely precipitated with the iron. A detailed procedure is given for the detection of gallium based on the above method; it can also be used for obtaining pure gallium salts from natural materials.

S. K. T.

**Hahn's Iron Titration Method and Rosenmund's Modification Thereof.** E. RUPP (*Apoth. Ztg.*, 1924, 39, 422—423; from *Chem. Zentr.*, 1924, ii, 512).—The success of Hahn and Windisch's iron titration method (A., 1923, ii, 262) depends on the purity of the thiosulphate solution; an increase in the amount of potassium iodide is frequently but not invariably of value. At present the usefulness of the method is limited.

F. A. M.

**Prussian-blue Reaction.** E. SCHULEK (*Pharm. Zentralh.*, 1924, 65, 693—694).—The presence of even small amounts of ammonium chloride hinders or entirely prevents the formation of

Prussian-blue in the usual test for small amounts of cyanide. In such cases the solution should be distilled with boric acid and the distillate tested as usual. [Cf. *B.*, 1925, 40.] A. R. P.

**Determination of Nickel by means of Dimethylglyoxime in Presence of Iron and Cobalt.** J. G. WEELDENBURG (*Rec. trav. chim.*, 1924, **43**, 465—473).—Tartaric and citric acids interfere with the determination of nickel by means of dimethylglyoxime in presence of iron and cobalt, the results obtained being too high. This is due to the simultaneous precipitation of an iron-cobalt-dimethylglyoxime compound of the formula  $\text{FeCoC}_{12}\text{H}_{19}\text{O}_6\text{N}_6$ . The properties of this substance are described and compared with those of the nickel compound. A method of determining nickel under the stated conditions is based on the reduction of the solution by warming with sodium hydrogen sulphite or sulphurous acid until the yellow colour of ferric iron has disappeared. Sodium hydroxide is then added until a permanent precipitate is formed; this is dissolved in a few drops of hydrochloric acid. To avoid atmospheric oxidation, the solution is treated with a reducing agent and diluted until not more than 0.1 g. of metal per 100 c.c. is present. Excess of dimethylglyoxime and a few g. of sodium acetate are added. The precipitate is allowed to settle, filtered, washed with dilute sulphurous acid, then with water, dried at 110—120°, and weighed. If the amount of iron and cobalt present is equal to or less than that of nickel, the quantity of dimethylglyoxime corresponding with the latter is sufficient, otherwise excess must be added. H. J. E.

**Ignition of Precipitates. II. Conversion of Molybdenum Sulphide into Oxide and the Volatility of Molybdenum Trioxide.** P. H. M.-P. BRINTON and A. E. STOPPEL (*J. Amer. Chem. Soc.*, 1924, **46**, 2454—2457).—Molybdenum trioxide is non-volatile below 500° and volatilises only very slightly between 500° and 600°. Hence the conversion of molybdenum trisulphide into the oxide in analysis may be carried out by heating the sulphide precipitate with the filter-paper at 600° in a crucible suspended in an improvised air-muffle, consisting of a large crucible with a disc of asbestos in the bottom. S. K. T.

**Determination of Uranium in Carnotite.** P. H. M.-P. BRINTON and R. B. ELLESTAD (*Ind. Eng. Chem.*, 1924, **16**, 1191—1192).—A rapid method of moderate accuracy for the determination of uranium in its ores depends on the fact that iron, vanadium, and the excess of lead used for precipitating the latter can be removed in one operation with lead nitrate and ammonium carbonate by precipitation under slight pressure. Any lead still in solution is removed as sulphide, the uranium precipitated as ammonium diuranate, and the precipitate freed from aluminium in the usual way. C. I.

**Potentiometric Determination of Vanadium, Chromium, and Iron in Presence of each other and its Application to Steel Analysis.** I. M. KOLTHOFF and O. TOMIČEK (*Rec. trav. chim.*, 1924, **43**, 447—456).—Whereas vanadic acid is reduced to



vanadyl salt and chromic acid to chromic salt by a ferrous salt in acid solution, only the vanadyl ion is oxidised to vanadic acid on titration with permanganate. The determination is most advantageously carried out at 70–80°. The method may be applied to the potentiometric determination of chromium and vanadium in presence of one another and details are given of the experimental method of determining vanadium and chromium in steel. [Cf. *B.*, 1924, 969.] H. J. E.

**Iodometric Determination of Vanadium.** A. E. STOPPEL, C. F. SIDENER, and P. H. M.-P. BRINTON (*J. Amer. Chem. Soc.*, 1924, **46**, 2448–2453).—The vanadium in a concentrated neutral solution of a vanadate may be accurately determined by adding to 10 c.c. an equal volume of 6*N*-mineral acid (*e.g.*, hydrochloric or sulphuric, but not acetic acid) and a few grams of potassium iodide and then, after considerable dilution, titrating with standard thio-sulphate solution. The liberated iodine is exactly equivalent to the reduction of the vanadium to the quadrivalent vanadyl stage. The operations must be conducted without undue delay. To ensure all the vanadium being in the quinquevalent condition, it should be previously oxidised with alkaline hydrogen peroxide solution, the excess of the latter being destroyed by boiling. Small quantities of molybdenum do not interfere if phosphoric acid is used for the mineral acid, but the presence of tungsten causes low results. Uranium must be absent. S. K. T.

**Bismuth. I. Determination of Bismuth.** L. KÜRTHY and H. MÜLLER (*Biochem. Z.*, 1924, **147**, 377–384).—A method for the determination of bismuth suited to biological application is described. The bismuth is precipitated from neutral solution as the phosphate by addition of a known excess of diammonium hydrogen phosphate, and, after 1 hour, is separated by centrifuging. The excess of phosphate is then determined by colorimetric comparison with a standard solution, utilising the blue colour which develops on adding molybdic acid, quinol, and sodium carbonate. The excess of phosphate may also be determined by titration with 0.1*M*-bismuth nitrate solution, using potassium iodide, which gives a yellow colour with bismuth nitrate, as an internal indicator. J. P.

**Boiling-point Correction Chart for Normal Liquids with Special Application to Petroleum Products.** W. H. BAHLKE and R. E. WILSON (*Ind. Eng. Chem.*, 1924, **16**, 1131–1132).—Where distillations of unassociated paraffin hydrocarbons are made at temperatures which vary from those at which the b. p. are required, the necessary corrections may be made from the given chart prepared from accurate vapour pressure observations. D. G. H.

**Analysis of Naphthalenesulphonic Acids and Naphthalene.** W. S. CALCOTT, F. L. ENGLISH, and F. B. DOWNING (*Ind. Eng. Chem.*, 1924, **16**, 1190; cf. *A.*, 1924, ii, 208).—Manipulative details, omitted in the previous paper, are given for the determination of

the naphthalene carbon by oxidation of the naphthalene residue to phthalic anhydride, and of the sulphonic acid sulphur by isolation of the soluble barium sulphonates and gravimetric determination of barium. [Cf. *B.*, 1924, 1007.] W. A. S.

**Determination of Anthracene in Anthraquinone.** H. F. LEWIS (*Ind. Eng. Chem.*, 1924, **16**, 1184).—When a solution of anthracene in "oleum" is heated, charring takes place, but a similar solution of anthraquinone remains yellow. The anthraquinone containing anthracene is dissolved in "10% oleum" heated at 150°, then poured into water and filtered. The colour of the filtrate is compared with those of solutions of potassium dichromate and cobalt chloride, standardised against prepared mixtures of anthracene and anthraquinone. An accuracy of 0.1%, up to 7% of anthracene, is claimed. W. A. S.

**Determination of Invert-sugar by the Reduction Titration Method in Liquids containing Sucrose.** M. A. H. VAN DEN HOUT, P. A. NEETESON, and A. L. VAN SCHERPENBERG (*Chem. Weekblad*, 1924, **21**, 578—582).—The possible errors in Schoorl's method have been investigated. Sucrose reduces Fehling's solution, but the extent of the reduction is at first constant and finally diminishes with increasing concentration of sucrose. The concentration of the Fehling's solution markedly affects the results. The previous history of the flasks employed is also a factor, constant results being obtained only after boiling out with sodium hydroxide and washing; the hydrogen-ion concentration of the distilled water used for dissolving is of influence, so that this should be made alkaline before use. The time of boiling has little effect, but cooling should be as rapid as possible. The amount of potassium iodide added and the time elapsing after acidification before titration both affect the results. The quantity of starch used should be constant. Salts, and especially those of the alkaline earths, have some influence; the latter should be removed as oxalates. S. I. L.

**Determination of Starch using Malt.** T. CHRZASZCZ (*Z. Unters. Nahr. Genussm.*, 1924, **48**, 306—311).—The starch containing grist is heated with water at 106°; the hydrogen-ion concentration is then adjusted to about  $p_H$  5, and the mash cooked in an autoclave. It is then cooled to 70°, malt extract is added, and a temperature of 65° to 70° is maintained until the liquid and grist cease to give a colour reaction with iodine. After cooling and diluting, a portion of the filtrate is hydrolysed with hydrochloric acid, neutralised with sodium hydroxide, and the reducing power determined by the usual methods. The determination is made on duplicate samples, the first being used for the iodine test during diastatic action. Correction is made for the malt extract added. G. S. W.

**Determination of Copper Value of Celluloses.** E. BENESCH (*Chem.-Ztg.*, 1924, **48**, 861).—Following the method described by Adanti (*A.*, 1916, ii, 155), 3—4 g. of cellulose are placed in a 1 litre

Erlenmeyer flask with 50 c.c. of Fehling's solution, washed down with 50 c.c. of water. Boiling is continued for 15 minutes, the mouth of the flask being covered with a glass dish; the mass is then collected under suction in a small Büchner funnel on a double layer of "quantitative" filter-paper. It is washed until free from Fehling's solution, then transferred together with the filter-paper to a large beaker, using 100 c.c. of water. Oxidation is effected by the addition of 25 c.c. of a solution of 10 g. of ferric ammonium sulphate in 10% sulphuric acid until the previously red filter-paper is completely colourless. The liquid is filtered off through the same funnel and the mass washed six or seven times with 50 c.c. of water by decantation until free from iron. The amount of ferrous salt in the filtrate is titrated with permanganate at a temperature above 50° and the result corrected by a control titration of 25 c.c. of the same iron alum solution diluted with 200 c.c. of water.

J. F. B.

**Determination of Tartaric Acid by Precipitation as Calcium Tartrate.** M. FRANÇOIS and C. LORMAND (*J. Pharm. Chim.*, 1924, [vii], **30**, 276—283).—Gravimetric determination of tartaric acid as the calcium salt (cf. A., 1923, ii, 129) is directly applicable to cream of tartar, potassium sodium tartrate, complex lithium mixtures containing tartaric acid, and potassium borotartrate. With tartar emetic, the antimony must first be eliminated, preferably with hydrogen sulphide. With potassium ferric tartrate, the iron should be removed, either as sulphide by the addition of ammonium sulphide and acetic acid, or as basic ferric acetate.

J. K.

**Determination of Citronellal in Citronella Oil.** J. DUPONT and L. LABAUNE (*Amer. Perf. Essent. Oil Rev.*, 1924, **19**, 257—258).—By acetylation with acetic anhydride and sodium acetate, the total quantity of compounds capable of acetylation is obtained. Acetylation is then effected on the oil remaining after treatment with hydroxylamine hydrochloride and sodium carbonate. The difference between the acetylation values is an indication of the citronellal content.

CHEMICAL ABSTRACTS.

**Determination of Cineole in Essential Oils by Cocking's Process.** L. S. CASH and C. E. FAWSITT (*J. Proc. Roy. Soc. N.S. Wales*, 1923, **57**, 157—159).—Cocking's method (A., 1920, ii, 645) gives more accurate results than other methods provided the oil contains at least 65% of cineole. Cineole was added to various eucalyptus oils to give a content of 65—95% of cineole, and f.p.-specific gravity curves were drawn. It is concluded that the cineole content of an oil should be capable of determination with a maximum error of 2%.

W. T. K. B.

**Phenolphthalin as a Reagent for Hydrocyanic Acid.** J. STAMM (*Arch. Pharm. Chem.*, **4**, 18; from *Chem. Zentr.*, 1924, ii, 515).—Alkaline phenolphthalin solution (2 drops in 5 c.c. of water) is a sensitive reagent for hydrocyanic acid or hydrogen peroxide

and can be utilised, in the absence of oxidising agents, for detecting hydrocyanic acid. F. A. M.

**Fluorescein as a Reagent for Hydrocyanic Acid.** J. STAMM (*Arch. Pharm. Chem.*, 4, 25; from *Chem. Zentr.*, 1924, ii, 515—516).—Fluorescein is oxidised to fluorescein by hydrocyanic acid in alkaline solution and in presence of very dilute copper sulphate. On adding to 4 c.c. of very dilute potassium cyanide solution, the same volume of the reagent (0.00025% of fluorescein) and 2 drops of 1 : 2000 cupric sulphate, a brilliant green fluorescence is shown at once. The reagent is prepared by dissolving fluorescein in alcoholic aqueous sodium hydroxide solution and heating with zinc dust on the water-bath until decolorised, followed by dilution with aqueous alcohol. After keeping in the dark for 12 hours, the solution is filtered and suitably diluted. Other oxidising agents besides hydrocyanic acid also give the reaction. F. A. M.

**Micro Determination of Carbamide and Ammonium Salts by Titration with Hypobromite.** B. POHORECKA-LELESZ (*Bull. Soc. Chim. biol.*, 1924, 6, 773—787).—Carbamide and ammonium salts may be determined by micro methods in which the sodium hypobromite used in decomposing these compounds is measured by iodometric titration in cold, or by alkalimetry in hot solutions. The former process is recommended for determining ammonia in the micro Kjeldahl method, the method being applied direct to the neutralised product from the acid digestion, thus eliminating the necessity of distillation. J. P.

**Analysis of Cyanamide in its Calcium Compound.** R. FOSSE, P. HAGENE, and R. DUBOIS (*Compt. rend.*, 1924, 179, 408—410).—The cyanamide is hydrolysed by means of dilute nitric or hydrochloric acid and a portion of the resulting solution, made slightly alkaline with ammonia and diluted to known volume, is treated with methylxanthidrol in presence of acetic acid. The xanthylcarbamide thus formed is dried and weighed. H. J. E.

**Influence of Colloids in the Reductase Test.** A. I. VIRTANEN (*Z. Unters. Nahr. Genussm.*, 1924, 48, 141—151).—The influence of colloidal adsorption of the methylene-blue on the rate of reduction in milk was examined by means of a series of tests under different colloidal conditions. Decrease of the adsorption surface by coagulation by electrolytes caused no decrease in the time of reduction, nor was the time increased by the addition of normal milk colloids in the form of condensed milk and cream. A considerable decrease in the rate of reduction was obtained in the presence of foreign colloids, especially in the case of gelatin. Increase of the continuous phase by addition of water up to 20% had no influence. [Cf. *B.*, 1924, 960.] G. S. W.

## General, Physical, and Inorganic Chemistry.

**The Displacement Law of Arc and Spark Spectra.** W. F. MEGGERS, C. C. KIESS, and F. M. WALTERS, jun. (*J. Opt. Soc. Amer.*, 1924, 9, 355—374).—A review of the laws which have been found to govern the structures of practically all spectra is given, and illustrated by six tables, including the multiplets of  $\text{Sc}^+$ ,  $\text{Ti}^+$ ,  $\text{V}^+$ ,  $\text{Cr}^+$ ,  $\text{Mn}^+$ , and  $\text{Fe}^+$ . The work of the Bureau of Standards on spark spectra is shown to prove the displacement law of Kossel and Sommerfeld.  
C. W. B.

**Spectrum Regularities for Scandium and Yttrium.** W. F. MEGGERS (*J. Washington Acad. Sci.*, 1924, 14, 419—430).—Examples of multiplets in the arc and spark spectra of scandium and yttrium are given. The doublets in the spectrum of  $\text{Sc I}$ , triplets in the spectrum of  $\text{Sc II}$ , doublets in the spectrum of  $\text{Y I}$ , triplets in the spectrum of  $\text{Y II}$ , Zeeman effect for  $\text{Y I}$  and  $\text{Y II}$  are classified in tables.  
C. W. B.

**Intensity Measurements in Flame Spectra.** C. E. BLEEKER and I. A. BONGERS (*Z. Physik*, 1924, 27, 195—202).—A comparison has been made of the relative intensities of the lines of the diffuse and sharp series of rubidium and caesium when excited in flames of different temperatures and with various concentrations of metallic chlorides in the flames. The intensity relations are unaffected by such changes, and the intensities of each pair of lines composing a doublet are also uniformly in the ratio 1 : 2.  
S. B.

**Doublets of the Alkali Metals.** F. J. DE WISNIEWSKI (*Compt. rend.*, 1924, 179, 1316—1317).—A formula,  $\Delta\gamma = \alpha_z/n^3 \cdot (1 - 0.5/n)$ , is given for the width of the successive doublets in the principal series. This is simpler than that previously given (*Physikal. Z.*, 1923, 24, 294).  $\Delta\gamma$  is the difference in frequency of the two lines of the doublet,  $n$  the numerical order of the doublet (Thitz's notation), and  $\alpha_z$  a constant for each element. Calculated and observed values are given, showing good agreement.  
L. L. B.

**Line Spectrum of Nitrogen.** F. CROZE (*Compt. rend.*, 1924, 179, 1603—1605; cf. A., 1914, ii, 600).—The lines emitted by  $\text{N}^+$  as distinct from neutral  $\text{N}$  and  $\text{N}^{++}$  have been resolved by the aid of the Zeeman effect. Although the complete  $\text{N}^+$  spectrum cannot yet be laid down, there is evidence of series of simple lines and of three series of terms with triple multiplicity disclosed by the presence of multiplets of the types  $ps$ ,  $pd$ ,  $df$ ,  $pp'$ ,  $dd'$ ,  $p'd'$ ,  $p'p''$ ,  $p''s$ .  
W. A. C.

**Low-voltage Arc Spectra of Copper.** A. G. SHENSTONE (*Nature*, 1924, 114, 934).—The absorbed lines of copper vapour are : 3247.55, 3273.97, 2492.14, 2441.63, 2244.24, 2225.67, 2165.06, and, with slight uncertainty, 2181.68, 2024.33 Å.  
A. A. E.

**Spark Spectrum of Iron in the Schumann Region.** L. and E. BLOCH (*Compt. rend.*, 1924, 179, 1396—1399).—The spark spectrum of iron in the region 1855—1505 Å. was re-examined: 253 lines are recorded, more than half of which are new. The lines of carbon and nitrogen given by Simeon and by Hopfield and Leefson were used as primary and the lines of aluminium as secondary standards. The absolute precision is not greater than that of the standards, *i.e.*, 0.2 Å., but the differences between successive lines are accurate to a few hundredths of this unit. H. T.

**Ultra-violet Spectrophotometry.** T. R. MERTON (*Proc. Roy. Soc.*, 1924, A, 106, 378—384).—A method is described for the preparation of optical "wedges" of platinum, by the cathodic sputtering of the metal on to a quartz plate in a vacuum. These may be used for spectrophotometry throughout the range of the quartz spectrograph, in the same manner as wedges of neutral-tinted glass are used in the visible. S. B.

**Absorption Measurement in the Ultra-violet by Photographic Photometry.** H. LEY and F. VOLBERT (*Z. wiss. Phot.*, 1924, 23, 41—51).—The photometric method of Henri gives satisfactory results agreeing with those of an independent method (A., 1923, ii, 519). The plate factor is practically independent of the wave-length of the light within the region studied (3900—2300 Å.) and the extinction coefficient,  $\epsilon$ , is independent of the intensity of the light. L. J. H.

**Irregularity of the  $L\alpha$ -Doublet in the X-Ray Spectra.** B. B. RAY (*Phil. Mag.*, 1924, [vi], 48, 707—711).—Measurements were made of the change in the wave-length of the  $L$ -doublet of the elements of atomic numbers between 41 and 92. When these differences were plotted against the atomic numbers, changes of slope were obtained in the regions Pd (46), Ce (58), and La (71), results which in a general way support the Bohr theory. Calculations made on the  $L\alpha$ -doublet show that both lines undergo similar changes, pointing to a similarity between the two orbits (*cf.* Landé, A., 1924, ii, 511). H. T.

**Döppler Effect of Arc and Spark Lines.** H. KREFFT (*Physikal. Z.*, 1924, 25, 352—366).—A summary of the work done in this field up to date. L. J. H.

**Döppler Effect in Canal Rays of Hydrogen.** H. KREFFT (*Ann. Physik*, 1924, [iv], 75, 513—520).—Supplementary to previous work (this vol., ii, 3). Additional observations have been made on the Döppler effect of  $H_\beta$ . The intensity distribution of the Döppler effect is not the same immediately in front of the cathode as at some distance behind it. Probably the canal rays are not yet in equilibrium at the cathode. Addition of oxygen to the discharge space reduces the range of velocities to which the Döppler effect is limited, but the addition of nitrogen produces no effect. With increasing current strength, the maximum velocity decreases. Variations also take place in the intensity maxima.

If a spark gap be introduced in circuit with the discharge tube a strengthening of the intensity maximum at higher velocity, due to accelerated atoms, takes place. M. S. B.

**Paschen-Back Effect in Hydrogen.** H. FALKENHAGEN (*Z. Physik*, 1924, 28, 1—10).—A theoretical discussion of the changes in the Zeeman pattern of the Balmer lines with the application of very intense magnetic fields. S. B.

**Inverse Stark Effect in Sodium Vapour.** R. LADENBURG (*Z. Physik*, 1924, 28, 51—68).—The effect of an intense electrical field on the *D*-line absorption of sodium vapour has been studied, under the dispersion of a Lummer-Gehrcke plate. The construction of a sodium vapour lamp, designed to emit the *D*-lines without self-reversal, is described. The light from this lamp passed between two plane electrodes maintained at potential differences of up to 160,000 volts/cm., and the space between the electrodes contained sodium vapour at pressures of the order of  $10^{-5}$  mm. Observations in directions perpendicular to the lines of force showed that the electrical field shifted both absorption lines equally to the red. The shift of the parallel component of  $D_2$  is greater than that of the perpendicular component and is 0.025 Å. for 160,000 volts/cm. It is proportional to the square of the field strength. The Stark effects here recorded are in agreement with those predicted by the Bohr theory for non-hydrogenic orbits when the applied external field is small in comparison with the atomic fields. S. B.

**Absorption of Cathode Rays in Aluminium Foil.** H. M. TERRILL (*Physical Rev.*, 1924, 24, 616—621).—Between 18 and 52 kv., Lenard's equation,  $I/I_0 = e^{-ax}$ , where  $x$  is the thickness of the aluminium, holds. Within the range of velocities, 8.09— $12.23 \times 10^9$  cm./sec., the values of  $a$  are given by Thomson's approximate expression,  $av^4 = 0.268 \times 10^{44}$ , where  $v$  is the mean of the velocities before and after penetrating the foil. A. A. E.

[Intensity and Distribution of] **Light Emission from the Striated Discharge.** R. SEELIGER and J. ÔKUBO (*Physikal. Z.*, 1924, 25, 337—342). L. J. H.

[Theory of the Diffusion of Positive and Negative Ions to the Walls of a Discharge Tube.] W. SCHOTTKY (*Physikal. Z.*, 1924, 25, 342—348). L. J. H.

**Energy Consumption in Ionisation by X-Rays of Different Wave-lengths.** L. GREBE and L. KRIEGESMANN (*Z. Physik*, 1924, 28, 91—94).—Measurements have been made of the energy in the form of X-rays of different wave-lengths required to produce a given degree of ionisation in air. It is found that the ratio energy/ionisation decreases exponentially with increasing wave-length of the X-rays. S. B.

**Mobility of Actinium Active Deposit Ions.** H. A. ERIKSON (*Physical Rev.*, 1924, 24, 622—626; cf. this vol., ii, 6).—When actinium active deposit ions are drawn through a stream of air between

two metal plates maintaining an electric field of more than 100 volts/cm., two depositions are observed corresponding with ionic mobilities of 4.35 and 1.55 cm./sec./volt/cm. The results indicate that the ions are, respectively, (a) atomic actinium-*A* and -*B*, and (b) actinium-*B*, and possibly -*A*, after union with a neutral molecule, presumably air. The mobility of an ion is determined chiefly by the charge, the structure of the ion, and the nature of the medium, but is practically independent of the mass. A. A. E.

**Mobility in Air of Ions Produced in Another Gas.** G. C. GRINDLEY and A. M. TYNDALL (*Phil. Mag.*, 1924, 48, [vi], 711—719).—Accurate measurements were made of the mobility of ions produced directly in air and of ions produced in another gas and measured in air. No sensible differences could be detected (cf. Wellisch, A., 1909, ii, 299). H. T.

**Visible Radiation from Solid Targets.** P. D. FOOTE, W. F. MEGGERS, and R. L. CHINAULT (*J. Opt. Soc. Amer.*, 1924, 9, 541—543).—An attempt to show if it were possible to excite a visible or ultra-violet line spectrum by bombarding targets of copper, carbon, platinum, and iron with 1000-volt electrons. The results are negative; in every case the first negative carbon group appeared despite every precaution with vacuum technique. These bands are enhanced by the presence of nitrogen. If the electron current is such that the target becomes heated, an almost imperceptible volatilisation is sufficient to excite the resonance lines of the element. C. W. B.

**Proof of the Invariance under the Lorentz Transformation of the Equation of Motion of the Electron.** L. PAGE (*Physical Rev.*, 1924, 24, 627—630).—Mathematical. A. A. E.

**Photo-electric Effect for Submicroscopic Mercury Drops.** E. WASSER (*Z. Physik*, 1924, 27, 203—225).—The photo-electric effect for small mercury drops varies in character with their radius. The normal effect (expulsion of negative charges) is observed with particles of radius larger than  $1.9 \times 10^{-5}$  cm., whilst for particles smaller than  $1.2 \times 10^{-5}$  cm. radius the inverse effect (expulsion of positive charges) takes its place. Measurements of the charges acquired have been made, and it is stated that these may be considerably less than the charge corresponding with the loss or gain of an electron (the minimum charge found was about  $e/8$  in the inverse, and  $e/2$  in the normal effect). Such results support Ehrenfest's belief in the existence of a "sub-electron." S. B.

**Effect of Adsorption of Gases on the Density of Mercury Droplets.** E. WASSER (*Z. Physik*, 1924, 27, 226—236).—No explanation of the results recorded in the previous abstract can be based on the supposition of density variations in the droplets, due to adsorbed gas films on their surface. The phenomena are the same in carbon dioxide and in nitrogen, although both gases would not be expected to give films of the same thickness. Also, to



achieve an explanation, films of several hundred molecules in thickness must be assumed, a supposition not consonant with modern views on adsorption. S. B.

**Photo-electric Emission of Selenium.** W. DEL REGNO (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 163—167).—The author's experiments fail to reveal any differences between the emission of selenium in the dark and under the influence of light and hence justify the assumption that free electrons play no part in the phenomenon. Confirmation is also furnished of the previous conclusion that the electrical conductivity exhibited by selenium under the influence of light is an effect of purely electronic character and is not due to any chemical transformation, such as the conversion of one allotropic form into another. T. H. P.

**Photo-electric Response of Potassium at Low Temperatures.** J. W. HORNBECK (*Physical Rev.*, 1924, 24, 631—638; cf. Ives, A., 1924, ii, 444).—The current-wave-length curve at  $-180^\circ$  is shifted by 80—500 Å. towards the shorter wave-lengths with respect to the  $20^\circ$  curve. Monochromatic heating and cooling curves run approximately parallel to the temperature axis except between  $-80^\circ$  and  $-100^\circ$ , where a change of crystal structure is known to take place. A. A. E.

**Thermionic Work Function of Oxide-coated Platinum.** C. DAVISSON and L. H. GERMER (*Physical Rev.*, 1924, 24, 666—682).—Measurements of the thermionic work function of platinum coated with the oxides of barium and strontium by a calorimetric and a temperature variation method give results in agreement, but insufficiently accurate to determine whether or not an electron within the metal possesses the thermal energy  $3kT/2$ . A. A. E.

**X-Ray Emission of Electrons from Metal Films, with special Reference to the Region of the Absorption Limit.** L. SIMONS (*Proc. Physical Soc.*, 1924, 37, 58—70; cf. A., 1924, ii, 140).—Particulars are given of an experimental quantitative investigation of absorption and ionisation phenomena exhibited by electrons emitted from gold and silver films exposed to X-rays, and the correlation of these phenomena with the photo-electric equation  $(mv^2/2)_{K,L,M, \text{etc.}} = h\nu - h\nu_{K,L,M, \text{etc.}}$  is discussed. The author has determined directly the aggregate number of  $\beta$ -rays of all types emitted by the films when exposed to X-rays of wave-lengths between  $388 \times 10^{-11}$  cm. and  $871 \times 10^{-11}$  cm., and has shown that no selective change in the average energy of the rays occurs when the  $K$ -fluorescence spectrum is excited. It is suggested that this is thus due to a re-grouping of the numbers and energies of the  $\beta$ -ray constituents, together with the additional emission of the  $K$ -group of minimum individual energy. The origin of  $\delta$ -rays is discussed from the respective points of view of thermionics, recoil electrons, and impact electrons, and it is concluded that these rays are impact electrons the most frequent energy of which is little greater than 3.5 volts and independent of the exciting wave-length and of the

nature of the emitting substance. They appear to be influenced, at the time of their emission, by the scattered X-rays. J. S. G. T.

**Magnetic Spectra of Iron and Nickel Wires at Wave-lengths of a Centimetre.** W. ARKADIEV (*Z. Physik*, 1924, 28, 11—28).—Previous measurements of magnetic absorption spectra of metallic wires for Hertzian waves of about 1 cm. wave-length have been used to test theories developed in other papers (*Ann. Physik*, 1919, 58, 105). The inconstancy of the form of the magnetic spectrum of iron and nickel is attributed to variations in the magnetic properties of ferromagnetic materials. S. B.

**Magnetic Properties of Thin Films of Ferromagnetic Metals Produced by the Evaporation Method.** A. J. SORENSEN (*Physical Rev.*, 1924, 24, 658—665).—The maximum value of the intensity of magnetisation of films of iron, nickel, and cobalt of thickness 20—300  $m\mu$  is of the same order of magnitude as for bulk metal. The remanence is high for iron and cobalt, but low for nickel. There is an abrupt change in the high values of the coercive force at a thickness of 55, 70, and 200  $m\mu$  for iron, cobalt, and nickel, respectively. A. A. E.

**New Phenomenon in the Diamagnetism of Gases.** A. GLASER (*Ann. Physik*, 1924, [iv], 75, 459—488).—A very sensitive method is described by which the magnetic susceptibilities of hydrogen, nitrogen, and carbon dioxide have been determined at different pressures. Down to a certain pressure, which differs for each gas, the decrease in magnetic susceptibility is directly proportional to the decrease in pressure. Below this pressure, however, there is a deviation in such a direction that the susceptibility is higher than is to be expected from the proportionality law. Ultimately, as the pressure and susceptibility both approach zero, they again become directly proportional to each other. The phenomenon is explained by supposing that, when the pressure becomes sufficiently reduced, it is possible for orientation of the molecule to take place under the influence of the magnetic field. This results in a relative increase of the susceptibility. The pressure at which this effect will begin to make itself felt depends on the relation between the time taken for orientation of the molecule and the interval between successive molecular collisions producing disorientation. It will therefore depend on the inertia of the molecule, that is, on the molecular weight, and on the strength of the magnetic field. M. S. B.

**Origin of the Satellites of Mercury Lines.** E. P. METCALFE and B. VENKATESACHAR (*Nature*, 1925, 115, 15—16).—Lines arising from isotopes must satisfy two conditions: (a) the intensities of the several isotope lines in the radiation from a thin layer must be in the ratio of the concentrations of the respective isotopes, (b) the radiation from the end of a long column should be distinguished by the equalisation of the brightness of corresponding lines when the column is sufficiently long for the lines to be "saturated." The second consideration, when applied to the line 5461 Å., indicates

that the line  $-0.024 \text{ \AA.}$  must be excluded from the isotopic group of satellites. Also, the components of  $5769 \text{ \AA.}$ , but not of  $5971 \text{ \AA.}$ , appear to satisfy the second condition. A. A. E.

**Mass Ratio of Isotopes in Chemical Elements.** F. M. JAEGER and D. W. DIJKSTRA (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 393—406).—Pure tetraethylsilicane was made from silica from various sources, terrestrial and meteoric. The specific gravity of all the samples was the same within a few units in the third decimal place per cent. Even this discrepancy was apparently due to traces of impurities as indicated by comparison of refractive indices. The ratio of the isotopes must therefore be the same whatever the origin of the silicon. L. J. H.

**Separation of Isotopes by the Ionic Migration Method.** J. KENDALL and J. F. WHITE (*Proc. Nat. Acad. Sci.*, 1924, 10, 458—461).—Using the apparatus already described (A., 1923, ii, 282), the method has been tested with non-isotopic mixtures of salts with ions of slightly different mobilities. Complete separation is easily effected with mixtures of iodide and thiocyanate, and barium and calcium, the differences in ionic mobilities being 16% and 8%, respectively. Considerable partial separation is attained with mixtures of barium and strontium, and iodide and chloride, the differences in ionic mobilities being, respectively, 5% and 1%. Assuming the two isotopic chlorine ions to possess different mobilities, the method should give at least a partial separation, but experiments with sodium chloride were indecisive. It is suggested that a mass-spectrograph may be used to detect such a separation. In the case of lead, which possesses radioactive isotopes, the distribution of the radioactive component in an activated sample of lead salt could be determined at intervals during the course of the experiment. J. S. C.

**Rare Gases of the Atmosphere.** H. JEFFREYS (*Nature*, 1924, 114, 934).—The tendency of a gravitating planet to collect heavier molecules and in certain circumstances to lose lighter ones cannot solely account for the rarity of the inert gases; possibly the ability of the other elements to form stable and liquid compounds has co-operated (cf. Aston, this vol., ii, 18). A. A. E.

**Artificial Disintegration of Elements.** E. RUTHERFORD and J. CHADWICK (*Proc. Physical Soc.*, 1924, 36, 417—422).—The method previously employed (cf. A., 1921, ii, 293) was improved by observing the particles ejected at right angles to the direction of bombardment. This enables particles with a range of only 7 cm. (or less for light atoms) to be observed. Hydrogen nuclei from the presence of hydrogen, and scattered  $\alpha$ -particles have not this penetration at this angle, whilst the particles from disintegration are ejected in all directions (cf. A., 1922, ii, 682). In addition to the cases previously reported, disintegration was found in the light elements neon, magnesium, silicon, sulphur, chlorine, argon, and potassium, but not in the case of hydrogen, helium, lithium, carbon, or oxygen. Of the heavier elements, nickel, copper, zinc,

selenium, krypton, molybdenum, palladium, silver, tin, xenon, gold, and uranium failed to give the effect. Elements from calcium to iron have not at present given conclusive results. The comparative ranges of the ejected particles suggest that the nuclei of the even-numbered light elements are stable, whilst those of the odd-numbered light elements are comparatively unstable. An estimate of the field of force within the atom (about three million volts for aluminium) is deduced from these ranges. L. J. H.

**Absorption and Scattering of  $\gamma$ -Rays.** E. A. OWEN, N. FLEMING, and W. E. FAGE (*Proc. Physical Soc.*, 1924, **36**, 355—366).—The absorption and scattering of  $\gamma$ -rays from radium filtered through 23 mm. of lead have been measured in magnesium, aluminium, zinc, tin, and lead. On the assumption that the mean effective wave-length of the radiation employed is 0.021 Å., the experimental results are consistent with the following statements: (1) When  $\gamma$ -rays traverse matter, the characteristic radiations of the absorbing medium are excited. (2) The atomic fluorescent absorption coefficient of  $\gamma$ -rays depends on the wave-length of the incident radiation and the atomic number according to the law  $\omega\pi/\rho = K\lambda^3 N^4$  which holds for X-rays. (3) The absorption in light elements is due almost entirely to scattering. (4) The pure atomic scattering absorption coefficient is proportional to the atomic number of the absorber. (5) In addition, a true absorption exists, the atomic coefficient of which is proportional to the atomic number.

Compton's formula would account for the experimental results if the wave-length of the incident radiation were 0.020 Å., but Jauncy's formula would require the value 0.029 Å. L. J. H.

**Effective Wave-lengths of  $\gamma$ -Rays.** J. A. GRAY (*Nature*, 1925, **115**, 13).—The author's conclusions are summarised as follows: (i) If the secondary  $\beta$ -rays produced in light elements by the hard  $\gamma$ -rays of radium-*C* are recoil electrons, with an energy given by the quantum theory of scattering, the effective wave-length of the  $\gamma$ -rays must be much smaller than that usually accepted. Thus no theory, as at present developed, can account for the properties of scattered  $\gamma$ -radiation. (ii) The internal atomic absorption coefficient of the hard  $\gamma$ -rays of radium-*D* is 0.67, as compared with an external coefficient of about  $3 \times 10^{-21}$ . On disintegrating, one atom of radium-*D* in five emits a  $\gamma$ -ray. (iii) The number of atoms of an element emitting one or more types of monochromatic  $\gamma$ -rays may be only a small fraction of the total number disintegrating and a large part of the  $\gamma$ -ray energy emitted may be due to white radiation. (iv) A knowledge of the wave-lengths and relative intensities of the lines in the spectrum of the  $\gamma$ -rays is not, in itself, sufficient for the determination of effective wave-lengths which can be used to interpret the results of experiments on  $\gamma$ -rays. A. A. E.

**Scattering and Absorption of  $\gamma$ -Rays.** J. A. GRAY (*Nature*, 1925, **115**, 86; cf. preceding abstract).—Four assumptions, for

which there is some evidence, are specified which lead to a reasonable explanation of experimental results on the scattering and absorption of hard  $\gamma$ -rays. It is believed that  $\gamma$ -rays possess a "range"; this would indicate that the scattering of  $\gamma$ -rays is a scattering of "corpuscles." As a correction, it is stated that only one in every seven radium-*D* atoms emits a  $\gamma$ -ray on disintegration.

A. A. E.

**Magnetic Spectrum of  $\beta$ -Rays of High Velocity from Mesothorium II.** D. YOVANOVITCH and J. D'ESPINE (*Compt. rend.*, 1924, 179, 1162—1163).—The existence of high-velocity rays ( $\beta=0.998$  and  $\beta=0.985$ , velocity of light taken as unity) from mesothorium II has been completely proved (cf. A., 1924, ii, 447).

H. T.

**$\gamma$ -Radiation of Mesothorium II.** J. THIBAUD (*Compt. rend.*, 1924, 179, 1322—1324).—In a previous study (cf. this vol., ii, 10) of the secondary  $\beta$ -ray spectra from uranium, lead, and tungsten, excited by the  $\gamma$ -radiation from mesothorium, three lines were found in the latter with energies corresponding with 580,700, 908,200, and 962,700 volts, respectively. The first of these was due to thorium-*B*, and it was suggested that the other two were due to mesothorium II.

A study of the primary  $\beta$ -ray spectrum of mesothorium II confirms this view, on the supposition that this spectrum is due to the photo-electric effect of the  $\gamma$ -radiation during disintegration. According to this hypothesis, the primary  $\beta$ -ray spectrum should be similar to the secondary  $\beta$ -ray spectrum from the element 89. This is found to be the case.

A further study of the secondary  $\beta$ -ray spectrum from lead gave two lines in the  $\gamma$ -radiation of 333 and 459 kv., respectively, confirming the results of Broglie and Cabrera (A., 1923, ii, 109).

The energy, frequency, and wave-length of four lines in the characteristic  $\gamma$ -ray spectrum of mesothorium II are given.

L. L. B.

**Distribution of Electrons among Atomic Levels.** E. C. STONER (*Phil. Mag.*, 1924, [vi], 48, 719—736).—A distribution of electrons in the atom is suggested in which the number of electrons associated with a sub-level is connected with the characterising inner quantum number. This leads to a greater concentration of electrons in the outer sub-groups and to an earlier completion of the inner sub-groups than given by the older Bohr distribution. The number of electrons in each completed level is equal to double the sum of the inner assigned quantum numbers, there being in the *K*, *L*, *M*, *N*, levels when complete 2, 8 ( $2+2+4$ ), 18 ( $2+2+4+4+6$ ), 32 . . . electrons. In the building up of elements, changes are made by the simple addition of electrons to the outer sub-levels without reorganisation of the group as a whole. Available evidence from intensities of X-ray lines, absorption of X-rays, magnetic properties, optical spectra, and chemical properties is given in support of the new distribution.

H. T.

**Striated Glow Discharge in Mercury Vapour.** K. T. COMPTON, L. A. TURNER, and W. H. MCCURDY (*Physical Rev.*, 1924, **24**, 597—615).—The theory of the glow discharge in a mono-atomic gas is considered, and certain predictions are verified in the case of mercury vapour. Striations are observed only when the current is small or a substance (*e.g.*, hydrogen) is present to remove excited atoms, which exist in the striations, but not in the intervening regions. Molecules of the compound  $\text{HgH}$  are apparently formed in the presence of excited atoms, since its band spectrum is strongly shown by the striations; it cannot, however, be excited by illuminating a mixture of mercury vapour and hydrogen with 2536 Å. resonance radiation. A. A. E.

**Fine Structure of Band Spectra of Sodium, Potassium, and Sodium-Potassium Vapours.** H. G. SMITH (*Proc. Roy. Soc.*, 1924, **A**, 106, 400—415).—Several of the absorption bands of sodium and potassium vapours and two of the bands peculiar to mixtures of these vapours have been examined under high dispersion. They have been separated into their *P*, *Q*, and *R* components. The corresponding moments of inertia have been calculated, and are in agreement with the supposition that the "sodium-potassium" bands are emitted by an  $\text{NaK}$  molecule. S. B.

**Regularities in Band Spectra.** S. DATTA (*Phil. Mag.*, 1924, [vi], **48**, 673—692).—The general equation  $\nu = A + mD + m^2C' + n(B' + 2b'm) + b'n^2$  (*cf.* Heurlinger, *Physikal. Z.*, 1919, **20**, 188; Deslandres, *A.*, 1902, ii, 373), in which *n* and *m* are simple integers having a definite physical meaning (*n* defining quantum changes and *m* the orbit of the atom), is theoretically deduced. Simplified forms are given in which (i) the rotational energy of the molecule is neglected, when  $\nu = A + Bm + Cm^2$ , and (ii) where the molecules are all in the same dissociated state, when  $\nu = A + Bn + Cn^2$ . The general equation has been applied with good agreement to the first positive nitrogen bands. An attempt has been made to explain the afterglow bands and to link up the photo-electric currents observed by Brandt (*Diss.*, Berlin) with the ionisation of mercury by ultra-violet radiation of the first positive bands corresponding to the limiting orbits. H. T.

**New Variety of Spectra.** W. H. MCVICKER, J. K. MARSH, and A. STEWART (*Phil. Mag.*, 1924, [vi], **48**, 628—636; *cf.* T., 1923, **123**, 642, 817, 2147; *A.*, 1924, ii, 712).—The Tesla luminescence spectrum of benzene consists of more than 70 fine bands falling into eight groups each reproducing exactly the same system of bands differing in position by approximately 100 Å. External conditions, *e.g.*, pressure, temperature, and timing of the transformer, have little effect. By comparison with Hartley's absorption data (*A.*, 1908, ii, 243) it is shown that the Tesla luminescence spectrum represents a reversal of the former, *i.e.*, the Fraunhofer effect is shown with a complex organic compound. H. T.

**Infra-red Absorption of Ice.** E. K. PLYLER (*J. Opt. Soc. Amer.*, 1924, 9, 545—555).—The spectral transmission of a crystal of ice 0.5 cm. thick has been determined for the ordinary and extraordinary rays, and also for sections cut so that the incident energy was about equally divided into the ordinary and extraordinary rays. The extraordinary ray does not exhibit any general absorption in the region from  $0.75\ \mu$  to  $1.15\ \mu$ , but the ordinary ray shows general absorption for this region which probably extends into the visible. One mm. of ice at  $1\ \mu$  absorbs 5% of the energy for the extraordinary ray and about 47% for the ordinary ray. Each ray has the corresponding absorption bands as found in liquid water, but the bands for ice are shifted toward the long wave-lengths.

C. W. B.

**Absorption Spectrum of Sulphur Vapour and Molecular Constitution.** V. HENRI and M. C. TEVES (*Compt. rend.*, 1924, 179, 1156—1159).—Using a continuous spark under water as a background, the absorption spectrum of sulphur at different pressures and at temperatures between  $100^\circ$  and  $1000^\circ$  was examined. Below  $250^\circ$ , where only  $S_8$  and  $S_6$  molecules are present, between 2700 and 2300 Å. continuous absorption results. Above  $250^\circ$ , where  $S_2$  molecules appear and under a pressure of 0.05 mm., a band spectrum between 2927 and 2713 Å. was observed. Increase of pressure increases rapidly the number of these bands, which extend through the region 2475—3700 Å. These bands can be separated into three distinct regions: (A) between 3700 and 2794 Å., where is produced a fine structure corresponding with a quantisation of the molecular rotation, (B) between 2794 and 2592 Å., where the spectrum consists of narrow bands without fine structure, and (C) between 2592 and 2475 Å., where broad continuous bands are obtained. From the lines in the A region, the moment of inertia of the normal molecule,  $S_8$ , and the active molecule were calculated. The former is  $12.6 \times 10^{-40}$  and the latter  $13.8 \times 10^{-40}$ .

The limit 2592 Å. corresponds with an internal transformation of the sulphur molecule requiring 102,100 cal./g.-mol., and that at 2475 Å., 110,000 cal./g.-mol.

H. T.

**Ultra-violet Absorption Spectra of Ketens and of their Dimerides.** G. C. LARDY (*J. Chim. Phys.*, 1924, 21, 281—307).—The absorption spectra of ketens consist of two bands, one very intense, in the ultra-violet, and the other at the limit of the visible spectrum and analogous to that of acetone. The positions of the bands depend on the substituent group, the displacement being towards the visible spectrum and increasing with the molecular weight. The exaltation of the specific displacement above the normal indicates that the non-saturation and hence the velocity of polymerisation increases in the order keten ( $\text{CH}_2\text{:C:O}$ ), diphenyl-, dipropyl-, and diethyl-keten, respectively. The intensity of the absorption of the first band indicates that the lability (or velocity of reaction with other compounds) of keten and its aliphatic

derivatives is approximately equal to that of acetone, whilst that of the diphenyl derivatives is much greater.

The absorption spectra of a number of  $\alpha$ - and  $\beta$ -diketones, and derivatives of diketocyclobutane have been determined.  $\alpha$ -Diketones such as diacetyl have an absorption band similar to that of acetone but displaced towards the red. Non-enolic derivatives of diketocyclobutane show two absorption bands, one in the ultra-violet, and a second generally resembling that of the group  $\text{:C:O}$ , of which the intensity is roughly equal to that of acetone for the lower homologues, but is much more intense for the dimethyl diphenyl derivative. The first band has been resolved into three or four bands. Diketodiphenylcyclobutane shows two absorption bands, one very intense due to the enolic form, and corresponding to the band given by the enolic form of acetylacetone, and a second comparatively faint, indicating that in solution in hexane about 12% of the compound is present in the ketonic form. The absorption spectra indicate that diketodimethylcyclobutane in solution in ether is present entirely in the enolic form, and possibly in the dienolic form. It gives two bands, one corresponding with that of acetone and the other with that of acetylacetone. A comparison of these spectra with those given by the dimeric forms of ketens indicates that the latter in solution do not exist as  $(\text{CH}_2\text{:CO})_2$ , but

entirely in the form  $\begin{array}{c} \text{CH}_2\text{:CO} \\ | \quad | \\ \text{CO-CH}_2 \end{array}$  in equilibrium with a very small

amount of the corresponding enolic form. The relations existing between the diazo compounds, the ketens, the azides, and the carbimides are discussed theoretically. W. H.-R.

**Influence of Magnetic and Electrical Fields on Ultra-violet Fluorescence of Iodine.** O. OLDENBERG (*Z. Physik*, 1924, **27**, 189—194).—The intensity maximum in the ultra-violet fluorescence spectrum of iodine is slightly shifted towards the red by a strong magnetic field, but the spectrum at 3460 Å. which appears only in presence of foreign gases is unaffected. An electrical field has no influence on these spectra. S. B.

**Fluorescence of Metallic Compounds of Hæmatoporphyrin.** C. DHÉRÉ, A. SCHNEIDER, and T. VAN DER BOM (*Compt. rend.*, 1924, **179**, 1356—1358).—The zinc compound of hæmatoporphyrin is obtained by addition of zinc hydroxide to the ammoniacal liquid and is precipitated by acetic acid, whilst the tin compound is prepared by the action of stannous chloride. Their alcoholic solutions exhibit fluorescence in the red-yellow, showing two bands, and this spectrum of each is characteristic and differs from that of hæmatoporphyrin. The lead and cadmium compounds (cf. Milroy, A., 1919, i, 178) possess fluorescence in the same region, not so the copper, iron, and cobalt compounds. F. M. H.

**Luminescence of Solid Nitrogen and Argon.** J. C. McLENNAN (*Nature*, 1925, **115**, 46—47).—Polemical and explanatory, partly on a question of priority (cf. Vegard, A., 1924, ii, 805). A. A. E.



**Spectroscopic Study of the Luminescent Oxidation of Phosphorus.** H. J. EMELÉUS and W. E. DOWNEY (*J. Chem. Soc.*, 1924, **125**, 2491—2495).—Phosphorus burning under various conditions always emits light with fundamentally the same spectrum; the higher the temperature of the oxidation the broader are the spectrum bands and the greater is the intensity of the light in the visible region.

The following bands were observed when phosphorus burned in a gas containing 80% of oxygen: 2390, 2475, 2530, 2630, 3275 Å.; the flame temperature was 800°. The same bands were emitted, but resolved into narrow bands, when the burning took place in air under reduced pressure, the flame temperature being 125°. The glow emits the same bands as the low-temperature flame, but they are less intense. These results support those of Centnerszwer and Petrikaln (A., 1912, ii, 709) but not the more recent results of Petrikaln (A., 1924, ii, 289). S. K. T.

**Spectra of Luminescence of Grignard Compounds.** R. T. DUFFORD, D. NIGHTINGALE, and S. CALVERT (*J. Opt. Soc. Amer.*, 1924, **9**, 405—409; cf. A., 1923, ii, 714).—By the use of a spectro-scope of high aperture ratio it is possible to photograph the chemiluminescence spectra of Grignard compounds. In all cases, they prove to be continuous. In certain cases, unstable oxidation products of the type  $\text{ROMgX}$  are obtained which are strongly fluorescent in ultra-violet light; but in these cases the spectra are either banded, or in any case not identical with the chemiluminescence spectra. Hence it is argued that the mechanisms of their formation are dissimilar. C. W. B.

**Luminescence in the Ingleside Calcites Affected by Acids.** W. P. HEADDEN (*Amer. J. Sci.*, 1924, [v], **8**, 509—517).—Certain specimens of colourless, transparent calcite phosphoresce in sunlight after exposure to radium emanation; lack of responsiveness in sunshine is attributed to variability in the efficiency of the latter (*Proc. Colo. Sci. Soc.*, **11**, 399). Specimens of calcite containing a yellow core of organic material are now found to be responsive only after washing with commercial hydrochloric acid and then exposing to radium emanation; unresponsive colourless calcite becomes responsive after the same treatment. When the coloured variety becomes ineffective, it is renewed by washing with acid, although less permanently and less strongly. Eventually a period of unresponsiveness is reached which is succeeded by one of responsiveness. The material then becomes permanently unresponsive. Other peculiar phenomena are recorded. The history of the sample has a large influence on its behaviour. Change in atomic structure is offered as the only explanation. S. K. T.

**Theory of the Decay of  $\alpha$ -Ray Luminescence.** E. E. WITMER (*Physical Rev.*, 1924, **24**, 639—643).—Approximate and exact expressions are developed for the decay of luminosity in substances which exhibit luminescence under  $\alpha$ -ray bombardment. A. A. E.

**Relation between the Depolarisation of the Scattered Light and the Kerr Effect in Liquids.** W. H. MARTIN (*J. Physical Chem.*, 1924, **28**, 1284—1290).—Gauss' theory (*Z. Physik*, 1923, **17**, 353) of the relation between the depolarisation factor of the scattered light and the Kerr constant of electric double-refraction has been tested for fifteen liquids. The values of the depolarisation factors calculated from theory agree with experimental measurements except in the case of chloroform, water, and methyl alcohol. Measurements of the depolarisation factor for nitrobenzene made in a magnetic field of 5000 gauss failed to discover any change in the degree of polarisation of the scattered light. M. B. D.

**Activation of Chlorine by Electric Discharge.** K. SCHAUM and A. FELLER (*Z. wiss. Phot.*, 1924, **23**, 66—71).—Chlorine may be activated by electric discharge of all kinds as discovered independently by Venkataramaiah (*A.*, 1923, ii, 149). The activated chlorine reacts more rapidly with toluene, especially as regards the attack of the side chain. L. J. H.

**Presentation of the Periodic System.** W. PALMAER (*Z. physikal. Chem.*, 1924, **110**, 685—704).—Priority is claimed for the arrangement of elements in periods determined by  $2n^2$  where  $n=1, 2, 3$ , or  $4$ . A property of the elements showing marked periodicity is the normal electrode potential. In cases where the element has more than one valency, the potential corresponding to the lowest valency is considered. Any system of classification must be based on the valencies of the elements, especially towards oxygen. The author's periodic table consists of eight groups, the first seven of which are subdivided into a primary and a secondary group. The eighth group has one principal sub-group and three subsidiary sub-groups. Hydrogen and the alkali metals occupy the principal sub-group of Group I. The rare earths are arranged in the principal sub-groups of Groups III (boron, aluminium) and IV (carbon etc.). There is no zero group, the inert gases occupying the principal sub-groups of Group VIII. The subsidiary sub-groups of Group VIII are occupied by iron and related elements. Various arguments in support of the arrangement are put forward. J. S. C.

**Fine Structure of the Free Benzene Molecule.** J. BECKENKAMP (*Z. anorg. Chem.*, 1924, **139**, 220—232).—The structure of the benzene molecule previously described (cf. *A.*, 1924, ii, 754) is based on two assumptions, *viz.*, the principle of closest packing and the arrangement of the hydrogen atoms in the spaces between the carbon atoms of a graphite structure. Neither of these assumptions is fully justified when the low atomic weights of carbon and hydrogen are considered. It is now assumed that the carbon atoms in the surface of a benzene crystal are arranged in an individual lattice very similar to that of graphite; with the help of Bragg's space lattice for the benzene crystal and certain principles previously described (cf. *A.*, 1924, ii, 32, and *loc. cit.*), two possible arrangements of the hydrogen atoms in the crystal arise. The

most probable one is that in which the centres of gravity of the carbon atoms form a spacial six-membered ring of the  $\rho_2$  type, whilst the hydrogen atoms, which lie with their axes perpendicular to the main axis of the molecule, form a plane ring. The thirty valency electrons are distributed as follows. One comes between each pair of carbon atoms. One is attached to each carbon atom on the side towards the interior of the molecule; three of these are above and three below the normal plane of the molecule. The attraction of these electrons by the atomic kernels and their repulsion by the binding electrons mentioned above control the elastic equilibrium of the molecule. The remaining electrons are distributed three on the outer surface of each carbon atom; one of these lies in the normal plane through the molecule and holds the hydrogen atom, whilst the other pair lie above or below this plane in alternate atoms. The latter are enantiomorphs, and according as the upper set or lower set is substituted, should give rise to optically active molecules.

This structure is correlated with the formerly proposed structure of graphite. In the benzene crystal, electrodynamic forces appear to have a large influence, whereas in graphite and diamond electrostatic forces are mainly concerned. The cleavage of diamond is now explained electrodynamically and three possible methods of twin formation are deduced.

S. K. T.

### Compressibility, Internal Pressure, and Chemical Affinity.

E. SAERENS (*J. Chim. Phys.*, 1924, **21**, 265—280).—If the affinity of chemical combination produces an internal pressure on the atoms concerned, the contraction of volume will be greater if the elements are easily compressible. Thus caesium is more compressible than lithium, and the contraction in the formation of caesium chloride is much greater than with lithium chloride. In a compound, the internal pressure is equally divided among the atoms, and the specific compressibility of the elements in a given binary halogen compound is constant and equal to that of the compound. In the halides of the alkali and alkaline-earth metals, the metal on combination undergoes a contraction of volume with increase of internal pressure, and the compressibility of the compound is less than that of the free metal. In the case of silver, thallium, lead, copper, etc., combination results in expansion with decrease of internal pressure, and the compressibility of the compound is greater than that of the metal. There is no essential difference between chemical affinity and the affinity of cohesion.

W. H. R.

**Determination of Molecular Fields. I. Viscosity.** J. E. JONES (*Proc. Roy. Soc.*, 1924, **A**, 106, 441—462).—The temperature variation of the viscosity of gases can be explained on the assumption that the repulsion and attractive forces between molecules each vary with an inverse power of the distance. The attractive forces are supposed to follow an inverse cube law, whilst the repulsive force may be assumed to vary with any power between

15 and 25, viscosity measurements alone being insufficient to provide a unique solution. S. B.

**Determination of Molecular Fields. II. Gaseous Equations of State.** J. E. JONES (*Proc. Roy. Soc.*, 1924, **A**, 106, 463—477; see preceding abstract).—The molecular model employed in the previous paper has also been used in the investigation of the equation of state for argon. To explain existing data in this way, even larger indices in the inverse power law governing the repulsive force have to be assumed than were necessary for the explanation of viscosity values. It is suggested that the molecular fields determined by the two methods are not strictly comparable. S. B.

**Heat of Combustion of Glycogen.** R. MEIER and O. MEYERHOF (*Biochem. Z.*, 1924, **150**, 233—242).—The following heats of combustion are given: *Mytilus* glycogen, water-free, 3820.5 (0.9 g.); hydrate, 3800; dissolved, 3789 cal. (0.9 g.). Frog glycogen, water-free, 3807 (0.9 g.); hydrate, 3786; dissolved, 3775.5 cal. (0.9 g.). J. P.

**Anomalous Dispersion in the Field of X-Rays.** E. HJALMAR and M. SIEGBAHN (*Nature*, 1925, **115**, 85—86).—The lattice constants of calcite and gypsum have been compared, a series of spectral lines with wave-lengths from 0.7 up to 5.2 Å. being used. When values of  $d_1/d_2 = \sin \phi_2 / \sin \phi_1$  are plotted against wave-length, the graph shows two marked discontinuities coincident with the wave-lengths of the absorption edges of calcium and sulphur. A. A. E.

**Compton Effect.** D. L. WEBSTER and P. A. ROSS (*Nature*, 1925, **115**, 51).—Experiments designed to test the reality of the Compton effect gave spectra which showed the Compton-theory lines as strongly as in earlier investigations. A. A. E.

**Influence of Atomic Arrangement on Refractive Index.** W. L. BRAGG (*Proc. Roy. Soc.*, 1924, **A**, 106, 346—368).—The refractive indices of certain birefringent crystals have been calculated, on the assumption that the atoms composing the crystal are ionised, and that each type of atom, when polarised by the electrical force associated with radiation, acts as an electrical doublet with a characteristic moment, determined by a constant  $\lambda$ .

The indices of calcite, aragonite, and alumina have been successfully calculated on this theory, with the help of X-ray data concerning the relative positions of the atomic centres. It is shown that it may later be possible, conversely, to obtain information about crystal structure from refractivity data, although examination of the values for alkali halides shows that the simple theory here developed is limited in its application, and that the "constant"  $\lambda$  may vary with the nature of the surrounding atoms. S. B.

**Theoretical Calculation of Rhombohedral Angle of Calcite etc.** W. L. BRAGG and S. CHAPMAN (*Proc. Roy. Soc.*, 1924, **A**, 106, 369—377).—The rhombohedral angle ( $\alpha$ ) of calcite,  $101^\circ 55'$ ,

is not determined by the symmetry of the crystal. The authors assume that calcite is an assemblage of ions, held in their equilibrium positions by the interplay of the attractive electrostatic forces, and of repulsive forces of some kind, which are effective over a small range only. The electrostatic energy of the system may then be calculated for various values of  $\alpha$ , and it is found that the angle giving a minimum energy is within  $3^\circ$  or  $4^\circ$  of the observed angle. The alteration of  $\alpha$  with substitution of other metals for calcium is quantitatively explained. S. B.

**Effect of Cold Rolling on Structure of Cubic Crystals.** F. WEBER (*Z. Physik*, 1924, **28**, 69—90).—Plates of iron and aluminium have been subjected to cold rolling and the resulting crystal deformations analysed by the X-ray method. The chief effect of the rolling is to cause a translatory motion along the glide planes of the crystals. When the deforming forces applied are great, a rotation of the component crystals also takes place about some important crystallographic direction. S. B.

**Atomic Structure of Two Intermetallic Compounds.** E. A. OWEN and G. D. PRESTON (*Proc. Physical Soc.*, 1924, **36**, 341—348).—Magnesium silicide has a face-centred cubic lattice of silicon atoms of side  $6.391 \text{ \AA}$ , symmetrically intermeshed with a simple cubic lattice of magnesium atoms of side  $3.19 \text{ \AA}$ . The density from X-ray data is  $1.95 \pm 0.05 \text{ g./c.c.}$  Aluminium antimonide has a face-centred cubic lattice of antimony atoms of side  $6.126 \text{ \AA}$ , intermeshed with an identical lattice of aluminium atoms. The density from X-ray data is  $4.23 \pm 0.04 \text{ g./c.c.}$  L. J. H.

**Crystal Structure of Mercuric Sulphide.** I. N. H. KOLKMEIJER, J. M. BLIJVOET, and A. KARSEN (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 390—392).—Black precipitated mercuric sulphide is of face-centred cubic structure like zinc sulphide. The lattice parameter is  $5.85 \times 10^{-8} \text{ cm.}$ , the density is 7.69, and the radius of the atomic domain of mercury is  $1.51 \times 10^{-8} \text{ cm.}$  There are four molecular groups per unit cell. L. J. H.

**X-Ray Analysis of Mother-of-Pearl.** J. H. SHAXBY (*Compt. rend.*, 1924, **179**, 1602—1603; cf. A. Dauvillier (*ibid.*, 819); W. L. Bragg, A., 1924, ii, 373).—Laue diagrams, taken with a silver anticathode, show pseudo-hexagonal symmetry in the plane of stratification, whilst at right angles to the latter a rectangular arrangement of atoms is indicated. The structure is identical with that found by Bragg for aragonite. W. A. C.

**Crystal Structure of Cuprite and Rutile.** G. GREENWOOD (*Phil. Mag.*, 1924, [vi], **48**, 654—663).

**Crystalline Form of Organic Derivatives of Arsenic.** II. G. GILTA (*Bull. Soc. chim. Belg.*, 1924, **33**, 532—538).—A detailed crystallographic examination has been made of the potassium, ammonium, and lithium salts of *p*-aminophenylarsinic acid (cf. A., 1923, i, 407). Potassium salt, anhydrous: orthorhombic, [ $a : b : c = 0.778011 : 1 : 0.758124$ ], conchoidal fracture. The causes

of the occurrence of abnormal faces are discussed. Lithium salt, anhydrous: monoclinic,  $[a:b:c=0.944731:1:0.830419, \beta=91^\circ 16']$ . Ammonium salt, dihydrate: orthorhombic,  $[a:b:c=1.037944:1:0.657969]$ , conchoidal fracture. W. E. E.

**Crystal Form and the Crystal Lattice.** M. YAMADA (*Sci. Rep. Tôhoku Imp. Univ.*, 1924, **13**, 53—74).—A mathematical paper in which the crystal forms of substances are derived from the structure of the lattice by means of the surface energy relationships of Born and Stern (A., 1919, ii, 418). Assuming a homopolar lattice and that the potential energy of the mutual action of a pair of atoms in the lattice is negligible except in the case of the two nearest atoms, Wulff's polyhedron (i.e., the crystal form) is a cube for the simple cubic lattice, a cubo-octahedron for the face-centred cubic lattice, a rhombic dodecahedron for the space-centred cubic lattice, and an octahedron for the diamond lattice. If the assumption is made that the range of atomic action reaches the second nearest atoms, the shapes of the polyhedra are modified slightly, the cube having its corners cut off by octahedral planes, the cubo-octahedron having its cubic planes enlarged or diminished, the rhombic dodecahedron having its corners replaced by planes of the cube, and the octahedron undergoing slight changes of shape. The calculated shapes agree well with those found for some of the elements under ideal conditions. A. R. P.

**Crystal Structure of Dolomite.** R. W. G. WYCKOFF and H. E. MERWIN (*Amer. J. Sci.*, 1924, [v], **8**, 447—461).—The Laue diagram for dolomite is of a lower symmetry than that for calcite, indicating that dolomite is not a solid solution of calcite and magnesite, but is a definite crystalline species. The symmetry is either  $C_4^2$  or  $Ci_2$ ; the positions of the carbon and the oxygen atoms were not determined. Pure magnesium and iron-rich dolomites have units of practically identical shapes and sizes.

S. K. T.

**Electrical Conductivity of Metals.** F. SIMON (*Z. Physik*, 1924, **27**, 157—163).—A theory is developed for the electrical conductivities of metals and their variations with temperature and physical conditions. These properties are regarded as being determined solely by the character of the outermost shell of electrons in the constituent atoms. S. B.

**Optical Properties of Amino-acids.** G. L. KEENAN (*J. Biol. Chem.*, 1924, **62**, 163—172).—Photomicrographs and crystallographic details are given of glycine, alanine, valine, leucine, serine, cystine, phenylalanine, tyrosine, tryptophan, and aspartic and glutamic acids. C. R. H.

**Thermal Expansion of Bismuth Crystals.** J. K. ROBERTS (*Proc. Roy. Soc.*, 1924, **A**, **106**, 385—399).—The coefficients of thermal expansion of bismuth crystals are constant between the ordinary temperature and  $240^\circ$ . The values given are: perpendicular to the crystal axis,  $12.0 \times 10^{-6}$ ; parallel to the axis,

$16.2 \times 10^{-6}$ ; mean  $13.4 \times 10^{-6}$ . Over the range of  $30^\circ$  lying between  $240^\circ$  and the melting point, the expansion falls off very markedly. An explanation of this fact is considered, based on the idea that a certain number of the atoms may here possess sufficient energy to dissociate themselves from their neighbours in the lattice. The linear law connecting the specific heat of pure solids with temperature, even up to their melting point, makes the explanation untenable, and the phenomenon is probably to be traced to the presence of impurities. S. B.

**Changes in State of Aggregation and Polymorphism. II. Microscopical Study of Transition Processes.** K. SCHAUM and W. RÖRIG (*Z. anorg. Chem.*, 1923, **132**, 77—89; cf. A., 1922, ii, 264).—An attempt has been made to determine the rate of transition from one crystalline form of a substance to another, by studying the behaviour of a thin layer of the substance when observed under the microscope with the aid of polarised light. The method has been tested by determinations of the linear velocity of crystallisation, both along a thin-walled tube inoculated at one end, and also radially from a point on a plate on which the molten material was spread. Suitable compounds for studying the rate of transition are difficult to find. Benzil-*o*-carboxylic acid, forming a yellow modification, which is a true benzil compound, at higher temperatures, and a white isomeride, resembling a lactone, at lower temperatures, has been examined. Tautomeric transformation was found to take place in the completely dry, crystalline state. In the gaseous condition, transition only occurs slowly. From the molten acid the yellow form alone separates. Determinations of the velocity of crystallisation when the melt is seeded, in one case with the white variety, and in the other with the yellow, show that it is much slower in the first than in the second case. No difference of solubility in chloroform has been found between the two varieties, possibly owing to an immediate transformation to the less soluble form on contact with the liquid. Benzil-*o*-carboxylic acid forms a unary-pseudobinary system. 3-Phenylindazole appears to behave similarly.

A microscopical study has also been made of the separation of the constituents in the crystalline aggregates obtained by freezing fused mixtures of organic compounds. Such observations are rendered difficult by polymorphic changes. M. S. B.

**Heat of Transformation of Martensite.** W. SCHNEIDER (*Werkstoffausschusses Ver. deut. Eisenhüttenleute, Bericht*, 1923, No. 32).—The heat of transformation of  $\gamma$ -iron into  $\alpha$ -iron is computed to be 13.2 cal. per g., decreasing linearly with increasing carbon content, and vanishing at 6.68% C. If martensite is assumed to be a solid solution of  $\text{Fe}_3\text{C}$  in  $\alpha$ -iron, the heat of solution of  $\text{Fe}_3\text{C}$  is 33.2 cal. per g. CHEMICAL ABSTRACTS.

**Atomic Heat of Silver at High Temperatures.** A. MAGNUS and A. HODLER (*Z. physikal. Chem.*, 1924, **110**, 188—191).—The specific heat of silver has been determined at temperatures between the ordinary temperature and  $900^\circ$ . The variation of the atomic

heat with temperature is given by  $C_p = 6.047 + 7.49 \times 10^{-4}t + 7.12 \times 10^{-7}t^2$ . The value of  $C_v$  calculated from  $C_p$ , after first passing through a maximum, diminishes linearly with increasing temperature, in good agreement with the equation of Born and Brody (*Z. Physik*, 1922, 8, 205),  $C_v = 3R(1 - 3\sigma RT)$ , where  $\sigma$  has the value  $5.53 \times 10^{-5}$ . J. S. C.

**Investigations of Specific Heat at Low Temperatures.** F. LANGE (*Z. physikal. Chem.*, 1924, 110, 343—362).—A convenient apparatus for the determination of specific heats at low temperatures is described. The specific heats of quinol, quinone, quinhedrone, tungsten, iodine, and the two forms of tin were determined over a range of temperature 20—300° Abs. The specific heats of iodine and white and grey tin were also investigated over the range 9—14° Abs., employing the apparatus of Simon and Lange (*A.*, 1923, ii, 458), the measurements verifying the reported transition of iodine at the temperature of liquid hydrogen. Calculations of the chemical constants of tungsten and diatomic iodine give the values  $3.68 \pm 0.72$  and  $3.37 \pm 0.20$ , respectively. The data for tin are in agreement with the Nernst heat theorem. J. S. C.

**Flow of Single Crystals.** W. GEISS (*Z. Physik*, 1924, 29, 78—80; cf. Schönborn, *ibid.*, 1922, 8, 377).—The rate of movement of a tungsten crystal under different loads has been studied as a function of the time, the load being applied for 1 or 2 hours. With relatively small loads, the flow velocity decreases with time, and a consolidation of the material takes place which results in an increase in the elasticity limit. By increasing the load, the initial velocity is increased, but the retardation decreases until it becomes zero, that is, the flow velocity is constant. This is the extension limit. With still higher loads, the flow velocity increases with time, and plastic deformation begins above the elasticity limit. The exponential relation between the velocity of flow  $v$ , the load  $P$ , and the time of application  $t$  is given by the following equation,  $v = A \cdot e^{B(P-P_s)t} \cdot [e^{C(P-P_E)} - 1]$ , where  $A$ ,  $B$ , and  $C$  are constants, and  $P_s$  and  $P_E$  represent the loads at the extension limit and the elasticity limit, respectively. M. S. B.

**Molecular Weight of Selenium Dioxide in Ethyl Alcohol.** E. B. R. PRIDEAUX and G. GREEN (*J. Physical Chem.*, 1924, 28, 1273—1278).—The molecular weight of selenium dioxide by the elevation of the boiling point of ethyl alcohol, using the figure for constant molar elevation of 11.9, was found to be 122.6 (mean of 44 determinations), instead of the theoretical value 111.2. There is no trend in the molecular weights up to a concentration of 55 g. in 100 g. of alcohol. After a correction for the volatility of selenium dioxide has been applied, the mean molecular weight is found to be 117.5. M. B. D.

**Specific Heat of Bromine at Low Temperatures and its Chemical Constant.** R. SUHRMANN and K. VON LÜDE (*Z. Physik*, 1924, 29, 71—77).—The molecular heat of bromine at



constant pressure, between the temperatures  $20.45^{\circ}$  and  $154.9^{\circ}$  Abs., as determined in a vacuum calorimeter, increases from 3.52 to 12.64 cal./mol. over this range. With the help of these values and the vapour-pressure curve deduced from the observations of other investigators, the value of  $i$  has been found equal to  $2.546 \pm 0.10$  (referred to atmospheres), and the heat of vaporisation at absolute zero 10980 cal./mol. (cf. Eucken, Karwat, and Fried, this vol., ii, 98). M. S. B.

**Determination of the Molecular Thermal Conductivity and the Molecular Heat of Diatomic Gases at Low Temperatures.** E. SCHREINER (*Z. physikal. Chem.*, 1924, **112**, 1—67).—The molecular heats of nitrogen, oxygen, and carbon monoxide were determined and no deviation from the normal value was observed on lowering the temperature to  $64^{\circ}$  Abs. This result is not in agreement with those of Scheel and Heuse (A., 1913, ii, 183) and of Eucken (A., 1913, ii, 474), who, working with these gases at temperatures not lower than  $80^{\circ}$  Abs., found that some loss of molecular heat had already occurred. The method employed of determining molecular heats depends essentially on a knowledge of molecular heat conductivity. The experimental determination of this value is based on that of Knudsen (A., 1911, ii, 368) and is described and discussed in detail. L. F. G.

**Theory of Degraded Gases and Null Point Energy.** K. BENNEWITZ (*Z. physikal. Chem.*, 1924, **110**, 725—767).—Mathematical. The laws of thermodynamics and the extended correspondence principle are not sufficient to determine whether an ideal supercooled gas will possess energy at absolute zero. Equations are deduced for the entropies and chemical constants of degraded gases. A complete thermodynamical survey of the equation of state is made and the limiting forms are compared at  $T=0$  and  $T=\infty$  on the assumptions of the existence and absence of energy at absolute zero. The existence of null point energy is further considered in reference to the integrated Clausius—Clapeyron equation. J. S. C.

**Revised Trouton Rule for the Heat of Vaporisation and the Quantum Theory.** A. BYK (*Z. physikal. Chem.*, 1924, **110**, 291—317).—The “constant” of the Trouton rule diminishes rapidly at low temperatures. A mathematical theory is developed, the problem being treated from the point of view of the author’s quantum theory of corresponding states (*Ann. Physik*, 1921, [iv], 66, 157; 1922, [iv], 69, 161) and Bakker’s theory of the heat of vaporisation. An equation is derived expressing the Trouton ratio as a universal function of the reduced temperature and volume. The values calculated for more than forty liquids ranging from hydrogen to stannic chloride are in fairly close agreement with those actually determined. J. S. C.

**Entropy of Condensed Gases at the Absolute Zero.** A. EUCKEN and F. FRIED (*Z. Physik*, 1924, **29**, 36—70; cf. this vol., ii, 98).—The integration constant  $i_k$  of the thermodynamic

formula for chemical equilibrium has been determined for a number of homogeneous and heterogeneous reactions. The values thus obtained are more exact than by any previous determinations, and they show that the relationship  $i_k = \Sigma i$ , required by Nernst's heat theorem, is not in general fulfilled. This necessitates a finite value for the entropy of a substance in the solid state at the absolute zero, and it has been shown that, for hydrogen, and probably for a number of other substances, this entropy is probably of the order of  $R \log_e 2$ . M. S. B.

**Constant  $i$  of the Thermodynamic Vapour-pressure Equation for Polyatomic Molecules.** A. EUCKEN, E. KARWAT, and F. FRIED (*Z. Physik*, 1924, 29, 1—35).—A theoretical paper in which the value of the integration constant of the thermodynamic vapour-pressure equation,  $i$ , which is a function of the entropy constant of the gas, the entropy at absolute zero of the condensed liquid, and also of the specific heat at absolute zero, has been determined for a large number of gases, partly on the basis of recent determinations of the specific heat and vapour pressure at low temperatures. The mean error has also been calculated. The value of  $i$  by statistical methods has been compared with that determined optically from the band-spectra of the gases, hydrogen, nitrogen, oxygen, nitric oxide, carbon monoxide, hydrogen chloride, hydrogen bromide, hydrogen iodide, carbon dioxide, and water. In all cases, the difference between the two is greater than the experimental error. M. S. B.

**Chemical Constants of Chlorine, Bromine, and Iodine in the Monatomic and Diatomic States.** K. WOHL (*Z. physikal. Chem.*, 1924, 110, 166—187; cf. Simon, following abstract).—The differences between the observed and theoretical values of the chemical constants of iodine, bromine, and chlorine in the monatomic state increase with their heats of dissociation. The experimental values for the various constants are as follows, theoretical values being in parentheses: Cl, +1.66 (+0.73); Br, +2.07 (+1.27); I, +2.08 (+1.56); Cl<sub>2</sub>, +1.96; Br<sub>2</sub>, +2.86; I<sub>2</sub>, +3.44; HCl, -0.40. J. S. C.

**Chemical Constants of Monatomic Gases.** F. SIMON (*Z. physikal. Chem.*, 1924, 110, 572—586).—A comparison of the recently determined values of the chemical constants of fourteen elements with the theoretical values shows that the deviations increase with increasing heats of vaporisation. J. S. C.

**Physico-chemical Investigations on Compounds of the cycloHexane Series.** W. HERZ and W. BLOCH (*Z. physikal. Chem.*, 1924, 110, 23—39).—A number of physico-chemical constants of carefully purified compounds of the cyclohexane series have been determined. cycloHexanone: b. p. 155.9°/760.2 mm.,  $d^{20}_4$  0.9625,  $n^{19.3}_D$  1.45066, sp. ht. 0.433, surface tension in dynes/cm. at 45° ( $\gamma$ ) 32.33,  $\eta^{29.1}$  0.01549. o-Methylcyclohexanone: b. p. 164.9°/756.3 mm.,  $d^{20}_4$  0.9423,  $n^{16.7}_D$  1.44916, sp. ht. 0.436,  $\gamma^{45}$  29.61,

$\eta^{39.1}$  0.01217. *m*-Methylcyclohexanone: b. p.  $64.5^\circ/18.3$  mm.,  $d^0$  0.9309,  $n_D^{17.3}$  1.44635, sp. ht. 0.441,  $\gamma^{45}$  28.36,  $\eta^{39.1}$  0.01226. *p*-Methylcyclohexanone: b. p.  $60.5^\circ/16.8$  mm.,  $d^0$  0.9312,  $n_D^{15.7}$  1.44585, sp. ht. 0.441,  $\gamma^{45}$  28.91,  $\eta^{39.1}$  0.01234. cycloHexanol: m. p.  $22^\circ$ , b. p.  $161.1^\circ/751.3$  mm.,  $d^0$  0.9627,  $n_D^{20.7}$  1.46542, sp. ht. 0.417,  $\gamma^{45}$  31.37,  $\eta^{39.1}$  0.2032. *o*-Methylcyclohexanol: b. p.  $167.2^\circ/756.5$  mm.,  $d^0$  0.9458,  $n_D^{16.4}$  1.46215, sp. ht. 0.418,  $\gamma^{45}$  29.43,  $\eta^{39.1}$  0.06977. *m*-Methylcyclohexanol: b. p.  $76.0^\circ/16$  mm.,  $d^0$  0.9353,  $n_D^{16.3}$  1.46065, sp. ht. 0.422,  $\gamma^{45}$  27.13,  $\eta^{39.1}$  0.09676. *p*-Methylcyclohexanol: b. p.  $76.7^\circ/15.0$  mm.,  $d^0$  0.9328,  $n_D^{15.4}$  1.45916, sp. ht. 0.423,  $\gamma^{45}$  27.94,  $\eta^{39.1}$  0.1436. Methods for the calculation of other quantities from the above data are given. The influence of admixture with methyl alcohol, ethyl alcohol, and propyl alcohol on the density and viscosity of cyclohexanone and cyclohexanol has been investigated.

J. S. C.

**Melting Point of Platinum.** F. HOFMANN (*Z. Physik*, 1924, 27, 285—304).—The melting point of platinum has been redetermined, for use as a thermometric fixed point, by means of comparisons at three wave-lengths of the intensities of the black body radiation from an iridium resistance furnace, maintained successively at the melting points of gold and of platinum. The value adopted for the melting point of platinum is  $1771 \pm 2^\circ$ .

S. B.

**The Three-temperature Rule.** M. PRUD'HOMME (*J. Chim. Phys.*, 1924, 21, 242—246).—The rule connecting the m. p., b. p., and critical temperature (A., 1921, ii, 376) has been found to give fairly good results for a number of chemically different substances.

W. H.-R.

**Temperature Gradient in Gases at Various Pressures.** W. MANDELL and J. WEST (*Proc. Physical Soc.*, 1924, 37, 20—40).—Determinations have been made of the temperature gradients in air and hydrogen contained at various pressures ranging from atmospheric down to about 0.001 mm. in a cylindrical brass vessel 3.9 cm. long and 12 cm. in diameter, the end faces of which were maintained respectively at about  $180^\circ$  and  $50^\circ$ . The results definitely indicate the existence at low pressures of very large "temperature jumps" in the neighbourhood of the walls of the vessel. The general character of the results obtained is explained on the assumption of the presence on the walls of a gas film possessing properties arising from the attraction between molecules of the material of the wall and of the gas.

J. S. G. T.

**Superheating of Liquids.** F. B. KENRICK, C. S. GILBERT, and K. L. WISMER (*J. Physical Chem.*, 1924, 28, 1297—1307).—Various liquids, having boiling points ranging from  $-10^\circ$  to  $183^\circ$ , have been superheated  $50$ — $170^\circ$  by heating them in open capillary tubes at atmospheric pressure or by reducing the pressure on the liquids in closed capillary tubes at constant temperature. Various methods of treating both the tubes and the liquids are given and the conclusion is drawn that the initiation of bubbles from freshly-prepared capillary tubes is connected with nuclei loosely attached to the

walls of the vessel and to a property of the liquid in which there is an element of chance. Preparation of "mote-free" liquid and removal of adsorbed gases on the glass or dissolved gases in the liquid had no appreciable effect. The radius of the bubbles (calculated from the surface tension and the vapour pressure at the maximum temperature) which can exist in equilibrium with the liquids at the highest temperature varies from 2.5 to 16  $\mu\mu$ . A simple relation is given between the external pressure and the maximum temperature attainable at this pressure, which holds in the case of ether over a wide range of pressure. M. B. D.

**Experiments on the Carbon Arc. Vapour Pressures of Carbon.** H. KOHN and M. GUCKEL (*Z. Physik*, 1924, **27**, 305—357).—Measurements have been made of the surface brightness of the anode of the carbon arc burning in various gases at pressures between 0.05 and 5.0 atm. The maximum temperature of the anode is thus found to be independent of the nature of the surrounding gas, and presumably depends solely on the vapour pressure of carbon. The heat of sublimation of carbon can be calculated from the change in temperature of the anode with gas pressure, from the Clausius-Clapeyron equation, and is given as 139.2 kg.-cal.  $\pm 7\%$  (at the ordinary temperature), in agreement with the value of 141.4 for a monatomic vapour, obtained from the chemical constant (cf. Fajans, A., 1922, ii, 818). The temperature of the negative carbon has also been measured. Its limiting maximum value appears to be the same as that of the positive crater. S. B.

**Critical Pressure-ratio for Gases as affected by Variable Specific Heat.** W. J. WALKER (*Phil. Mag.*, 1924, [vi], **48**, 703—707; cf. *ibid.*, 1922, [vi], **43**, 589).—The critical pressure-ratio during maximum discharge conditions of gases through orifices under variable specific heat conditions has been deduced and takes the form  $p_2/p_1 = (2/m+1)^{m/(m-1)} \{1 + [3\lambda T_2(m-1)]/4(m+1)\}$ . At normal temperatures,  $[3\lambda T_2(m-1)]/4(m+1)$  is practically negligible. H. T.

**Viscosities of Gases [Hydrogen and Helium] at Low Temperatures.** P. GÜNTHER (*Z. physikal. Chem.*, 1924, **110**, 626—636).—The viscosities of hydrogen and helium have been determined at low temperatures (15—80° Abs.). The viscosity of hydrogen in the vicinity of 20° Abs. varies as  $T^{3/2}$ , in accordance with the Nernst theory. The behaviour of helium does not, however, conform to the theoretical requirements. J. S. C.

**Origin of Free Oxygen in the Air.** G. TAMMANN (*Z. physikal. Chem.*, 1924, **110**, 17—22).—An attempt is made to estimate the epoch in which free oxygen first appeared in the atmosphere. Oxygen, as such, is not found in lava or occluded in erupted rock. The possibility of molecules leaving the gravitational field of the earth is discussed and it is shown that the necessary velocity is 11 km./sec. From the mathematical treatment it appears that only the hydrogen molecule at very high temperatures is likely

to attain a velocity of this order. Free atmospheric oxygen probably made its appearance after the commencement of the solidification of the earth's upper crust. J. S. C.

**Volume in Liquid Mixtures.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, **140**, 399—404).—The values of  $\psi = (n^2 - 1)/(n^2 + 2)$  have been calculated for different concentrations of twelve binary liquid mixtures from the value of  $n$  for the mixture and from the values of  $\psi$  for each of the constituents according to the rule of mixtures. The two values thus obtained for each mixture agree fairly closely, but there is sufficient difference to indicate that the volume of mixtures is not strictly additive. Using the value of  $n$  for the solid salt, the volume of solutions of varying concentrations of potassium or sodium chloride in water agrees quite closely with that obtained by the rule of mixtures. A. R. P.

**Contraction of Ethyl Alcohol on Dilution.** H. P. FORAN (*J. Soc. Chem. Ind.*, 1924, **43**, 338—340r).—The percentage contraction,  $C$ , when ethyl alcohol is diluted with water is given by the relation  $C = 3(V/P - 1.02)$ , where  $V$  is the percentage increase in volume when the water is added and  $P$  the percentage decrease in strength.  $P$ ,  $V$ , and  $V/P$  must not exceed 45%, 90%, and 1.90, respectively. S. K. T.

**Vaporisation of Liquid Mixtures.** J. F. KING and S. P. SMEDLEY (*J. Physical Chem.*, 1924, **28**, 1265—1272).—Three methods are described for determining the exact composition of the constant-evaporating mixtures of two miscible liquids. The constant-evaporating mixture for carbon tetrachloride and ethyl alcohol at 20° was found to contain 17.4% of ethyl alcohol by volume. The densities at 20°/4° for various mixtures have been tabulated. The methods are: determination of the maximum vapour pressure by Smith and Menzies' "submerged bubblet" method, change in the refractive index after evaporation, and density change after a given amount of air has been bubbled through the liquid. M. B. D.

**Determination of the Vapour Pressures and of the Composition of the Vapour Phases in Equilibrium with Aqueous Solutions of Hydrogen Chloride and Hydrogen Bromide at Different Temperatures.** M. WREWSKY, N. SAWARITZKY, and L. SCHARLOFF (*Z. physikal. Chem.*, 1924, **112**, 97—108).—The compositions of the vapour phases have been determined at about 20°, 55°, and 80°. A wide range of concentrations of the solutions was employed. The partial pressures of acid and water, respectively, are calculated. For both series of solutions, the total vapour pressure falls with increasing concentration to a minimum and then rises sharply. This sudden rise is due to the partial pressure of the halogen compound, which is negligible until the region of the minimum is reached, but then increases extremely rapidly. The compositions of the constant-boiling hydrogen chloride solutions agree very closely with those recorded by Roscoe and Ditmar (*Annalen*, 1860, **116**, 214). L. F. G.

**Equilibrium between Liquid and Gaseous Phases of Aqueous Solutions of Hydrogen Chloride and of Hydrogen Bromide.** M. WREWSKY (*Z. physikal. Chem.*, 1924, **112**, 109—116).—Theoretical. The change of vapour pressure of binary solutions with temperature and heat of formation is examined, and an expression derived with which the data available for hydrogen chloride, bromide, and iodide solutions are shown to be in agreement (cf. preceding abstract). L. F. G.

**Determination of the Boiling and Condensation Curves of Mixtures of Hydrochloric Acid and Water under a Pressure of 760 mm.** E. CARRIÈRE and ARNAUD (*Compt. rend.*, 1924, **179**, 1265—1267).—The results given correlate (1) boiling point with percentage of hydrogen chloride in the boiling liquid for the range 19—110—100°, and 41·9—20·15—0·03% HCl, and (2) temperature of distillation with percentage of hydrogen chloride in the distillate, for the range 20°—110°—100° and 100—20·15—0%. The results agree with those of Roscoe and Dittmar (*T.*, 1859, **12**, 128) and conform to the Gibbs-Konovalov law (cf. A., 1923, ii, 555). T. H. P.

**Equilibrium between Vapour and Liquid of Aqueous Solutions of Ammonia.** M. WREWSKY (*Z. physikal. Chem.*, 1924, **112**, 117—127).—Theoretical. Data now available (cf. this vol., ii, 101, and above) are shown to be in agreement with values calculated from thermodynamic considerations. L. F. G.

**Influence of Thin Surface Films on the Evaporation of Water.** G. HEDESTRAND (*J. Physical Chem.*, 1924, **28**, 1245—1252).—The rate of evaporation of water into dry air from a surface of 18·2 sq. cm. at 20° has been measured. The amount of water evaporated for a given rate of flow was found to vary with the height of the edge of the vessel above the water surface. The evaporation increases with increased rate of flow of the dry air up to a limiting value. Films 1 mol. thick of palmitic and oleic acids were formed on the water surface by dissolving them in benzene and allowing it to evaporate. No change was observed in the rate of evaporation. Saponin solutions, which have a very low surface tension, due to adsorbed molecules at the interfacial surface, also had no effect. Salt solutions lowered the rate of evaporation in the ratio of the partial pressure of the solution to that of pure water. The surface films formed by adsorbed substances at the interfacial surfaces or by unimolecular layers must therefore follow the thermal agitation of the water molecules and do not exist as an impermeable layer on the surface. M. B. D.

**Behaviour of the Simple Halides with Water.** N. V. SIDGWICK (*J. Chem. Soc.*, 1924, **125**, 2672—2674).—The suggestion that the maximum covalency of an element depends on its position in the periodic table (A., 1924, i, 506) is shown to explain the various reactions of simple halides in aqueous solution, viz., ionisation, hydrolysis, either of the type  $XCl \rightarrow XOH + HCl$  or  $XCl \rightarrow XH + HOCl$ , and no reaction. It is shown that hydration should facilitate

ionisation and that elements with a maximum covalency of four should form uni- and bi-valent cations, whereas those with a co-valency of six should also form tervalent ions. When ionisation is no longer possible, the water tends to attach itself to the molecule and to react with the halogen (*e.g.*, silicon tetrachloride). Carbon tetrachloride does not react because it cannot ionise and has a complete octet in which the carbon, unlike the silicon in silicon tetrachloride, is exerting its maximum covalency so that the molecule cannot take up water. Nitrogen trichloride reacts with water with formation of hypochlorous acid by offering its unshared pair of electrons to the hydrogen of the water, producing  $\text{Cl-N}(\text{Cl}_2) \rightarrow \text{H-O-H}$ , which then decomposes. S. K. T.

### Critical Solution Temperature of Ternary Mixtures. A.

BOUTARIC and G. CORBET (*Compt. rend.*, 1924, **179**, 1319—1322).—The miscibility of water with binary mixtures of phenol, aniline, salicylic acid, and benzoic acid has been examined. Where the two substances are chemically similar (*e.g.*, benzoic and salicylic acids), the critical solution temperature is a linear function of the composition. Experiments have also been made on the miscibility of phenol with mixtures of various alcohols and water. L. L. B.

### Diffusion in Mixed Crystals. H. BRAUNE [with H. HELLWEG]

(*Z. physikal. Chem.*, 1924, **110**, 147—165).—The lattice structure of crystals necessitates the vibration of atoms about equilibrium positions, their mean centres of gravity being fixed. The electrical conductivity of solid salts and the phenomenon of diffusion demonstrate the possibility of the atoms changing position. The probability of this is, however, small, and diffusion takes place in solid bodies only with measurable velocity in the neighbourhood of the melting point. Mixed crystals of the metals of the copper group are particularly suitable for diffusion experiments, since they form no intermetallic compounds and are apparently completely miscible. On the assumption that the rate of diffusion is dependent on the amplitude of atomic vibration, the expression is derived  $D_T = Ce^{-3/2 T_s/T}$ , where  $D_T$  is the diffusion coefficient at temperature  $T$ ,  $T_s$  the m. p.,  $b$  a constant, and  $C$  a constant characteristic of the substance. A description of the experimental technique for the determination of the diffusion of gold into silver is given, the values of  $D_T$  at various temperatures being in close agreement with the above expression. Copper diffuses more readily into those silver-gold alloys which are rich in the former metal. The alteration in the electrical conductivity of solid electrolytes with temperature may be represented by the formula  $\kappa = Ce^{-\beta/T}$ . J. S. C.

### Cast Alloys of Aluminium containing Small Amounts of

**Magnesium.** S. DANIELS (*Ind. Eng. Chem.*, 1924, **16**, 1243—1249).—The effect of the addition of small proportions of magnesium to aluminium which contains silicon and iron as impurities appears to be the formation of magnesium silicide,  $\text{Mg}_2\text{Si}$ . The equilibrium between silicon, iron, and aluminium is materially

altered, the iron existing chiefly or entirely as  $\text{FeAl}_3$ . [Cf. B., 1925, 73.] C. I.

**Hardness of Copper-Tin Alloys.** O. BAUER and O. VOLLENBRUCK (*Z. Metallk.*, 1924, **16**, 426—429).—The curve showing the hardness of copper-tin alloys rises slowly with increase of tin to 13.9%, the limit of the solid solution, then rapidly to a maximum at the point corresponding with  $\text{Cu}_3\text{Sn}$ ; it then falls rapidly to a point corresponding with  $\text{Cu}_6\text{Sn}_5$ , after which the slope is gradual to pure tin. A slight kink occurs in the downward portion of the curve at  $\text{Cu}_3\text{Sn}$ . [Cf. B., 1925, 73.] A. R. P.

**Gold-Copper Alloys.** E. SEDSTRÖM (*Ann. Physik*, 1924, [iv], **75**, 549—555).—The thermoelectric power against copper, heat conductivity, and electrical resistance of gold-copper alloys, prepared by fusion in a vacuum, have been determined. The heat conductivity was calculated from the thermoelectric effect by Borelius' method (*ibid.*, 1917, **52**, 398; 1918, **56**, 338). The results confirm the existence of a compound  $\text{AuCu}$  (cf. Kurnakov, Shemtschushni, and Zasedatelev, *J. Inst. Metals*, 1916, **15**, 305). The alloys which approximate to this composition are extremely brittle. A similar study has been made of a number of other alloys, but the results are recorded elsewhere (*Dissertation*, Stockholm, 1924).

M. S. B.

**Coefficients of Thermal Expansion for Aluminium Alloys and Alloys of Nickel-Iron and Cobalt-Iron.** K. HONDA and Y. OKUBO (*Sci. Rep. Tōkoku Imp. Univ.*, 1924, **13**, 101—107).—A table showing the mean coefficients of linear expansion of aluminium, magnesium, and eleven light aluminium alloys for several temperature ranges from 20° to 500° is given, together with curves showing the variation of this coefficient in the iron-nickel and iron-cobalt alloys with the nickel and cobalt content, respectively. A very pronounced minimum in the first-named series occurs with 35% Ni, corresponding with the so-called "Invar" alloys; the cobalt curve, on the other hand, is fairly flat and more or less regular. [Cf. B., 1925, 73.] A. R. P.

**Influence of Indifferent Gases on the Saturated Vapour Concentrations of Liquids.** F. POLLITZER and E. STREBEL (*Z. physikal. Chem.*, 1924, **110**, 768—785).—The alteration in the saturated vapour concentration of a liquid in presence of a compressed, chemically indifferent gas is due to two factors, the pressure exerted on the liquid and the solvent action of the gas on the vapour. The former causes an increase in the partial pressure over the liquid, independent of the nature of the gas and depending only on the pressure exerted. The second factor causes an increase characteristic of the gas concerned. The influence of hydrogen, air, and carbon dioxide on the vapour pressure of water and of hydrogen and nitrogen on the vapour pressure of liquid carbon dioxide has been investigated over a pressure range up to 200 kg./cm.<sup>2</sup>. An equation is derived representing the increase in vapour pressure as a function of the total pressure. Deviations



are ascribed to the solvent action of the compressed gas. In the case of water this is negligible for hydrogen, small for air, and considerable for carbon dioxide. J. S. C.

**Supersaturation of Gases in Liquids.** F. B. KENRICK, K. L. WISMER, and K. S. WYATT (*J. Physical Chem.*, 1924, 28, 1308—1315).—When water is saturated with oxygen and carbon dioxide, at concentrations corresponding with about 16 atm., bubbles do not form in an appreciable time when the pressure is reduced to 1 atm. at the ordinary temperature, but only after heating at about 60°. Colloidal platinum favours the formation of bubbles in water supersaturated with oxygen, but rapidly loses its effectiveness. Although carbon dioxide is thirty times as soluble as oxygen, the average time before bubble formation is about the same for the two gases when they are at the same temperature and when the supersaturation corresponds with the same equilibrium pressure. Nitrogen produced in solution by the reaction between hydrazine sulphate, ferric alum, and sulphuric acid at an equilibrium pressure of about 100 atm. can be brought to atmospheric pressure for an appreciable time without bubbles forming in the body of the liquid. M. B. D.

**Temperature of Steam Evolved from a [Boiling Aqueous] Solution.** E. REISSMANN (*Z. angew. Chem.*, 1924, 37, 899—903).—An aqueous solution of calcium chloride was boiled in a vessel, the vapour space being jacketed by an electrically heated oil-bath. The temperatures of the boiling solution, vapour, and oil-bath were read over a period and the results plotted graphically. If the temperature of the bath is above or below that of the solution, that of the vapour is intermediate between the two, and if the temperature of the bath is varied the three curves intersect at a point. In this way, and from a comparison of the behaviour of pure water under similar conditions, it is proved that the steam leaves the boiling solution at the temperature of the solution, and not at 100°. The author concludes with a reply to Schreiber's assertion to the contrary. (Cf. *Z. techn. Physik*, 1923, 19.)

W. T. K. B.

**Rate of Absorption and Equilibrium of Carbon Dioxide in Alkaline Solutions.** R. V. WILLIAMSON and J. H. MATHEWS (*Ind. Eng. Chem.*, 1924, 16, 1157—1161).—The absorption of carbon dioxide increases with the rate of flow of the alkaline liquid and is very sensitive to any disturbance of the surface, whilst doubling the rate of flow of gas results in a very marked decrease in the effectiveness of the liquid. The rate of absorption of carbon dioxide is greatly increased by increasing the concentration of the potassium hydroxide, but is almost independent of the potassium carbonate concentration. It corresponds with the absorption in distilled water plus an amount proportional to that of hydroxide and inversely proportional to that of hydrogen carbonate present. The rate of absorption with potassium carbonate solution increases to a maximum at 70—75° and then decreases, and is directly proportional to the partial pressure of the carbon dioxide. D. G. H.

**Principles of Gas Absorption.** W. K. LEWIS and W. G. WHITMAN (*Ind. Eng. Chem.*, 1924, **16**, 1215—1220).—The “two-film” theory of the absorption of gas by a liquid assumes that the rate of absorption depends only on the rate of diffusion through the stationary films at the intersurface in which convection is absent. This rate is given by the general equation  $dW/Ad\theta = k_g(P_g - P_i) = k_L(C_i - C_L)$ , in which  $P$ ,  $C$  are the concentrations of the solute in the gas and liquid and  $g$ ,  $i$ ,  $L$  refer to the gas, interface, and liquid, respectively. This equation is capable of simplification in cases of very high solubility (gas-film diffusion only significant) and very low solubility (liquid-film diffusion significant), and also for conditions in the case of intermediate gases where Henry’s law holds good. [Cf. *B.*, 1925, 55.] C. I.

**Absorption of Carbon Dioxide and Ammonia from Gas Bubbles.** P. G. LEDIG (*Ind. Eng. Chem.*, 1924, **16**, 1231—1233).—The rate of absorption of carbon dioxide in potassium hydroxide solution increases slowly with increasing concentration of the latter up to 9*N*. Beyond this point, the increase becomes very rapid and no theory can be put forward to explain the discontinuity. With sodium hydroxide, the rate of absorption diminishes when the concentration exceeds 4*N*. [Cf. *B.*, 1925, 69.] C. I.

**Effect of Gas Velocity and Temperature on Rate of Absorption.** R. T. HASLAM, R. L. HERSHEY, and R. H. KEEN (*Ind. Eng. Chem.*, 1924, **16**, 1224—1230).—The values for the “overall” absorption coefficients of sulphur dioxide and of ammonia in water in a particular absorption tower with varying gas velocities and temperatures were determined. From these on the “two-film” theory the individual film coefficients were calculated and experimental support was obtained to many of Lewis and Whitman’s deductions (cf. above), in particular that the film conductivity is a function of the ratio of density to viscosity and that the molecular diffusivities of all solutes, under similar conditions, are the same. [Cf. *B.*, 1925, 55.] C. I.

**Comparative Absorption Rates for Various Gases.** W. G. WHITMAN and D. S. DAVIS (*Ind. Eng. Chem.*, 1924, **16**, 1233—1236).—The “overall” rates of absorption under similar conditions for oxygen, sulphur dioxide, ammonia, and hydrogen chloride in water and for ammonia in 2.3*N*-hydrochloric acid were determined. It is shown that on Lewis and Whitman’s theory the results obtained in the first and last cases can be applied to the calculation of the other three and that these calculated results agree closely with those experimentally obtained. The “two-film” theory of absorption is thus strongly supported. The same constant is obtained by determining the rate of escape of a gas from solution as by measurement of the rate of absorption, the two processes being practically the same. [Cf. *B.*, 1925, 55.] C. I.

**Mechanism of Absorption of Moderately Soluble Gases in Water.** H. G. BECKER (*Ind. Eng. Chem.*, 1924, **16**, 1220—1224).—The absorption constants for oxygen and nitrogen in air-free

water were determined by measuring the reduction of pressure within a gas bubble passing through a vigorously agitated column of water. The rate of solution can be expressed in the form  $dw/dt = a - bw$ . The rate of absorption at the surface of a volume of water stirred by means of an agitator was found to vary directly with the speed of stirring, but conditions of perfect mixing were unattainable. Experiments on the absorption of various gases at a stationary surface showed that carbon dioxide, hydrogen, and hydrogen sulphide form a saturated surface layer. Chlorine and some other gases do not, the difference being probably due to the varying effects on the density, viscosity, and surface tension of the liquid produced by the solution of the gas. [Cf. *B.*, 1925, 55.] C. I.

**Mists from Chemical Reactions. II. Absorption of Chemical Mists.** H. REMY and K. RUHLAND (*Z. anorg. Chem.*, 1924, **139**, 51—68).—The absorption of moist chemical mists by aqueous salt solutions depends on many factors; that of dry mists ("colloidal dust") is dependent only on the vapour pressure of the salt solution. The curve representing the absorption of dry sulphuric anhydride mists by sulphuric acid solutions of varying concentration runs parallel with the b. p.-concentration curve of the acid. A maximum is observed in each case with approximately 98% acid solutions. Sulphuric acid solutions below 5% absorb moist sulphuric anhydride mists better than water; the absorption decreases as the acid concentration rises above this strength. Viscosity effects cause a very variable absorption as the acid becomes highly concentrated; heat of solution also exerts some influence. Exactly similar results were obtained for the absorption of wet and of dry ammonium chloride mists in ammonium chloride and in calcium chloride solutions. S. K. T.

**Mists from Chemical Reactions. III. Examination for Electric Charge.** H. REMY and C. KOCH (*Z. anorg. Chem.*, 1924, **139**, 69—80).—Ammonium chloride and sulphuric anhydride mists do not carry electric charges. The temporary small negative charges which these fogs acquire after bubbling through water are due to the charging of the fog-bearing gas ("bubble effect"; cf. Coehn, *Z. Elektrochem.*, 1923, **29**, 1). The size of this charge depends on the amount of fog absorbed by the water. Pure air assumes a relatively large negative charge when bubbled through 0.0001N-ammonium chloride or sulphuric acid which changes to a small positive value as the concentration increases to N. S. K. T.

**Adsorption of Arsenious Acid by Hydrated Aluminium Oxide.** J. H. YOE (*J. Amer. Chem. Soc.*, 1924, **46**, 2390—2397).—Aluminium hydroxide adsorbs arsenious acid very rapidly for the first few minutes, after which the rate drops; after 24 hours an equilibrium is apparently reached, although further slight adsorption takes place after 232 hours. The adsorbed quantities agree with the usual adsorption formula in the case of adsorption periods of 24 and 72 hours, but not in the case of 232 hours; the latter,

however, is probably not a simple case of adsorption. The lower the temperature of precipitation of the hydroxide the greater is its adsorptive capacity, this effect being greater over the range 0—50° than over 50—100°. Boiling the precipitate also reduces its adsorptive power. The effect of high temperature may be to cause the formation of a more compact precipitate. S. K. T.

**Adsorption by Precipitates.** H. B. WEISER (*J. Physical Chem.*, 1924, **28**, 1253—1264).—The amounts of potassium, barium, and aluminium chlorides, and potassium alum required to precipitate negative arsenious sulphide sol at various concentrations have been determined in the presence of phenol and isoamyl alcohol. These non-electrolytes increase the amount of barium chloride required, decrease the amount of potassium chloride, and have no effect in the case of the other two salts, contrary to the results of Kruyt and van Duin (*A.*, 1914, ii, 182). Although the amount of barium chloride required for precipitation is greater, the actual quantity of barium carried down by the sol is less, and, with concentrations of barium chloride less than the precipitation value, this amount follows the usual adsorption isotherm. Positive hydrous ferric and chromic oxide sols in the presence of these non-electrolytes show a slight diminution in the amounts of potassium chloride, oxalate, and sulphate required for precipitation. The adsorption of a non-electrolyte by the particles of a sol lowers its stability and at the same time it reduces the adsorption of the precipitating ion of the electrolyte added to it to produce coagulation. These two factors act in opposite directions and the amount of electrolyte required for precipitation is determined by the preponderance of either one or the other. M. B. D.

**Effects of Gas on the Resistance and Resistance-Temperature Coefficient of Sputtered Platinum Films.** F. W. REYNOLDS (*Physical Rev.*, 1924, **24**, 523—531).—Sputtered platinum films are assumed to contain adsorbed hydrogen; decrease of the resistance of a film on contact with oxygen is due partly to removal of hydrogen and partly to adsorption of oxygen, but the effects obtained depend on the conditions under which the film was produced. A. A. E.

**Temper Colours.** C. W. MASON (*J. Physical Chem.*, 1924, **28**, 1233—1244).—The author criticises the views of Mallock (*Proc. Roy. Soc.*, 1918, **A**, **94**, 561), Hinshelwood (*A.*, 1923, ii, 29), and Raman (*Nature*, 1922, **109**, 105). Temper colours are due to interference of light reflected in a similar manner to Newton's rings from the two surfaces of a film of a compound of the metal which is formed on its surface. Explanations using diffraction or selective reflection are inadequate and also inconsistent with the behaviour of the colours. The colour is increased by a reticulated or granular structure and a moderate degree of opacity of the film. If the film is itself coloured, it obscures the interference colours in the case of thicker films. (Cf. this vol., ii, 138.) M. B. D.

**"Temper" Colours [of Steel].** R. C. GALE (*J. Soc. Chem. Ind.*, 1924, **43**, 349—352T).—The thickness of the temper colours on steel as determined by direct weighing, assuming that the density of the film is 5.25 g. per c.c., varies from  $4.2 \times 10^{-7}$  cm. for a pale straw colour to  $21.3 \times 10^{-7}$  cm. for a dark purple. The figures do not agree with those calculated by Tammann from the thickness of an air layer of similar colour, and if the colours were due to interference then the refractive index of the film would vary from 2.53 to 0.63. Again, a blue film becomes purple or yellow when gently polished, and other evidence is adduced which seems to show that the films are granular. (Cf. Mason, preceding abstract; Hinshelwood, this vol., ii, 138.) A. R. P.

**Interfacial Tension of some Aqueous Solutions against Oils, as Corrected for Specific Gravity.** R. L. HOWARD and T. SOLLMAN (*J. Physical Chem.*, 1924, **28**, 1291—1296).—When surface tensions are measured by the Donnan pipette (A., 1900, ii, 201), a correction should be applied for the difference in density between the solutions and the oil. Surface tensions are given for solutions of sodium halides, sulphate, citrate, and carbonate, sucrose, glycerol, chloral hydrate, ethyl alcohol, carbamide, soap, bile salts, saponin, and tannin in water. M. B. D.

**[Uni-molecular Films of Sodium Oleate on Water.] Determination of the Constant  $N$  of Avogadro.** P. L. DU NOÛY (*Phil. Mag.*, 1924, [vi], **48**, 664—672).—Determinations of the surface tension of dilute aqueous solutions of sodium oleate after keeping for two hours show that three decided minima always occur at the concentrations 1/750,000, 1/1,220,000, and 1/1,390,000, respectively. It is suggested that these three minima correspond with the three possible modes of orientation of the molecules on the surface, unimolecular layers being in each case realised. Hence from these three minima it is possible to calculate the three dimensions of the sodium oleate molecule, from which  $N$  can be determined, a value  $6.008 \times 10^{23}$  being obtained. H. T.

**Phase Boundary Forces at the Gas-Liquid Surface of Separation. II. Adsorption and Orientation of Molecules of Aliphatic Compounds.** A. FRUMKIN (*Z. physikal. Chem.*, 1924, **111**, 190—210).—By the arrangement previously described (A., 1924, ii, 462) the potential difference set up at the surface of separation between air and solutions of a large number of aliphatic compounds has been determined. The solutions were made conducting by the addition of potassium chloride, which, except at high concentrations, does not affect the values found. The typical curve obtained by plotting the potential difference  $\epsilon$  against the concentration  $c$  for organic non-electrolytes or weak electrolytes conforms closely to the equation  $\epsilon = Ac/(1 + Be)$ ,  $A$  and  $B$  being constants, which is of the form of the Langmuir adsorption isotherm. For neutral salts, however, the curve is represented by an expression which recalls the Freundlich adsorption isotherm. In homologous series of organic compounds, for example, aliphatic acids, alcohols,

ketones, and esters, increase in the number of carbon atoms brings about a diminution in the concentration at which a given charge may be reached, and the relative charge is the same for each carbon atom. The value of  $\epsilon_{\infty}$ , however, is practically identical for each member of the series. Acids, alcohols, ketones, esters, and amines give positive charges to the surface of the solution. Halogen substitution compounds and neutral salts give, for the most part, a negative charge. The general behaviour runs parallel with the effect on the surface tension and is therefore related to the adsorption of the substance at the air-water surface of separation.

Accepting the views of Langmuir and Harkins on the orientation of adsorbed molecules by surface forces, the results may be explained by supposing that in pure water the oxygen molecule is oriented towards the surface giving a negative charge. In solutions of aliphatic compounds which give a positive charge, the hydrocarbon radicals, having no tendency to hydrate, take up a position at the surface, but in the halogen derivatives the halogen is adsorbed at the surface giving a negative charge. Since increase in the number of carbon atoms does not increase the maximum charge, the linking C—C must be completely non-polar in character. To the linkings C—O, C—Cl, and C—N a definite polarity must be ascribed, the carbon atom in each case being positive. M. S. B.

**Orientation of Ammonium Iodide Crystals on the Surface of Muscovite.** M. ROYER (*Compt. rend.*, 1924, 179, 1610—1612; cf. Gaubert, A., 1924, ii, 549).—A drop of warm saturated solution of ammonium iodide is spread on a freshly-prepared cleavage surface of the mica, the lower temperature of which causes rapid crystallisation without formation of unoriented crystals. The crystals are invariably cubic, never octahedral. Unlike other alkali halides, ammonium iodide on a given fresh cleavage orients itself in one position only. A side of the triangular contour (normal to a triad axis of the cube) lies parallel to the mica plane (010), whilst all the apices point either in one direction or the opposite. When crystals are deposited on successive cleavages, the orientation is sometimes all in one direction and sometimes all in the other. It is inferred that muscovite is of triclinic symmetry, but is built up of laminations twinned at  $180^\circ$  to one another, the resulting crystal being pseudo-monoclinic. W. A. C.

**Permeability of Membranes.** W. D. BANCROFT and C. GURCHOT (*J. Physical Chem.*, 1924, 28, 1278—1283).—A preliminary paper showing that the permeability of membranes is closely connected with their coagulability when prepared in the colloidal state. Copper ferrocyanide membranes are coagulated by low concentrations of methyl alcohol and of acetic acid, thereby becoming permeable to sugar. Alcohols and acids coagulate a copper ferrocyanide sol whilst alkalis peptise a copper ferrocyanide gel. The results of Barlow (A., 1905, ii, 507; 1906, ii, 273), Walden (A., 1893, ii, 203), and Czapek (*Ber. deuts. bot. Ges.*, 1910, 28, 159) are shown to be due to coagulation of the membrane by the alcohols or acids employed. M. B. D.

**Theory of Osmotic Pressure, Membrane Potential, and Coagulation of Colloids. Colloidal Chromium Hydroxide.** N. BJERRUM (*Z. physikal. Chem.*, 1924, **110**, 656—684).—Equations have been deduced for the osmotic pressures of colloidal ions; observations on colloidal solutions of chromium hydroxide are in approximate agreement with these. Determinations of membrane potential show that the relationships existing between this quantity and the activities of the ions ( $H^+$  and  $Cl^-$ ) on different sides of the membrane are in agreement with Donnan's theory. The membrane potentials calculated from the observed osmotic pressures are approximately half the measured values. From the osmotic pressure measurements it is calculated that the colloidal chromium particle consists on the average of 1000 chromium atoms and carries about 30 free charges. The amount of adsorbed anion (chloride) shows that the total charge carried by the colloid is about 240. For complete coagulation, the necessary amount of ferrocyanide corresponds exactly with the total charge on the colloid, whilst about 15% excess of ammonium or potassium sulphate is required. The change in the conductivity on addition of ammonium sulphate has been measured. Commencement of coagulation is indicated by a sudden break in the curve obtained on plotting conductivity against c.c. of ammonium sulphate. An apparatus is described for the determination of osmotic pressures, membrane potentials, and the activities of the ions on both sides of the collodion membrane. J. S. C.

**Effects of Dilution on Colloids.** W. KOPACZEWSKI (*Compt. rend.*, 1924, **179**, 628—629).—Certain colloidal solutions give, on dilution, conductivity values greater than would be expected as a result of dissociation. It is suggested that the union between ions and molecules in the solution is not a simple chemical change. Some biological aspects of the experimental results are indicated.

H. J. E.

**Theory of Elasticity of Colloidal Solutions.** E. SZEGVARI (*Z. physikal. Chem.*, 1924, **108**, 175—184; cf. following abstract).—When the elasticity limit in solids is overstepped the tension completely disappears, but in a colloidal solution in motion the tension at the elasticity limit is maintained, and represents a flow-elasticity. The relation between the resistance value,  $w$ , the velocity gradient,  $G$ , in the liquid, the flow-elasticity,  $\delta$ , and the true viscosity,  $\eta$ , is expressed by  $w = \delta/G + \eta$ . This formula is in good agreement with the experimental results obtained using Couette's apparatus, but, for agreement with those obtained by Hess' method, the addition of a constant to  $G$  is required. By reference to the experimental data for benzopurpurin and vanadium pentoxide sols it is shown that, whilst true viscosity increases proportionally with concentration, or with addition of electrolyte, and in the latter case only very slowly, the rate of increase of elasticity also increases rapidly. The two quantities therefore appear to be independent of one another. Under the conditions prevailing in the Ostwald

viscosimeter, the influence of the elasticity of the sol on the result is of the same order as that of the viscosity. M. S. B.

**Viscosity and Elasticity of Colloidal Solutions.** H. FREUNDLICH and E. SCHALEK (*Z. physikal. Chem.*, 1924, **108**, 153—174).—The viscosity of various sols has been examined by Hess' method of comparison of the rate of flow of the sol with that of water through horizontal capillary tubes under the influence of varying pressures (cf. Rothlin, A., 1920, ii, 18) and by Couette's method, as modified by Hatschek (A., 1913, ii, 835), in which an external revolving cylinder drags round an internal concentric cylinder on account of the viscosity of the liquid between. A number of sols, especially hydrophobic sols, for example, arsenic trisulphide, lanthanum oxide, zirconium oxide, calcium fluoride, a sulphur sol, and an aluminium oxide sol, obeyed Poiseuille's law, that is, they behaved like true solutions. A different aluminium oxide sol and a cerium oxide sol showed slight deviations from Poiseuille's law. Greater deviations were shown by an old ferric oxide sol, and much greater divergence by vanadium pentoxide, benzopurpurin, cotton-yellow, gelatin, and sodium stearate. With increasing pressure, or with increasing angular velocity, according to the method of measurement, the apparent coefficient of viscosity, or the resistance value, decreased. This is attributed to a shearing elasticity of the sol which becomes less important relatively to the true viscosity coefficient as the velocity gradient in the sol increases. It has been previously shown by Freundlich and Seifriz (*Z. physikal. Chem.*, 1923, **104**, 233) that most sols displaying deviations from Poiseuille's law possess an extension elasticity. The sols which show the greatest deviations, and therefore the greatest elasticity, appear to be those which consist of non-spherical particles. The elasticity apparently increases with age and with the addition of electrolytes, and decreases with dilution. In the case of vanadium pentoxide sols, the increase in double refraction runs parallel with the increase in apparent viscosity, but does not appear to be related to the size of the particles.

Since only low pressures are operative in the Ostwald viscosimeter, it is evidently not suitable for the measurement of the viscosity of sols. M. S. B.

**Colloidal Arsenic Sulphide.** A. BOUTARIC and M. VUILLAUME (*J. Chim. Phys.*, 1924, **21**, 247—264; cf. A., 1924, ii, 405).—The absorption of light by arsenic sulphide sols is expressed by the relation  $\log I_0/I = k/\lambda^n$ , where  $I_0$  and  $I$  are the intensities of the incident and transmitted rays of wave-length  $\lambda$ . The constant  $n$  increases regularly with diminishing wave-length, being 3.3 for  $\lambda = 640 \mu\mu$  and 12.0 for  $\lambda = 530 \mu\mu$ , and it is equal to 4 (the Rayleigh constant for absorption by colourless particles of small size compared to  $\lambda$ ) when  $\lambda = 620 \mu\mu$ . The absorption is the result of (1) a simple absorption following the law of Rayleigh, and (2) a selective absorption in the region of  $\lambda = 620 \mu\mu$ , and due to reflection from the surface of the granules. Absorption due to (1) is increased and that due to (2) is decreased by increase in the size of the granules.



When the sols are prepared by passing hydrogen sulphide into a solution of arsenious oxide, the size of the granules increases with the concentration of the arsenic and with the time of passage of the hydrogen sulphide, a slow current of which gives much larger granules than a rapid one.

The densities and viscosities of sols of different concentration have been determined, and indicate that the viscosity formula of Einstein applies accurately to sols of infinite dilution.

The flocculation of these sols has been studied spectrophotometrically by periodically measuring the coefficient of absorption, which first increases rapidly and then reaches a limiting value. At this point, a gel is produced in an unstable condition, and flocculation may occur at any moment and is favoured by factors such as rapid stirring. The slightest excess of hydrogen sulphide greatly retards the flocculation by alkali chlorides and aluminium chloride, accelerates it in the case of the chlorides of barium, strontium, and calcium, and has little effect with manganese or magnesium chlorides. Rise of temperature produces a similar effect, but the presence of excess of arsenic trioxide has little effect. In all cases, the speed of flocculation increases both with the concentration of the electrolyte after mixing, and with that of the added solution, unless this is very dilute. For a given concentration of electrolyte, increased colloid concentration raises the velocity of flocculation with the chlorides of potassium, barium, magnesium, and manganese, and diminishes the velocity with cadmium and aluminium chlorides.

W. H.-R.

**Dispersion of Colloidal Electrolytes in Relation to Mineral Exchanges in Cells.** W. MESTREZAT and (MLLE.) M. JANET.—(See i, 198.)

**Determination of the Size of Invisible Particles in Emulsoid Sols.** H. R. KRUYT and H. J. C. TENDELOO (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 377—381).—The conductivity, viscosity, and the cataphoretic velocity of 0.5% sols of starch, to which varying quantities of various electrolytes were added, were measured. This leaves only  $\phi$ , the relative volume of the particles, and  $r$ , their radius, undetermined in Smoluchowski's equation for charged particles,  $(\eta_s - \eta_0)/\eta_0 = \frac{5}{2} \phi [1 + \omega/r\zeta_2 \cdot (\zeta D/2\pi)^2]$ , in which  $\eta_s$  and  $\eta_0$  are the viscosities of the sol and dispersent, respectively,  $\omega$  is the specific resistance,  $\zeta$  is the potential difference in the surface double layer, and  $D$  is the dielectric constant. By taking the results with different concentrations of electrolytes present in pairs and solving for  $\phi$  and  $r$ , it is found that these are constant whichever combination be taken, that is,  $\phi$  and  $r$  are not affected by the charge. As a mean,  $r$  is found to be, in this case, 7  $\mu$ .

L. J. H.

**Titration Curve of Gelatin.** W. R. ATKIN and G. W. DOUGLAS (*J. Soc. Leather Trades Chem.*, 1924, 8, 584—596).—The  $p_H$  values of 1% gelatin solutions to which varying amounts of acid or alkali have been added are plotted against the amount of acid or alkali

combined with the gelatin. From  $p_H$  1.7 the amount of combined hydrochloric acid rises sharply with decreasing  $p_H$ . From the isoelectric point  $p_H$  4.7 to  $p_H$  1.7 the curve is rather flatter whilst from  $p_H$  4.7 to  $p_H$  7.7 the amount of sodium hydroxide fixed increases continuously. From  $p_H$  7.7 the curve is an almost perfect sigmoid. Sigmoid curves have been obtained by Harris (A., 1924, ii, 73) for certain proteins, and the authors consider that the gelatin curve is the result of the merging of two sigmoid curves into one another between  $p_H$  4.7 and  $p_H$  7.7. The acid portion of the titration curve represents approximately the titration curve of the free amino groups in gelatin with hydrochloric acid and the alkaline portion represents the titration of the free carboxyl groups with sodium hydroxide. From the first curve the basic dissociation constant is 0.0002 and the acid dissociation constant is found similarly to be  $2 \times 10^{-6}$ . From the alkaline portion of the curve,  $p_H$  4.7 to  $p_H$  7.7, it is found that the equivalent weight of gelatin is 3290. The more alkaline portion of the curve  $p_H$  7.7 to  $p_H$  12.6 gives 2060. A keto-enol transformation appears to be involved in this region. Wilson's second isoelectric point for gelatin (cf. A., 1923, i, 68) is due to neutral salt effects. The point of inflection at  $p_H$  7.7 appears to represent the commencement of the introduction of alkali into the  $-\text{CO}\cdot\text{NH}-$  group, in which there has been a molecular rearrangement into the enol form  $-\text{C}(\text{OH})\cdot\text{N}-$ , the hydroxyl then combining with alkali.

D. W.

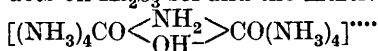
**Physico-chemical Examination of Medicinal Silver Preparations.** H. SCHLEE and W. THIESSENHUSEN (*Z. angew. Chem.*, 1924, **37**, 837—845, 855—860; cf. A., 1924, i, 1262).—Equal concentrations of aqueous solutions of various silver preparations (dispargen, fulmargin, protargol, collargol, iodcollargol, solargyl) have about the same conductivity (about  $2.5 \times 10^{-5}$  for 0.031% solutions and  $1.0 \times 10^{-3}$  for 2% solutions), this being roughly proportional to the silver content. The determination of the conductivity and of the silver-ion concentration affords a means of detecting the presence of electrolytes which do not yield silver ions and of roughly estimating their quantity. The size of the colloidal particles present in the solutions varies between 21 and 27  $\mu\mu$ , except for solargyl, in which they measure 59  $\mu\mu$ . Their number is, in general, proportional to the silver content, and varies between  $1 \times 10^9$  and  $76 \times 10^9$  per c.c. of the 1% solutions. The above determinations were also made on solutions which had been kept for several months. In every case, a sediment had formed, increasing in quantity with increasing concentration of the solutions and causing a diminution in the silver content of the solutions. The silver-ion concentration had diminished (except in the case of collargol and of concentrated solutions of dispargen and solargyl), the conductivity had increased, the number of colloidal particles had decreased, and the size of the latter had remained constant or had increased slightly. Silver hydrosols, freshly prepared in water and  $N/1000$  sodium hydroxide by Bredig's electrical pulverisation method, were also examined. The quantity of silver going into colloidal solution

increases with the time of pulverisation, although not always in strict proportion. The same applies to the silver-ion concentration (except in dilute alkaline sols), conductivity, and number of the colloidal particles, the size of which is about  $20\ \mu\mu$  in pure water and  $29\text{--}40\ \mu\mu$  in the alkaline medium. From the high silver-ion concentration of the hydrosols (about  $0.1$  mg. of ion per litre), it is assumed that part of the silver pulverised goes into colloidal solution in the combined state. These hydrosols rapidly form flocculent precipitates, a phenomenon in which atmospheric carbon dioxide appears to play a part.

W. T. K. B.

**Influence of Valency on Coagulation and Cataphoresis.** H. FREUNDLICH and H. P. ZEH (*Z. physikal. Chem.*, 1924, **114**, 65).—The influence of complex cobalt salts with uni- to sexa-valent cations on the cataphoresis and coagulation of an  $\text{As}_2\text{S}_3$  sol has been examined. The coagulative power ( $\gamma$ ) of the salts increases with increasing valency of the cation. From curves expressing the relation between the electrokinetic potential  $\zeta$  and the concentration  $c$ , the concentrations which correspond with a fixed  $\zeta$  value have been derived. In agreement with Freundlich's adsorption theory of coagulation, these concentrations ( $c$ ) vary with the valency of the cations in the same manner as the coagulation values. The adsorption theory is applicable to the uni-, bi-, ter-, and quadri-valent cations, but unexplained deviations occur with the sexa-valent cation.

Similar observations were made on the influence of salts with complex cyanide ions on a  $\text{Fe}_2\text{O}_3$  sol. Here also the parallelism between  $\gamma$  and  $c$  is complete. The inference that the different anions are equally adsorbed in equimolar concentration proves, however, to be valid only to a limited extent. In particular,  $\text{Au}(\text{CN})_2'$  acts more weakly than  $\text{Au}(\text{CN})_4'$  and  $\text{Cu}(\text{CN})_4'''$  than  $\text{Fe}(\text{CN})_6'''$ . In contrast to earlier work, the authors'  $\zeta$ - $c$  curves show no initial rise of  $\zeta$  potential except where the multivalent anion  $\text{Fe}(\text{CN})_6'''$  acts on  $\text{As}_2\text{S}_3$  sol and the multivalent cation



acts on  $\text{Fe}_2\text{O}_3$  sol. The observed behaviour is attributed to the value of the  $\zeta$  potential possessed by the original pure sol.

N. H. H.

**Influence of Colloids on the Cathodic Overvoltage of Hydrogen and Metals.** C. MARIE and G. LEJEUNE (*Compt. rend.*, 1924, **179**, 679—682; cf. A., 1909, ii, 124).—The energy required to liberate zinc, nickel, or lead is increased when a colloid such as gelatin is added to the solution. The colloid reduces the amount of the metal deposited by a given current. With copper, mercury, or silver, on the other hand, the energy difference is small. It was to be expected that the addition of colloid to an acid solution of the metal would increase the quantity of the latter deposited. This may be the case for low concentrations of hydrogen ions, but experiment shows that it is not so for greater concentrations. The

phenomenon apparently undergoes inversion at a certain limiting concentration.

T. H. P.

### **Influence of Intensive Drying on Internal Change. II.**

A. SMITS (*Z. physikal. Chem.*, 1924, **111**, 161—170; cf. A., 1922, ii, 358).—The mechanism of the changes in a unary system, which produce the phenomena observed after intensive drying, has been discussed. Regarding the substance as a mixture of at least two different kinds of molecules, it is possible that the internal equilibrium between these, which would otherwise change with change of temperature, may be fixed by the drying, so that the same equilibrium is thereafter maintained at all temperatures. Alternatively, the position of equilibrium may be moved, after a certain degree of dryness is reached, because the reaction in one direction is delayed by the absence of water more than the reaction in the contrary direction. The latter view appears to be supported by the experiments of Dixon and Baker on the influence of drying on the reactivity of different substances. Their results might be explained by postulating the existence of an internal equilibrium between active and inactive molecules which is shifted by drying in such a way that all the molecules become inactive (Smits, *Versl. Kon. Akad. V. Wet.*, 1923, **32**, 345). The experiments of Coehn (A., 1923, ii, 206) on the effect of drying upon the equilibrium between hydrogen and chlorine on the one side, and hydrogen chloride on the other, when under the influence of ultra-violet light, may probably be similarly explained.

M. S. B.

### **Measurement of the Second Dissociation Constants of Dibasic Acids, with Special Reference to Tartaric Acid.**

T. PAUL (*Z. physikal. Chem.*, 1924, **110**, 417—434).—The expression of A. A. Noyes (A., 1893, ii, 365), connecting the first and second dissociation constants of dibasic acids with the hydrogen-ion concentration and molarity of dilute aqueous solutions of the corresponding acid sodium or potassium salts, is deduced. The concentration of the hydrogen ion in solutions of sodium and potassium hydrogen tartrates has been determined by conductivity methods at 18°, and by the method of sugar inversion at 76°. Assuming  $k_1$  for tartaric acid to have the value  $0.97 \times 10^{-3}$ , as determined by Ostwald and Walden from conductivity measurements at both temperatures, values of  $k_2$  are calculated. The  $k_2$  values obtained by the catalytic method diminish with increasing dilution of the acid salt and reach a constant limiting value  $2.7 \times 10^{-5}$  at  $v=1000$ . The  $k_2$  values from conductivity measurements increase with increasing dilution and attain the same limiting value at roughly the same dilution. These variations are ascribed to the incomplete ionisation of the salt in the more concentrated solutions. Measurements of the rates of sugar inversion and of electrical conductivity show that the value of  $k_1$  for tartaric acid is  $0.97 \times 10^{-3}$  at 18° and 76°. Values of  $k_2$  for tartaric acid obtained by other investigators are given, the values ranging from  $2.9 \times 10^{-5}$  to  $7.5 \times 10^{-5}$ .

J. S. C.

**Theory of Binary Electrolytes.** W. SEMENTSCHENKO (*Z. physikal. Chem.*, 1924, **112**, 128—134).—An expression is derived which connects the degree of dissociation of an electrolyte with the dilution and with the dielectric constant of the solvent. Ostwald's dilution law and Walden's law result as special cases. The expression is used to develop quantitatively the hypothesis of dissociated complexes in connexion with anomalous conductivity (cf. Steele, McIntosh, and Archibald, A., 1905, ii, 222).

L. F. G.

**Dilution Laws and Distribution Coefficients of Strong Electrolytes from the Debye Theory.** P. GROSS and O. HALPERN (*Physikal. Z.*, 1924, **25**, 393—397).—The dilution laws for strong electrolytes and the distribution coefficients of such compounds between two immiscible solvents have been treated from the standpoint of the Debye theory. Existing data have been used to verify the relations deduced.

S. B.

**Electrometric Study of Hydrolysis.** P. JOB (*Compt. rend.*, 1924, **179**, 1317—1319).—The hydrolytic equilibrium in salt solution is displaced by the addition of strong acids or bases, and the displacement measured electrometrically (A., 1924, ii, 512). An atmosphere free from carbon dioxide is essential. In the case of solutions of alkali acetates (except at the neutral point), the formula  $B = C_H(1 + AC_H/K + C_H)$  is used, where  $B$  is the concentration of the added hydrochloric acid,  $C_H$  the hydrogen-ion concentration,  $A$  is the concentration (dilute enough for complete dissociation) of the acetate, and  $K$  is the dissociation constant of acetic acid. The value obtained for  $K$  is  $3.5 \times 10^{-5}$ , i.e., almost double that usually adopted. Reasons are given for this discrepancy. The value obtained for the hydrolytic constant of the acetate is  $2.6 \times 10^{-10}$ .

L. L. B.

**Affinity Constant of some Organic Bases.** M. BOURGUAUD and A. DONDELINGER (*Compt. rend.*, 1924, **179**, 1159—1161).—The affinity constants of twenty-seven amines were calculated from measurements of the degree of hydrolysis of their hydrochlorides. Aniline has a smaller affinity constant than indanylamine and the latter smaller than benzylamine. Qualitatively this order can be explained by the more symmetrical structure of aniline and the closer proximity of the nitrogen atom to the phenyl radical. Substitution of one or two methyl groups lowers the affinity constant although the first only plays the part of a negatifying radical. The positive ethyl group sometimes lowers, sometimes raises the value of the constant. The indanyl group always acts in a negative manner. Substitution in the para position by the methyl group has very slight influence on the value of the constant (cf. Walker, *Z. physikal. Chem.*, 1899, 319).

H. T.

**Theory of the Isoelectric Point.** R. KUHN (*Z. physikal. Chem.*, 1924, **114**, 44—48).—The values obtained for the isoelectric point of amphoteric electrolytes by viscosity minimum and similar physical methods do not always agree with those obtained from Michaelis' formula  $h_1 = \sqrt{K_a K_w / K_b}$ , where  $h_1$  is the hydrogen-ion

concentration,  $K_a$  and  $K_b$  are the acidic and basic dissociation constants, and  $K_w$  is the ionic product for water. The author puts forward the formula  $h_0 = h_1 \sqrt{\tan \alpha_1 / \tan \alpha_2}$ , where  $h_0$  is the hydrogen-ion concentration determined by the viscosity or other method,  $h_1$  that obtained as above, whilst  $\tan \alpha_1$  and  $\tan \alpha_2$  are the tangents of inclination of the viscosity etc. curves for points with equal ordinates on both sides of the minimum or maximum. N. H. H.

**Electrometric Titration of Acids.** F. AUERBACH and E. SMOLCZYK (*Z. physikal. Chem.*, 1924, **110**, 65—141).—Equations are derived representing the change in the  $p_H$  value on titration of solutions of monobasic, dibasic, and tribasic organic acids with alkali. It is shown that in the case of a dibasic acid the existence of two sigmoid portions on plotting  $p_H$  against c.c. alkali depends on the ratio of the values of the first and second dissociation constants. If  $K_1 : K_2 < 16$ , the form of the curve is that of a monobasic acid. The process of electrometric titration may be employed to determine the various dissociation constants. Equations are derived whereby the concentrations of the components of mixtures of two monobasic acids, a monobasic acid and a dibasic acid, two dibasic acids, or a dibasic acid and a tribasic acid, may be determined from a knowledge of the dissociation constants and the results of an electrometric titration. The influence of errors of observation on the final result is dealt with.

A form of the quinhydrone electrode suitable for electrometric titration is described. The total electrolyte concentration must always be kept below 0.1 *M* in order to avoid the inherent "salt error."

The values for the dissociation constants of the various acids at 20° are found to be: benzoic,  $6.5 \times 10^{-5}$ ; acetic,  $1.86 \times 10^{-5}$ ; lactic,  $1.33 \times 10^{-4}$ ; tartaric,  $K_1$   $8.96 \times 10^{-4}$ ,  $K_2$   $7.46 \times 10^{-5}$ ; malic,  $K_1$   $3.86 \times 10^{-4}$ ,  $K_2$   $1.39 \times 10^{-5}$ ; succinic,  $K_1$   $6.86 \times 10^{-5}$ ,  $K_2$   $3.97 \times 10^{-6}$ ; citric,  $K_1$   $1.03 \times 10^{-3}$ ,  $K_2$   $2.53 \times 10^{-5}$ ,  $K_3$   $1.51 \times 10^{-6}$ . Oxalic acid is too strong an electrolyte to permit of the determination of  $K_1$  and  $K_2$  by this method. Owing to the activity of formic acid as a reducing agent, the quinhydrone electrode cannot be employed for the electrometric titration of this acid.

The applicability of the method to the determination of the individual concentrations in mixtures of two acids has been tested by experiments with known mixtures of the following acid pairs: acetic and lactic, tartaric and acetic, tartaric and lactic, tartaric and malic, citric and tartaric, citric and malic. The concentrations thus found are in excellent agreement with the actual values.

The concentration of an organic acid in presence of its salts may be determined by addition of a small known excess of strong acid, e.g., hydrochloric, followed by an electrometric titration. The occurrence of the first maximum in the value of  $\Delta\epsilon/\Delta x$  ( $\epsilon$  being the potential of the hydrogen electrode and  $x$  the amount of added alkali) indicates the neutralisation of the excess of strong acid, and the occurrence of the second maximum, the neutralisation of the total acid. The method has been successfully applied to the

determination of lactic, tartaric, malic, and citric acids in presence of their sodium salts and to the determination of a mixture of tartaric and malic acids in presence of sodium malate and tartrate.  
J. S. C.

**Calculation of the Work of Chemical Changes involving Variable Concentrations.** C. FRENZEL (*Z. physikal. Chem.*, 1924, **110**, 547—558).—Mathematical. An expression for the maximum work in homogeneous gas reactions is derived. The expression may be represented graphically.  
J. S. C.

**Equilibrium across a Parchment Membrane in the Case of Sodium Chloride in Presence of Sodium Caseinate.** P. A. SPORING (*J. Chem. Soc.*, 1924, **125**, 2316—2319).—Purified sodium caseinate, neutral to phenolphthalein, was selected as an example of an electrolytic colloid of complicated constitution and placed in one compartment of a distribution vessel. Separated from it by a parchment membrane was an equal volume of aqueous sodium chloride. After equilibrium had been attained the two solutions were analysed. The ionic product  $[Na][Cl]$ , on the caseinate side of the membrane is found to be always greater than on the other side if the caseinate is assumed to be completely dissociated. To give a constant ionic product, a dissociation value of 0.6—0.8 for sodium caseinate must be assumed. The results are in fair agreement with the theory of membrane equilibrium in its simplest form.  
C. I.

**Solubilities of Vanillin.** C. E. MANGE and O. EHLEH (*Ind. Eng. Chem.*, 1924, **16**, 1258—1259).—Solubility curves for vanillin in aqueous alcohol and aqueous glycerol are drawn. The latter dissolves very little more vanillin than water alone and the solutions exhibit considerable supercooling. Concentrated solutions of vanillin in glycerol or in a mixture of glycerol and alcohol deposit a heavy white precipitate of vanillin glyceride, which is easily hydrolysed into glycerol and vanillin by addition of water and heating. Generally speaking, if the solution contains as much water as vanillin, precipitation of the glyceride will not occur.  
W. T. K. B.

**System Zinc Sulphate-Water.** C. R. BURY (*J. Chem. Soc.*, 1924, **125**, 2538—2541).—Data obtained for the solubility of zinc sulphate hexahydrate between 11° and 61° differ (below 25°) from those of Cohen (cf. A., 1900, ii, 184), whose figures must refer to some other hydrate. The latter agree with the data obtained for the monoclinic heptahydrate between 7° and 23°. The transition of the hepta- to the hexa-hydrate takes place at 24.8°. The monohydrate is probably formed when the hexahydrate is warmed at about 60° (cf. A., 1897, ii, 250).  
S. K. T.

**Determination of the Solubilities of Sparingly Soluble Substances. II. Solubilities of the Oxides of Beryllium, Aluminium, Zinc, Cadmium, Lead, Copper, and Silver in Water.** H. REMY and A. KUHLMANN (*Z. anal. Chem.*, 1924, **65**, 161—181).—The solubilities of the above oxides were deter-

mined by the conductometric titration and conductivity methods, a correction being applied in the latter case for the carbon dioxide content of the water. The results obtained by the respective methods were (in mg. per litre): aluminium oxide, 0.94, 1.04; zinc oxide, 2.92, 3.06; cadmium oxide, 4.80, 5.00; lead dioxide, 12.39, 12.34; copper oxide, 5.46, 5.39; silver oxide, 25.29, 24.80. The solubility of beryllium oxide, 0.20 mg. per litre (conductometric titration; the conductivity method failed), is very much smaller than that of magnesium oxide (cf. this vol., ii, 30), which is in accordance with the general relationship between the solubilities of the oxides of the metals in the first column of the second group of the periodic table.

S. K. T.

**Sulphurous Acid and its Salts. II. Decomposition of Sulphites at Red Heat.** F. FOERSTER and K. KUBEL (*Z. anorg. Chem.*, 1924, **139**, 261—292).—Calcium and sodium sulphites decompose at 650° and 600°, respectively, according to the equation:  $4M_2SO_3 \rightleftharpoons 3M_2SO_4 + M_2S$ . Above 900°, the dissociation  $M_2SO_3 \rightleftharpoons M_2O + SO_2(\alpha)$  disturbs the equilibrium. For the calcium compound, this dissociation is perceptible at 650° and is almost complete at 1100°. The residue contains calcium sulphate besides oxide, probably because the equilibrium  $3SO_2 \rightleftharpoons 2SO_3 + S$  becomes effective at high temperatures. With sodium sulphite, the equilibrium ( $\alpha$ ) is not fully established after 2 hours' heating at 1200°. The rate of decomposition of sodium sulphite is much greater than that of the calcium salt at the same temperature. For the former, it increases rapidly between 600° and 700°; for the latter it increases rapidly between 650° and 700°, but only very slowly between 700° and 800°.

Magnesium sulphite decomposes at 300° according to the equation:  $4MgSO_3 = [2MgSO_4 + 2MgSO_2] = 2MgSO_4 + MgS_2O_3 + MgO$ , the magnesium sulphoxylate being regarded as an intermediate product; partial decomposition of the thiosulphate,  $MgS_2O_3 = MgSO_3 + S$ , and dissociation of the sulphite,  $MgSO_3 \rightleftharpoons MgO + SO_2$ , also take place, especially at higher temperatures. [Cf. *B.*, 1925, 39.]

S. K. T.

**Sodium and Potassium Salts of Sulphurous Acid.** F. FOERSTER, A. BROSCHE, and C. NORBERG-SCHULZ (*Z. physikal. Chem.*, 1924, **110**, 435—496).—Sodium and potassium salts of sulphurous acid have been prepared and separated in an atmosphere of hydrogen. Solubility determinations, also in a hydrogen atmosphere, have been made over a range of temperature extending from the cryohydric point almost to the boiling point. Sodium sulphite exists as a heptahydrate and as the anhydrous salt. No evidence for the existence of the reported decahydrate was obtained. Solubility data show that the cryohydric point is  $-3.45^\circ$  and the transition temperature of the heptahydrate  $33.4^\circ$ . The retarded transition renders the determination of this temperature by thermometric and dilatometric methods impossible. Sodium pyrosulphite crystallises from acid solutions and there appears to be no evidence for the existence of  $NaHSO_3$ . The solubility data for sodium



pyrosulphite show that this crystallises out from aqueous solutions as  $\text{Na}_2\text{S}_2\text{O}_5$  from the boiling point to  $5.5^\circ$  (stable), or to  $-4.8^\circ$  (metastable), as  $\text{Na}_2\text{S}_2\text{O}_5 \cdot 7\text{H}_2\text{O}$  from  $+5.5^\circ$  to the cryohydric point  $-9.05^\circ$  (stable), and as  $\text{Na}_2\text{S}_2\text{O}_5 \cdot 6\text{H}_2\text{O}$  from  $+3.8^\circ$  to the cryohydric point  $-9.79^\circ$  (metastable). Some evidence was obtained as to the existence of  $\text{Na}_2\text{S}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$  and  $3\text{Na}_2\text{S}_2\text{O}_5 \cdot \text{H}_2\text{O}$  but no conclusive proof.

Potassium sulphite forms no hydrate as recorded in the literature. The cryohydric point is  $-45.5^\circ$ . Solubility determinations show that potassium pyrosulphite exists only as the anhydrous salt. A double salt,  $\text{K}_2\text{S}_2\text{O}_5 \cdot 4\text{KHSO}_3$ , crystallises out from such solutions over the temperature range  $-4^\circ$  to  $+4^\circ$ . The hydrogen sulphite itself is non-existent. The above salts are perfectly stable in dry air and give off no sulphur dioxide. Cryoscopic measurements show that in aqueous solution the pyrosulphites are hydrolysed according to the scheme  $\text{S}_2\text{O}_5'' + \text{H}_2\text{O} \rightleftharpoons 2\text{HSO}_3'$ . J. S. C.

**Displacement of the Maximum Solubility and the Existence of Solubility Constants.** A. COLSON (*Compt. rend.*, 1924, 179, 1399—1404).—Measurements of the solubility of calcium sulphate in dilute nitric and sulphuric acids have been made at different temperatures. The solubility curves show no maxima. Measurements of the heats of solution of calcium sulphate in dilute nitric and sulphuric acids at  $16$ – $17^\circ$  gave 18.5 cal. and 10 cal. per g., respectively. H. T.

**Equilibrium  $\text{Fe}'' + \text{Ag}' \rightleftharpoons \text{Fe}''' + \text{Ag}$ .** N. A. TANANAEV (*Z. physikal. Chem.*, 1924, 114, 49—58).—The reaction studied in the complete absence of air is shown to be reversible and gives the well-defined equilibrium constants  $K_0$ , 0.0018;  $K_{25}$ , 0.0061;  $K_{45}$ , 0.0110. The heat of reaction is 7868 cal. for 1 g.-atom of silver. Van't Hoff's equation connecting change of equilibrium with temperature is applied and gives satisfactory agreement with the experimental results. N. H. H.

**Reciprocal Salt Pair  $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightleftharpoons \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$ .** J. B. ROBERTSON (*J. Soc. Chem. Ind.*, 1924, 43, 334—338T).—The equilibrium diagram for the above system at  $25^\circ$ ,  $50^\circ$ , and  $100^\circ$  was constructed from investigations on the systems  $\text{KCl}$ – $\text{K}_2\text{Cr}_2\text{O}_7$ – $\text{H}_2\text{O}$ ,  $\text{NaCl}$ – $\text{Na}_2\text{Cr}_2\text{O}_7$ – $\text{H}_2\text{O}$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ – $\text{Na}_2\text{Cr}_2\text{O}_7$ – $\text{H}_2\text{O}$  and  $(\text{K}, \text{Na})$ – $(\text{Cl}, \text{Cr}_2\text{O}_7)$ – $\text{H}_2\text{O}$ , together with Reinders' results for the system  $\text{NaCl}$ – $\text{KCl}$ – $\text{H}_2\text{O}$  (*Z. anorg. Chem.*, 1915, 93, 202). Potassium dichromate and sodium chloride are the compatible salt pair at all temperatures; as the temperature increases the areas on the diagram representing potassium and sodium chlorides increase considerably at the expense of the area representing potassium dichromate. The sodium dichromate area is always very small. S. K. T.

**Binary System Sodium Metasilicate–Silica.** G. W. MOREY and N. L. BOWEN (*J. Physical Chem.*, 1924, 28, 1167—1179).—The system sodium metasilicate–silica has been investigated by heating a few mg. wrapped in platinum foil at constant temperature until

equilibrium is reached, and quenching by dropping into mercury. The m. p. of the metasilicate is  $1088^{\circ}$  and the thermal diagram shows a maximum corresponding with sodium disilicate,  $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ , at  $874^{\circ}$ . The eutectic metasilicate-disilicate is at  $840^{\circ}$  and 37.5 mol.-% of silica and the eutectic disilicate-quartz is at  $793^{\circ}$  and 65 mol.-% of silica. The results are compared with those of previous workers for potassium and lithium metasilicates. M. B. D.

**Thermal Analysis of the System Lithium Fluoride-Magnesium Fluoride.** G. TACCHINI (*Gazzetta*, 1924, **54**, 777—780).—As the proportion of magnesium fluoride in this system is increased the solidifying point falls gradually from  $840^{\circ}$ , the value for pure lithium fluoride, to the minimum,  $669^{\circ}$ , for about 60 mol.-% of magnesium fluoride, and then rises slowly to  $690^{\circ}$  for 75.71 mol.-% of the latter. The curve then rises steeply to reach  $1060^{\circ}$  with 86.59 mol.-% of magnesium fluoride. Extrapolation gives for the m. p. of magnesium fluoride the approximate value  $1400^{\circ}$  (cf. Beck, *Metallurgie*, 1908, **5**, 504). The form of the diagram and the absence of an eutectic in all the mixtures examined would indicate the existence of mixed crystals in all proportions of the components or at least in mixtures containing up to 75 mol.-% of magnesium fluoride. Since the lithium and magnesium salts are of different crystalline forms, being respectively cubic and tetragonal, it is probable that two series of mixed crystals are formed and that the curve of incipient solidification exhibits an angle, with a miscibility gap. T. H. P.

**Equilibrium Diagram of the Copper-Tin System.** T. ISIHARA (*Sci. Rep. Tohoku Imp. Univ.*, 1924, **13**, 75—100).—The equilibrium diagram of the copper-tin series of alloys has been reinvestigated by means of the electrical resistance method and microscopical examination. The maximum solubility of tin in copper at the ordinary temperature is 11% and this solid solution undergoes a progressive transformation at temperatures between  $480^{\circ}$  and  $580^{\circ}$ , according to the percentage of tin. The  $\beta$  solid solution decomposes below  $510^{\circ}$  into  $\alpha + \delta$ , whilst the  $\gamma$  constituent decomposes below  $580^{\circ}$  into an eutectoid mixture of  $\delta + \eta$ . The constituent  $\delta$  is the compound  $\text{Cu}_3\text{Sn}$ ,  $\eta$  is a solid solution of tin in  $\text{Cu}_3\text{Sn}$ , and  $\epsilon$  is the compound  $\text{CuSn}$ , which apparently exists in two forms having a transformation point at  $180^{\circ}$  similar to the A2 point in steel. A. R. P.

**Secondary Crystallisation of Steel.** E. SCHEIL (*Z. anorg. Chem.*, 1924, **139**, 81—107).—From a comparison of the rates of crystallisation and of formation of crystal centres in a carbon-iron alloy as a function of temperature, it is shown that the phenomena observed in the formation of pearlite by the transition of steel in the solid state are interpreted more easily by Vogel's theory (A., 1912, ii, 744) than by that of Howe (*Proc. Amer. Soc. Testing Materials*, 1911, 263). From the same point of view, assuming that martensite is a solution of carbon in an unstable form of  $\alpha$ -iron, the equilibrium curve of the austenite-martensite

system is discussed. This curve is of Roozeboom's first type. Benedicks' experiments on the chilling of an austenite steel in liquid air (*J. Iron and Steel Inst.*, 1908, 251) are also satisfactorily explained. Fränkel and Heymann's assumption that austenite first changes to martensite on tempering (A., 1924, ii, 490) is not supported, and the existence of the carbide  $\text{FeC}_{8-10}$  could not be confirmed. S. K. T.

**System Sodium Carbonate-Sodium Sulphate-Water.** W. A. CASPARI (*J. Chem. Soc.*, 1924, 125, 2381—2387).—The solid phases characterising this system include the two decahydrates and mixed crystals thereof, anhydrous sodium sulphate, the hydrates,  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$  and  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , and a double salt  $\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$ , which latter has a wide field of stability from  $26.1^\circ$  to the b. p. The conditions of equilibrium in which these phases take part have been examined in detail. The double salt, which forms thick prisms ( $d=2.59$ ) which deliquesce in moist air, is stable in contact with its own solution above  $67^\circ$ . C. I.

**Equilibria in the System : Mercuric Chloride, Ammonium Chloride, Potassium Chloride, and Water at  $25^\circ$ .** Y. OSAKA and K. ANDO (*Z. physikal. Chem.*, 1924, 110, 786—798).—The following double salts and solid solutions have been found and the conditions for their existence determined:  $\text{HgCl}_2 \cdot \text{KCl} \cdot \text{H}_2\text{O}$ ,  $\text{HgCl}_2 \cdot 2\text{KCl} \cdot \text{H}_2\text{O}$ ,  $2\text{HgCl}_2 \cdot \text{KCl} \cdot 2\text{H}_2\text{O}$ ,  $\text{HgCl}_2 \cdot \text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$ ,  $\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$ ,  $3\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$ ,  $9\text{HgCl}_2 \cdot 2\text{NH}_4\text{Cl}$ ,  $\text{HgCl}_2 \cdot (\text{K}, \text{NH}_4)\text{Cl} \cdot \text{H}_2\text{O}$  (complete),  $\text{HgCl}_2 \cdot 2(\text{K}, \text{NH}_4)\text{Cl} \cdot \text{H}_2\text{O}$  (complete),  $3\text{HgCl}_2 \cdot (\text{K}, \text{NH}_4)\text{Cl} \cdot 2\text{H}_2\text{O}$  (a gap),  $3\text{HgCl}_2 \cdot 2(\text{K}, \text{NH}_4)\text{Cl} \cdot \text{H}_2\text{O}$  (gaps),  $(\text{K}, \text{NH}_4)\text{Cl}$  (a gap). For the system  $\text{HgCl}_2$ - $\text{KCl}$ - $\text{H}_2\text{O}$  see Foote and Levy (A., 1906, ii, 231), and the system  $\text{HgCl}_2$ - $\text{NH}_4\text{Cl}$ - $\text{H}_2\text{O}$  see Meerburg (A., 1908, ii, 676). J. S. C.

**System : Copper Nitrate-Ammonium Nitrate-Water.** G. MEIJER (*Rec. trav. chim.*, 1924, 43, 397—398).—At  $30.5^\circ$  the two nitrates form no compound; the diagram shows that addition of solid ammonium nitrate to a saturated solution of copper nitrate at this temperature increases the solubility of the latter, thus indicating the formation of a complex. H. J. E.

**System : Cupric Nitrate-Ammonium Nitrate-Water.** F. A. H. SCHREINEMAKERS, G. BERKHOFF, and K. POSTHUMUS (*Rec. trav. chim.*, 1924, 43, 508—511; cf. Meijer, preceding abstract).—The equilibrium cupric nitrate-ammonium nitrate-water has been studied at  $40^\circ$  and  $30^\circ$  by analysis of the solid phases and corresponding residues. The existence of a hydrate  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  is inferred from the data at  $40^\circ$ . Evidence for this has also been obtained in the system cupric nitrate-nitric acid-water. The double salt  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{NH}_4\text{NO}_3$  is decomposed by water and cannot coexist with ammonium nitrite. A transition point has been found at  $27.1^\circ$ . F. M. H.

**Equilibria between Sodium, Alkaline-earth Metals, and their Chlorides in the Fused State.** K. JELLINEK and J. CZERWINSKI (*Z. physikal. Chem.*, 1924, 110, 192—236).—The equi-

librium,  $2\text{Na} + \text{ECl}_2 \rightleftharpoons 2\text{NaCl} + \text{E}$ , where E denotes the alkaline-earth metals, calcium, strontium, or barium, has been investigated at  $1000^\circ$ , the metals being distributed between the two phases, fused salts and molten lead. The actual experimental method consists essentially in the electrolysis of the fused chlorides, the molten lead serving as cathode whilst a carbon rod dipping into the fused salt acts as anode. Employing this electrochemical method, the same state of equilibrium is set up for the reaction  $\text{K} + \text{NaCl} \rightleftharpoons \text{Na} + \text{KCl}$  as was obtained by Jellinek and Tomoff (A., 1924, ii, 658) by purely chemical methods. In the case of experiments with the alkaline-earth metals, application of the experimental numbers to the mass law expression leads to an inconstant value. Constancy is, however, obtained if it be assumed that whilst the alkaline-earth metals and chlorides are present as simple atoms and molecules, respectively, sodium exists in the molten lead phase principally as  $\text{Na}_2$  and that sodium chloride exists in the fused salt phase as  $\text{Na}_2\text{Cl}_2$ . The fact that freezing-point curves of lead-alkali metal alloys and lead-alkaline-earth metal alloys exhibit maxima corresponding with  $\text{Na}_{2x}\text{Pb}_y$ ,  $\text{Ca}_x\text{Pb}_y$ , etc., respectively, is interpreted as being in support of this assumption. The temperature coefficient of the equilibrium constant is found to be extremely small. It is shown that the experimental numbers obtained in a study of the equilibrium  $\text{Pb} + \text{CdCl}_2 \rightleftharpoons \text{PbCl}_2 + \text{Cd}$  (Lorenz, Fraenkel, and Silberstein, A., 1924, ii, 258) conform to the requirements of the law of mass action.

J. S. C.

**Equilibrium between Lithium, Barium, and their Chlorides in the Molten State.** K. JELLINEK and J. CZERWINSKI (*Z. anorg. Chem.*, 1924, **139**, 233–236).—By a slight modification of the method previously employed (cf. A., 1924, ii, 658) the equilibrium  $2\text{Li} + \text{BaCl}_2 \rightleftharpoons \text{Ba} + 2\text{LiCl}$  was examined at about  $850^\circ$ . The mass-action law is obeyed; lithium chloride appears to combine with the barium chloride in the fused mass. Metallic lithium dissolved in lead appears to exist as double molecules or as  $\text{Li}_2\text{Pb}_n$ . Using previously published data, the equilibrium constant of the reaction  $2\text{Na} + \text{Li}_2\text{Cl}_2 \rightleftharpoons 2\text{Li} + \text{Na}_2\text{Cl}_2$  is calculated.

S. K. T.

**In-, Uni-, and Multi-variant Equilibria.** XXVII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amst.*, 1924, **27**, 441–450).—Theoretical (cf. A., 1924, ii, 389, 601).

L. J. H.

**System Chromium Oxide–Chromium Hydroxide–Chromite–Sodium Hydroxide.** E. MÜLLER (*Z. physikal. Chem.*, 1924, **110**, 363–383; cf. A., 1923, ii, 71).—Excess of chromium oxide or hydroxide was shaken with aqueous sodium hydroxide solutions of various concentrations for several days. From time to time samples of the turbid liquid were extracted and centrifuged, the chromium in the clear liquid and the water in the precipitate being determined. In all cases, it was found that the solubility was dependent on the time of agitation, rising to a maximum and then falling to a constant value. Both the maximum and final solubilities attain their highest

values at a sodium hydroxide concentration  $14N$ . These facts are interpreted on the assumption that chromium hydroxide is a "solid liquid" in which simple and polymerised molecules are present in homogeneous solution. On account of the magnitude of the internal friction, equilibrium is only slowly attained. The ageing process does not so much consist in the enlarging of single particles as in a progressive change during polymerisation and is thus essentially chemical in character.

J. S. C.

**System Lead Hydroxide-Lead Oxide-Plumbite-Sodium Hydroxide Solution.** E. MÜLLER [with E. REISSMANN and O. BALLIN] (*Z. physikal. Chem.*, 1924, **114**, 129—155).—By treatment of precipitated lead hydroxide with sodium hydroxide solution the following solid phases are formed according to the conditions: yellow and red forms of the oxide,  $PbO$ , and a crystalline sodium plumbite. From the solubilities of these substances in sodium hydroxide solutions of varying concentrations, an equilibrium diagram has been constructed which, however, gives uncertain results at low concentrations of alkali. It is doubtful whether the sodium plumbite is  $Na_2PbO_2$  or  $NaHPbO_2$ . The preparation of a crystalline hydroxide,  $Pb(OH)_2$ , is also described. The amorphous hydroxides are thought to be supercooled liquids.

N. H. H.

**Le Chatelier Principle and its Application to the Crystallisation Processes in Binary Systems.** R. RUER (*Z. physikal. Chem.*, 1924, **110**, 60—64).—The solidus and liquidus curves for binary mixtures are considered from the point of view of the principle of mobile equilibrium.

J. S. C.

**Reactivity of Solid Phases.** J. A. HEDVALL (*J. Physical Chem.*, 1924, **28**, 1316—1330).—The author summarises previous work on the reactivity, diffusion, and recrystallisation of solid phases and surveys his own results (1913—1924). The heating curves of mixtures composed of the reacting solids in powder form indicate when a reaction is taking place. Metallic oxides can form both compounds and solid solutions, *e.g.*, Rinman's green. The temperature of thermal dissociation of a compound can be determined by this method. The rate of reaction depends on the size of the grains, large grains giving a small rate. Sometimes the reaction product forms an impermeable film; *e.g.*, the reaction between calcium oxide and copper sulphate does not go to completion, but the mixture requires regrinding several times. Very intense reactions occur on heating mixtures of a peroxide of an alkaline-earth with other oxides. The heat of reaction, intensity, and temperature of the beginning of the reaction are tabulated for alkaline-earth oxides with various metallic carbonates and sulphates.

M. B. D.

**Specific Heats of Aqueous Solutions of Hydrogen Chloride and Ammonia at Various Temperatures.** M. WREWSKY and A. KAIGORODOFF (*Z. physikal. Chem.*, 1924, **112**, 83—89).—An apparatus for the determination of specific heats which obviates errors due to evaporation has been employed with aqueous solutions

of hydrogen chloride and of ammonia at 3°, 20°, 40°, and 60° over a range of concentrations varying from very dilute to nearly saturated. At constant temperature, the specific heat of hydrogen chloride solutions decreases with increasing concentration, but with ammonia at low temperatures, the specific heat decreases to a minimum and then increases. At higher temperatures, the minimum becomes flatter and finally disappears, the specific heat increasing approximately linearly with increase of ammonia content. For both solutions, the specific heat for constant composition increases with the temperature, except at very low concentrations, when it first passes through a minimum. The occurrence of such minima is explained by the presence of the minimum, at 40°, in the specific heat of water. From the deviations between the observed specific heats of these solutions and those calculated from the law of mixtures, it is concluded that the temperature coefficient of their heats of formation is a function which decreases with rising temperature. L. F. G.

**Specific Heats of Aqueous Solutions of Hydrogen Chloride and Ammonia at Various Temperatures, etc. I—V.** M. WREWSKY and others (*Z. physikal. Chem.*, 1924, **113**, 490—491; cf. preceding abstract).—Errata. G. M. B.

**True Specific Heats of Salt Solutions (Cadmium Iodide, Ammonium Nitrate, and Zinc Sulphate).** E. COHEN, W. D. HELDERMAN, and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1924, **112**, 135—140).—The true specific heats of solutions of various concentrations of cadmium iodide (19°), ammonium nitrate (32·3°), and of zinc sulphate (19°) were determined with an accuracy of 0·05% by the use of an adiabatic electrical calorimeter previously described (A., 1920, ii, 584). The values obtained agreed closely with those calculated from an equation in which specific heat is expressed as a function of concentration. L. F. G.

**Heats of Formation of Aqueous Solutions of Hydrogen Chloride and Ammonia at Different Temperatures.** M. WREWSKY and N. SAWARITZKY (*Z. physikal. Chem.*, 1924, **112**, 90—96).—Heats of solution and dilution have been determined at various temperatures. The results obtained are more complete than those of Thomsen and of Berthelot. The heats of formation of very concentrated solutions vary considerably with the composition, but the variations are relatively small when dilute solutions are formed. At constant temperature, the molecular heat of solution of ammonia is practically constant over a large concentration interval. The molecular heat of solution of hydrogen chloride increases with rise of temperature, whilst that of ammonia decreases. L. F. G.

**Heats of Combustion of Normal Substances.** W. JAEGER and H. VON STEINWEHR (*Z. physikal. Chem.*, 1924, **114**, 59—64).—The authors criticise as somewhat arbitrary the decision of the

"Commission pour l'Établissement d'un étalon thermochimique" in 1922 to take as the heat of combustion of benzoic acid the value obtained by Dickinson (*Bull. Bur. of Standards*, 1915, **11**, 190) in preference to those of other workers, notably Fischer and Wrede (*Z. physikal. Chem.*, 1909, **69**, 218). The electrical method used by the latter for determining the heat value of the calorimeter is said to be more trustworthy than the calorimetric method used by Dickinson.

N. H. H.

**Electrical Conductivity of Fused Sodium Hydroxide.** K. ARNDT and G. PLOETZ (*Z. physikal. Chem.*, 1924, **110**, 237—242).—The electrical conductivity of fused sodium hydroxide has been determined at temperatures between 320° and 450° (m. p. of sodium hydroxide, 318°) in a silver apparatus, a brief description of which is given. As the samples of caustic soda were found to contain small amounts of sodium chloride and carbonate, the effect of addition of these substances on the conductivity has been investigated. The value of the conductivity of pure sodium hydroxide was then determined after a small extrapolation, from the values for the impure substance. At temperatures 320°, 350°, 400°, and 450° the values of  $k$  are, respectively, 2·12, 2·38, 2·82, and 3·27.

J. S. C.

**Fused Electrolytes.** W. BILTZ and W. KLEMM (*Z. physikal. Chem.*, 1924, **110**, 318—342).—The electrical conductivities of a number of fused chlorides have been determined over a considerable range of temperature. Descriptions of the various forms of apparatus employed and of the experimental technique are given. With the exception of zinc chloride, the conductivity is a linear function of the temperature. The conductivities of the alkali chlorides decrease with increasing molecular weight. The chlorides of beryllium, zinc, and mercury have very low conductivities, whilst magnesium and cadmium chlorides possess conductivities of the same order of magnitude as those of the alkaline-earths.

J. S. C.

**Temperature Coefficient of the Mobility of Ions in Liquids.** F. A. LINDEMANN (*Z. physikal. Chem.*, 1924, **110**, 394—398).—From a consideration of the collisions between the ions and the solvent molecules, an equation is derived for the migration velocity which involves the velocities and masses of the solvent molecules and ions, the absolute temperature, and the mean free path. For equal temperatures and free paths the equation requires that the mobilities should be greatest for light ions and constant for heavy ions. The fact that ions of light elements do not obey this rule may be due to hydration or more probably that the free path is not the same for all ions. If by hydration is meant an increase in the density of the solvent in the vicinity of the ions the theory implies its occurrence. If, however, it be understood to mean that solvent molecules are combined with the ion and travel with it, the above considerations are not applicable.

J. S. C.

**Effect of Boric Acid on the Solubility in Water and on the Conductivity of  $\gamma$ -Pyronecarboxylic Acids.** P. E. VERKADE (*Rec. trav. chim.*, 1924, **43**, 879—893).—In opposition to Borsche (A., 1917, i, 117), meconic acid is considered to be 3-hydroxy-4-pyrone-2:6-dicarboxylic acid; in aqueous solution, it probably gives an equilibrium mixture of keto and enol forms. Comenic acid (3-hydroxy-4-pyrone-6-carboxylic acid) also gives an equilibrium mixture of keto and enol forms, in which the former predominates. In the presence of boric acid, the solubilities of meconic and chelidonic acids in water are increased, whereas the solubility of comenic acid is unchanged; hence the first two acids form complexes with boric acid, but the last does not (cf. A., 1903, ii, 288; 1910, ii, 275; 1911, ii, 261). The boric acid complex of chelidonic acid is probably an oxonium compound. Sulphuric acid conforms to the rules of Böeseken and Verkade respecting the influence of boric acid on the electrical conductivity of acids in aqueous solution (A., 1916, ii, 595). Meconic and chelidonic acids, however, in the presence of boric acid, show, at high concentration, an abnormally large decrease in conductivity. Although in all other such cases an increase has been observed, the present result is considered to support the conclusion that these acids form complexes with boric acid.  
W. E. E.

**Conductivity and Catalytic Action of the three Strong Halogen Acids in Methyl and Ethyl Alcohol.** H. GOLDSCHMIDT and P. DAHL (Z. physikal. Chem., 1924, **114**, 1—22).—The conductivities of hydrochloric, hydrobromic, and hydriodic acids and of their sodium salts in methyl and ethyl alcohols have been measured at 25°. The increase of  $\Lambda$  with dilution differs in both alcohols, being greatest for sodium chloride and least for hydriodic acid. Kohlrausch's law of independent ionic migration velocities is found to hold. For the three acids the influence of water on  $\Lambda_\infty$  is the same. In both alcohols equally concentrated solutions of the acids catalyse ester formation to the same degree. Consideration of the reaction kinetics shows that in both alcohols complete dissociation of the acids in solutions of finite concentration is not quite reached, this being more evident with ethyl alcohol.

N. H. H.

**Adsorption and Cataphoresis.** C. FROMAGEOT (*Compt. rend.*, 1924, **179**, 1404—1406).—The velocity of cataphoresis of carbon particles in solutions of organic acids and their sodium salts depends only on the hydrogen-ion concentration increasing as the latter decreases. It is not affected by the extent to which the acid or its salt is adsorbed. It is inferred that organic acids are adsorbed in the form of non-dissociated molecules and that adsorption takes place directly on the carbon surface and not through the medium of a double layer.  
H. T.

**Experiments on the Conductivity and Ionisation of Electrolytes.** O. SCARPA (*Gazzetta*, 1924, **54**, 860—875).—The experiments illustrate the conductivity of electrolytes without the aid of



electrodes, the electrical resistance of electrolytes in motion, the action of a fixed magnetic field on a moving electrolyte, and the action of a fixed magnetic field on a jet of an electrolyte traversed by an electric current.

T. H. P.

**Formation and Ionisation of Compounds of Casein with Alkali.** I. Transport Numbers of Alkali Caseinate Solutions. II. Conductivities of Alkali Caseinate Solutions. III. Electrochemical Behaviour of Racemic Casein. D. M. GREENBERG and C. L. A. SCHMIDT (*J. Gen. Physiol.*, 1924, 7, 287—301, 303—316, 317—326).—I. In the electrolysis of solutions of the alkali caseinates at constant  $p_H$  the quantity of casein deposited is directly proportional to the current and inversely proportional to the amount of the combined alkali. The transport numbers of the ions of alkali caseinate solutions have been measured by Hittorf's direct method, and the results support the view that the current is carried by the alkali metal as cation and by casein as anion.

II. By a method of extrapolation of results at certain dilutions, the conductivity at infinite dilution and at different temperatures has been obtained; from these data, the mobility of the casein ion is calculated. The average value, 45.3 at 30° (that of lithium is 43.7 at 30°), agrees well with the results from the transport number experiments. A linear relationship exists between the conductivity of alkali casein solutions and temperature.

III. The results of experiments on the conductivity of alkali solutions of casein and "racemic" casein, and the nitrogen distribution in these substances, are discussed from the point of view of protein racemisation. From the data obtained, and from the fact that the isoelectric point of "racemic" casein is at  $p_H$  4.3 (that of casein is at  $p_H$  4.55), it is concluded that, save for hydrolysis of amide groups, racemic casein is not a degradation product of casein.

H. J. C.

**Electro-endosmosis.** II. F. FAIRBROTHER (*J. Chem. Soc.*, 1924, 125, 2495—2501).—The calculation of potential gradient in electro-endosmosis experiments from the observed current flow and the resistance of the electrolyte is inaccurate, since the amount of current flowing through a fine capillary tube or the pores of a powder is influenced by surface effects. Electrolytes in Jena glass powder (grains 0.2—0.25 mm. diameter) show an increased conductivity of several units per cent., the increase being greatest in dilute solutions and negligible in solutions of strong acids. 0.1*N*-Potassium chloride solution is not free from surface conductivity effects. With carborundum powder (grains 0.2 mm. diameter), the alternating current resistance of carborundum-electrolyte mixtures depends on the conductivity of the electrolyte and, in very dilute solutions, the resistance of the electrolyte is of the same order as that of the carborundum.

J. W. B.

**Electric Transport in a Ferric Oxide Hydrosol.** H. PUIG-GARI (*I. Congreso Sudamer. Quím.*, 1924; reprint).—The transport of material in a ferric oxide hydrosol ( $p_H$  3.8) is in agreement with

the ordinary laws of electrolysis when the current intensity is less than 0.01 amp.

G. W. R.

**Influence of Neutral Salts on the Potential of the Hydrogen Electrode in Contact with a Hydrochloric Acid Solution.** L. MICHAELIS and M. MIZUTANI (*Z. physikal. Chem.*, 1924, **112**, 68—82).—The change of activity of the hydrogen ions in very dilute hydrochloric acid solution, as influenced by the addition of neutral salts, was examined by a modification of a method previously used (A., 1921, ii, 56; 1923, ii, 824). In general, with increasing salt concentration, the potential difference rises to a maximum in the region 0.2—0.3*N*, and then falls, so much so in some cases that the solution would appear to be more "acid" in the presence of salt than alone. From the results obtained with the alkali chlorides the effect of the different alkali ions is correlated systematically with atomic weight. Data are also given for the effect of various mixtures of chlorides on 0.01*N*-hydrochloric acid.

L. F. G.

**Electromotive Behaviour of Aluminium.** I. A. SMITS (*Z. Elektrochem.*, 1924, **30**, 423—435).—When a pure aluminium electrode, previously immersed in an aluminium sulphate solution, is transferred to another of the same concentration, but saturated also with mercuric chloride, in an atmosphere of nitrogen, its potential first becomes more positive and then more negative than in the original state. At the same time a grey mercury deposit forms on the electrode, and there is probably an equilibrium set up between a liquid and solid amalgam and the electrolyte solution. After remaining at a maximum negative potential for some time, the surface becomes bright, due to the complete covering of the electrode by a liquid amalgam, and the potential begins to fall again. The presence of the mercury makes the aluminium more active. It therefore dissolves in water, leaving the mercury poorer in aluminium, and the potential becomes more positive. The whole process takes place more quickly with a polished electrode than with one etched with hydrochloric acid and washed with distilled water. It is considered that in the second case aluminium hydroxide acts as a retarder. In the presence of the nitrate ion the action on the polished electrode is retarded, whilst the potential of the etched electrode remains positive indefinitely, as if no mercury had been precipitated on it. If, however, it is washed and transferred to a pure aluminium chloride solution, it immediately takes on a large negative potential, which increases on keeping. This shows that mercury has actually been present in the electrode and that the nitrate ion has completely inhibited the usual reactions.

The electromotive behaviour of an aluminium electrode in aqueous aluminium chloride solutions of different hydrogen-ion concentrations has also been studied. The aluminium becomes most passive between the hydrogen-ion concentrations  $10^{-0.5}$  and  $10^{-8.5}$  but never behaves as a hydrogen electrode, showing that, under the conditions of the experiments, the aluminium is never covered

with an insulating film of oxide, but always behaves as a metallic electrode.

The results are explained in accordance with the author's views on electromotive equilibria, as deduced from his theory of allotropy.  
M. S. B.

**Phase Boundary Potentials.** L. MICHAELIS and A. FUJITA (*Z. physikal. Chem.*, 1924, **110**, 266—284).—Theoretical equations for the *E.M.F.* of cells involving immiscible liquids are developed, and the *E.M.F.* of a large number of such cells experimentally determined. The investigations cover concentration cells with the following liquid junctions; (1) benzyl alcohol saturated with water, (2) dilute electrolyte solution saturated with benzyl alcohol, cells consisting of aqueous solutions of different electrolytes at one and the same concentration separated by benzyl alcohol saturated with water, cells containing mixed electrolytes, and cells using toluene saturated with water as liquid junction. J. S. C.

**Theory of the Bioelectric Cell.** R. HÖBER (*Z. physikal. Chem.*, 1924, **110**, 142—146).—Bioelectric systems are set up in living matter, the protoplasmic membrane separating the protoplasm with its dissolved salts from the exterior solution. Systems consisting of two aqueous electrolyte solutions separated by some immiscible organic liquid are not suitable for purposes of comparison, the *E.M.F.* of the cell thus formed being influenced by the organic or inorganic nature of the dissolved electrolytes, whereas, when living tissue (apple and liver) is used as intermediate substance the resulting *E.M.F.* is independent of the character of the electrolytes concerned. Cells in which gelatin, coated with gelatin tannate ( $p_H$  7.1) and euglobin on the alkaline side of the isoelectric point, replace the organic liquid behave in an analogous manner to the apple and liver systems. Protein cells therefore serve as satisfactory models for bioelectric systems. J. S. C.

**Influence of Anions on the "Passivability" of Metals.** V. ROTHMUND [with F. EISENKOLB and R. STEINHERZ] (*Z. physikal. Chem.*, 1924, **110**, 384—393).—The passivity of nickel and tin in solutions of acids has been established. A small anode of the metal is set up against a large platinum cathode in acid solution and a current applied. The abrupt fall in the current strength as the applied potential passes through a critical value corresponds with the entry of the metal into the passive state. Under these conditions, the metal may actually go into solution even when passive.

Nickel becomes passive in solutions of sulphuric, perchloric, nitric, acetic, phosphoric, citric, oxalic, tartaric, boric, and hydrofluosilicic acids, the necessary potential (0.34 volt) being practically independent of the nature and concentration of the acid. The metal also becomes passive in solutions of thiocyanic and the halogen acids, the critical potential being, however, much higher.

Tin becomes passive in solutions of sulphuric, hydrofluosilicic, and the halogen acids but not in nitric, iodic, perchloric, or acetic

acid. The metal goes into solution to form stannous salts from both the active and passive states.

J. S. C.

**Electrolysis of Potassium-Sodium Alloys.** R. KREMANN and R. G. VON REHENBURG (*Z. physikal. Chem.*, 1924, **110**, 559—571).—Passage of an electric current through fused sodium-potassium alloys results in an accumulation of sodium at the anode and of potassium at the cathode. Measurements carried out with alloys containing 63—75% potassium show that the percentage separation at first increases rapidly with increasing current density and subsequently approaches asymptotically a limiting value.

J. S. C.

**Electrolysis of Molten Alloys. III. Lead-Cadmium and Lead-Sodium Alloys.** R. KREMANN, H. KIENZL, and R. MARKL (*Monatsh.*, 1924, **45**, 133—139).—A lead-cadmium alloy, containing 57% of lead, was subjected in the molten state (300°), in a capillary tube, to the action of a current of density 0.67 amp./mm.<sup>2</sup>, for 72 hours, then cooled, the current being maintained until the continuity of the metal in the capillary was broken by contraction. Passing from cathode to anode, the lead content was found to have alternately decreased and increased in the sense that the whole strip formed a series of electrolytes in which cadmium was carried to the cathode, lead to the anode, the lowest lead content observed being 43%, the highest 72%. A lead-sodium alloy, containing 90% of lead, showed no electrolytic effect at the ordinary temperature, but in the molten state at 370° sodium accumulated at the cathode, lead at the anode.

F. G. W.

**Electrolysis of Molten Alloys. IV. Sodium-Mercury Alloys.** R. KREMANN, R. MÜLLER, and H. KIENZL (*Monatsh.*, 1924, **45**, 157—176).—When an electric current is passed through a column (diameter 1.0—1.5 mm.) of molten sodium amalgam at 240°, the sodium content is increased at the cathode and decreased at the anode. The effect increases with current density up to 4.5 amp./mm.<sup>2</sup>, thereafter being independent of current density, and equilibrium is attained in 3 hours. The greater the original sodium content of the amalgam, the greater the difference between anode and cathode compositions. The effect is also greater, the longer the column of alloy, but a limit is reached at about 35 cm. It is concluded that the final structure of the column is the result of equilibrium between the forces due to the applied current and those of diffusion, which tend to homogenise the alloy column.

F. G. W.

**Electrolysis of Molten Alloys. V. Potassium, Calcium, and Cadmium Amalgams.** R. KREMANN, R. MÜLLER, and H. ORTNER (*Monatsh.*, 1924, **45**, 177—186).—As in the case of sodium amalgam (cf. preceding abstract), passage of an electric current through a column of potassium amalgam at 240° produces an increase in potassium content at the cathode, the effect being similarly influenced by the various factors involved. The magnitude of the effect, however, is about twice as great as for sodium amalgam,

and is attributed to the more electropositive character of potassium and to the lower rate of diffusion which corresponds with the greater atomic volume. With calcium and cadmium amalgams similar, although smaller, variations were observed. F. G. W.

**Application of the Method of Electrolysis with the Mercury Dropping Cathode.** J. HEYROVSKY (*Compt. rend.*, 1924, **179**, 1267—1268; cf. A., 1924, ii, 598, 599; this vol., ii, 43).—This method is useful for studying ionic relations in solutions in cases where reversible cells cannot be used owing either to the low concentrations of the metals in solution or to the attackability by water or passivity of the electrodes. The solubility product and degree of ionic complexity of alkali zincates and plumbites are readily determinable by this means, which serves also to investigate inorganic or organic reductions in aqueous or non-aqueous solutions. T. H. P.

**Electrolytic Polarisation. II. Cathodic Overvoltage of Mercury.** S. GLASSTONE (*J. Chem. Soc.*, 1924, **125**, 2646—2656).—The extrapolation method for the determination of the overvoltage of the lead cathode (cf. A., 1924, ii, 600) is extended to the mercury cathode in acid solution. Of the three overvoltage states observed by Newbery (T., 1922, **121**, 7), only the highest state has been obtained with certainty. At low current densities, when the electrolyte is not too dilute, the potential of the mercury cathode measured by the direct method (cf. Lewis and Jackson, A., 1906, ii, 648) is almost equal to the instantaneous back *E.M.F.*, and hence the true overvoltage may be calculated from the former. At high current densities direct and extrapolated overvoltages differ; the divergence increases as the concentration of the electrolyte is decreased, but diminishes with increase of temperature. The cathodic overvoltage of mercury in sulphuric acid at such current densities does not itself vary greatly as the concentration of the electrolyte changes from *N*/50 to 6*N*. At 10° the variation of the true overvoltage of mercury in a *N*-sulphuric acid electrolyte with current density is expressed by the equation  $E = 0.955 + 0.028 \log I$  ( $I$  = current density in milliamp./cm.<sup>2</sup>). The minimum overvoltage is almost independent of the hydrogen-ion concentration of the electrolyte. With dilute electrolytes it is found that oxygen diffusing from the anode may influence the rate of fall of the back *E.M.F.* of the mercury cathode in a manner which depends on the material of the electrode vessel and the current density. Coating the glass surface with paraffin wax or stearic acid, or digestion with concentrated acid reduces the effect, whilst heating with alkali increases it. J. W. B.

**Electrochemistry of Non-aqueous Solutions. IV. Attempts to Deposit certain Metals of the Earths and Alkaline-earths from Anhydrous Pyridine.** R. MÜLLER, F. HÖLZL, W. KNAUS, F. PLANISZIG, and K. PRETT (*Monatsh.*, 1924, **44**, 219—236; cf. A., 1922, ii, 612; 1923, ii, 287).—The conditions of electrolysis are similar to those described in previous communications (*loc. cit.*),

either platinum or mercury being used as cathode. The potentials given (unless otherwise stated) refer to a silver electrode in 0.1*N*-silver nitrate in pyridine. Using a platinum cathode, magnesium was deposited from a saturated solution of magnesium bromide at 18° and from a solution saturated at 60° at about 1.8 volts. The grey coating of magnesium becomes covered with a coherent skin—a magnesium-pyridine compound—if the current is interrupted. This hinders further passage. Deposition on mercury is more difficult. Calcium is deposited on platinum from a solution of the nitrate saturated at 18°, but the formation of a calcium-pyridine compound rapidly stops the current. Zinc is deposited rather readily, but the measurement of potential is difficult, partly owing to bad conductivity. Solutions of zinc iodide, 0.1*N* and saturated, have the same decomposition potential, 1.60 volts. Cadmium iodide is only slightly soluble in pyridine and the solutions conduct extremely badly. The decomposition potential of a saturated solution at 25° is about 3.3 volts. Similar data are recorded for beryllium and aluminium.

A. C.

**Electrochemistry of Non-aqueous Solutions. V. Attempts to Deposit certain of the Heavy Metals from Anhydrous Pyridine.** R. MÜLLER, R. HÖNIG, and A. KONETSCHNIGG (*Monatsh.*, 1924, **44**, 237—245; cf. preceding abstract).—Copper is deposited from a solution of cuprous iodide saturated at 25° (17.4 g. CuI per litre of solvent) at a potential of 2.8 volts. A green deposit (cuprous compound) separates at the anode. Solutions of manganous chloride, 0.1 and 0.168*N* (saturated at 25°), show very indefinite decomposition potentials of about 2 volts. A solution of ferrous bromide, saturated at 25° (4.87 g. of salt per litre), shows a decomposition potential of about 1.05 volts. The deposited metal appears to be in the passive state and dissolves only with difficulty in dilute hydrochloric and nitric acids. Other difficulties in the electrolysis of metals of this class in organic solvents arise from the low solubility of the salts, the poor conductivity of the solutions, and the tendency to form complexes with the solvent. The solution of cuprous iodide in pyridine deposits yellow crystals of a compound of the salt and solvent. The compound  $\text{MnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , stated by Varet to be rose-coloured, is white when entirely anhydrous.

A. C.

**Electrochemical Aspects of the Oxidising Properties of Sulphur Dioxide.** S. R. CARTER and F. JAMES (*J. Chem. Soc.*, 1924, **125**, 2231—2240).—The capacity of sulphur dioxide to act as an oxidising or reducing agent in solutions containing ferrous and ferric ions has been studied electrochemically. Measurements of electrode potentials for the half cells,  $\text{Pt}|\text{H}_2\text{SO}_4, \text{H}_2\text{SO}_3, xN\text{-HCl}$ , and  $\text{Pt}|\text{H}_2\text{SO}_3, \text{S}, xN\text{-HCl}$  show that an increase in acid concentration is accompanied by a rise in the sulphur dioxide potential, whilst under the same conditions there is a diminution in the ferri-ferrous potential. Experiments on the cathodic reduction of sulphur dioxide in acid solution show that hydrogen sulphide is not formed as a primary product. As the cathode potential is

reduced from 0.7 volt to 0.1 volt a very small current passes with separation of sulphur (but not hydrogen sulphide). At 0.1 volt a marked increase in the current density takes place. This is in agreement with Jellinek's work on the electrode potential of mixtures of hydrogen sulphate and hydrosulphite in neutral or faintly acid solution. It is probable therefore that the primary product of reduction of sulphur dioxide in acid solution is hyposulphurous acid. C. I.

**"Reaction-influencing" Ions in Light and Dark Reactions.** H. VON EULER and E. RUDBERG (*Z. physikal. Chem.*, 1924, **110**, 243—250).—The interpretation of results of previous studies on reaction velocities (A., 1923, ii, 547, 840) is discussed and the question of the existence of active ions in very small concentration raised. It is thought that a study of certain photochemical reactions may throw some light on the problem. J. S. C.

**Temperature-coefficients of Thermal and Photochemical Reactions.** N. R. DIAR (*Z. anorg. Chem.*, 1924, **139**, 194—204).—A résumé of previous work from which conclusions are drawn contrary to those recently arrived at by van Thiel (A., 1922, ii, 754). S. K. T.

**Propagation of the Explosion Wave.** P. LAFFITTE (*Compt. rend.*, 1924, **179**, 1394—1396).—The effect of a sudden change in the diameter of the tube on the explosion wave has been examined for mixtures of carbon disulphide and of hydrogen with oxygen (cf. Campbell, T., 1922, **121**, 2483). After a certain interval of disturbance the explosion wave was re-formed. This interval was dependent on the diameter of the second tube, varying in length from 8 cm. for a 13-mm. tube to 100 cm. for a 44-mm. tube, when the diameter of the first tube was constant at 7 mm. H. T.

**Influence of Nitrogen Dilution on the Speed of Flame.** O. C. DE C. ELLIS (*J. Chem. Soc.*, 1924, **125**, 2674).—If the speed of flame in the author's experiments (cf. Campbell and Ellis, A., 1924, ii, 746; Ellis and Stubbs, *ibid.*, 747) is proportional to one additive constant of the constituent gases, it must be proportional to any other. Thermal conductivity is not accurately additive. J. W. B.

**Detonation Limits of Gaseous Mixtures.** R. WENDLANDT (*Z. physikal. Chem.*, 1924, **110**, 637—655).—The minimum concentrations of hydrogen and carbon monoxide for the detonation of hydrogen-air, and carbon monoxide-oxygen mixtures are 18—19% and 38—39%, respectively. Carbon monoxide-air mixtures exhibit only pseudo-detonation, the maximum velocity corresponding with a 40% carbon monoxide content. [Cf. B., 1925, 88.] J. S. C.

**Formation and Thermal Decomposition of Carbonyl Chloride.** M. BODENSTEIN and H. PLAUT (*Z. physikal. Chem.*, 1924, **110**, 399—416).—The equilibrium constant of the reaction  $\text{CO} + \text{Cl}_2 \rightleftharpoons \text{COCl}_2$  has been determined at temperatures between

349° and 452°. The variation of this with temperature is given by  $\log K_c = -5710/T + 5.46$ . Measurement of the velocities of the direct and opposing reactions indicates that the reaction occurs entirely in the homogeneous gas phase and takes place according to the equation suggested by Christiansen (A., 1923, ii, 62); the rate of formation of carbonyl chloride is given by  $v_1 = k_1 \sqrt{[\text{Cl}_2]}([\text{CO}][\text{Cl}_2] - K[\text{COCl}_2])$  and the rate of decomposition by  $v_2 = k_2 \sqrt{[\text{Cl}_2]}([\text{COCl}_2] - [\text{CO}][\text{Cl}_2]/K)$ ,  $K$  being the value of the equilibrium constant  $[\text{COCl}_2]/[\text{CO}][\text{Cl}_2]$ . In the case of the latter reaction, certain corrections must be applied to the experimental observations. The value of the ratio  $k_2/k_1$  is in excellent agreement with the value of  $K$  at the same temperature. It is shown that the experimental results are in accordance with the following reaction scheme : (i)  $\text{Cl}_2 \rightleftharpoons 2\text{Cl}$ ; (ii)  $\text{Cl} + \text{Cl}_2 \rightleftharpoons \text{Cl}_3$ ; (iii)  $\text{Cl}_3 + \text{CO} \rightleftharpoons \text{COCl}_2 + \text{Cl}$ . Systems (i) and (ii) remain in a state of equilibrium whilst (iii) determines the reaction velocity.

J. S. C.

**Transformation of Diamond in a Vacuum at High Temperatures.** P. LEBEAU and M. PICON (*Compt. rend.*, 1924, **179**, 1059—1061).—The transformation of diamond into graphite is comparatively slow in a high vacuum at 1500—1900°, being incomplete after 1 hour, in marked contrast to the rapid transformation in the presence of gases (cf. Friedel and Ribaud, A., 1924, ii, 474). Above 2000° the change is much more rapid, but the swelling up and disintegration which occur in the presence of gases are not always observed. The speed of transformation of different specimens varies greatly, and is probably influenced by the presence of traces of impurities.

W. H.-R.

**Kinetics of Macro-crystal Formation in Tungsten by Union of Small Crystals.** H. ALTERTHUM (*Z. physikal. Chem.*, 1924, **110**, 1—16).—An aggregate of small crystals tends to pass into the more stable system consisting of a few large crystals. Owing to the small free energy involved and the extremely slow rate of diffusion in solids the velocity of this change is very small at the ordinary temperature. In presence of foreign substances, the small crystals become coated with a film and macro-crystal formation is prevented. Rods consisting of a large number of tungsten crystals were found to consist of a few large crystals after being heated for some time at 3000° in an atmosphere of hydrogen. The time necessary for the production of these large grains is not constant and with the rods employed at 3200° varied from 45 to 70 minutes. The number of crystals produced depends also on the concentration of water vapour in the hydrogen. Various theoretical points are discussed.

J. S. C.

**Induction Periods in Chemical Reactions.** R. P. SANYAL and N. R. DHAR (*Z. anorg. Chem.*, 1924, **139**, 161—193).—The induction period of the reaction between arsenious and iodic acids is curtailed by (1) excess of iodic acid, (2) increase in the concentrations of the reactants, (3) addition of a trace of arsenic acid, (4)



addition of many mineral acids, and (5) exposure to sunlight; it is prolonged by addition of mercuric chloride or by violent shaking. The fraction of the iodine liberated increases with the arsenious acid concentration and passes through a maximum. The iodine appears on the surface of the solution even if the latter is covered with benzene or hydrogen; occasionally it appears at a nucleus on the glass.

The induction period of many reactions was followed by measuring the conductivity of the mixed solutions, which attains a maximum at the termination of the period. Some reactions showed no maximum, *e.g.*, reduction of iodic acid with ferrous sulphate, when insoluble  $\text{Fe}(\text{OH})\text{SO}_4$  is probably formed etc. The reduction with hydroxylamine hydrochloride showed a period of induction, but the conductivity did not attain a maximum until after the appearance of the iodine; this is attributed to decomposition of the hydroxylamine in aqueous solution as well as to oxidation by iodine. Sulphur is deposited from acid solutions of sodium thiosulphate while the conductivity remains fairly constant. No induction period was found for the decomposition of chlorine water, nor for the action of bromine water on oxalic and tartaric acids. With mixtures of sodium thiosulphate, hydrochloric acid, and arsenious acid, the arsenic trisulphide is probably formed immediately but is precipitated only when its solubility limit in presence of hydrochloric acid is reached (*cf.* Forbes, Estill, and Walker, A., 1922, ii, 271). It is concluded from experiments on the oxidation of organic acids by permanganate that an apparent period in which no reaction takes place can be produced in very slow reactions when the method of following the changes during the period is not very sensitive. Skrabal's conclusions on the reaction between potassium permanganate and oxalic acid could not be supported (*cf.* A., 1905, ii, 17).

S. K. T.

**Velocity of Reaction in Mixed Solvents. VII. Influence of the Base on the Velocity of Saponification of Esters in Methyl Alcohol Mixtures.** W. I. JONES, H. McCOMBIE, and H. A. SCARBOROUGH (*J. Chem. Soc.*, 1914, 125, 2590—2595).—The velocity of saponification of methyl *n*-butyrate and *o*-chlorobenzoate by lithium, barium, and tetramethylammonium hydroxides in methyl alcohol–water mixtures is measured and compared with the results obtained for potassium hydroxide (*cf.* T., 1923, 123, 2688); the curves are divisible into linear sections. All four bases give points of inflection at compositions corresponding with the complexes,  $2\text{MeOH}, \text{H}_2\text{O}$  and  $\text{MeOH}, 3\text{H}_2\text{O}$ , whilst lithium hydroxide gives one corresponding with  $2\text{MeOH}, 2\text{H}_2\text{O}$ , and the other bases at points corresponding with  $\text{MeOH}, \text{H}_2\text{O}$  and  $\text{MeOH}, 2\text{H}_2\text{O}$ . The results indicate that the process of saponification is not mainly promoted by hydroxyl ions but by the formation of a complex between the ester and the base and its subsequent decomposition. The ratio  $k_{\text{KOH}}/k_{\text{base}}$  is calculated in each case, and lithium and tetramethylammonium hydroxides yield results which support the view that the velocity of saponification depends on two factors, the

relative proportion of base existing as hydroxide and methoxide, and a steric factor including the influence both of the ester and of the base.

J. W. B.

**Diazoamino Conversion.** H. GOLDSCHMIDT, S. JOHNSEN, and E. OVERWIEN (*Z. physikal. Chem.*, 1924, **110**, 251—265).—The influence of various acids on the rate of the diazoamino conversion in aniline solution has been investigated. In presence of strong acids the rate of reaction is roughly proportional to the acid concentration. With weak acids, there is no such proportionality, the velocity coefficients increasing more rapidly than the acid concentration. The deviations from proportionality apparently become larger as the strengths of the acids diminish. 1 : 3 : 5-Dinitrobenzoic acid, however, behaves abnormally in this respect. In all cases, the variation in reaction velocity with the change in the acid concentration  $c$ , may be represented by the expression  $k = ac + bc^2$ , where  $k$  is the unimolecular velocity coefficient and  $a$  and  $b$  are constants characteristic of the acid. Addition of water causes a diminution in reaction velocity in presence of strong acids, but produces an increase when the catalyst is a weak acid. Conductivity measurements in aniline solution show that the value of the molecular conductivity passes through a minimum as the dilution is increased, and that in all cases the conductivity is increased on addition of water. The effect of addition of various bases on the conductivity of a number of acids in aniline solution has been investigated. The experimental results are interpreted as being in favour of the hypothesis that the active catalyst in the diazoamino conversion is the ion,  $C_6H_5 \cdot NH_3^+$ .

J. S. C.

**Velocity of Oxidation of the Metals and the Structure of Coloured Oxide Films.** D. H. BANGHAM and J. STAFFORD (*Nature*, 1925, **115**, 83—84).—Despite Mallock's observations (*Proc. Roy. Soc.*, 1918, **A**, **94**, 566), it is considered proved that interference is the true explanation of metallic temper colours since there is a close approximation between the rate of reaction of the metal with oxygen, assuming interference to be the cause (Tammann), and that in the case of zinc directly determined. In the case of copper the primary formation (as required by the interference theory) of a coherent, tightly clinging film must be ascribed to cuprous, and not cupric, oxide (cf. Hinshelwood, *A.*, 1923, **ii**, 29) on account of the lattice similarity of copper and cuprous oxide, and the consequent formation of the latter with the minimum disturbance. Calculation of the thicknesses of air films corresponding with such cuprous oxide films gives results closely approximating to known colour ranges. Hinshelwood's observations that successive oxidations and reductions of a copper surface led to an intensification of the film colours produced, and to a correspondingly greater rate of fixation of the oxygen; also that the amounts of oxygen required to form purple, blue, and green films remain in constant ratio, are explained if the treatment causes a roughening of the surface, whereby the effective area of the metal is increased (cf. Mason, this vol., **ii**, 108; Gale, *ibid.*, 109.)

A. A. E.

**Formation of Nitrous Acid from Nitric Acid and Nitric Oxide.** E. ABEL and D. HARASTY (*Z. anorg. Chem.*, 1924, **139**, 1—39).—The velocity of the reaction  $\text{HNO}_3 + \text{H}_2\text{O} + 2\text{NO} = 3\text{HNO}_2$  was followed by bubbling nitric oxide through nitric acid and examining the solution after a series of time intervals by the usual methods (cf. A., 1912, ii, 1093). The reaction is heterogeneous (the velocity of reduction is decreased by decreasing the glass surface of the apparatus) and is autocatalysed by the nitrous acid, which acts as a superposed positive and negative catalyst; it accelerates the reduction when its concentration is small and retards it as the concentration becomes larger. The velocity increases with increasing velocity of the nitric oxide stream and with decreasing volume of the solution of the reactants. The latter effect is mainly due to change in the hydrogen-ion concentration of the nitric acid; the nitrate-ion concentration has only a small influence. Sodium sulphate retards the reaction and in moderately large concentrations practically stops it. S. K. T.

**Hydrolysis of Esters of Ketonic Acids.** A. SKRABAL, F. PFAFF, and H. AIROLDI (*Monatsh.*, 1924, **45**, 141—155).—A detailed discussion of published data on the hydrolysis of esters of lævulic, acetoacetic, and pyruvic acids. Measurements of the rate of hydrolysis of ethyl lævulate in presence of hydrochloric acid and sodium hydroxide gave values of  $k$ , for normal hydrogen- and hydroxyl-ion concentration respectively, of 0.00156 and 7.7, whilst corresponding values for ethyl pyruvate, derived from similar measurements in presence of hydrochloric acid, water, and phosphate buffer solutions, were 0.00816 and  $1.1 \times 10^5$ . F. G. W.

**Rate of Hydrolysis of Ethyl Orthocarbonate.** A. SKRABAL and M. BALTADSCHEWA (*Monatsh.*, 1924, **45**, 95—104).—The hydrolysis of ethyl orthocarbonate takes place in the two stages: (i)  $\text{C}(\text{OEt})_4 + \text{H}_2\text{O} = \text{CO}(\text{OEt})_2 + 2\text{EtOH}$ ; (ii)  $\text{CO}(\text{OEt})_2 + \text{H}_2\text{O} = \text{CO}_2 + 2\text{EtOH}$ . The velocity of (ii) is small in presence of hydrogen ions (cf. A., 1918, ii, 11), but is proportional to the concentration of hydroxyl ions present. Measurements made in presence of sodium carbonate gave  $k=1.6$  for  $[\text{C}]_{\text{OH}}=1.0$ . For methyl carbonate, the corresponding constant is 7.0. The rate of reaction (i) is not influenced by hydroxyl ions, and  $k_w=3.4 \times 10^{-4}$ . Measurements in potassium dihydrogen phosphate/disodium hydrogen phosphate, and sodium acetate/acetic acid buffer solutions showed the rate of reaction (i) to be proportional to the concentration of hydrogen ions present, and for  $[\text{C}]_{\text{H}}=1.0$ ,  $k=1.2 \times 10^4$ . F. G. W.

**Acceleration of the Catalysis of Mixtures of Hydrogen and Oxygen by Oxygen Carriers and by the Alternating Current.** K. A. HOFMANN and A. DOLDE (*Ber.*, 1924, **57**, [B], 1969—1976; cf. A., 1922, ii, 276, 490).—The rate of formation of water from mixtures of oxygen and hydrogen at platinum contacts continuously wetted by an aqueous electrolyte is diminished by the formation of a comparatively inactive platinum hydride from the hydrogen originally dissolved in the atomic state and of platinum oxide which

is produced even when ozone is present in the gaseous mixture. The formation of these substances can be avoided by the aid of an alternating current. After a short induction period, the platinum develops its maximum activity. The union of absorbed hydrogen atoms with oxygen molecules at a platinum surface occurs instantaneously, but time is required for the passage of the hydrogen and oxygen molecules to the metal. Since hydrogen diffuses about four times as rapidly as oxygen through the liquid, the union is delayed for lack of oxygen, and a platinum contact, even if previously primed with oxygen, rapidly becomes a strong Pt—H pole in the presence of electrolytic gas. This defect may be obviated by the introduction of a rapidly reducible and quickly oxidisable oxide which is adsorbed by platinum. For this purpose, the addition of a small amount of vanadium sulphate to 0.1*N*-sulphuric acid is effective; titanium sulphate, uranyl sulphate, and ferric ammonium sulphate are unsuitable. In all probability an oxide containing quadrivalent vanadium is produced. By this means a given platinum contact is brought to its maximum activity, which is developed with mixtures containing 33% of oxygen and not, as in the case of *N*-sulphuric acid alone, with 40% of oxygen. H. W.

**Heterogeneous Catalysis.** W. E. GARNER (*Nature*, 1924, **114**, 932).—A brief discussion of the bearing of results already published (Blench and Garner, *T.*, 1924, **125**, 1288) on the mechanism of heterogeneous catalysis. Differences in the heats of absorption of oxygen by carbon at various temperatures are held to indicate a widely differing energy content of the surface carbon atoms, of which the valencies are far from being saturated by neighbouring carbon atoms. The effect of surface atoms lying in an exposed position in initiating or maintaining chemical processes is considered. A. A. E.

**Corrosion of Metals.** E. MAASS and E. LIEBREICH (*Z. angew. Chem.*, 1924, **37**, 897—899).—A theoretical survey of the principal factors, both chemical and electrochemical, concerned in the corrosion of metals in contact with electrolytes. Feeble polarisation of either sign favours corrosion, up to the point at which protection is afforded by actual evolution of hydrogen. Electrochemical effects are, however, often masked by the formation of a protective coating of some insoluble compound of the metal. W. T. K. B.

**Action of Salt Solutions on Iron and Steel in the Presence of Oxygen.** U. R. EVANS (*J. Soc. Chem. Ind.*, 1924, **43**, 315—322r).—The corrosion of iron and steel by drops of 0.1*N*-aqueous salt solutions was observed. The area under the centre of the drop becomes anodic and is attacked, whilst the outer portions, which are exposed to the air, become cathodic. Salt solutions (*e.g.*, potassium chloride) which yield soluble anodic and cathodic products (*e.g.*, ferrous chloride and potassium hydroxide, respectively) tend to increase the velocity of corrosion; where the products mix, a ring of ferrous hydroxide is formed which is oxidised to ferric hydroxide and spreads as a membrane over the surface. Outside

this membrane the iron is unattacked. When the cathodic product only is insoluble, as in the case of zinc sulphate, the cathodic area is protected from diffused oxygen and the rate of corrosion is slightly diminished; insoluble anodic products cling to the metal surface and practically prevent corrosion, although the edges of the protecting skin may fail to adhere in places and localised corrosion then takes place. Potassium chromate causes passivity, but localised corrosion is caused by the presence of large quantities of chlorides and to some extent by sulphates and more especially nitrates.

S. K. T.

**Anodic Oxidation of Gold. III.** F. JIRSA and J. JELINEK (*Chem. Listy*, 1924, 18, 334—337).—The ionic product of auric hydroxide deduced from its solubility in nitric acid was found to be  $[\text{Au}^{+++}][\text{OH}]_3 = 5.5 \times 10^{-46}$ , a value that is in fair agreement with that previously deduced from its solubility in sulphuric acid ( $9 \times 10^{-46}$ ). The solubility of auric hydroxide in water is  $2.4 \times 10^{-12}$  mol. per litre and its affinity constant, calculated on the assumption that in sulphuric acid solution it exists as  $\text{HAu}(\text{SO}_4)_2$ , is  $1.1 \times 10^{-6}$ ; it is therefore about as strong a base as hydrazine hydrate. The potential of gold in a solution of auric nitrate was found to be 1.37 volts, which agrees closely with previously calculated figures.

A. R. P.

**Photochemistry of the Halogens. Action of Light on the Reactions of Iodine or Bromine with Potassium Oxalate.** A. BERTHOUD and H. BELLENOT (*J. Chim. phys.*, 1924, 21, 308—350). The reaction of iodine with potassium oxalate ( $\text{K}_2\text{C}_2\text{O}_4 + \text{I}_2 = 2\text{KI} + 2\text{CO}_2$ ) has been investigated, the course of the reaction being determined by titration of the unchanged iodine. In the dark, the velocity of the reaction is proportional to the concentrations of the oxalate and of the iodine, and inversely proportional to the concentration of potassium iodide. The temperature coefficient of the velocity constant in the dark ( $k_{t+10} : k_t$ ) is 4.36 for the range  $69.5^\circ$  to  $78^\circ$ , the high value being partly due to the increasing dissociation of the complexes  $\text{I}_3'$  as the temperature rises. The reaction is due entirely to the  $\text{I}_2$  molecules and not to the complexes. The reaction is accelerated by light of all visible wave-lengths and does not follow the law of Grotthuss. In the case of red light where the absorption is weak, the velocity of the reaction is proportional (1) to the concentration of oxalate, (2) to the square root of the concentration of iodine, (3) to the square root of the intensity of the incident light, and (4) inversely proportional to the concentration of potassium iodide. In blue light where the absorption is almost total, (1), (3), and (4) still apply, but the velocity in this case is inversely proportional to the square root of the concentration of iodine. A complicated explanation of these facts is possible if it is assumed that the light activates only the  $\text{I}_2$  molecules, causing these to split up into atoms which may either react with the oxalate, recombine to form  $\text{I}_2$  molecules, or combine with  $\text{I}'$  ions to form complexes according to the scheme  $2\text{I} + \text{I}' \rightarrow \text{I}_3'$ . The temperature coefficient of the reaction in light is 3.18 for the range  $25$ — $40^\circ$ ; if account is taken of the

increased dissociation of the complexes as the temperature rises, the coefficient becomes 2.90, which is still a very high value.

In the dark, the reaction with bromine is similar to that with iodine, the temperature coefficient being 5.99 for the range 0—11.5°. The reaction is accelerated only by light of shorter wave-length than green, and the velocity is again proportional to the concentration of oxalate and to the square root of the intensity of the light. The concentration of potassium bromide, however, has little effect, indicating that the light activates the complexes  $\text{Br}_3'$  and  $\text{Br}_3\text{K}'$ , as well as the  $\text{Br}_2$  molecules. In dilute solutions of bromine in which the absorption is weak, the velocity of the reaction is again proportional to the square root of the concentration of bromine, but in concentrated solutions in which the absorption is complete the velocity is independent of the bromine concentration. If traces of ammonium salts are present, a period of induction occurs until the ammonium ions are destroyed. The temperature coefficient is again high, 2.04 for the range 0—15°. W. H. R.

**Influence of Aqueous Vapour Pressure and Wave-length on the Photochemical Formation of Hydrogen Chloride.** A. COEHN and G. JUNG (*Z. physikal. Chem.*, 1924, **110**, 705—724).—Mixtures of hydrogen and chlorine containing water vapour equivalent to  $10^{-7}$  mm. of mercury exhibit no photochemical combination on exposure to rays of the visible spectrum. On raising the water content to the equivalent of  $10^{-5}$  mm. mercury, an 88% yield of hydrogen chloride is obtained. Perfectly dry gaseous mixtures on exposure to the short ultra-violet rays,  $\lambda > 300\mu\mu$ , react quantitatively in a few minutes. The maximum wave-length producing the photochemical combination of moist gaseous mixtures is found to be  $540\mu\mu$ . J. S. C.

**Example of Photochemical Reaction-coupling ( $\text{COCl}_2 + \text{H}_2$ ) and the Photochemical Decomposition of Formaldehyde.** G. BREDIG and A. VON GOLDBERGER (*Z. physikal. Chem.*, 1924, **110**, 521—546).—Exposure of mixtures of carbonyl chloride and hydrogen to ultra-violet light results in the 97% decomposition of the carbonyl chloride according to the scheme  $\text{COCl}_2 \rightarrow \text{CO} + \text{Cl}_2$ , followed by  $\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl}$ . In the absence of hydrogen, the equilibrium mixture under similar conditions contains about 4% of carbon monoxide and chlorine. It was hoped to obtain formaldehyde according to the scheme  $\text{COCl}_2 + 2\text{H}_2 \rightarrow \text{CH}_2\text{O} + 2\text{HCl}$ . At 10°, minute traces of this substance were obtained and none at all at 80°. The walls of the reaction vessel were observed to be coated with a white to brown deposit. The photolysis of pure gaseous formaldehyde was therefore studied at 80° and 195°. Carbon monoxide and hydrogen were the chief decomposition products. Small amounts of methane and carbon dioxide were observed and at the higher temperature a sugary substance was formed on the walls. The decomposition cannot apparently be represented by any simple stoichiometric expression. At 80°, the decomposition follows the unimolecular law but at 195°, and for high concentrations of vapour, all light is absorbed and the rate of reaction is independent of

concentration. The failure to obtain formaldehyde from carbonyl chloride is explained on the assumption that on formation it undergoes a polymerisation to solid products and also suffers a photochemical decomposition. J. S. C.

**Quantity of Ultra-violet Light Energy required to render developable a Grain of Photographic Silver Bromide.** P. S. HELMICK (*J. Opt. Soc. Amer.*, 1924, 9, 521—540).—For 2537 Å., the average quanta per grain is  $731 \pm 14$ , for 2653 Å.  $514 \pm 11$ ; for 3131 Å.  $510 \pm 16$ , for 3650 Å.  $555 \pm 13$ . Thus small energies are more efficient in producing developable grains than large energies. Determinations are made of the absorption of the silver bromide and the gelatin in an ordinary photographic emulsion. C. W. B.

**Photographic Blackening Curve.** W. MEIDINGER (*Z. physikal. Chem.*, 1924, 114, 89—113).—The dependence of the velocity of development on the concentration of the components of a "metol" developer has been studied and the law of mass action thereby demonstrated. Addition of bromide ion retards development up to a limiting value, from which it is inferred that development is a surface reaction and that the grains adsorb bromide ion which forms a protection against the developer. Addition of iodide ion eventually stops development, whilst chloride ion is without effect. The relation between constitution and developing properties is discussed for the hydroxy-benzenes and -naphthalenes. It is shown that in a developer the hydroxyl groups must be arranged so as to allow the quinone structure to be formed on oxidation. Blackening increases with duration of development up to a limiting value. In making these last measurements a correction for fog is applied. The results obtained by "physical" development are discussed and compared with the ordinary process. The action of  $\alpha$ -rays is approximately proportional to the mass of the silver bromide in the plate layer.

In an examination of three types of plate (Agfa "Spezial," "Reproduktion," and "Diapositiv") the covering power of the emulsions was determined. For the same emulsion, the same degree of blackening corresponds with a constant separation of silver irrespective of the times of development and exposure. Grain size alone is not a criterion of sensitiveness, which may be altered considerably in the same plate by treatment with acids and alkalis. The blackening curve for the "Spezial" and "Reproduktion" plates was determined by grain counting and titration and the light absorption is interpreted in terms of the quantum theory. N. H. H.

**Latent Photographic Image. I. Relation between Light Frequency and Number of Developable Centres.** F. C. TOY (*Phil. Mag.*, 1924, [vi], 48, 947—961).—By applying the laws of reflection and absorption to the case of a "single layer" photographic plate, the relative quantities of light energy, of different frequencies, absorbed by the grains when equal intensities of each are incident, are calculated; hence the number of quanta absorbed

is determined. It is shown experimentally that, except at low exposure, the relative number of developable centres produced by different frequencies is equal to the relative number of quanta absorbed. It is suggested that the departure from this equality at low exposures is due to the fact that the development does not then give a true record of the extent of the light action.

C. W. B.

**Action of Ultra-violet Light on "Dye and Textile Fibre" Systems.** P. HEERMANN (*Chem.-Ztg.*, 1924, 48, 813—814, 834—835).—It is proposed to classify "dye and textile fibre" systems into four classes according to their susceptibility to light of various wave-lengths. The behaviour has been examined with reference to sunlight transmitted through glass (3500—30000 $\lambda$ ), direct sunlight (3000—40000 $\lambda$ ) and ultra-violet light such as that obtained by means of a mercury vapour lamp (1800—6000 $\lambda$ ). These classes, termed "micro-," "macro-," "homo-," and "mesotropic" are, respectively, most susceptible to light of short wave-length, long wave-length, all wave-lengths, and to the ultra-violet light present in sunlight. The majority of synthetic organic dyes are included in the "microtropic" class. The action of ultra-violet light on textile materials such as cotton, artificial silks, linen, jute, wool, and silk is closely related to the fading of dyed materials. The action of sunlight and weathering cannot, however, be satisfactorily determined by means of artificial sources of illumination. [Cf. *B.*, 1925, 68.]

A. J. H.

**Chemical Combination of Helium.** E. H. BOOMER (*Nature*, 1925, 115, 16; cf. Manley, this vol., ii, 57).—Mixtures of helium with mercury, iodine, sulphur, and phosphorus vapours have been examined under the influence of electron bombardment and in the presence of surfaces cooled by liquid air. The helium disappears much more quickly than under the ordinary conditions in a discharge tube. Solid substances, believed to be compounds of helium, were obtained which suddenly liberate the original amount of helium when warmed to  $-70^{\circ}$  in the cases of mercury and iodine, and  $-125^{\circ}$  in the cases of sulphur and phosphorus.

A. A. E.

**Compounds of Gold with Nitrogen.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 46—49; from *Chem. Zentr.*, 1924, ii, 18; cf. Weitz, A., 1915, ii, 39).—Explosive gold ("knallgold") is held by the author to be a mixture of gold amidine,  $\text{NH}\cdot\text{Au}\cdot\text{NH}_2$ , and gold iminochloride,  $\text{NH}\cdot\text{AuCl}$ .

G. W. R.

**Isomorphous Relations between Beryllium and Magnesium Compounds.** F. ZAMBONINI and G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 218—222).—Magnesium lanthanum nitrate,  $\text{Mg}_3\text{La}_2(\text{NO}_3)_{12}\cdot 24\text{H}_2\text{O}$ , forms, with the corresponding beryllium lanthanum compound, mixed crystals containing as much as about 19% of the latter. In their simple compounds, however, beryllium and magnesium appear to be isomorphogenous only in special cases.



Such slight tendency towards isomorphism is in accord with the different atomic structures proposed for these two metals by Bohr.  
T. H. P.

**Reduction of Magnesium Sulphate.** W. ALTHAMMER (*Kali*, 1924, **18**, 112—114; from *Chem. Zentr.*, 1924, ii, 165).—Magnesium sulphate is quantitatively reduced when heated with an equivalent amount of carbon at 750°. About 40% of the sulphur is obtained in the free state. Even with a fivefold excess of carbon no magnesium sulphide is obtained but simply an increase in the yield of free sulphur. The primary reaction is according to the equation  $\text{MgSO}_4 + \text{C} = \text{MgO} + \text{SO}_2 + \text{CO}$ . The production of sulphur follows the reversible secondary reactions:  $2\text{CO} + \text{SO}_2 = \text{S} + 2\text{CO}_2$  and  $\text{CO}_2 + \text{C} = 2\text{CO}$ . Illuminating gas, hydrogen, carbon dioxide, benzene vapour, acetylene, and producer gases all reduce magnesium sulphate at 650—700°. The effect of producer gases depends principally on their hydrogen content. In the case of reduction with hydrogen, over 70% of the sulphur present is obtained in the free state.  
G. W. R.

**Crystal Structure of Mercuric Sulphide.** II. N. H. KOLKMEIJER, J. M. BIJVOET, and A. KARSEN (*Rec. trav. chim.*, 1924, **43**, 894—896; cf. *ibid.*, 677).—The agreement between the Debye-Scherrer photographs of cubic (black) and trigonal (red) mercuric sulphides is due to identity in the dimensions of the octahedral and basal planes respectively. Neither  $\beta'$  mercuric sulphide nor any other modification described by Allen and Crenshaw is distinct from the black and the red forms.  
W. E. E.

**Double Nitrates of Metals of the Cerium Group with Copper and with Cadmium.** G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 246—250).—*Lanthanum copper nitrate*,  $2\text{La}(\text{NO}_3)_3 \cdot 3\text{Cu}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , forms hygroscopic, pale blue, trigonal crystals,  $d^{10}$  2.227, which are melted in their water of crystallisation by the heat of the hand, and form mixed crystals with the analogous lanthanum magnesium nitrate. *Cerium copper nitrate*,

$2\text{Ce}(\text{NO}_3)_3 \cdot 3\text{Cu}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ ,  
forms highly deliquescent, pale blue crystals,  $d^{10}$  2.237.

T. H. P.

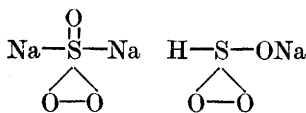
**Allotropy of Germanium Dioxide.** J. H. MÜLLER and H. R. BLANK (*J. Amer. Chem. Soc.*, 1924, **46**, 2358—2367).—An allotropic form of germanium dioxide, quantitatively insoluble in boiling water and stable towards acids (*e.g.*, hydrofluoric) and alkalis, is prepared by heating at 200—1100° for 4 hours the oxide obtained by the evaporation of an aqueous solution of the oxide. The maximum yield under these conditions, and probably also the maximum velocity of transition, occurs when the heating is carried out at 380°. This insoluble variety, which must be the stable modification at the ordinary temperature, is reconverted into the soluble form by fusion. The yields obtained by heating the soluble oxide at 280° increase with duration of heating up to a maximum conversion of about 15%; this probably indicates the presence of

a second soluble allotropic form in the soluble oxide obtained by evaporation. The m. p. of any variety is between  $1090^{\circ}$  and  $1100^{\circ}$ . The oxide may be purified from sulphates by ignition above  $950^{\circ}$  for about 36 hours; chlorides are removed by repeatedly moistening the oxide with water, evaporating, and igniting at  $950^{\circ}$  (cf. Nichols, A., 1923, ii, 571). S. K. T.

**Pharmacological Properties of Tin Hydride and Germanium Hydride.** F. PANETH and G. JOACHIMOGLU.—(See i, 197.)

**New Oxides of Nitrogen.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 20—33; from *Chem. Zentr.*, 1924, ii, 17—18; cf. A., 1914, ii, 39).—When nitrogen is burnt in the high-tension flame arc or when ammonia is burnt with a platinum catalyst at low red heat, nitrogen isdioxide,  $\text{N}=\text{O}=\text{O}$  is the primary product. This is in contradiction to the assumption that nitric oxide is the only oxide of nitrogen stable at high temperatures. The lighter colour which is observed when nitrogen peroxide is passed through a hot tube is not to be attributed to decomposition into nitric oxide and oxygen but to the formation of the lighter coloured nitrogen isdioxide. G. W. R.

**Reactions between Nitrous and Sulphurous Acids.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 1—19; from *Chem. Zentr.*, 1924, ii, 16—17; cf. A., 1907, ii, 23, 700).—The reactions of sulphites and hyposulphites can be explained on the assumption that they are differently constituted. For the sodium salts, the



accompanying formulæ are given. The fact that normal sulphites do not react with nitrites is explained by steric hindrance, owing to the central position of the sulphur atom. The reactions of nitrites and nitrous acid with sulphites and sulphurous acid are discussed from this point of view. The different reactions are best explained by assuming for nitrous acid the formula  $\text{N}(\text{OH})_3$ . By successive replacement of the hydroxyl groups by sulphonie acid groups, dihydroxylaminesulphonic acid, hydroxylaminedisulphonic acid, and nitrilosulphonic acid are formed. In the presence of an indifferent acid, nitrososulphonic acid tends to form with nitrous acid, nitrosulphonic acid,  $\text{O}:\text{N}(\text{OH})\cdot\text{SO}_3\text{H}$ , with liberation of nitric oxide. This acid is stable in sulphuric acid solution. It is also formed by reduction of nitrosulphonic acid by copper or mercury in sulphuric acid solution. It yields nitric oxide and sulphuric acid on decomposition. Nitrosulphonic acid is decomposed according to the equation  $\text{O}:\text{N}\cdot\text{SO}_3\text{H} + \text{H}_2\text{O} = \text{NOH} + \text{H}_2\text{SO}_4$ . The hyponitrous acid thus formed rapidly decomposes, yielding nitrous oxide and water. G. W. R.

**Monochloroamine.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 50—78; from *Chem. Zentr.*, 1924, ii, 162—163; cf. A., 1909, ii, 232; Marckwald and Wille, A., 1923, ii, 558).—In the reaction whereby monochloroamine is formed from sodium hypochlorite and aqueous ammonia, ammonium hypochlorite is

not produced. Monochloroamine may be distilled in a vacuum without decomposition from the products of the above reaction in the presence of 50% zinc chloride solution. Concentrated aqueous solutions of monochloroamine on being kept at low temperatures deposit yellow crystals which appear to be chlorine hydrate. Monochloroamine is decomposed by strong ammonia solution, yielding ammonium chloride and nitrogen. In the presence of strong alkalis, hydrazine is produced according to the equation  $\text{NH}_2\text{Cl} + \text{NH}_3 + \text{NaOH} = \text{N}_2\text{H}_4 + \text{NaCl} + \text{H}_2\text{O}$ . The yield of hydrazine is increased by the presence of formaldehyde, sugars, gum, or gelatin. The chlorine of monochloroamine may be replaced by the sulphonic acid group, using sodium sulphite. With sodium hydrogen sulphite, however, sulphonation does not take place even in the presence of sodium hydroxide. In the reaction between sodium hydroxide and monochloroamine, it is probable that some tri-imide,  $\text{N}_3\text{H}_3$ , is formed.

G. W. R.

**Composition of Nitrogen Iodide.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 34—45; from *Chem. Zentr.*, 1924, ii, 18).—The precipitate obtained by the reaction of potassium iodide solution with aqueous ammonia, which has the composition  $\text{NH}_3\text{NI}_3$ , when washed with water yields ammonia and nitrogen iodide. The original precipitate on being dried loses half its ammonia, yielding the explosive compound,  $\text{NHI}_2$ , considered by the author to be a molecular compound of 2 mols. of nitrogen iodide and 1 mol. of ammonia. The ammonia-nitrogen iodide compound reacts with sodium hydroxide according to the following equations: (i)  $\text{NH}_3\text{NI}_3 + 4\text{NaOH} = \text{NH}_3 + 3\text{NaI} + 2\text{H}_2\text{O} + \text{NaNO}_2$ ; (ii)  $\text{NH}_3\text{NI}_3 + 3\text{NaOH} = \text{N}_2 + 3\text{NaI} + 3\text{H}_2\text{O}$ . With sodium sulphite the following reaction takes place:  $\text{NH}_3\text{NI}_3 + 3\text{Na}_2\text{SO}_3 + 3\text{H}_2\text{O} = 2\text{NH}_3 + 3\text{HI} + 3\text{Na}_2\text{SO}_4$ . The precipitate obtained by the action of potassium iodide on chloroamine solution in the presence of ammonium chloride is similar to that obtained from the action of iodine on aqueous ammonia.

G. W. R.

**Ozone from Flames.** H. VON WARTENBURG (*Z. physikal. Chem.*, 1924, 110, 285—290; cf. Riesenfeld and Beja, A., 1924, ii, 470).—Manchot's criticism (A., 1924, ii, 543) of the author's assumption that the formation of ozone in flames containing oxygen and hydrogen is preceded by the formation of hydrogen peroxide and its decomposition into water and oxygen atoms (A., 1921, ii, 107) is considered. Oxygen atoms are certainly present in such flames and these in some way form ozone, since Riesenfeld (A., 1924, ii, 470) has shown that the quantities of ozone are far too large to be explained on the assumption of thermal formation from oxygen. Atomic oxygen may result from some partial reaction following a primary addition of molecules, or by means of molecular collisions whereby translational energy is converted into chemical energy. The question of an electron effect in the absence of an accelerating electric field is also discussed.

J. S. C.

**Formation of Ozone and Hydrogen Peroxide in the Oxygen-hydrogen Flame.** E. H. RIESENFELD (*Z. physikal. Chem.*, 1924, **110**, 801—807).—Dry mixtures of hydrogen and oxygen have been burned at the end of a silica tube 0.2—0.4 mm. in diameter, and the gases immediately cooled, the amounts of ozone and hydrogen peroxide formed being determined. The small dimensions of the flame permit a much more efficient cooling than was obtained by other investigators, the amounts of ozone and hydrogen peroxide being consequently much greater. The ratio  $[O_3]/[H_2O_2]$  is found to decrease as the hydrogen content of the burning gases increases, becoming zero when a gas mixture of the composition  $H_2:O$  is attained. With mixtures richer in hydrogen much more hydrogen peroxide is obtained and it therefore seems unlikely that this latter substance is to be regarded as the precursor of ozone. A more plausible hypothesis is that ozone is produced by collisions between ionic or atomic oxygen and molecular oxygen and that the presence of hydrogen peroxide is due to collisions between oxygen ions or atoms and hydrogen molecules. J. S. C.

**Reduction of Sulphuric Acid to Hydrogen Sulphide.** A. VILA (*Compt. rend.*, 1924, **179**, 1163—1165).—When sulphuric acid vapour mixed with hydrogen is passed over silica heated at 700—900° quantitative reduction to hydrogen sulphide takes place. H. T.

**Formation and Decomposition of Polythionates.** F. FOERSTER (*Z. anorg. Chem.*, 1924, **139**, 246—260).—Criticism of Josephy's work (*A.*, 1924, ii, 470) in the light of previous work by the author (*cf. A.*, 1923, ii, 23) and others. S. K. T.

**Reaction between Arsenious Anhydride and Chlorine.** L. CAMBI [with P. M. VOLTOLIN] (*Giorn. Chim. Ind. Appl.*, 1924, **6**, 527—532).—The experimental results show that the products of the interaction of chlorine and arsenious anhydride in presence of water represent the resultant of the two reversible reactions,  $AsCl_3 + Cl_2 + (2.5 + n)H_2O \rightleftharpoons 0.5As_2O_3 + nH_2O + 5HCl$ ; and  $0.5As_2O_3 + 3HCl \rightleftharpoons AsCl_3 + 1.5H_2O$ . The final result corresponds with the former equation when the proportion of water present is high and approximately with the latter when little water is used, liquid trichloride being formed in this case. Application of the reaction to the preparation of calcium and lead arsenates is considered. [*Cf. B.*, 1925, 97.] T. H. P.

**Reaction between Ferrous Salts and Cuprous Salts.** R. C. WELLS (*Amer. J. Sci.*, 1924, **8**, 428—433).—In the reduction of cuprous salts with ferrous hydroxide the main reaction corresponds with the equation,  $3FeO + 2CuCl = 2Cu + Fe_2O_3 + FeCl_2$ , especially when cuprous chloride is present in excess. With decrease of the latter, the reaction is:  $4FeO + 2CuCl = 2Cu + Fe_3O_4 + FeCl_2$ . Investigation of the effect of the hydrogen-ion concentration shows that the reaction  $Cu^+ + Fe^{2+} \rightleftharpoons Cu + Fe^{3+}$  results in the separation of copper at  $p_H > 5.0$ . H. T.

**Ruthenium Oxides.** L. WÖHLER, P. BALZ, and L. METZ (*Z. anorg. Chem.*, 1924, **139**, 205—219).—The methods previously proposed for the preparation of ruthenium pentahydroxide are shown to be erroneous. Debray and Joly's method (A., 1888, 559, 920) yields the tetrahydroxide; reduction of the tetroxide and of potassium ruthenate with alcohol gives the dioxide mixed with an explosive organic compound of ruthenium; Remy's method (A., 1923, ii, 329) gives the sesquioxide mixed with more or less dioxide. Pure ruthenium dioxide may be prepared by heating ruthenium sesquichloride,  $\text{Ru}_2\text{Cl}_3$ , at 600—700° in oxygen; the sesquichloride is obtained by the action of chlorine on finely divided ruthenium at 400—600°, or by the reduction of sodium ruthenium chloride,  $\text{Na}_2\text{RuCl}_5$ , at 400° in hydrogen. Hydrogen peroxide solution reduces ruthenium tetroxide solution, and oxidises ruthenium trihydroxide to the tetrahydroxide, which when heated (<800°) in a vacuum yields the pure dioxide. Treatment of potassium ruthenate with carbon dioxide or nitric acid gives a mixture of ruthenium tetroxide and tetrahydroxide. Ruthenium is the most easily oxidised of the noble metals; the vapour pressure of the dioxide is 15 mm. at 1000°, decomposition into metal and tetroxide taking place at higher temperatures. Ruthenium trihydroxide loses oxygen and water when placed in a vacuum; when carefully dehydrated in carbon dioxide it yields a mixture of dioxide and metal. The monoxide is not formed by the direct oxidation of the metal, nor by the reduction of the tetroxide in hydrogen. S. K. T.

**Compounds of Carbon Monoxide with Ruthenium Salts.** W. MANCHOT and J. KÖNIG (*Ber.*, 1924, **57**, [B], 2130—2133).—Ruthenium tri-iodide is converted smoothly by carbon monoxide at 240—250° into the compound,  $\text{RuI}_2(\text{CO})_2$ , in which the carbon monoxide is retained with remarkable firmness. Ruthenium tribromide is less readily transformed at 270—290° into the substance,  $\text{RuBr}_2(\text{CO})_2$ , whereas the corresponding chloro compound is formed only slowly and incompletely from ruthenium trichloride at 270°. Aqueous or alcoholic solutions of ruthenium trichloride or tribromide absorb carbon monoxide slowly.

The facilitation of the chlorination of ruthenium at 360—440° by the presence of carbon monoxide depends on the formation of the compound just described and its decomposition with the production of finely-divided ruthenium. H. W.

**Ozone.** G. M. SCHWAB (*Z. physikal. Chem.*, 1924, **110**, 599—625).—A convenient form of apparatus for the preparation of pure ozonised oxygen by the customary silent discharge method is described. The gas so obtained contains about 15% of ozone. On cooling by means of liquid air two liquid phases result, the upper light blue layer being a saturated solution of ozone in oxygen and the lower dark blue layer a saturated solution of oxygen in ozone. At -183° the latter phase contains 70% of ozone, and on fractionation pure ozone is obtained. The critical solution temperature is -158°.

The mean value for the molecular weight by volumetric methods (determination of iodine liberated from potassium iodide in presence of boric acid) is 49.1 and the value given by the Dumas vapour density method 47.9. The following physical constants have been determined: b. p.  $-112.3^{\circ}$ , m. p.  $-251.4^{\circ}$ , critical temperature  $-5^{\circ}$ , critical density 0.54, critical volume 89.4 c.c./mol.,  $d^{183}_{20} 1.71 \pm 0.05$ . The expansion between  $-192^{\circ}$  and  $-80^{\circ}$  is given by  $v_T = 0.512 + 0.000456T + 0.0000039T^2$ ,  $T$  being the absolute temperature. The calculated critical pressure is 67 atm. The question of the structure of ozone is discussed and it is shown that the most probable formula is  $O=O=O$ . [Cf. Riesenfeld and Schwab, A., 1922, ii, 761.] J. S. C.

**Formation of Nitric Oxide by purely Electrical Means.** G. M. SCHWAB and S. LOEB (*Z. physikal. Chem.*, 1924, **114**, 23—43).—An apparatus is described in which nitrogen and oxygen are made to react at 6 mm. pressure in a cold direct current discharge with an oxide cathode. The velocity of formation of nitric oxide is constant for nitrogen percentages of 20 to 80, outside which limits it falls towards zero. The velocity of decomposition depends on the form of discharge but in an unreproducible manner. Interpreted kinetically, the results show that the optical absorption law can be closely applied to the activation of a component without regard to the energy distribution in the discharge. It is concluded that the greater part of the energy taken from the oxygen serves to activate the nitrogen by impact of the oxygen ions on the nitrogen molecules, whilst the energy absorbed by the latter for which the absorption law applies is, under the experimental conditions, only a small part of the current energy, which is mainly lost by reflection from the electrodes. N. H. H.

**Test of the Efficiency of a Stirring Contrivance.** W. A. ROTH (*Z. physikal. Chem.*, 1924, **110**, 57—59).—The efficiency of a stirring device may be determined by embedding a little coloured salt (e.g., potassium permanganate) in sodium sulphate which is introduced into the agitated liquid, the time necessary for the solution to assume a homogeneous tint being noted. Quantitative determinations may be carried out by measurement of the electrical conductivity in various parts of the solution or by titration of small samples with oxalic acid. Alternatively, the permanganate may be enclosed in silver gauze or "cellon" paper. J. S. C.

**Trustworthy Shaking Machine.** A. G. MILLIGAN (*J. Chem. Soc.*, 1924, **125**, 2674—2675).—The bottle carrier is supported on four springy laths of straight-grained ash allowing a limited horizontal displacement and exerting a strong restoring force at the end of each stroke, and thus very little power is needed and the danger of stoppage at a dead point eliminated. J. W. B.

**Apparatus for Physical Chemistry Laboratories.** O. SCARPA (*Gazzetta*, 1924, **54**, 876—887).—Descriptions are given of apparatus for measuring coefficients of diffusion in liquids and

surface tension of liquids, and of a tonometer for measuring dissociation pressures and the depression of the vapour pressures of liquids.

T. H. P.

**Modifications in Laboratory Apparatus.** T. S. PATTERSON (*J. Soc. Chem. Ind.*, 1924, **43**, 281—283T).—The following apparatus is described and figured: (a) A water condenser which can be suspended in the neck of a flask and containing a centre tube down which additions may be made to the contents of the flask during a reaction. (b) A simple extractor working at the b. p. of the solvent, and less fragile than the Soxhlet type. (c) A simple pressure equaliser. (d) A device for absorbing fumes, consisting of a modified calcium chloride tower packed with pumice; a suitable absorbent, contained in a dropping funnel at the top, is allowed to trickle down the tower. (e) A simplified vacuum distillation receiver of the rotating type. (f) A test-tube stand with a wedge-shaped base, enabling moisture from the tubes to drain away rapidly. A large number of holes in the die of a sodium-wire press hastens the preparation of sodium-wire.

S. K. T.

**Apparatus for the Accurate Determination of Solubilities.** E. COHEN, W. A. T. DE MEESTER, and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1924, **112**, 150—155).—An apparatus is described and figured which is similar to one previously used (cf. A., 1923, ii, 386), but suitable for determinations carried out at normal pressure and higher temperatures. The solubilities of thallium sulphate at 30°, 40°, and 60° and of silver nitrate at 30° have been determined by this method. The former values are within about 0.2% of those of Berkeley (A., 1904, ii, 648), but the solubility of silver nitrate is 73.82 g. per 100 g. of solution, compared with 73 obtained by Schreinemakers and de Baat (*Arch. Néerland.*, 1910, [ii], **15**, 415).

L. F. G.

**Calorimeter for the Electrical Adiabatic Determination of Heats of Solution.** E. COHEN, A. L. T. MOESVELD, and W. D. HELDERMAN (*Z. physikal. Chem.*, 1924, **112**, 141—149).—An improved form of an apparatus previously used (A., 1920, ii, 584) is described and figured; it has given results reproducible to within about 0.3%. The method of employing it where a negative heat of solution occurs is explained. Three determinations of the molecular heat of solution of ammonium nitrate gave the values —3579, —3583, and —3589 cal., respectively.

L. F. G.

**Apparatus for the Catalytic Dehydrogenation of Alcohols.** S. G. WILLMOTT (*Analyst*, 1925, **50**, 13—16).—The usual laboratory methods for preparing aliphatic aldehydes were found unsatisfactory, never giving yields of more than, e.g., 20% of the theoretical quantity for propaldehyde, but by dehydrogenating the alcohol, using an improved form of Neave's apparatus (A., 1909, ii, 835), an average yield of 30% was obtained in this case. The alcohol vapour is passed at a controlled speed through a pre-heater into the dehydrogenation tube (at 300°) containing the copper catalyst; for small operations copper-bronze may be used.

D. G. H.

**Theories of Strong Electrolytes and their History.** J. J. VAN LAAR (*Z. anorg. Chem.*, 1924, **139**, 108—134).—A mathematical paper in which Debye's theory (cf. A., 1923, ii, 459, 617, 724, 827) is correlated with the Rudolphi-van't Hoff laws (cf. *Archives Teyler*, 1900, [ii], **7**, 1).  
S. K. T.

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## Mineralogical Chemistry.

**Constitution of the Silicates. Chlorites.** V. ISKYUL (*Private Pub.*, Petrograd, 1917).—Analyses of the following minerals are given, together with data regarding the solubility of the silica in acid and alkali, and considerations of constitution: forsterite, olivine, glinkite, enstatite, bronzite, anthophyllite, actinolite, serpentine, chrysotile, antigorite, melanite, and pyrope garnet, clinocllore, leuchtenbergite, penninite, rhodochrome, tabergite, corundophyllite, and prochlorite. Olivines are classed as orthosilicates; on ignition, the reactions, (a)  $\text{Fe}_2\text{SiO}_4 + \text{O} = \text{Fe}_2\text{O}_3 + \text{SiO}_2$ ; (b)  $\text{Mg}_2\text{SiO}_4 + \text{SiO}_2 = 2\text{MgSiO}_3$ , occur. The solubility of amphibole silica is twice as great as that of pyroxene silica. Experiments with serpentine indicate the occurrence of the reaction,  $\text{H}_4\text{Mg}_3\text{Si}_2\text{O}_9 = 2\text{H}_2\text{O} + \text{Mg}_2\text{SiO}_4 + \text{MgSiO}_3$ . The serpentines are classed as metasilicates. The experiments support Vernadsky's theory that the chlorites are salts, and complex compounds of these salts, of the acids of the formula  $\text{Al}_2\text{Si}_{m+2}\text{O}_{2m-n+7}(\text{OH})_{2n}$ .

### CHEMICAL ABSTRACTS.

**Composition of Melilite.** A. N. WINCHELL (*Amer. J. Sci.*, 1924, 8, 375—384).—It is suggested that all minerals of the melilite group conform to the general type  $\text{R}_2\text{O}_7$  (R including silicon), the dominant members being gehlenite ( $\text{Ca}_2\text{Al}_2\text{SiO}_7$ ) and akermanite ( $\text{Ca}_2\text{MgSi}_2\text{O}_7$ ). In substituted members,  $\text{Fe}''$  replaces part of the magnesium and  $\text{Fe}'''$  part of the aluminium. Alkalis present may be assigned either to  $\text{Na}_2\text{Si}_3\text{O}_7$ , or  $\text{NaAl}_3\text{SiO}_7$ . Contrary to the views of Buddington and Schaller, grossularite and andradite are not miscible with melilites. Excess of silica may exist in the interatomic spaces of the molecules. This increases the density but has little effect on the index of refraction.

H. T.

**Sincosite, a New Vanadium Mineral.** W. T. SCHALLER (*Amer. J. Sci.*, 1924, [v], 8, 462—480).—A new vanadium mineral, sincosite, from Sincos (Peru), is described. It probably belongs to the uranite group; its chemical composition is  $\text{V}_2\text{O}_4 \cdot \text{CaO} \cdot \text{P}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  ( $x=4$  or  $5$ ). Traces of selenium are also present. It occurs as small, brittle, green crystals ( $d\ 2.84$ ), which closely resemble crystals of torbernite in shape, habit, and optical properties. Most of the crystals are uniaxial, but some are biaxial; nearly all become biaxial on keeping, this form probably corresponding with a lower hydrate. They revert to the uniaxial form when stored in a desiccator over dilute sulphuric acid.

S. K. T.

**Analysis of the New Germanium-Gallium Mineral Germanite.** F. W. KRIESEL (*Chem.-Ztg.*, 1924, 48, 961—963).—

The finely-ground mineral is dissolved in a mixture of nitric and sulphuric acids and the solution is evaporated until the former is expelled; hydrochloric acid is added and the germanium distilled off as tetrachloride while a current of chlorine is passed through the apparatus. The distillate is treated with hydrogen sulphide, the germanium sulphide dissolved in ammonium sulphide, reprecipitated by the addition of sulphuric acid, collected, washed with dilute acid, dried, and ignited; the oxide residue is reoxidised with nitric acid and heated repeatedly with ammonia until of constant weight. Arsenic is removed from the residue in the distillation flask by a second distillation in the presence of a stream of sulphur dioxide and the remaining liquid is used for the determination of lead, copper, iron, and zinc. A second but much larger portion of the mineral is dissolved as before and the solution is repeatedly evaporated with hydrochloric acid to remove germanium, then electrolysed to remove copper and arsenic, and finally evaporated with nitric and sulphuric acids to dryness. Iron, aluminium, and gallium are precipitated in the aqueous solution of this residue by the basic acetate process, cadmium, cobalt, nickel, manganese, magnesium, and calcium being determined in the filtrate. The iron precipitate is dissolved in dilute sulphuric acid, the solution reduced with hydrogen sulphide, the excess of which is boiled off, and, after neutralisation with sodium carbonate, the gallium is precipitated by boiling with cuprous oxide. The precipitate is dissolved in nitric acid, the copper removed with hydrogen sulphide, and the gallium separated from aluminium by addition of sodium acetate and arsenite followed by saturation of the solution with hydrogen sulphide. The gallium-arsenic sulphide precipitate is dissolved in nitric acid, which is removed by evaporation with hydrochloric acid and the arsenic is precipitated as sulphide, the gallium being recovered from the filtrate by addition of ammonia. For the determination of molybdenum, a third portion is dissolved in nitric acid, the solution filtered, treated with ferric nitrate, neutralised with sodium carbonate, diluted considerably, and boiled, the precipitate of basic iron salts dissolved in hydrochloric acid, and the molybdenum precipitated as sulphide, which is dissolved in ammonium sulphide, reprecipitated, and subsequently dissolved in nitric acid. The solution is evaporated with hydrochloric acid and sulphur dioxide to expel arsenic and the molybdenum eventually precipitated as lead molybdate. Tungsten trioxide, silica, titanium dioxide, and barium sulphate are determined in the material insoluble in aqua regia. An analysis of a clean specimen of germanite by the above process gave the following (percentage) figures: Cu, 45.39; Pb, 0.66; Zn, 2.58; Fe, 4.56; Ge, 8.70; S, 30.65; As, 4.13; Ga, 0.76;  $\text{SiO}_2$ , 0.23;  $\text{WO}_3$ , 0.18;  $\text{TiO}_2$ , 0.004; Mo, 1.282; Mn, 0.02; Ni, 0.001; Co, 0.013; Cd, 0.07; CaO, 0.12; MgO, 0.055; C, 0.136; Ag and Au, 0.005. The mineral occurs fairly intimately mixed with tetrahedrite, which itself contains 0.14% Ge.

A. R. P.

## Analytical Chemistry.

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**Multiple Gas Analysis Apparatus.** M. N. J. DIRKEN (*J. Scientific Instruments*, 1924, 2, 55—60).—The ordinary apparatus is modified so that the rate of working is doubled whilst the same accuracy is attained. The absorption vessel, which is an improved Shipley and Henderson type, can be readily detached from the burette and placed in a shaking machine while another is put in its place. By this means four or five sets of absorption vessels may be used in rotation. A new sampling tube containing no stopcocks and a new method of collecting and transferring gas samples are described.

S. K. T.

**Hæmoglobinometer.** K. BÜRGER.—(See i, 177.)

**Economic Anode for Rapid Electro-analysis.** A. LASSIEUR (*Bull. Soc. chim.*, 1924, [iv], 35, 1530—1532).—The anode described by Bertiaux (A., 1924, ii, 695) is criticised partly on account of the inferior deposits obtained, especially with antimony, zinc, and lead, on the perforated foil, but mainly on account of the cost of the heavy platinum-iridium foil and of the possibility of errors introduced by the use of silver supports. The latter source of error may be eliminated by substituting special steel for the silver. A more economic rotating anode is described in which a thin platinum wire is attached to a suitable glass agitator. This anode cannot be used for the analysis of brasses and bronzes containing lead in which the lead is deposited on the anode as lead peroxide, but the conditions have now been determined for the successive deposition of copper and lead in the metallic state. Anodes with large surfaces and oxidising powers are not always advantageous in electro-analysis.

R. B.

**Automatic Gas Analysis.** L. LÖWENSTEIN (*Z. physikal. Chem.*, 1924, 110, 799—800).—A method is described for the accurate determination of small quantities of hydrogen, methane, etc., in presence of a large excess of oxygen (or *vice versa*), in which the gases, after passing through a combustion chamber, enter a hair hygrometer, the alterations in the length of the fibre being an indication of the water content (*i.e.*, of the hydrogen or oxygen content of the original gas).

J. S. C.

**Gasometric Determinations by Combustion with Copper Oxide.** I. J. ŠVÉDA (*Chem. News*, 1925, 130, 1—5).—Hydrogen and carbon monoxide are completely burnt to water and carbon dioxide, respectively, whilst methane remains unchanged when brought into contact with copper oxide at 280—290°. In order to analyse a mixture of these gases confined over mercury in a eudiometer, a miniature platinum-wound electric furnace containing a mixture of 3 parts of cupric oxide and 1 part of ceric oxide is introduced into the gas and the temperature adjusted by a pre-

determined external resistance to 280—290°. A slight error is introduced into the analysis by the adsorption of a certain amount of carbon dioxide by the furnace, but the volume after combustion of pure carbon monoxide is practically the same as before. The furnace is made by winding a few turns of platinum wire, 0.16 mm. thick, around a narrow porous crucible made of Marquardt paste, covering the wire with a further quantity of the paste, packing the crucible with the oxide mixture, and drying by heating it to redness. After use, the cupric oxide may be regenerated by heating the furnace at a red heat in air. A. R. P.

**Determination of the Hydrogen-ion Concentration of the Soil.** (1) W. R. G. ATKINS. (2) R. M. BARNETTE, D. J. HISSINK, and J. VAN DER SPEK.—(See i, 220.)

**Acid-Base Titrations and Equilibria of Weak Bases and Acids.** L. J. HARRIS (*Nature*, 1925, 115, 119—120).—By determining the volume of standard alkali or acid required to titrate a solute over a given  $p_H$  range or to a given  $p_H$  end-point, substances with feebly acidic or basic properties can be determined to an accuracy of the same order as that of an ordinary acid-base titration. It is possible to resolve a compound titration curve into its components and determine a number of acids and bases or ampholytes present simultaneously in a mixture, even when partial overlapping occurs. The method has been applied to determinations of proteins in solution, to determinations of molecular weights and dissociation constants, and to the detection of chemical changes. For glycine and arginine, accurate values of  $\alpha$  in the equation  $[H^+] = \alpha[\text{free HCl}]$  have been calculated.

A. A. E.

**Use of Aminosulphonic Acid as a Standard in Volumetric Analysis.** L. HERBOTH (*Arch. Pharm.*, 1924, 262, 517—519).—Aminosulphonic acid is easily prepared (cf. Hofmann, "Lehrbuch der anorg. Chemie," 4th ed., 1922, 174) by saturating a concentrated solution of hydroxylamine hydrochloride with sulphur dioxide. The crystals (decomp. 205°) are anhydrous and quite stable in air. The compound yields ammonia when treated with sodium hydroxide and its barium and mercurous salts are sparingly soluble. It can be satisfactorily used as a standard in alkalimetry in either 0.1N- or 0.01N-solution, with dimethylaminoazobenzene, methyl-red, phenolphthalein, or rosolic acid as indicator. W. A. S.

**Conductivity of Water.** F. BORDAS and F. TOUPLAIN (*Ann. Falsif.*, 1924, 17, 516—524).—The conductivity of a water affords the best physical test of its composition. The presence of even small numbers of hydrogen and hydroxyl ions allow of the passage of a current, and dissolved gases, particularly carbon dioxide, appreciably increase the conductivity. If, however, as much as 300 mg. of a salt per litre is present the effect of the dissolved gas disappears. D. G. H.

**Determination of Water in Mixtures of Ether, Alcohol, and Water.** R. K. NEWMAN (*J. Soc. Chem. Ind.*, 1924, 43, 285—287T).—A measured volume of the mixture is boiled and the vapour passed over calcium carbide and then through concentrated sulphuric acid. The acetylene formed from the water is collected in a Schiff nitrometer over potassium hydroxide solution and measured. The other constituents are retained by the acid. The apparatus is swept out with a stream of carbon dioxide, which is also used to remove any acetylene dissolved in the acid. From the results of experiments made by this method, it is concluded that ether dried over sodium for six months still contains 0.14% by weight of water.  
S. K. T.

**Determination of Minute Quantities of Iodine in Biological Material.** F. C. KELLY and A. D. HUSBAND.—(See i, 183.)

**Use of Iodic Acid and Potassium Hydrogen Carbonate for the Preparation of Standard Solutions.** M. RUSZKOWSKI (*Roczniki Farmacji*, 1924, 2, 108—109; from *Chem. Zentr.*, 1924, ii, 215).—For the volumetric determination of thiosulphate the author recommends the use of iodic acid. The iodic acid is allowed to react with potassium iodide solution and the iodine thus liberated is titrated with the thiosulphate solution.  
G. W. R.

**Determination of Oxygen in Organic Compounds. II.** H. TER MEULEN (*Rec. trav. chim.*, 1924, 43, 899—904).—Modifications of the catalytic hydrogenation method of determining oxygen (A., 1922, ii, 717) are described, which render it applicable to organic compounds containing one or more of the elements nitrogen, sulphur, and halogens.  
W. E. E.

**Rapid Determination of Sulphur.** F. KÜHL (*Z. anal. Chem.*, 1924, 65, 185—186).—The sulphur is dissolved in a known volume of hot standard sodium hydroxide solution, and, after cooling, is oxidised to sodium sulphate by addition of hydrogen peroxide; the excess of alkali is then titrated with standard hydrochloric acid.  
S. K. T.

**Detection of Sulphur Dioxide, Nitrogen Dioxide, and some Acids.** E. EEGRIWE (*Z. anal. Chem.*, 1924, 65, 182—185).—Well-known qualitative reactions are modified so as to increase their sensitivity. Sulphur dioxide is detected by lowering into the gas a rod thinly coated with a layer of moist zinc nitroprusside which has been rendered transparent by exposure to ammonia (test for ammonia). The coating turns rose to deep red, according as the concentration of sulphur dioxide is small or large. If the rose-coloured layer is allowed to dry, it becomes white and the change is then more readily observed. Nitrogen dioxide is detected by holding in the gas a drop of 1% aqueous benzidine hydrochloride solution on a glass rod and then adding it to a drop of 0.04% aqueous  $\beta$ -naphthol solution. A red colour develops which changes to rose- or dark red-violet on addition of ammonia. A drop of 20% aqueous ammonium molybdate solution held in silicon tetra-

fluoride on a piece of paper turns yellow, first on the edges, then throughout, in the absence of hydrogen sulphide. Tests, based on this reaction, are described for silicates and fluorides. S. K. T.

**Colorimetric Determination of Ammonia in Urine.** A. P. ORR.—(See i, 184.)

**Determination of Silica in Plant Material.** D. R. NANJI and W. S. SHAW.—(See i, 214.)

**Colorimetric Determination of the Inorganic Phosphorus of Serum.** R. ESSINGER and P. GYÖRGY.—(See i, 178.)

**Colorimetric Determination of Phosphorus.** C. RIMINGTON.—(See i, 183.)

**Sources of Error in the Determination of Phosphoric Acid by the Molybdate-Magnesia Method.** J. M. McCANDLESS and J. Q. BURTON (*Ind. Eng. Chem.*, 1924, **16**, 1267—1270).—Discrepancies in the gravimetric analysis of materials with a high phosphoric acid content (*e.g.*, superphosphates with 45—50% of phosphoric acid) are avoided by carefully testing the neutrality of the ammonia solution of the yellow precipitate prior to adding the magnesia mixture. A solution which is neutral to litmus gives correct results, an excess of acid giving high, and an excess of ammonia low results. If the solution is neutral or slightly alkaline before adding the magnesia, the precipitate remains white after strong ignition and contains only faint traces of molybdenum, but when hydrochloric acid is in excess the ignited precipitate is blue and contains an appreciable amount of molybdenum oxide. The origin of the latter is discussed, and exact details are given for carrying out the analysis. W. T. K. B.

**Determination of Small Quantities of Arsenic and its occurrence in Urine and in Fish.** H. E. COX (*Analyst*, 1925, **50**, 3—13).—Preliminary digestion of the organic material is best carried out by the Swedish method, where sulphuric and nitric acids are added in such a way as to preclude the formation of any large quantities of carbon which may retain or adsorb arsenic. Subsequent determination may be by Ramberg's process when not less than 0.01 mg. of arsenic is present. All traces of nitrous acid must first be removed, ammonium oxalate is then added, and the mixture boiled to expel sulphuric acid fumes. Hydrochloric acid, ferrous sulphate, and potassium bromide are then added before distilling into water, with subsequent titration of the distillate with potassium bromate solution. For quantities of arsenic less than 0.01 mg. the Marsh-Berzelius method is more trustworthy. Normal urine was found to contain up to 0.58 mg. of arsenic per litre, and fish, especially plaice, up to 3 parts per million. D. G. H.

**Distillation of Arsenious, Antimonious, and Stannic Chlorides.** K. RÖHRE (*Z. anal. Chem.*, 1924, **65**, 109—128).—The distillation of arsenious chloride from solutions strongly acid with hydrochloric acid is accelerated by the addition of calcium or aluminium chloride, but zinc, copper, and cadmium chlorides

have little effect. Phosphoric and sulphuric acids, whilst accelerating the volatilisation of the arsenic, tend to retain part as sulphate or phosphate. The most favourable procedure for the distillation of arsenious chloride solutions which do not contain antimony consists in slowly heating the solution containing calcium chloride and much hydrochloric acid at 130°, cooling somewhat, adding more hydrochloric acid, and again distilling up to 130°. If antimony is present, the distillation is effected at water-bath temperature while a current of carbon dioxide is passed through the apparatus for 2 hours. Quinquevalent arsenic is most satisfactorily reduced by means of pyrogallol previously to distillation. Antimonious chloride may be distilled from solutions containing much sulphuric acid provided that hydrobromic acid is slowly dropped into the flask during the distillation, which is conducted at 180°. Stannic chloride may also be distilled under these conditions. A. R. P.

**Electrical Determination of Soil Alkali.** A. F. JOSEPH, F. J. MARTIN, and J. S. HANCOCK.—(See i, 222.)

**Iodometric Micro Determination of Sodium.** M. BÁLINT (*Biochem. Z.*, 1924, 150, 424—443).—The sodium is precipitated by the addition of an alkaline solution of potassium pyroantimonate, centrifuged in the presence of 20% alcohol, and washed with 50% alcohol. It is then treated with 2% potassium iodide solution and the liberated iodine is titrated. Serum is first ashed (cf. Bálint and Petow, A., 1924, ii, 500; Kramer and Tisdall, A., 1921, ii, 463).  
J. P.

**Determination of Sodium in Serum.** B. KRAMER and I. GITTLEMAN.—(See i, 180.)

**Separation of Small Quantities of Calcium from Large Amounts of Magnesium.** V. RODT and E. KINDSCHER (*Chem.-Ztg.*, 1924, 48, 953—954, 964—965).—Details are given of a critical study of the oxalate and sulphate methods of separating calcium from magnesium. In the former method, the calcium may fail entirely to precipitate under any conditions when its actual amount is small and a preponderating quantity of magnesium is present, the precipitate obtained consisting entirely of magnesium oxalate. Precipitation of calcium sulphate by addition of alcohol to a solution of the mixed sulphates, evaporation to dryness of a solution of the mixed chlorides with sulphuric acid followed by an alcohol extraction, and digestion of the dried chlorides with sodium sulphate solution containing alcohol all gave very low figures. The best results (1 to 5% low) were obtained by evaporating the chloride solution to dryness with just sufficient dilute sulphuric acid or lithium sulphate to convert the calcium present into sulphate and extracting the moistened residue with methyl alcohol containing 10% of ethyl alcohol. The residual calcium sulphate is dissolved in dilute hydrochloric acid and converted to oxalate in the usual way. [Cf. B., Mar.]  
A. R. P.

**Simplification in the Detection of Certain Cations.** P. SACCARDI (*Annali Chim. Appl.*, 1924, 14, 303—305).—Separation

of copper from cadmium in qualitative analysis may be effected by taking advantage of the fact that the electrolytic solution tension of iron is intermediate between those of copper and cadmium, the former, but not the latter, being displaced from its salt solutions by iron. The blue ammoniacal solution remaining after removal of the bismuth is rendered acid with hydrochloric acid and then shaken with iron filings, the copper being deposited in a few minutes; without removal of the filings, hydrogen sulphide is passed into the liquid and precipitates the cadmium.

To separate tin from antimony, the mixed sulphides are dissolved in hydrochloric acid and the solution is treated with a little magnesium and divided into two parts. (1) If tin is present, addition of mercuric chloride solution causes the formation of a brown or white precipitate of mercurous chloride and metallic mercury; another method of detecting tin consists in rendering the solution strongly acid with concentrated hydrochloric acid and boiling it with a trace of arsenious anhydride, brownish-black arsenic being precipitated. (2) With excess of chlorine water, antimony is precipitated as the pentoxide.

T. H. P.

**Separation of Cadmium from Zinc by Means of Hydrogen Sulphide.** G. LUFF (*Z. anal. Chem.*, 1924, **65**, 97—109).—Ammonium sulphate assists, whilst ammonium chloride retards, the precipitation of cadmium and zinc as sulphides from acid solutions. For the separation of cadmium from zinc by this procedure, a minimum amount (7 to 8 c.c.) of strong hydrochloric acid ( $d$  1.18) or sulphuric acid ( $d$  1.836) per 100 c.c. of solution is necessary; cleaner separations are effected if the solution contains ammonium sulphate and is saturated with hydrogen sulphide at 80° and then somewhat diluted with cold water. Under these conditions, the cadmium sulphide is precipitated in the form of orange-red, microscopic, six-sided tablets and rosettes. Cadmium sulphide is usually converted into sulphate for weighing, but it may also be converted into cadmium diammonium ferrocyanide, which is dried at 110° and weighed. The salt forms hexagonal prisms insoluble in dilute ammonia and is obtained by precipitation of a warm ammoniacal solution of cadmium and ammonium chlorides with potassium ferrocyanide. [Cf. *B.*, Mar.] A. R. P.

**Electrolytic Separation of Copper, Antimony, and Bismuth from Lead.** A. LASSIEUR (*Compt. rend.*, 1924, **179**, 632—634).—Under the conditions recommended by Schoch and Brown (*A.*, 1916, ii, 578), the lead deposit is too heavy owing to the presence of hydroxide. This may be obviated by working with a solution containing 15—20% of concentrated hydrochloric acid, using an auxiliary potential of 440 millivolts, or preferably with a 2.5% solution of hydrofluoric acid and 400 millivolts. In presence of lead, bismuth may be quantitatively deposited in presence of nitric acid and hydroxylamine hydrochloride with an auxiliary potential of 200—240 millivolts. The separation of lead from copper presents little difficulty; antimony, when present in the quinquivalent condition, furnishes a good deposit in presence of hydrochloric



acid, but, from its tervalent compounds, adherence is usually poor. The auxiliary potential needed for antimony is 240 millivolts; deposition of lead does not begin below 350 millivolts and is, in presence of antimony, satisfactory only when the concentration of lead is less than 0.2 g. per 100 c.c. H. J. E.

**Conversion of Cupric into Cuprous Sulphide by Heating in a Current of Hydrogen.** F. L. HAHN (*Z. anal. Chem.*, 1924, **65**, 134—137).—Polemical. The temperature range for the conversion of cupric sulphide into cuprous sulphide by heating in hydrogen is at most only 60°, and correct results cannot be obtained by the method recommended by Wilke-Dörfurt (A., 1924, ii, 785). Good results are obtained only when a mixture of hydrogen and hydrogen sulphide is employed and the cuprous sulphide cooled in an atmosphere of carbon dioxide containing methyl alcohol vapour (cf. Hahn, A., 1917, ii, 543). A. R. P.

**Determination of Small Quantities of Copper in Tissues.** A. N. CURRIE.—(See i, 183.)

**Oxidimetric Determination of Manganese in Hydrofluoric Acid Solution.** II. J. HOLLUTA and J. OBRIST (*Monatsh.*, 1924, **44**, 209—218; cf. A., 1921, ii, 522).—Some important differences between the authors' method (*loc. cit.*) and that of Metzger and Marrs (A., 1912, ii, 94; 1913, ii, 344) are pointed out. The method is shown to be trustworthy in the presence of large or small quantities of most of the important metals with the exception of calcium, aluminium, chromium, and bismuth. Copper must be in the cupric form, whilst antimony retards the reaction considerably. The presence of arsenate ions accelerates it, and it is thought possible that under suitable conditions arsenic may be substituted for hydrofluoric acid. Magnesium in larger amounts causes the formation of a white precipitate and lengthens the reaction period somewhat. The presence of bismuth disturbs owing to separation of basic salts at the low acidity required by the method. Aluminium in small quantities may be present, but not calcium. Less permanganate is required as the quantity of calcium increases, the probable cause being the formation of a double fluoride of calcium and manganese as well as adsorption effects, especially when large amounts of calcium are present. The colour of the chromium ions hinders a correct spectroscopic determination of the end-point under the conditions prescribed. Attempts to substitute hydrofluosilicic, phosphoric, or arsenic acid for hydrofluoric did not show promising results. Methods of modifying the reaction by making it the basis of electrometric and potentiometric processes are suggested (cf. Müller and Wahle, A., 1923, ii, 881). A. C.

**Determination of Manganese.** G. BERTRAND.—(See i, 223.)

**Determination of Iron in Small Quantities of Biological Substances.** M. M. MURRAY.—(See i, 183.)

**Analysis of Germanite.** F. W. KRIESEL.—(See ii, 153.)

**Determination of Bismuth.** W. AUTENRIETH and A. MEYER.—(See i, 182.)

**Bromometric Determinations.** W. MANCHOT and F. OBERHAUSER (*Z. anorg. Chem.*, 1924, **139**, 40—50).—Ferrous iron in solution is determined by adding standard hypobromite solution, acidifying, adding excess of arsenious acid solution, and titrating back with bromine (or bromate) after adding phosphoric acid. Nitrites are oxidised to nitrates with a known excess of bromine in presence of sodium hydrogen carbonate, a reaction which is complete in 5 minutes. Excess of alkali arsenite is added and titrated back with bromine after acidification. Cobalt may be determined similarly after precipitation as potassium cobaltinitrite. Tin is oxidised in hydrochloric acid solution with bromine, and hydrogen peroxide with hypobromous acid, the added reagent being titrated back in the usual manner. Carbamide is determined in the same way as ammonia, but the hypobromite mixture is allowed to react for 10—15 minutes. Sulphurous acid, hydrogen sulphide, and thiosulphates are now determined by allowing the solution to flow under the surface of a hypobromite solution, which is then titrated as above. Hypochlorites may also be determined bromometrically. Solutions of arsenious acid acidified with hydrochloric acid may be used in these titrations when the latter are carried out in acid solution.

[With H. WETTSTEIN.]—The bromine-vapour pressures of 0.1*N*-solutions of bromine in hydrochloric acid, potassium bromide, and acetic acid solutions decrease with increasing concentration of the latter solutions, and are greater in hydrochloric acid solutions than in potassium bromide solutions of the same normality. Bromine solutions in *N*-potassium bromide are the most suitable for general use (cf. A., 1924, ii, 274, 507).

S. K. T.

**Selective Determination of Vanadium in Presence of Iron and Chromium.** I. Determination of Vanadium in Presence of Iron. K. SOMEYA (*Z. anorg. Chem.*, 1924, **139**, 237—245).—The vanadium in a vanadium steel may be determined by a modification of Knop's method of determining iron (cf. A., 1924, ii, 351). The alloy, which must not contain tungsten, but may contain manganese, chromium, molybdenum, small amounts of copper, etc., is dissolved in sulphuric acid; a slight excess of potassium permanganate is added and the solution decolorised with a few drops of sulphurous acid solution; 15 c.c. of phosphoric acid mixture and 3 drops of diphenylamine sulphate solution (*loc. cit.*) are then added, the whole is diluted to 120—200 c.c. and titrated at 100° with 0.1*N*-ferrous sulphate solution in dilute sulphuric acid until the violet-blue solution becomes bright greenish-blue. With very large proportions of iron the end-point is not distinct. Allowance must be made for oxidation of the indicator. The end-point is practically independent of the acid concentration, although hydrochloric acid must not be used. Kelley and Conant's method (A., 1916, ii, 274) may also be used with the diphenylamine internal indicator.

S. K. T.

**Colour Reaction for Glycerol.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1924, **61**, 1497—1498).—By oxidation with permanganate

and treatment with Schiff's reagent, glycerol gives a positive coloration in 0.04% solution. The common organic acids do not interfere. S. I. L.

**Determination of Sugar in Blood.** (1) M. GILBERT and J. C. BOCK. (2) E. G. B. CALVERT.—(See i, 179.)

**Determination of Free Sugar in Total Blood.** H. BIERRY and L. MOQUET.—(See i, 179.)

**Colorimetric Determination of Sugar in Blood.** F. J. PATON.—(See i, 180.)

**Differentiation of Citric from Tartaric Acid.** W. PARRI (*Giorn. Chim. Ind. Appl.*, 1924, 6, 537—538).—With a sulphuric acid solution of phosphomolybdic and vanadic acids, citric acid gives a deep blue coloration, which becomes green on heating but resumes its original colour on cooling. This reaction, which is disturbed to some extent by the presence of other compounds, serves for the detection of a small proportion of citric acid in tartaric acid. [Cf. B., 1925, 114.] T. H. P.

**Colour Reaction, Supposed Specific for Formaldehyde, Produced by Glyoxylic Acid.** FOSSE and A. HIEULLE (*Compt. rend.*, 1924, 179, 636—638).—Glyoxylic acid yields with Schryver's reagent an intense magenta-red; this coloration has hitherto been considered specific for formaldehyde. The reaction is extremely sensitive, being given by 0.001 mg. of glyoxylic acid at a concentration of 1 in  $10^6$ . The author considers that the presence of formaldehyde in green leaves cannot be regarded as proved.

H. J. E.

**Effect of different Ammonium Salts in Rothera's Reaction.** H. W. VAN URK (*Pharm. Weekblad*, 1925, 62, 8—10).—Saturated solutions of many ammonium salts containing acetone were treated with ammonia and sodium nitroprusside; the test is most sensitive in presence of ammonium sulphate. There is no relation between the solubility and the sensitiveness. S. I. L.

**Action of Sodium Nitroprusside on Acetone and Acetaldehyde.** H. W. VAN URK (*Pharm. Weekblad*, 1925, 62, 2—8).—The colorations given by pure acetone and pure acetaldehyde in presence of sodium nitroprusside in alkaline and acid solutions are tabulated; acetone gives an orange-yellow colour in alkaline solution, changing to purplish-red on acidifying, acetaldehyde reddish-purple in alkaline solution, nearly discharged on acidifying. The latter reaction is attributed to aldol formation, which is reversed in acid solution. Both reagents give green colorations on warming the alkaline solution. In ammoniacal solution acetaldehyde gives no coloration, acetone a violet ring; for testing for acetone in urine, ammonium salts should be present, but alkali tartrates or acetates are not necessary. S. I. L.

**Colour Test for Aniline and Toluidine.** H. D. MURRAY (*Chem. News*, 1925, **130**, 23).—The amine is dissolved in warm 50% sulphuric acid and a saturated solution of potassium dichromate is added. When no further change in colour takes place, the solution is poured into a large excess of water, and rendered alkaline with ammonia. Three colour stages are noticed, (i) on the addition of the dichromate, (ii) on pouring into water, and (iii) on making alkaline. Aniline gives purple, purple, and dark purple; *o*-toluidine, blue, purple to orange-yellow, and bright blue; *m*-toluidine, green, brown, and dark purple; *p*-toluidine, reddish-brown, straw-colour, and later darkens slightly. The di-substituted tertiary amines give no colour change on pouring into water. I. E. B.

**Interference of Ammonia with the Hypochlorite Reaction for Aniline.** E. S. WEST (*Ind. Eng. Chem.*, 1924, **16**, 1270—1271).—The inhibitory effect of a relatively low concentration of ammonia and its salts on the formation of a violet coloration when calcium hypochlorite is added to an aqueous solution of aniline is due to its reaction with the hypochlorite and to its effect on the coloured product. The effect is largely avoided by acidifying the solution or by removing the ammonia by aëration (after making alkaline, if ammonium salts are present) before adding the hypochlorite. Sodium chloride and other salts also interfere with the reaction if present in very high concentrations. W. T. K. B.

### **Directive Influence of Substituents in the Benzene Ring.**

**I. Chemical Determination of the Meta Isomeride in some Disubstituted Derivatives of Benzene.** A. W. FRANCIS and A. J. HILL (*J. Amer. Chem. Soc.*, 1924, **46**, 2498—2505).—When bromine in aqueous solution (or acidified bromate-bromide solution) is added to a mixture of an *o*-, *m*-, and *p*-derivative of aniline or phenol, the *m*-derivatives are completely converted into tribromo compounds, whilst the *o*- and *p*-derivatives yield dibromo compounds. The consumption of bromine by a mixture of isomerides is therefore a measure of the proportion of *m*-isomeride present. The method can be extended to nitro compounds by subjecting these to a preliminary reduction with titanous chloride, and is accurate to 0.5%. In the case of *o*- and *m*-toluidines, *o*-phenylenediamine, *o*-aminophenol, and *p*-phenetidine, the bromine titration must be carried out below 0° to prevent formation of deeply coloured oxidation products which mask the end-point. Precipitation of partly-brominated products can be avoided by the use of sufficient solvent (alcohol); this difficulty is greatest with *p*-compounds. The carboxyl, sulphonic, and aldehyde groups are readily displaced by bromine, except at low temperatures, from *o*- and *p*-amino and hydroxy derivatives, the last-named group giving rise to carbon monoxide. Quinol does not absorb bromine at ordinary temperatures, and pyrocatechol, *p*-phenylenediamine, and *p*-aminophenol are indifferent at 0°. Resorcinol is brominated quantitatively, but mixtures of it with quinol give low results unless a large excess of bromine is present. *m*-Phenylenediamine decomposes on bromination, but if mixed with an equal amount of resorcinol,

both compounds are tribrominated quantitatively, without decomposition. Phloroglucinol yields first a precipitate of the tribromo derivative, which then redissolves with formation of the compound  $C_6Br_3(OBr)_2 \cdot OH$ , and this is finally converted into the compound  $C_6Br_3(OBr)_3$ . Both of these are reconverted into the tribromo derivative by potassium iodide, so that they do not interfere with the determination of phloroglucinol by this method. F. G. W.

**Detection and Determination of Indican in Urine.** S. N. GORE.—(See i, 186.)

**The Tryptophan-Aldehyde Reaction.** E. KOMM (*Z. physiol. Chem.*, 1924, **140**, 74—79).—In the reaction previously described (A., 1923, ii, 194), the maximum intensity of colour is attained only after 5 days in the case of pure solutions of tryptophan, but is reached in a few hours in the presence of gelatin. The following substances also accelerate the intensification of the colour; oxidising agents, proline, proteins, and polypeptides containing proline or proline derivatives. E. S.

**Determination of Uric Acid by Benedict's method.** H. COHEN.—(See i, 184.)

**Determination of Uric Acid in Urine.** AUFRECHT.—(See i, 187.)

**Colour Reactions of Cryogenine with Heavy Metals.** L. BORNET (*J. Pharm. Chim.*, 1924, [vii], **30**, 356—358).—Saturated aqueous solutions of cryogenine react with neutral solutions of certain metallic salts as follows. Copper salts give a red coloration; mercury salts give a peach colour followed by a violet precipitate which, if the solution is shaken with benzene or ether, collects as a violet ring at the junction of the liquids. Ferric salts give a reddish-brown coloration, and a red colour is given by moderate quantities of chromates and dichromates in presence of hydrochloric acid. The sensitiveness is increased if one or two drops of hydrogen peroxide are added after the reagents are mixed. S. K. T.

**Determination of Urobilin in Human Excreta.** OPITZ and BREHME.—(See i, 187.)

**Fluorescent Oxidation Products of Bilirubin and their Importance as Sources of Error in Tests for Urobilin.** K. H. BARRENSCHEEN and O. WELTMANN.—(See i, 187.)

**Determination of Cholesterol and its Esters in Tissues.** II. J. A. GARDNER and F. W. FOX.—(See i, 182.)

**Colorimetric Determination of Lycopin.** S. J. B. CONNELL.—(See i, 214.)

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## General, Physical, and Inorganic Chemistry.

**Law of Variation with Temperature of the Conductivity of Solid Salts, and Possible Relationship to the Characteristic Spectrum of the Metal of the Salt.** P. VAILLANT (*Compt. rend.*, 1925, 180, 206—208).—If the liberation of electrons which carry the current which flows when an *E.M.F.* is applied to a layer of a solid salt (cf. A., 1924, ii, 456) is caused by the absorption of radiant energy produced by a monochromatic radiation of wave-length  $\lambda$ , then the coefficient  $K$  which connects the densities of the liberated electrons,  $n_1$ , with that of the particles giving rise to them,  $n$ , ( $Kn=n_1^2$ ) should vary with temperature and follow the same law as this radiation, viz.,  $K=K_0e^{-hc/\nu T\lambda}$ , where  $h$ =Planck's constant,  $c$ =velocity of light. The wave-lengths,  $\lambda$ , calculated in this way for the salts of sodium, potassium, and lithium are, within the limits of experimental error, those of the chief lines in the spectra of the elements.

J. W. B.

**Exceptionally Intense Absorption of a Radiation by the Emitting Atom.** M. DE BROGLIE and J. THIBAUD (*Compt. rend.*, 1925, 180, 179—180; cf. A., 1922, ii, 104).—Electrons arising from the re-absorption of fluorescent rays emitted in the radiator itself yield more intense rays than those directly emitted under the influence of exciting rays. This is demonstrated by a comparison of the  $K$ -radiation of tungsten (double  $\alpha$ ) and the  $K$ -fluorescent rays of the ionised element (copper, mercury, iodine, and barium). The relative intensity of the second increases with the atomic number, *i.e.*, in a reverse sense to that required by the laws of Bragg and Moseley. Atoms which emit  $\gamma$ -rays show the greatest probability of absorbing this radiation and converting it into photo-electrons. (Cf. Ellis, A., 1921, ii, 422.)

J. W. B.

**Excitation of Spark Spectra.** S. WERNER (*Nature*, 1925, 115, 191—192).—The vapour of the element under investigation is allowed to escape into a high vacuum from a small hole in a crucible heated to 1000°, the vapour being exposed to bombardment by a strong current of electrons (200—500 ma.). Besides the arc spectra, the spark spectra of sodium, potassium, cadmium, and zinc were observed with considerable intensity. In the case of lithium, few only of Morand's lines (A., 1924, ii, 509) were verified, but most of Schüller's results (*Naturwiss.*, July 11, 1924) were confirmed. A scheme is given of the terms of the doublet spectrum, in which the effective quantum numbers of the various terms are very similar to those for helium. With an accelerating potential of 150—200 volts, the intensity of the line 5485 Å. decreased very rapidly relatively to the arc lines. The spark spectrum of lithium was also excited, but with a smaller relative intensity, together with the arc spectrum, by means of an arc between the crucible and anode.

A. A. E.

**Line Spectrum of Nitrogen and Ionised Oxygen.** F. CROZE (*Compt. rend.*, 1925, **180**, 277—279).—In an earlier paper (*ibid.*, 1924, **179**, 1603) it was shown that in the spectrum of ionised nitrogen the most important triple combination terms are multiplets  $p_3d_3$ ,  $pp'_3$ ,  $p'_3d'_3$ ,  $d_3d'_3$ . In the present paper,  $p_3s_3$ ,  $d_3f_3$  are added. Following the rule of alternation, the line spectrum of ionised oxygen ( $O^+$ ) should be due to combinations of pairs of terms. The author's work on the Zeeman effect (A., 1914, ii, 600) using Landé's rules (*Z. Physik*, 1923, **15**, 189) gives quadruple combinations in the visible region. They are, as in nitrogen, of the type  $ps$  (Landé),  $pd$ ,  $df$ ,  $pp'$ ,  $p'd'$ ,  $dd'$ .  
R. A. M.

**Conditions for Appearance, and Structure, of Bands of Silver between  $\lambda=3330$  and  $\lambda=3358$ .** E. BENGTSSON and E. SVENSSON (*Compt. rend.*, 1925, **180**, 274—276; cf. A., 1924, ii, 78).—The arc spectrum of silver chloride in an atmosphere of hydrogen has been photographed in the second order, using a concave grating. It can be expressed as two Deslandres series  $P$  and  $R$ . The absent member  $m=0$  is taken as origin. If  $F$  and  $f$  are initial and final energy states of the molecule,  $n$  and  $m$  correspond respectively with nuclear and rotational vibrations;  $P(m)=F(nm)-f(n'm+1)$  and  $R(m)=F(nm+1)-f(n'm)$ . Two relations are given corresponding with the initial and final states of the molecule emitting light:  $h/8\pi^2A'=6.3$ , and  $h/8\pi^2A''=6.6$ , where  $h$  is the Planck constant,  $A'$  and  $A''$  are moments of inertia. Similar results were obtained with gold and copper (A., 1924, ii, 78).

The conditions for appearance of the bands and the size of the moment of inertia lead to the view that a dipole  $AgH$  is present.

R. A. M.

**Excitation of Forbidden Spectral Lines.** P. D. FOOTE, T. TAKAMINE, and R. L. CHENAULT (*Nature*, 1925, **115**, 265).—The mercury line  $1S-2p_1$  (Paschen's notation), the corresponding line of zinc, and both  $1S-2p_1$  and  $1S-2p_3$  of cadmium have been excited in the positive column of a hot-cathode discharge. The spectrum observed was of the arc type, only a few spark lines appearing. The cadmium lines 2239, 2267, 2307, and 2329 Å. (belonging to the group  $2p-2p_1$ ) were sharply absorbed by the positive glow. An unknown absorption line at 3086.7 was observed.

A. A. E.

**Mercury Line 2270 Å. ( $1S-2p_1$ ).** T. TAKAMINE and M. FUKUDA (*Physical Rev.*, 1925, [ii], **25**, 23—29).—The mercury line 2270 Å. was excited with an intensity intermediate between that of 2302 ( $2p_2-9d_2$ ) and 2323 ( $2p_2-8d_2$ ) by means of the branched arc of a mercury lamp of suitable form. In a heavy condensed discharge the lines 2270 and 2345 ( $2p_3-5s$ ) are shifted about 0.1 Å. towards the red whereas 2564 ( $2p_2-4S$ ) is displaced by an equal amount in the opposite direction.

A. A. E.

**Cathode Spectra of Metals and their Salts.** M. KIMURA and G. NAKAMURA (*Japan. J. Phys.*, 1924, **3**, 29—41).—The spectra

were obtained by using a vacuum tube with an aluminium anode and a cathode consisting of salts, chiefly chlorides, of the metals. The tube was excited by an induction coil or high-tension transformer and the glow at the cathode was focussed on the slit of the spectroscope. The results for magnesium, tin, and lead are shown in plates. The spectra resembled those of the spark. Zinc, cadmium, and bismuth presented the characteristics of the arc. Calcium, strontium, and barium gave only a few lines of their spectra. Tin gave both long and short lines, the former being ascribed to  $\text{Sn}^+$ , the latter to  $\text{Sn}^{++}$ .  
E. B. L.

**Cathode Spectra of Metals.** M. KIMURA and G. NAKAMURA (*Japan. J. Phys.*, 1924, 3, 43—44).—Similar results to those obtained with tin (cf. preceding abstract) were found for cadmium, aluminium, zinc, and lead. Long lines were attributed to singly ionised atoms and shorter lines to atoms with two positive charges. E. B. L.

**Regularities in the Arc Spectrum of Niobium.** W. F. MEGGERS (*J. Washington Acad. Sci.*, 1924, 14, 442—446).—The data for the arc spectrum of niobium have been examined from the point of view of certain properties of spectral lines in multiplet structures, such as constant wave-number differences, temperature classification, intensity rules accompanying transitions of azimuthal and inner quantum numbers, and Zeeman effect. The spectrum appears to possess structures similar to that of vanadium (Meggers, A., 1923, ii, 673; 1924, ii, 365). The ultimate rays which are most sensitive for the purposes of chemical analysis are 4100.99, 4079.73, and 4058.99 Å.  
M. S. B.

**Spectrum of Iron.** M. A. CATALÁN (*Anal. Fis. Quím.*, 1924, 22, 398—408; cf. A., 1924, ii, 435).—Six new multiplets formed with terms previously known have been found in the spectrum of iron. Ten new levels, only partially classified, originating two sets of multiplets, are also shown. Complete data, including also the results of Laporte (A., 1924, ii, 364), are given in tabular form.

G. W. R.

**Spark Spectrum of Potassium.** W. DAHMEN (*Z. Physik*, 1924, 29, 264—266).—Measurements of wave-lengths in the spark spectrum of potassium between 3400 and 7000 Å. have been made. Potassium electrodes in argon at a few mm. pressure were employed. The mean error in measurement was  $3/1000$  Å. The resemblance of the spark spectrum of potassium to the arc spectrum of argon shows at least a qualitative agreement with Kossel and Sommerfeld's displacement law (A., 1919, ii, 378).  
M. S. B.

**Connexion between the Spectra of Argon and Ionised Potassium.** T. L. DE BRUIN and P. ZEEMAN (*Nature*, 1925, 115, 116—117).—An examination of the results of Dahmen (cf. preceding abstract) with ionised potassium. The difference of about 847 is not characteristic, but that of about 1696 is present as 1712; also, 418.2 replaces 414. Some groups have been found



of regularly distributed lines exhibiting a regular distribution of intensities. Five examples of "quintets" are given. A. A. E.

**Spark Spectra of Tungsten and Mercury in the Extreme Ultra-violet.** BAYEN (*Compt. rend.*, 1925, 180, 57—59).—The spark spectra of tungsten and mercury in the region between 1850 and 2100 Å. have been investigated and a large number of new lines are tabulated.  
W. H.-R.

**Spark Spectrum of Tungsten in the Schumann Region.** L. and E. BLOCH (*Compt. rend.*, 1925, 180, 133—135).—A list is given of some 360 lines in the spark spectrum of tungsten between 1826 and 1453 Å.  
G. M. B.

**Electromagnetic Analysis of Positive Rays.** R. DÖPEL (*Ann. Physik*, 1925, [iv], 76, 1—28).—The positive rays were produced in the usual manner, the gas streaming through a fine capillary into the discharge bulb or cylinder and thence through the cathode into the inspection chamber maintained at the highest possible vacuum. The parabolas obtained by combined electric and magnetic deflection were observed on a willemite screen, and the energy along the line obtained when the magnetic field alone was used was measured by a sensitive thermo-couple. With a sufficiently high discharge potential energy curves for hydrogen show maxima on the positive side at distances approximately in the ratio 1 :  $\sqrt{2}$  : 2 and are attributed to molecules, fast atoms, and slow atoms. On the negative side, only fast and slow atoms are obtained, the negatively charged molecules being less stable. Addition of oxygen increases the relative number of molecules.

In addition to the usual features, the parabolas showed  $H_2^-$  molecules and  $He^-$  atoms. From the nature of the beading on the parabolas the author deduces the existence in the dark space of  $H_4$ ,  $O_4$ ,  $N_4$ , and  $He_2$ .  
E. B. L.

**Asymmetric Emission of Electrons by X-Rays.** W. SEITZ (*Physikal. Z.*, 1924, 25, 547—550).—The asymmetrical emission of electrons from a metal film placed in a beam of X-rays was examined by means of thin films of five different metals, sputtered on celluloid. The number of electrons emitted from the surface from which the X-rays emerged was always greater than from the surface on which the X-rays were incident, but the ratio of these two quantities decreased with increasing atomic weight. By retaining the slowest electrons by means of a retarding electric field or by means of a thin layer of a non-conductor painted on the film, the asymmetry was increased, being greater the smaller the atomic weight. Further, the magnetic spectra of the incident and emergent beams of electrons from a thin copper foil were simultaneously photographed. The maxima in both spectra corresponded with the same electron velocities, and the intensity of slow electrons was greater on the incident side, whilst that of the fastest electrons was greater on the emergent side. The asymmetry thus appeared to depend chiefly on the fast photo-electrons and not, or only to a small extent, on the slower Compton electrons.  
L. F. B.

**Electronic Bombardment of Metal Surfaces.** H. E. FARNSWORTH (*Physical Rev.*, 1925, [ii], 25, 41—57).—Curves constructed to show the ratio of secondary (emergent) to primary (incident) electron current as a function of the primary velocity depended on the previous heat treatment of the metals copper, silver, gold, tungsten, platinum, palladium, magnesium, and aluminium, but characteristic curves were obtained after heating the metals of higher m. p. to redness for some time. Velocity distribution curves of the secondary electrons are also given. Variation in the treatment of the copper surface and the effect of simultaneous exposure to radiation from a silica mercury arc were also studied.

A. A. E.

**Resonance Radiation and the Correspondence Principle.** C. G. DARWIN (*Nature*, 1925, 115, 81—82).—A discussion of the effect of the results of Wood and Ellett (*Proc. Roy. Soc.*, 1923, A, 103, 396) on the validity of the quantum theory, and a consideration of modifications. A well-known classical theorem, on application of the correspondence principle, specifies that if an atom can emit circular waves of equal frequency in either sense, then it can also emit linear waves. There is, however, no direct evidence for the emission of purely circular or linear waves from a single atom in the absence of a magnetic field; in presence of such a field, the degeneracy disappears. The theorem is not consonant with the physical reality of Bohr's orbits, but a new conception arises that a definite statement of phase is required; if this is so, it is not surprising that the older theory fails. Modifications concerning the conception of emission without disturbance of the existing ideas of quantised orbits of the electrons are considered and a serious difficulty in the hypothesis is specified.

A. A. E.

**Simple Method for Quantitative Studies of Ionisation Phenomena in Gases.** I. LANGMUIR and H. A. JONES (*Science*, 1924, 59, 380—383).—A simple type of tube contains no grid, the filament being mounted axially within a cylindrical electrode and passing through holes in the centres of end plates within, but not touching, the cylinder. The current-voltage curves obtained yield practically full information regarding the number and distribution of velocities of the electrons in the ionised gas. Experiments with argon and mercury vapour permit the recognition of five distinct classes of electrons in the ionised gas: (a) Primary electrons from the cathode. (b) Electrons scattered through small angles by elastic collisions (for mercury, none were observed). (c) Electrons which suffer a definite loss of energy; for mercury vapour, Eldridge's results (*Physical Rev.*, 1922, 20, 456) are confirmed. (d) Secondary electrons of moderate velocity, probably due to photo-electric emission from atoms of gas, ultra-violet radiation being produced from atoms excited by primary electrons. (e) Secondary electrons of low velocity, produced in by far the greatest number. Experiments are in progress using hydrogen, helium, nitrogen, neon, and carbon monoxide.

A. A. E.

**Width of Rays in the Balmer Series in the Oscillating Discharge.** (MLLE.) M. HANOT (*Compt. rend.*, 1925, 180, 54—56).—The width of the  $H_\beta$  and  $H_\gamma$  rays in the Balmer series in hydrogen has been determined. If the capacity and potential are  $C$  and  $V$ , respectively, and if the period of the oscillating discharge is  $T$ , the wave-length of the latter may be written  $\lambda = VT$ . The width of the lines increases with increasing  $C$  and  $V$ , and with decreasing  $T$  (or  $\lambda$ ). No change in the width of the lines occurs if  $C$  and  $T$  are simultaneously changed so that  $C/T$  remains constant, or if  $V$  and  $T$  are simultaneously changed so that  $V/T$  is constant. The maximum intensity of the current  $I_0 = 2\pi CV/T$ , and, if  $C$ ,  $V$ , and  $T$  are all varied, a smooth curve is obtained if the width of a given line is plotted against  $I_0$ . The curve for the one line may be derived from that for the other by multiplying the ordinate (representing width of line) by a constant factor. W. H.-R.

**Mobilities of the Positive Ions in Helium.** H. B. WAHLIN (*Proc. Nat. Acad. Sci.*, 1924, 10, 475).—The value of the mobility observed depends on the time that elapses between the formation of the ion and the instant it enters the field in which the mobility is measured. Having checked the results of previous workers in the case of air, the author has applied the same method to a mono-atomic gas, helium, and finds the ratio of the mobilities of the aged to the unaged ion to be approximately  $1:\sqrt{3}$ , which, on the assumption that the mobility varies inversely as the square root of the mass, indicates a cluster of three helium atoms. E. B. L.

**Mobility of Negative Ions in Flames by the Hall Effect Method.** J. S. WATT (*Physical Rev.*, 1925, [ii], 25, 69—74).—For a flame containing potassium carbonate, the mobility of negative ions decreased from 26 m./sec. for 1 volt/cm. when the potential gradient was 1 volt/cm., to 16 m./sec. for a gradient of 30 volts/cm. For a salt-free flame the values were 26.5 m./sec. for 5 volts/cm. and 16 m./sec. for 50 volts/cm. The mobility was scarcely affected by wide variation of concentration. The Hall effect varies slightly with the direction of the magnetic field, the asymmetry being greater the greater the amount of salt in the flame. A. A. E.

**Disturbing Influence of an Electric Field on the Zeeman Effect in Spectral Lines.** H. C. UREY (*Z. Physik*, 1924, 29, 86—90; cf. *Kgl. Danske Videnskab. Selsk. math.-fys. Medd.*, 1924, 6, 2).—In continuation of previous work on the Zeeman effect in hydrogen, the degeneration of the atomic or ionic system for certain values of the magnetic field, in the absence of an electric field, has been discussed mathematically. The state under consideration is reached when certain frequencies in the motion of the atom, namely, the frequency of precession of the orbit of the electron in its plane, and the frequency of precession of the plane of the orbit round an axis parallel to the magnetic field, become equal to one another. The difficulties and limits are considered of an experimental study of the phenomenon by examining the behaviour with a varying magnetic field, combined with an electric field at right-

angles, too weak to affect appreciably the energy of the system composed of the positive nucleus and negative electron.

M. S. B.

**Distribution of Electric Field in Metal Arcs and the Stark Effect observed in Arcs of Silver, Copper, Magnesium, Chromium, Nickel, Cobalt, Iron, and Ten other Metals.** H. NAGAOKA and Y. SUGIURA (*Japan. J. Phys.*, 1924, 3, 45—73).—The authors produced a stable arc by using a 500 volt d.c. generator with a large inductance and capacity across the electrodes. The potential drop across the arc was measured and from it the electric field and its gradient were deduced. For obtaining Stark effect they found a small drop of metal the preferable form of anode; in the case of silver, copper, magnesium, zinc, cadmium, and aluminium the lines belonging to the same series are similarly affected. In iron there are six types of change due to the electric field, but it is the spark and not the arc lines which are affected. This method can be employed for sorting the lines as in the Zeeman effect. Many new lines were observed, due to the presence of the strong electric field. The spectra are reproduced in a set of plates.

E. B. L.

**Life of Metastable Helium.** F. M. KANNENSTINE (*Astrophys. J.*, 1924, 59, 133—141).—The life of metastable helium atoms is  $1/140$  second. The critical frequency was independent of the pressure over a large range of pressure, a condition which is considered to be caused by a long-lived abnormal atom. The departure of the critical frequency—pressure curve from a straight line at low pressures is interpreted from the point of view of diffusion of the atoms from the arc space. The abnormal atoms are stable in pure helium, but revert to the normal atoms in the presence of impurities, *i. e.*, in circumstances in which the selection principle is violated.

A. A. E.

**Life of Metastable Helium.** A. J. DEMPSTER (*Astrophys. J.*, 1924, 59, 142—147; cf. preceding abstract).—A mathematical consideration of Kannenstine's experiments (*ibid.*, 1922, 55, 345) supports the view that at the higher pressures the metastable state is destroyed only by collision with some impurity, and tends to discredit the suggestion that radiation is handed on from atom to atom.

A. A. E.

**Life Periods of Excited Atoms.** W. GERLACH and W. SCHÜTZ (*Physikal. Z.*, 1925, 26, 33—35).—On a basis of measurements of thermal energies and of the energy of the Zeeman separation, the limiting values of  $10^{-7}$  to  $10^{-9}$  second are deduced for the periods of existence of mercury and sodium atoms in the excited states Na  $2p$  and Hg  $2p_2$ .

F. G. T.

**Electric Field of Ions and Neutral Salt Action.** P. DEBYE and J. MCAULAY (*Physikal. Z.*, 1925, 26, 22—29).—Continuing previous work (A., 1924, ii, 387), it is shown that neutral salt action and the salting-out effect are to be attributed to changes in the

dielectric constant on dissolving solutes in a solvent. The electrical work term in the previously deduced expression for the osmotic pressure of dilute electrolyte solutions is a function of the dielectric constant of the solution. This latter is generally decreased by the addition of a non-electrolyte with a consequent variation in the electrical work term and so of the osmotic pressure. In the salting-out effect a rise of dielectric constant is produced by the precipitation of the non-electrolyte to counteract the increase of the electric field due to the addition of an electrolyte.

A mathematical treatment on this basis leads to an expression for the total osmotic pressure of a mixed solution of electrolyte and non-electrolyte of the form  $P = P_N + P_E + p$ , where  $P_N, P_E$  are the osmotic pressures of the non-electrolyte and electrolyte singly, and  $p$  is a term involving the dielectric constant of the solvent, the radius of the ions, and a coefficient in an interpolation formula for the effect of the non-electrolyte on the dielectric constant of the solvent. By use of cryoscopic data of Rivett for mixed solutions of sugar and electrolytes, it is shown that values are obtained from the above expression for ionic radii agreeing with accepted values.

An expression is also obtained for the activity of a non-electrolyte in the presence of an electrolyte. Application of this gives a calculated increase of 19% in the activity of a sugar solution on the addition of 0.4 mol. of potassium chloride per litre, which is in agreement with the rise of inversion velocity (15%) found by Arrhenius.

F. G. T.

**Possibility of Reproducing the Electrical Conditions of the Nitrogen Afterglow.** W. H. B. CAMERON (*Nature*, 1925, 115, 122).—Photographs through a neutral wedge of the spectrum of the afterglow at points 17.8 cm. apart in a tube through which glowing nitrogen was pumped showed no pronounced energy displacement. The  $\beta$ -group of the afterglow spectrum cannot be reproduced from discharge tubes containing nitrogen and argon; neither does the spectrum of the light from discharges through ammonia in high-pressure argon yield evidence of the occurrence of  $\alpha$ - or  $\beta$ -groups. Further, the band spectrum of iodine in the presence of high-pressure argon did not display the relative intensity changes characteristic of the afterglow. Thus, although there are several points of resemblance between the electrical conditions of the afterglow and those existing when a mild discharge is passed through high-pressure argon, specific effects in the former appear incapable of reproduction in the latter case.

A. A. E.

**Influence of Temperature on the Photo-electric Effect.** J. R. NIELSEN (*Physical Rev.*, 1925, [ii], 25, 30—40).—Millikan's suggestion that in the photo-electric effect the energy of the light is transferred to the free electrons of the metals as well as to the bound electrons is discussed. The expression  $h\nu_0 = \phi_p - E_k$  is deduced, where  $\nu_0$  is the threshold frequency,  $\phi_p$  is the gain in potential energy accompanying the transference of a free electron from the metal to the surrounding electron atmosphere, and  $E_k$  the average kinetic energy of a free electron within the metal. The

temperature variation of the threshold frequency or of the long wave-length limit is proportional to the Thomson coefficient. The photo-electric current from aluminium for 2537 Å. remained constant within 0.5% when the target was cooled from 400° to 100°.

A. A. E.

**Thomson Circuit in the Study of Magnetic Spectra.** N. NIKITIN (*Z. Physik*, 1924, 29, 288—293).—A method has been devised for the determination of the apparent magnetic permeabilities,  $\mu_k$  and  $\mu_n$ , of iron wire. This can be used for very thick wire and for very small quantities of material.  $\mu_n$  is less than  $\mu_k$  and the  $\mu_n$ -spectrum is much more complicated than the  $\mu_k$ -spectrum. The results are in agreement with the visco-elasticity theory (Arkadiev, *ibid.*, 1924, 27, 37).

M. S. B.

**Reversible Permeability.** R. GANS (*Z. Physik*, 1924, 29, 270—271).—Polemical against Uller (*Verh. deut. physikal. Ges.*, 1924, [iii], 5, 2).

M. S. B.

**The Constant  $\Delta$  in the Weiss-Curie Law.** B. CABRERA (*Anal. Fis. Quím.*, 1924, 22, 463—475).—Theoretical. The author discusses the theories of paramagnetism of Langevin and Ehrenfest. The reality of the magneton of Weiss as a natural unit implies that in any suggested organisation of electrons in the atom the resulting magnetic moment must always be a whole multiple of the magneton. The significance of the constant  $\Delta$  in the Weiss-Curie law is also discussed.

G. W. R.

**Thermo-magnetic Studies of certain Solutions.** A. DUPERIER (*Anal. Fis. Quím.*, 1924, 22, 383—397).—Determinations have been made of the value  $\Delta$  in the Weiss-Curie law  $\kappa(T+\Delta)=C$ , where  $\kappa$  is the molecular susceptibility, using solutions of nickel nitrate and manganese nitrate, respectively. For nickel the value of  $\Delta$  obtained is  $-2$ , and for manganese,  $-25$ . In each case the value is approximately constant. From these values and previous measurements of  $\kappa$ , the magneton number for nickel is found to be  $15.96 \pm 0.05$  and for manganese  $28.06 \pm 0.08$ . The magneton number thus found for nickel is identical with that found for the solid salts, whilst for manganese it is less by unity than that obtained for solid salts.

G. W. R.

**Magnetisation Numbers of the Rare Earths.** S. MEYER (*Physikal. Z.*, 1925, 26, 51—54).—The magnetic susceptibilities of a number of rare earth elements have been determined and agree with values obtained independently by B. Cabrera (private communication). Plotted against atomic number the values lie on two parabolic curves, maxima being occupied by the pairs Pr, Nd, and Dy, Ho. An attempt is made to correlate these values with the Bohr structure of these atoms. La, Lu, and Hf, in which the 6.6.6. and 8.8.8.8. electron groups are completed, are diamagnetic. Paramagnetism occurs in those atoms in which the 8.8.8.8. group is in course of completion. Ladenburg's view (A., 1920, ii, 301) that magnetic susceptibility is determined by the

arrangement of the inner rather than the valency electrons is confirmed.

F. G. T.

**Chemical Studies on the Isotopes of Lead.** H. BRENNEN (*Compt. rend.*, 1925, **180**, 282—284).—Dillon, Clarke, and Hinchy (A., 1922, ii, 710) recorded a partial separation of the isotopes of radioactive lead by means of the Grignard reaction on lead chloride, using the method of Soddy and Hyman (T., 1914, **105**, 1402) for atomic weight determination. The author has repeated the work using the method of Richards (A., 1908, ii, 281) for the atomic weight of lead. The fractionation through lead tetraethyl gave mean values 207.15 and 207.155 for ordinary lead and 206.87 and 206.88 for a mixture of equal parts of ordinary lead and radioactive lead (atomic weight 206.55). The method does not therefore result in a separation of the isotopes.

R. A. M.

**Atomic Weight of Silicon. Analysis of Silicon Chloride.** O. HÖNIGSCHMID and M. STEINHEIL (*Z. anorg. Chem.*, 1924, **141**, 101—108).—The silicon tetrachloride was purified by repeated fractional distillation in a high vacuum, and the purity tested by measurement of the vapour pressure at 0° (76.6 mm.). The resulting chloride was free from hydrochloric acid and higher chlorides. It was decomposed by sodium hydroxide solution, and the chlorine precipitated with silver nitrate. From the ratio  $\text{SiCl}_4 : 4\text{Ag}$  ( $\text{Cl} = 35.457$ ;  $\text{Ag} = 107.88$ ) a mean of four analyses gave  $\text{Si} = 28.105$ , with a mean deviation of  $\pm 0.003$ . The authors regard this as in favour of Baxter's value  $\text{Si} = 28.063$ , and against the generally-accepted former value 28.3.

L. L. B.

**Atomic Weight of Chlorine.** (Mlle.) E. GLEDITSCH (*J. Chim. physique*, 1924, **21**, 456—460).—No difference could be detected in the atomic weights of chlorine contained in carefully purified silver chloride prepared from (a) volcanic ammonium chloride produced in an eruption of Vesuvius, (b) water from a depth of 1573 m. in the Calumet and Hecla mines near Lake Superior, and (c) ordinary barium chloride.

W. H.-R.

**Atomic Weight of Zirconium.** O. HÖNIGSCHMID, E. ZINTL, and F. GONZÁLEZ (*Anal. Fis. Quím.*, 1924, **22**, 432—462).—The occurrence of hafnium together with zirconium has necessitated a revision of the atomic weight of zirconium. After removal of the greater part of the hafnium by fractional crystallisation of the potassium double fluorides and correction for the small amounts of hafnium remaining, as shown by X-ray examination, the mean value for the atomic weight of zirconium, determined by way of the bromide, is given as 91.22. This is in good agreement with the value obtained by Venable and Bell (A., 1924, ii, 690) and deducible from Aston's data for the isotopes of zirconium (A., 1924, ii, 690), assuming that the fourth isotope (96) is present in inappreciable amount.

G. W. R.

**Determination of the Atomic Weight of Selenium.** P. BRUYLANTS, F. LAFORTUNE, and L. VERBRUGGEN (*Bull. Soc. chim. Belg.*, 1924, **33**, 587—612).—Selenium was purified by several

repetitions of the following treatment: solution in nitric acid, evaporation of the solution to dryness, sublimation of the selenium dioxide obtained, and reduction of the sublimate with dry ammonia. The element was converted into hydrogen selenide by direct combination with hydrogen at  $700^{\circ}$  and by means of the action of water on aluminium selenide prepared by fusing the two elements together. In all cases the gas was purified by condensation in a mixture of solid carbon dioxide and alcohol. By direct weighing, a litre of hydrogen selenide was found to weigh at  $0^{\circ}$  and 760 mm. 3.6624 g. (mean of 53 determinations); the atomic weight of selenium is, therefore, 79.23.

A. R. P.

**Atomic Weight of Bismuth.** A. CLASSEN and G. STRAUCH (*Z. anorg. Chem.*, 1924, 141, 82—94).—The atomic weight of bismuth has been determined by means of the combustion of bismuth triphenyl, previously purified by distillation in a high vacuum. In contact with oxalic acid, the oxalate is formed (cf. Classen and Ney, A., 1921, ii, 119), which, by heating in a stream of oxygen, yields an oxide free from carbon. The apparatus employed was a modification of that devised by Richards, in which the initial weighing out, the combustion, and the final weighing all take place in the same vessel. As a mean of fifteen experiments, the value 208.989 was obtained for the atomic weight. This confirms the value 209 found by Classen and Ney, and contradicts that (208) given by von Schneider and Gutbier.

L. L. B.

**Distribution of Length of  $\alpha$ -Particles of Polonium in Oxygen and Nitrogen.** I. CURIE and N. YAMADA (*Compt. rend.*, 1924, 179, 761—763).—About four hundred particles were measured from nitrogen, a somewhat smaller number from oxygen; the general form of the curves of distribution of length is similar to that found with air by Curie (A., 1923, ii, 207). The difference in the actual values is attributed to the use of radiation from a greater mass of polonium than that employed hitherto, so that absorption at the surface of the radiation source may have occurred. The conclusion is reached that the difference in form between Bragg's oxygen and nitrogen curves is due to the law of variation of ionisation with length of the  $\alpha$ -particle.

H. J. E.

**Secondary  $\beta$ -Rays produced in a Gas by X-Rays.** P. AUGER (*Compt. rend.*, 1925, 180, 65—68; cf. A., 1924, ii, 286, 440).—When X-rays are passed into pure argon only secondary  $\beta$ -rays are produced, but, if the argon is diluted with hydrogen, tertiary  $\beta$ -rays of a few millimetres range are also formed. In krypton diluted with hydrogen, the tertiary rays have a range comparable with that of the secondary rays, and there are traces of quaternary  $\beta$ -rays. The tertiary rays start from the same origin as the secondary and are distinguished from the latter in that they are not affected by changes in the tension of the exciting X-rays. Their production is explained as follows: if the initial X-ray ionises an atom deeply (e.g., in the *K* shell) the vacant space is very soon taken by an electron from one of the outer shells (e.g., the *L* shell) with liberation of



energy. This energy may be given off as electromagnetic radiation, but generally this radiation is reabsorbed by the same atom with the loss of an electron from one of the outer layers, and this produces the tertiary  $\beta$ -ray. The process may be repeated, with emission of quaternary or  $\beta$ -rays, until the outermost shell of electrons is reached.

W. H.-R.

**Magnetic Spectrum of the High Speed  $\beta$ -Rays of Thorium- $B+C$ .** D. K. YOVANOVITCH and J. D'ESPINE (*Compt. rend.*, 1925, 180, 202—203).—The magnetic spectrum of the  $\beta$ -rays of thorium- $B+C$  is found to contain, in addition to those discovered by Meitner (A., 1922, ii, 732), a band of rapid, but feeble, rays extending to  $H\rho$  (gauss per cm.)=6800 with a strong doublet at 5480. In addition, there are two rays at 11,000 and 18,000 and probably another at 40,000. The values of the other rays are in good agreement with those obtained by Meitner. J. W. B.

**Absorption of  $\beta$ -Rays by Matter.** G. FOURNIER (*Compt. rend.*, 1925, 180, 284—287).—A mixture of radium- $D$  and - $E$  in equilibrium was used as a source so that the experiments were concerned only with the  $\beta$ -radiation from radium- $E$  and with a small quantity of a more absorbable  $\beta$ -ray. The coefficient of absorption,  $\mu/\rho$ , was measured for carbon, aluminium, copper, molybdenum, silver, and tin, using the expression  $I=I_0e^{-\mu/\rho \cdot m/s}$  where  $m/s$  is the mass of absorbing material per sq. cm.,  $\mu$  the ordinary absorption coefficient, and  $\rho$  the density of the material.  $\mu/\rho$  is independent of experimental arrangement and varies with the absorbent and with the velocity of the  $\beta$ -rays absorbed. The linear relation  $\mu/\rho=a+bN$  ( $a=15$ ,  $b=0.142$ ,  $N$ =atomic number) holds accurately for the principal  $\beta$ -radiation of radium- $E$  with the above elements absorbing. For the other  $\beta$ -rays the expression found to hold is  $\mu/\rho=65+0.615N$ , i.e., the constants are 4.33 times greater than before. R. A. M.

**Study of Characteristic Spectra of  $\gamma$ -Rays by Crystal Diffraction.** J. THIBAUD (*Compt. rend.*, 1925, 180, 138—140).—The results obtained previously for the frequencies of  $\gamma$ -rays, by the examination of the secondary  $\beta$ -radiations they excite, have been confirmed by a direct examination of their diffraction by a crystal by de Broglie's method. Examination of the radiation from radium in equilibrium with its products confirms the two lines found by Rutherford and Andrade near  $1^\circ 30'$  (A., 1914, ii, 698). The present experimental method has, however, extended the range of the observations to rays of an energy of at least 236,000 volts. The radiation from radiothorium showed four lines of wave-lengths 0.168, 0.145, 0.062, and 0.052 Å. Of these lines the last mentioned was also found by the examination of the  $\beta$ -spectrum excited in lead, together with two others of energy  $2.73$  and  $2.98 \times 10^5$  volts respectively which were not detected by the diffraction method. Confirmation of two of the lines enumerated is also found in the measurements of Meitner (A., 1922, ii, 416) and of Ellis (*ibid.*, 466). G. M. B.

**High-Energy  $\gamma$ -Ray from Thorium Disintegration Products.**

D. H. BLACK (*Nature*, 1925, 115, 226).—New measurements have been made of the spectra of thorium-*B*, -*C*, and -*D*. Two lines of high energy, viz.,  $2.55$  and  $2.62 \times 10^6$  volts, and possibly a third of slightly greater energy, have been observed. No lines appear between these and those of an energy of about  $0.8 \times 10^6$  volts.

A. A. E.

**Capacity for Emanating of Finely-divided Precipitates as a means of Determining Surface Variation.**

O. HAHN (*Annalen*, 1924, 440, 121—139).—The capacity for emanating possessed by a compound when mixed with an appropriate radioactive substance, *i.e.*, the ratio of the amount of emanation diffusing out at the ordinary temperature to the total amount the active material can theoretically give, increases with the degree of subdivision of the compound (cf. *Z. Elektrochem.*, 1923, 27, 189). The procedure previously described, which gave qualitative results, is now combined with Paneth and Vorwerk's method (*A.*, 1922, ii, 618), so that, when large quantities of active material are used, quantitative results are obtained. Investigations on ferric hydroxide hydrogels and alcogels are recorded. Gels precipitated in the cold have a higher emanation capacity than those precipitated in the hot, and moist gels than dry gels, although the reason of the latter is probably not the increase in the size of the crystals. The emanation capacity tends to zero on heating and its original value is not attained on cooling; it decreases rapidly with dry gels on ageing, whereas for moist alcogels it is constant and, for moist hydrogels, nearly so. The ageing phenomena in dry and moist hydrogels are reversible. The emanation coefficient of nickel hydroxide gels sinks extremely rapidly on drying; it is very sensitive to traces of impurities in this case.

S. K. T.

**Thoron.** B. BATSCHA (*Z. physikal. chem. Unterr.*, 1924, 37, 117—118; from *Chem. Zentr.*, 1924, ii, 1149).—An experiment is described for demonstrating the exponential character of the decay of thoron, showing that its half-value period is about 53 seconds.

G. W. R.

**Determination of Radium.** (MME.) P. CURIE.—(See ii, 241.)

**Decomposition of Mercury Atoms.** L. KAUL (*Metallbörse*, 14, 1432; from *Chem. Zentr.*, 1924, ii, 1049).—The conversion of mercury into gold (Miethe and Stammreich, *Naturwiss.*, 12, 597) is attributed to the loosening effect of the ultra-violet rays on the hydrogen atoms in the mercury atom, which is regarded as built up of hydrogen, helium, and carbon atoms. The hydrogen atoms are unable to resume their place in the system when the ultra-violet light is withdrawn, and by the removal of four hydrogen atoms the gold atom is formed.

R. B.

**Theory of the Periodic System.** A. SOMMERFELD (*Physikal. Z.*, 1925, 26, 70—74).—A theoretical paper in which is discussed the distribution of electrons among atomic levels according to the

scheme suggested by Stoner (this vol., ii, 85). This is compared with the Bohr distribution and its bearing on the optical and magnetic properties of the elements considered. F. G. T.

**Application of the Correspondence Principle to Degenerate Systems and the Relative Intensities of Band Lines.** E. C. KEMBLE (*Physical Rev.*, 1925, [ii], 25, 1—22).—In an attempt to harmonise the Kratzer half integral quantum numbers with the symmetry in the intensities of the two branches of the hydrogen chloride band at  $3.46\ \mu$ , treatment of the molecule as a degenerate system with but one quantum condition for two degrees of freedom led to an unsatisfactory formula. A modification is proposed and justified by treating the molecule as a non-degenerate system. Comparison between theory and experiment is fairly satisfactory if it is assumed that the lines possess a fine structure. A. A. E.

**Lack of Correspondence between Spectroscopic and Spectrophotometric Absorption Maxima.** H. GOMBOS (*Biochem. Z.*, 1924, 151, 7—14).—Absorption maxima of permanganate solutions determined spectroscopically and spectrophotometrically do not correspond. J. P.

**Photometric and Spectrophotometric Studies. IV. The Influence of Temperature on the Absorption Spectra of Borax and Phosphate Beads.** K. SCHAUM and M. FUNCK (*Z. wiss. Phot.*, 1924, 23, 73—78).—Study of the absorption spectra of borax and phosphate beads characteristically coloured with copper, nickel, cobalt, iron, chromium, and manganese shows that in most cases increase in temperature (cold to  $800$ — $850^\circ$ ) brings about a shift of the absorption band towards the red. In some individual cases, e.g., copper-borax, chromium-phosphate, and manganese-borax and -phosphate, the shift is very marked. In certain other cases, e.g., cobalt, the effect of temperature is very small. The results give no reliable information about the broadening of the bands nor the increase in the maxima on elevation of temperature. Considerable alteration in temperature brings about no constitutive change in the absorbing complex, although it considerably modifies the absorption spectrum. The investigation was carried out with a König-Martens spectrophotometer. Beads were prepared on a platinum wire, and could only be used for about 2 hours on account of their hygroscopicity. Beads having an accurately known content of colouring metal salt can be produced, but the preparation of such beads is useless, since they cannot be made plane-parallel. The influence of thickness and concentration was eliminated by using Weigert's "typical colour curve" method (cf. A., 1916, ii, 545). W. C.

**Influence of the CH-group on the Absorption of certain Organic Compounds below  $3\mu$ .** T. DREISCH (*Z. wiss. Phot.*, 1924, 23, 102—110).—Observations were made with a mirror spectrometer using benzene and chloroform in both the liquid and vapour states, and acetylene gas. Between  $2.486\mu$  and  $1.179\mu$  benzene and chloroform show four comparable bands in the liquid

state, and two comparable gaseous bands. An acetylene band at  $2.47\mu$  agrees with the benzene band at about  $2.48\mu$ , but a second acetylene band at  $1.56\mu$  was previously unknown, and falls between the benzene bands at  $1.688\mu$  and  $1.45\mu$ . There is no acetylene band corresponding with the benzene band at  $2.18\mu$ , which is characteristic of aromatic compounds. With one exception, due probably to insufficient resolution, the four liquid and the two vapour bands of benzene and chloroform show the same numerical relationship. The ratio of the absorption coefficients of similar bands due to benzene and chloroform is as 3 to 1. The acetylene band at  $2.47\mu$  fits in with the above proportion.

W. C.

**Ultra-violet Absorption Spectra of Hæmoglobin Derivatives. Chemical Constitution of Blood Pigments.** H. FRIEDLI (*Bull. Soc. Chim. biol.*, 1924, 6, 908—934).—An account is given of the ultra-violet absorption spectra (as far as  $2000\text{ \AA.}$ ) of pyrrole, indole,  $\alpha$ - and  $\beta$ -methylindole, hæmin,  $\alpha$ - and  $\beta$ -bromohæmin, hæmatin in acid and alkaline solution, hæmatoporphyrin dimethyl ether, mesoporphyrin, and of the anhydride and imide of hæmatic acid. The relation between the chemical constitution and the absorption spectra of these compounds is discussed. It is found that indole has a totally different spectrum from either pyrrole or benzene, from which it is derived. The methylindoles possess spectra very similar to that of indole itself; the position of the substituent methyl group has a small effect. Hæmin (on account, it is suggested, of the four pyrrole rings it contains) shows a strong ultra-violet absorption. Although no difference can be detected chemically, there is a marked difference spectroscopically between  $\alpha$ - and  $\beta$ -bromohæmin. The absorption in the ultra-violet of the compounds not containing an atom of iron (*e.g.*, hæmatoporphyrin) is considerably diminished. The spectra of the imide and anhydride of hæmatic acid are very different.

L. F. H.

**Absorption of [Ultra-]Violet Light by Organic Substances.** V. E. KEPIANKA and L. MARCHLEWSKI (*Bull. Soc. chim.*, 1924, [iv], 35, 1613—1618).—The coefficient of extinction, for a given wave-length, of an aqueous solution containing equimolecular quantities of benzoic acid and phenol is equal to the sum of the coefficients for solutions of the separate substances of the same concentration, in most cases to within 5%. The maximum deviation was 15%.

S. K. T.

**Absorption of Ultra-violet Rays by Methyl Derivatives of Naphthalene.** H. DE LÁSZLÓ (*Compt. rend.*, 1925, 180, 203—206).—The absorption spectra of mono- and di-methylnaphthalenes in the vapour state and in hexane solution are plotted. The introduction of the methyl group into the naphthalene causes a displacement of the spectrum towards the red which is greater with  $\beta$ - than  $\alpha$ -mononaphthalene derivatives, and with 2:6- than 2:7-dimethylnaphthalene. The spectra resemble generally those of naphthalene itself, consisting of a region A between  $3250$  and  $2950\text{ \AA.}$ , a region B between  $2950$  and  $2500\text{ \AA.}$ , and a very strong band in the

ultra-violet, at 2200 Å. In the state of vapour, the A region consists of continuous bands (resolution into lines being observed only in the case of  $\beta$ -methylnaphthalene) which can be grouped into several series with almost constant intervals. In the B region the bands are fused together, the absorption curve showing three maxima for the  $\beta$ -derivative and four for the  $\alpha$ -, whilst, in the vapour state, the  $\beta$ -derivative shows seven and the  $\alpha$ -derivative four continuous bands.

J. W. B.

**Spectrum of Carbon Monoxide at Very Low Pressures, and its Relation to the Spectrum of the Tails of Comets.** F. BALDET (*Compt. rend.*, 1925, 180, 271—273; cf. A., 1924, ii, 438).—The spectrum was obtained by the impact of slow electrons from an incandescent filament. Thirty bands are given between 5700 and 3080 Å., each having four principal edges. The positions are given sufficiently accurately by the Deslandres expression,  $\nu = (27.83/2 \cdot n^2 + 2197.24n) - (26.57/2 \cdot p^2 + 1493.66p) + 23529.0$ , where  $n$  varies from  $-3$  to  $0$  and  $p$  from  $+3$  to  $-9$ . The origin is taken at the most intense band beginning at 4248.55 with stronger edges at 4251.27, 4271.31, 4273.87. All the bands are similarly subdivided. The wave-number differences between the first and third, the second and fourth edges of the same band are practically constant ( $\Delta\nu = -126$ ). Between the first and second,  $\Delta\nu$  varies regularly but not linearly from  $\Delta\nu = -17$  at  $\nu = 18,000$  to  $\Delta\nu = -10$  at  $\nu = 31,000$ . The spectrum resembles closely the third group in that of air. Since the one may be due to a molecule  $N+O$  and the other to  $C+O$ , it seems possible that the influence of oxygen preponderates in both spectra. The spectrum is characteristic of comet-tails and may be called the third negative group of carbon. The first group was recorded by Deslandres (A., 1904, ii, 105) and the second by Deslandres and d'Azambuja (*ibid.*, 1905, 140, 917). R. A. M.

**Infra-red Absorption Spectrum of Ammonia.** K. SCHIERKOLK (*Z. Physik*, 1924, 29, 277—287).—The absorption spectrum of ammonia in the region from  $0.589\mu$  to  $14.4\mu$  has been studied by means of an apparatus of high dispersive power. In the short-wave portion of this region strong bands have been found at  $1.493\mu$  and  $1.935\mu$ , with a weaker one at  $1.643\mu$ . A strong band at  $2.22\mu$  shows two sharp maxima at  $2.202\mu$  and  $2.239\mu$ . The bands previously found by Coblentz ("Ultra-red Investigations") in the neighbourhood of  $3.0\mu$ ,  $6.0\mu$ , and from  $7.8\mu$  to  $15\mu$ , have been further resolved. The last forms a double band. Mean values for the moment of inertia of the ammonia molecule have been calculated from the absorption bands and compared with Eucken's value calculated from the vapour-pressure curve (*Jahrb. Radioakt.*, 1920, 16, 401). M. S. B.

**Structure of the so-called Ultra-violet Bands of Water Vapour.** G. H. DIEKE (*Nature*, 1925, 115, 194).—Results of a consideration of published data, to be given in detail elsewhere, are summarised. With the aid of the combination principle it is

possible to obtain the relative values of the rotational terms without any theoretical assumption concerning the structure of the molecule.

A. A. E.

**Ultra-violet Absorption Spectra of Ketens and their Dimerides.** II. G. C. LARDY (*J. Chim. physique*, 1924, **21**, 353—385; cf. this vol., ii, 87).—Details of the experimental data (*loc. cit.*) are given. Using solutions in hexane and, in some cases, in alcohol, the ultra-violet absorption spectra of the following substances are described in detail; keten, diethyl-, dipropyl-, and diphenyl-keten; tetraethyl-, tetrapropyl-, and tetra-allyl-diketocyclobutane; diphenyldimethyldiketocyclobutane; diketocyclobutane; diphenyldiketocyclobutane; the diethyl ester of 1:3-dimethyl-2:4-diketocyclobutane-1:3-dicarboxylic acid; acidimethyldiketocyclobutane; ethyl- and phenyl-carbimides; diethylcarbodi-imide; diacetyl. No difference exists between the absorption spectra of aldoketens of the type  $H_2C:C:O$  and ketoketens of the type  $R_2C:C:O$ . The absorption spectrum of keten has also been examined in the state of vapour, and consists of a number of fine bands occupying the same position as that of the wide band given by the substance in solution and corresponding with the group  $C:O$ .

W. H.-R.

**Fluorescence of Benzene Vapour by Monochromatic Excitation.** P. PRINGSHEIM and A. L. REIMANN (*Z. Physik*, 1924, **29**, 115—124).—The ultra-violet band fluorescence of benzene vapour, excited by different monochromatic radiations from the mercury, zinc, and cadmium arcs, has been examined. At the saturation pressure of 25 mm. at  $0^\circ$ , any active wave-length excites the same spectrum as that previously obtained under excitation by electrical discharge, or by light from the iron arc (McVickers and Marsh, T., 1923, **123**, 642, 817, 820). At lower pressures, less than 1 mm., some of the feeble bands, which do not stand in any clearly recognised series relation with the exciting line, or with one another, become intensified, whilst the stronger bands almost disappear. Raising the temperature to increase the saturation pressure, or adding another gas, gradually restores the original spectrum. At still higher pressures, for example 75 mm., and also in liquid benzene and concentrated solutions, the fluorescence appears to be a surface phenomenon, owing to the strong absorption of the exciting radiation. This accounts for the negative results of earlier investigators.

M. S. B.

**Phosphorescent Powers of Fluorescein.** B. BATSCHA (*Ber.*, 1925, **58**, [B], 187—193; cf. Trede and Wulff, A., 1922, ii, 245).—Fluorescein is brought into a highly phosphorescent condition when a small quantity of it is melted with tartaric or citric acid and the molten mass is allowed to cool. The phenomenon is excited by exposure to bright, diffused daylight, but persists only for 8—10 seconds. It appears to be connected with the viscosity of the mixture, since the citric acid preparations require to be cooled to  $-12^\circ$  (when they become hard instead of viscous) before the effect is obvious and, further, phosphorescence is no longer observed if the

mixtures are heated to about  $45^{\circ}$ . Mixtures of fluorescein and dextrose are, at most, faintly phosphorescent, but this property is acquired if acidic substances (oxalic or salicylic acid, potassium hydrogen oxalate, sodium hydrogen sulphate) are added. Pyrocatechol, quinol, normal sodium sulphate, sodium hydroxide, barium hydroxide, sodium carbonate, and disodium hydrogen phosphate do not produce this effect, but the action of the alkaline materials is rendered somewhat obscure by their behaviour towards dextrose itself. It is, however, established definitely that the phosphorescence of fluorescein is activated by substances with free hydrogen ions. Phosphorescence is excited in tartaric acid or dextrose which has been melted and cooled if exposed to the arc light, and the effect disappears if the specimens are warmed at  $45^{\circ}$ ; the phenomenon is much less readily excited and less intense in character than that observed in the presence of fluorescein. H. W.

**Examination of the Classical Dispersion Formula in the Case of Monatomic Gases and Vapours.** K. F. HERZFELD and K. L. WOLF (*Ann. Physik*, 1925, [iv], 76, 71–105).—A study of experimental results for the variation of refractive index with wave-length in the case of helium, neon, and argon, shows that they can be expressed satisfactorily by a dispersion formula of only one term in which the specific ("dispersion") frequency lies further in the ultra-violet than the long wave-length end of the absorption spectrum. The attempt to base a formula on the resonance frequency failed, but a formula with two terms, one of which involved the resonance frequency and the other the dispersion frequency, satisfied the cases of argon and helium.

The number of electrons in each atom causing the dispersion is much larger for argon than for neon, but the further increase for krypton and xenon is small. The authors consider that there is a real deviation from the classical formula and favour that of Wentzel. An integral relationship is established between the refractive indices for helium, neon, argon, krypton, and xenon, for very long wave-lengths. Mercury vapour shows a peculiarity at  $\lambda 7000 \text{ \AA.}$  in that there is anomalous dispersion but no absorption. E. B. L.

**Theory of Constitutive Colour.** E. ZINTL and A. RAUCH (*Ber.*, 1925, 58, [B], 234; cf. A., 1924, ii, 806).—The colour of all inorganic substances, including the elements, has been ascribed by Biltz (A., 1923, ii, 809) to the presence of incompletely saturated or weak electro-valency forces. H. W.

**Ionisation in the Wave of Propagation of Explosions.** A. E. MALINOWSKI (*J. Chim. physique*, 1924, 21, 469–478).—A rapid current of air mixed with hydrogen or hydrocarbon vapour was passed through an iron tube and the variations of pressure and ionisation were measured when the explosive wave proceeded normally, and when it was made to pass through a strong electric field. The explosion proper is preceded by an initial wave in which ionisation takes place, the degree of ionisation being reduced if the

wave passes through a strong electric field owing to the latter removing the ions or electrons. In the case of a mixture of air with benzene vapour, the explosion can be completely stopped if the initial wave passes between plates charged to a potential difference of about 110 volts. The degree of ionisation is greater in those places in which the velocity of the wave is increasing than where it is decreasing. Of the total number of ions ( $n_1$ ) produced, the greater number recombine and the resulting liberated energy maintains the explosion. But a small fraction ( $n$ ) of the ions ( $n/n_1 < 3.6 \times 10^{-5}$ ) are carried forward by the explosive wave from one layer to the next, and it is these ions that accelerate the explosion and can be removed by an electric field.

W. H.-R.

**Evolution of the Molecule of Nickelic Hydroxide in Contact with Water.** (MLLE.) S. VEIL (*Compt. rend.*, 1925, **180**, 211—213; cf. A., 1924, ii, 557).—Nickelic hydroxide and nickel sesquioxide show exactly similar, but slightly smaller, variations of the molecular coefficient of magnetisation on successive re-dissolution and re-precipitation as do the corresponding compounds of bivalent nickel.

J. W. B.

**Relation between the Critical Temperature and the Molecular Volume at Absolute Zero.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1925, **141**, 375—379).—Theoretical. Previous work (this vol., ii, 25; Van Laar, "Die Zustandgleichung von Gasen und Flüssigkeiten," 1924, 140) is used to deduce the relation  $V_0 \gamma p_k / T_k = 5.13$ , where  $V_0$  is the molecular volume at absolute zero,  $p_k$  and  $T_k$  the critical pressure and temperature, and  $\gamma = b_k / 2b_0$ , where  $b$  is the constant of Van der Waals. For most normal substances  $\gamma = 0.9$ , and the relation reduces to  $V_0 p_k / T_k = 5.7$ , whilst more accurately  $2\gamma = 1 + 0.038 \sqrt{T_k}$ . The above relations have been tested for a number of organic and inorganic compounds and the agreement is very satisfactory; in the case of elements the values of  $V_0 p_k / T_k$  are considerably greater than the theoretical value, but the values of  $V_0 \gamma p_k / T_k$  are in better agreement.

W. H.-R.

**Wave-length of Maximum Energy in the Sound Spectrum of an Explosion.** A. DUFOUR (*Compt. rend.*, 1924, **179**, 759—761).—Evidence is adduced in support of the relation established by Villard (*ibid.*, 1924, **179**, 617) between the wave of maximum energy and the mass of explosive used.

H. J. E.

**Double Refraction of Amorphous Liquids and Molecular Constitution.** D. VORLÄNDER and R. WALTER (*Physikal. Z.*, 1924, **25**, 571—573).—The double refraction of about 120 organic substances was measured when they were placed in a rotating cylinder apparatus at nearly constant temperature. The results for various types of molecules are given in terms of the "specific double refraction," which in the case of amorphous oils is given by  $D/u\eta$ , where  $D$  is the double refraction observed when the cylinder rotates with a velocity  $u$ , and  $\eta$  the coefficient of viscosity of the substance referred to water as unity. A curve is given showing



the connexion between the specific double refraction and the length of chain in the case of the fatty acids. L. F. B.

**Rotatory Power of Cholesteric Substances.** M. ROYER (*Compt. rend.*, 1925, **180**, 148—150; cf. A., 1923, ii, 223).—The enormous rotatory power of the cholesteric phase is due to a strong helical torsion in the substance, the rotatory power being smaller the larger the torsion. In a mixture of amyl cyanobenzylideneamino-cinnamate with cholesteryl benzoate (2.75 parts:1) this torsion diminishes as the temperature rises from the lower transition point to the higher temperature at which the cholesteric phase passes into the nematic phase. At the same time the rotatory power increases to seven times its initial value. The direction of the spiral torsion becomes reversed at this point, the rotatory power on either side of it for 5100 Å. being +135.8 and -135.8 turns per mm. In all other cases, optical rotatory power falls with rise of temperature. The cholesteric rotatory power differs in this from molecular rotation in crystals, which often rises with the temperature. On the other hand, cholesteric rotatory power is quite analogous to magnetic rotation and especially with respect to the dispersion, the passage from a large value  $+R$  to an equally large  $-R$  for adjacent wavelengths being paralleled only in magnetic rotatory dispersions. The light is in both cases circularly polarised. G. M. B.

**Ammonium Dimolybdomalate.** E. DARMOIS and A. HONNELAITRE (*Compt. rend.*, 1924, **179**, 629—632).—Ammonium dimolybdomalate reacts with substances which can combine with molybdic acid and these produce variations in its rotatory power. Hydroxy-acids, polyhydric alcohols, polyphenols, and phenolic acids exert marked influence. This appears to depend on the possession of two hydroxyl groups in adjacent positions (cf. Böeseken, A., 1921, i, 843). H. J. E.

**Varying Valency of Gold with Respect to Mercaptanic Radicles.** (SIR) P. C. RAY (*J. Indian Chem. Soc.*, 1924, **1**, 63—73).—Various products obtained as precipitates by addition of gold chloride to solutions of sulphur compounds in alcohol, ether, and acetone are formulated as containing bi-, quadri-, and sexa-valent sulphur together with bi-, ter-, quadri-, and quinque-valent gold. From diethyl disulphide two compounds,  $\text{Et}_2\text{S}_2\text{Au}_2\text{Cl}_4$  and  $\text{Et}_2\text{S}_2\text{Au}_4\text{Cl}_2$ . From monopotassium dithioethylene glycol,  $\text{C}_4\text{H}_8\text{S}_4\text{Au}_2\text{Cl}$ . Disodium dithioethylene glycol gave  $(\text{C}_2\text{H}_4\text{S}_2)_4\text{Au}_3\text{Cl}$  in ether,  $(\text{C}_2\text{H}_4\text{S}_2)_5\text{Au}_2$  in acetone. The following compounds are described from benzylidenedithioethylene tetrasulphide:  $2[\text{PhCHS}_4(\text{C}_2\text{H}_4)_2]\text{Au}_3\text{Cl}_4\text{Et}_2\text{O}$ ,  $6[\text{PhCHS}_4(\text{C}_2\text{H}_4)_2]\text{Au}_4\text{Cl}_3$ ,  $5(\text{C}_2\text{H}_4)_2\text{S}_2\text{Au}_3\text{Cl}_5\cdot 1.5\text{Et}_2\text{O}$ ,  $4[(\text{C}_2\text{H}_4)_2\text{S}_2]\text{Au}_3\text{Cl}_4\cdot 0.5\text{Et}_2\text{O}$ ,  $4[(\text{C}_2\text{H}_4)_2\text{S}_2]\text{Au}_3\text{Cl}_2$ ,  $3[(\text{C}_2\text{H}_4)_2\text{S}_2]\text{Au}_3\text{Cl}_2\cdot \text{EtOH}$ ,  $3[(\text{C}_2\text{H}_4)_2\text{S}_2]\text{Au}_3\text{Cl}_2\cdot \text{EtOH}$ ,  $3[(\text{C}_2\text{H}_4)_2\text{S}_2]\text{Au}_3\text{Cl}_2\cdot \text{EtOH}$ , Triethylene trisulphide gave  $(\text{C}_2\text{H}_4\text{S})_3\cdot 2\text{AuCl}_3$  and  $(\text{C}_2\text{H}_4\text{S})_3\cdot \text{AuCl}_2$ . G. M. B.

**Calculation of Molecular Diameters from Heat of Vaporisation and Surface Tension Data.** H. SIEK (*Physikal. Z.*, 1924, **25**, 545—546).—A formula is deduced connecting the diameter of a

molecule of a substance with its internal heat of vaporisation, and is used to calculate the molecular diameters for seventeen different substances. The values obtained are compared with those calculated from a modified form of an equation given by Ostwald and with values obtained by Kuenen from kinetic theory data. On the average the author's values are about 30% larger than those of Kuenen.

L. F. B.

**Crystal Structures of Ammonium Fluoferrate, Fluoaluminate, and Oxyfluomolybdate.** L. PAULING (*J. Amer. Chem. Soc.*, 1924, 46, 2738—2751).—Cubic crystals of ammonium fluoferrate, fluoaluminate, and oxyfluomolybdate have been examined by the spectral, Laue, and powder X-ray methods. The units of structure, based on a face-centred lattice, contain 4 mols. The values of  $d$  found are : ammonium fluoferrate 9.10 Å., fluoaluminate 8.40 Å., and oxyfluomolybdate 9.10 Å. The results closely resemble those for the chlorostannate. In oxyfluomolybdate oxygen and fluorine atoms are taken as crystallographically equivalent.

G. M. B.

**Electrical Conductivity of Rock Salt Crystal.** D. VON SEELEN (*Z. Physik*, 1924, 29, 125—140).—The electrical conductivity of natural rock salt crystals has been determined at temperatures from 15° to 500°. No experiments were made on chemically pure single crystals, and the material used could only be regarded as presenting roughly a crystal lattice structure. The conductivity varies with different specimens, with the direction of the current in relation to the crystal axes, and with the thickness of the layer. At low temperatures, it is very small. The results are affected to a slight extent by a dielectric polarisation, and after long passage of the current electrolytic polarisation is observed. Ohm's law is valid up to differences of potential of 200 volts. Transport measurements show that the conduction is electrolytic and that the current is carried solely by the sodium ion. The sodium separated at the cathode rapidly changes into hydroxide and carbonate, or bicarbonate. By determining the potential at different points inside the crystal, it has been shown that the fall of potential between the electrodes is not expressed by a straight line graph. The form of the curve does not change with the potential difference applied, but only with temperature. The effect therefore appears to be due to a variable resistance of the material. Charging and discharging phenomena have been studied and are in agreement with Maxwell's theory. The results show that conduction takes place by the formation of volume charges and not of electrical double layers.

M. S. B.

**Free-space Numbers.** I. R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, 141, 304—308; cf. A., 1923, ii, 801; 1924, ii, 520, 823).—The "free-space number,"  $\chi$ , is calculated by subtracting the "filled-space number,"  $\psi$ , from unity. Since  $\psi$  has been determined for a great number of compounds, the values of  $\chi$  have only to be tabulated; the figures obtained vary from 0.3601 for bromobenzene to 0.5401 for ethylene.

S. I. L.

**Hardening Phenomena in Metals as Revealed by X-Rays.**

E. SCHIEBOLD (*Z. Metallk.*, 1924, 417—425, 462—480).—A critical discussion and review of the work and theories of previous investigators on the effect of cold work in hardening metals and the use of X-rays in revealing the changes undergone by metals during plastic deformation is given and the opinion expressed that no satisfactory theory which will account for all the known facts of the mechanism of the hardening of metals by cold work has yet been advanced. Laue and Debye-Scherrer röntgenograms show that plastic deformation takes place as the result of pure translation of the crystals in an orderly geometric manner along slip or twinning planes combined with bending or tearing of the individual crystal grains, and, by observing the symmetry of the diagrams, it is possible to tell approximately the extent and nature of the deformation which the metal has undergone, as the symmetry of the figures is greater the severer the deformation. [Cf. *B.*, 1925, 103.]

A. R. P.

**Structure of Metals and its Physical Investigation.**

J. CZOCHRALSKI (*Z. Metallk.*, 1925, 17, 1—11).—A description is given of an attempt to elucidate the phenomena that occur during the deformation of a metal by investigating the behaviour of a single crystal of aluminium during distortion. Specimens in the shape of round or square rods exhibited after twisting about the long axis and after coiling characteristic reflection figures when polished and etched, the shape of the figures depending to a great extent on the deformation the metal had undergone. Laue photographs also showed this, but not nearly so clearly. A single crystal of aluminium twisted through  $360^\circ$  and again twisted back to its original shape gave almost the same Laue photograph as the original, but the star-like design was not so strongly marked and a polished and etched section showed the presence of twinned crystals along the boundaries of the specimen; annealing at  $620^\circ$  caused complete recrystallisation. From his results, the author expresses the opinion that Póányi's theory of the deformation of metals by the translation and parallel movement of the crystals does not agree with all the known facts. [Cf. *B.*, 1925, 175.]

A. R. P.

**Smectic Compounds and X-Rays.**

E. FRIEDEL (*Compt. rend.*, 1925, 180, 269—271; cf. *A.*, 1923, ii, 223; 1924, ii, 518).—Friedel and de Broglie found that smectic compounds like oleates give diffraction patterns with X-rays. McBain asserted that the results were due to crystalline oleates. The typical smectic compounds, ethyl *p*-azoxybenzoate, ethyl *p*-azoxycinnamate, pass from the crystalline to the smectic condition at temperature  $T_1$  and melt to the amorphous condition at  $T_2$ . Below  $T_1$ , normal X-ray spectra are shown, between  $T_1$  and  $T_2$  the results are of a special type characterised by equidistant planes in one direction. Above  $T_2$  no spectra were obtained. For ethyl *p*-azoxybenzoate  $S=19.9$ ,  $C=16.2$  and for ethyl *p*-azoxycinnamate  $S=23$ . A mixture of 15 parts of the former with 1 part of the latter gave

$S=20.6$ ,  $C=16.2$  where  $S$  and  $C$  are the distances between successive planes in the smectic and crystalline states, respectively ( $C$ =longest distance). The earlier work on solid soaps and pure oleates gave similar results. The only mesomorphs to show diffraction patterns are the smectic compounds.  
R. A. M.

**Determination of the Molecular Weights of Non-volatile Substances by the Isothermal Distillation of their Solutions.**

C. HRYWAKOWSKI (*J. Chim. physique*, 1924, **21**, 396—399).—The accuracy of the microscopical method of determining molecular weights due to Barger (T., 1904, **85**, 286) has been tested by experiments with aqueous solutions of carbamide and resorcinol. If a thermostat is used, the method gives results correct to 0.005 g.-mol., this degree of accuracy being about the same as that obtained by b. p. or f. p. determinations, but the microscopical method has the advantage of being applicable over a range of temperatures.

W. H.-R.

**Variation of the Molecular Weights of Sodium, Potassium, and Tellurium with Temperature.**

A. JOUNIAUX (*Bull. Soc. chim.*, 1924, [iv], **35**, 1607—1613).—From the previously published observations of other workers it is shown that sodium is monatomic over the temperature range 63.5—1063°; potassium is unimolecular near its m. p., but its complexity increases as the temperature rises. Tellurium is monatomic at 357° and becomes more complex at lower temperatures. It is diatomic at high temperatures (about 1500°).

S. K. T.

**Optical Constants of Solid Cæsium.** J. B. NATHANSON (*Physical Rev.*, 1925, [ii], **25**, 75—84).—The optical constants of cæsium with reference to air are, for light of wave-length 4550—6800 Å. (six values are tabulated), as follows: refractive index, 0.362—0.350 (minimum, 0.321 at 5890 Å.); coefficient of absorption, 2.37—4.34; reflecting power, 0.442—0.661; principal angle of incidence, 55°25'—63°20'; principal angle of azimuth, 38°32'—40°6'.

A. A. E.

**Thermoelectric Behaviour of Pure Iron at its Transition Points.** A. GOETZ (*Physikal. Z.*, 1924, **25**, 562—571).—A pure iron wire is heated by the passage of an alternating current. The wire consists of two uniform portions of different diameters, so chosen that when the wire is heated different modifications of iron may exist simultaneously in the two portions. The ratio of the diameters decides the particular modifications which may so exist for a given temperature of the thinner portion. The thermoelectric behaviour of the various modifications may thus be studied right up to the melting point. The results show that there is a big decrease in the thermoelectric power when iron passes from the  $\beta$  modification to the  $\gamma$  modification, and an increase when  $\gamma$ -iron changes to  $\delta$ -iron, thus showing that the space-centred cube structure is thermoelectrically positive with respect to the surface-centred cube structure.

L. F. B.

**Molecular Heats of Vaporisation.** M. PRUD'HOMME (*J. Chim. physique*, 1924, 21, 461—465).—The molecular heat of vaporisation ( $L$ ) at any temperature ( $T$ ) may be expressed by the relation (1),  $L = KT(T_c - T)/(T_c - T_1)$  where  $T_c$  is the critical temperature and  $T_1$  the boiling point, both on the absolute scale. This relation is tested for methyl alcohol. When plotted against  $T$ , the value of  $L/K$  rises to a maximum at  $T = T_c/2$ ; the value of  $K$  is a minimum at this point, but the minimum is flat so that  $K$  is approximately constant at this point, but increases greatly on either side. Empirically  $L$  may be expressed by the relation (2),  $L = a(T_c - T)^n$ , where, for methyl alcohol,  $\log a = 0.3381461$ , and  $n = 0.265$ ; the agreement between observed and calculated results is good to within  $100^\circ$  of the critical temperature. Combination of (1) and (2) shows that  $K$  may be expressed in the form  $K = (T_c - T)^{n-1} \cdot C/T$ , where  $C$  is a constant. The values of  $K$  at different temperatures are calculated for various substances; for nitrous oxide the value of  $L$  calculated for the b. p. indicates that the substance forms unassociated molecules on the basis of Trouton's Law.

W. H.-R.

**Density of Oxygen.** G. P. BAXTER and H. W. STARKWEATHER (*Proc. Nat. Acad. Sci.*, 1924, 10, 479).—The oxygen was weighed in a globe of about a litre capacity in the usual manner against a counterpoise of similar capacity, but with increased refinements. The balance case was wrapped in felt; it contained radium bromide to dissipate electrostatic charges, the balance room temperature was controlled to  $1^\circ$ , and the barometers were immersed in water at a constant temperature. The average of all the twenty-two experiments gave the density 1.42901 g./litre at  $0^\circ$ , 760 mm. of mercury, and sea level, latitude  $45^\circ$ : the g.-mol. volume is in consequence 22.415 litres.

E. B. L.

**Properties of Pure Hydrogen Peroxide. V. Vapour Pressure.** O. MAASS and P. G. HIEBERT (*J. Amer. Chem. Soc.*, 1924, 46, 2693—2700).—Direct measurements of the vapour pressure of hydrogen peroxide are summarised by the equation  $\log p = -(0.05223 \times 48530)/T + 8.843$ . The following constants are deduced: b. p.  $152.1^\circ$ , latent heat of evaporation, 341.5 cal., Trouton's constant, 27.3, critical temperature,  $459^\circ$ . G. M. B.

**Hardness of Manganese Steel.** C. BENEDICKS (*Nature*, 1925, 115, 230).—Shavings, obtained by means of quartz or alundum, from a non-magnetic specimen of manganese steel exhibited ferro-magnetism, but no lines due to  $\alpha$ -iron could be detected by X-ray analysis. It is nevertheless probable that mechanical stress causes a partial conversion of  $\gamma$ -iron into  $\alpha$ -iron. A. A. E.

**Property-Composition Curves of Binary Liquid Mixtures.** L. FRANK (*Z. physikal. Chem.*, 1924, 114, 257—274).—The possibility of interpreting property-composition curves in terms of the van der Waals equation is considered. The properties include vapour pressure, boiling point, specific volume, viscosity, surface tension, and partial pressure, and forty-three binary mixtures have

been examined. It has been found that the assumption of compound-formation or association can be frequently dispensed with, although in some cases, *e.g.*, chloroform-ether, carbon disulphide-acetone, mixtures of benzene with methyl alcohol, ethyl alcohol, acetic acid, and carbon disulphide, and nearly all mixtures with water, satisfactory results are not obtained. The mixtures with water are regarded as ternary mixtures, perhaps with  $(\text{H}_2\text{O})_m$  and  $(\text{H}_2\text{O})_n$ , whilst almost all other mixtures for which calculated and experimental values do not agree contain an associated component. On the other hand, the boiling point-concentration curves show fairly good agreement between calculated and observed values in the case of ether-methyl alcohol and ether-ethyl alcohol, although the alcohols are associated, and the viscosity values also seem to be largely unaffected by association. The vapour pressure-concentration curves for methyl alcohol-ethyl alcohol give good agreement, a fact for which the explanation suggested is that over the temperature range considered ( $20-100^\circ$ ), both components are associated to the same extent.

L. L. B.

**Determination of the Structural Composition of Alloys by a Metallographical Planimeter.** E. P. POLUSHKIN (*Trans. Amer. Inst. Min. Met. Eng.*, Dec. 1924, 19 pages).—The structural composition of an alloy of two or three constituents may be determined by planimetric measurement of the area occupied by each of the constituents on a few representative photomicrographs. This is accomplished by drawing a series of parallel lines at equal distances apart across the surface of the photograph so as to divide the constituents into a number of trapezoids, the total area of which is found by multiplying the distance between two succeeding lines by the sum of the medians of the trapezoids as measured by a recording planimeter. The volume occupied by a constituent of the alloy is then the same fraction of the total volume of the alloy as the area of the constituent is to the whole area of the photograph. If the density of each constituent is known, the weight of each present can be calculated and thus the composition of the alloy found. The application of the method to the analysis of some bismuth alloys and of cast iron is described; the results obtained agree reasonably closely with those found by chemical analysis.

A. R. P.

**Equilibrium in Solutions of the Isomorphous Salts,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , and  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ .** I. ZWEIGLÓWNA (*Roczniki Chemji*, 1924, 4, 331—341).—The solubilities of mixed crystals of these salts between  $0^\circ$  and  $6^\circ$  indicate that the double sulphates are miscible in all proportions and that, in chemical composition, the mixed crystals differ little from the solution, although the two component salts differ in solubility. If  $c_1$  and  $c_2$  indicate respectively the molecular concentrations of the two double sulphates in the solution, and  $x_1$  and  $x_2$  the molecular proportions of the two in the mixed crystals, the values of  $c_1/x_1$  and  $c_2/x_2$  are constant; from this it is inferred that the crystal molecule is identical with the simple chemical molecule. T. H. P.

**Relationship between Tensile Strength, Temperature, and Cold-work in some Pure Metals and Single Solid Solutions.**

D. H. INGALL (*J. Inst. Metals*, 1924, 32, 41—64).—The tensile strength of any uniform metal or alloy is a linear function of temperature (provided no allotropic or phase change takes place) up to a certain critical inflexion temperature beyond which the function is of a higher order. The critical inflection temperature of an alloy is that of the constituent with the lowest inflection temperature; it is the limiting temperature at which a metal retains its properties due to cold work and is possibly influenced by the size and distribution of the constituents. [Cf. *B.*, 1924, 836.] S. K. T.

**Allotropy of Glass.** H. LE CHATELIER (*Compt. rend.*, 1924, 179, 718—721).—The author claims that his equation representing the viscosity of glass as a function of temperature (*ibid.*, 1924, 179, 517) and the inference that the substance exists in another allotropic form below 800° are confirmed by the experimental work of English (*J. Soc. Glass Tech.*, 1924, 8, 205). Calculated values are compared with those obtained experimentally and a diagram indicates the points at which allotropic change occurs for three different types of glass. H. J. E.

**Solubility of Chlorine in Carbon Tetrachloride.** G.-M. SCHWAB and G. HANKE (*Z. physikal. Chem.*, 1924, 114, 251—256).—The solubility coefficient,  $s$ , has been determined by measuring the decrease in pressure with time of chlorine in an apparatus of known volume connected with a very small flask containing a small quantity of carbon tetrachloride. The value of  $s$  is found to be  $0.031 \pm 0.003$  at 19°. The “invasion” coefficient, which is defined as “the number of molecules which pass per second through 1 cm.<sup>2</sup> of surface with 1 atm. difference between the pressure in the gas phase and the osmotic pressure in the solution,” is also determined and is given as  $10^5 i = 2.2 \pm 0.5$  at 19°. L. L. B.

**Solubility of Yttrium Salts.** M. C. CREW, H. E. STEINERT, and B. S. HOPKINS (*J. Physical Chem.*, 1925, 29, 34—38).—The solubility of yttrium chloride, bromide, nitrate, and sulphate has been measured over a temperature range of 0—100°. There is no change in the hydration of these salts over this range. M. B. D.

**Solubilities of Calcium Soaps.** G. A. HARRISON (*Biochem. J.*, 1924, 18, 1222—1223).—The solubilities of the calcium soaps of oleic, palmitic, and stearic acids in alcohol, ether, chloroform, acetone, benzene, xylene, and light petroleum are given. S. S. Z.

**Piezochemical Studies. XXVI. Influence of Pressure on Solubility in the System Naphthalene-Tetrachloroethane.** E. COHEN, W. A. T. DE MEESTER, and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1924, 114, 321—333; cf. *A.*, 1923, ii, 746).—In the course of an earlier investigation (*ibid.*, 1919, 93, 385) it was found that the solubility could be expressed by means of a parabolic curve, and the existence of a minimum solubility was suggested.

This point has now been further investigated, using the system, naphthalene-tetrachloroethane, in which the solubility is strongly influenced by pressure. The two following equations are used to express the results: (1)  $c = \alpha + \beta p + \gamma p^2$  and (2)  $\log c = \alpha_1 + \beta_1 p + \gamma_1 p^2$ , where  $c$  is either the weight per cent. with respect to solvent or solution, or the molecular per cent. with respect to solution. In all cases, equation (1) gives better results than (2), especially where  $c$  is expressed as percentage by weight of the solvent. It has not been possible, however, to decide with any certainty whether the solubility passes through a minimum or not with rising pressure. The increase of solubility amounts to 10.5% for a pressure increase of 250 atm. Concordant results could only be obtained up to pressures of about 1000 atm., probably on account of the great increase of viscosity of the oil at higher pressures.

L. L. B.

**Absorption of Vapours by Charcoal.** E. URBAIN (*Compt. rend.*, 1925, 180, 63—65).—The absorption of chlorine, benzene, and chloropicrin vapours by compressed charcoals has been investigated. If  $v$  is the volume of the pores,  $V$  the volume actually occupied by the carbon, and  $\Phi$  the apparent volume of the charcoal,  $\Phi = v + V$ , and the "compactness"  $c$  is defined as  $c = V/\Phi$ . Increase in the compactness results in increased absorption in the case of chlorine, and diminished absorption with chloropicrin. With benzene, the absorption is a maximum at  $c = 0.300$  and decreases on either side. In the specimens examined  $c$  varied from 0.19 to 0.40. W. H.-R.

**Adsorption of Vapours by Alumina.** L. A. MUNRO and F. M. G. JOHNSON (*Ind. Eng. Chem.*, 1925, 17, 88).—The adsorptive power of alumina depends on its state of dehydration. When the water content is less than 7.2%, however, the adsorptive power remains constant. The adsorption of gases by alumina can be divided into three classes. Ether, ethyl alcohol, petrol, methyl alcohol, and benzene are never completely adsorbed; water and acetic acid are completely adsorbed until the alumina is within about 40% of saturation; sulphur dioxide and ammonia are completely adsorbed until the alumina has become saturated. Substances such as acetone, esters, and organic compounds containing halogens are catalytically decomposed by the alumina. M. B. D.

**Adsorption of Hydrogen and Hydroxyl Ions by Charcoal.** C. KROETZ (*Biochem. Z.*, 1924, 153, 173—184).—Using a series of buffer mixtures of different  $p_H$ , and taking the isoelectric point of charcoal to be that of the buffer mixture which does not change in reaction after adding excess of charcoal to it, it is found that blood charcoal has its isoelectric point at  $p_H$  7.58. An appreciable change in the reaction of a medium is brought about only when much charcoal is used and when the medium is only slightly buffered. The effect of therapeutic doses of charcoal on the  $p_H$  of the alimentary secretions is negligible.

H. D. K.

**Adsorption of Nitrogen Peroxide by Silica Gel.** R. C. RAY (*J. Physical Chem.*, 1925, 29, 74—86).—The adsorption iso-



therms for nitrogen peroxide by silica gel have been determined at 15°, 57°, 80°, and 100° at pressures varying from 11 to 490 mm. Gels containing between 5.16 and 4.68% of moisture have the same adsorptive capacity, but below these values the adsorptive power is considerably diminished, probably owing to an incipient fusion of the surface of the gel due to prolonged heating at a fairly high temperature. By repeated adsorption of nitrogen peroxide, the water is replaced by approximately the same volume of nitric acid and the adsorptive capacity of the gel is only slightly diminished.

M. B. D.

**Active Charcoal. III. Spacial and Stoichiometric Relations of Adsorption (Chemical Complex Formation).** O. RUFF and E. HOHLFELD (*Kolloid-Z.*, 1925, 36, 23—39; cf. A., 1923, ii, 411; 1924, ii, 334).—The adsorption curves of gases and dissolved substances by alder-wood charcoal, activated by steam, approximate to a series of intersecting straight lines. In several cases, the adsorption remains constant over a wide range of concentrations up to the saturation of the solution. Mercuric chloride, aniline, phenol, benzoic acid, fumaric acid, and, possibly, oxalic acid give adsorption curves with two marked changes of direction; the curve for thiocarbamide shows three, and those for caffeine and "saccharin" one such change. The adsorption curve of succinic acid consists of two inclined portions separated by a long interval of constant adsorption. With two exceptions, the breaks occur at points within one of the ranges 1.2 to 1.4, 2.25 to 2.6, and 4.0 to 4.6 millimols. per g. of charcoal. The areas of a postulated unimolecular layer of adsorbed substance at the same points are much less concordant. It is inferred that the adsorption depends on the number and valency of the active surface groups in the charcoal, rather than on the size of the adsorbed molecule. The adsorption curve for carbon dioxide near the temperature of condensation shows breaks at 2.6 and 5.3 millimols. per g. of charcoal. It is suggested that the activation of charcoal involves chemical changes at the surface and not a simple increase in surface area. Adsorption is regarded as a special case of molecular complex formation.

E. M. C.

**Adsorption by Aluminium Hydroxide Considered as a Solid Solution Phenomenon.** L. B. MILLER (*U.S. Pub. Health Repts.*, 1924, 39, 1502—1516).—The relationship of the Freundlich adsorption isotherm to adsorption by aluminium hydroxide is discussed. Precipitation of aluminium hydroxide was carried out in the presence of varying concentrations of negative ions (sulphate and oxalate), and it was found that varying adsorption of each ion took place dependent on the concentration of each ion present, thereby influencing the character of the floc formed. The total adsorption was practically constant at the same total negative-ion concentration regardless of the relative amounts of each ion present. The  $p_H$  is an important factor. Positive-ion concentration may also influence the efficiency of water clarification by alum. Alum floc behaves as a single phase.

CHEMICAL ABSTRACTS.

**Adsorption from Solution from the Standpoint of Capillarity.** I. W. A. PATRICK and D. C. JONES (*J. Physical Chem.*, 1925, 29, 1—10).—The adsorption of formic, acetic, benzoic, and *n*-butyric acids by silica gel containing 6.2% of moisture has been studied in various organic solvents. In general, adsorption of a solute increases as its solubility in the solvent decreases. Although nitrobenzene increases the surface tension, nevertheless it is strongly adsorbed from its solution in kerosene. The adsorption isotherm for acetic acid-carbon disulphide was investigated over the whole available range of concentration. The results are explained by assuming that the adsorbed phase wets the adsorbent and thus presents a highly concave surface to the rest of the solution from the capillaries in the gel. This concave surface decreases the solubility of the solute and hence causes a phase separation.

M. B. D.

**Sorption of Toluene and Acetic Acid and their Mixtures by Carbon.** A. M. BAKER and J. W. MCBAIN (*J. Amer. Chem. Soc.*, 1924, 46, 2718—2725; cf. T., 1921, 119, 454).—In the sorption of the vapours of toluene and acetic acid by sugar carbon maintained at a higher temperature than the liquid, saturation values are found which are nearly independent of the temperature of the carbon: 1 g. of toluene to 8 g. of carbon and 1 g. of acetic acid to 6 g. of carbon. With acetic acid, however, sorption rapidly diminishes above 180°. The amounts of the two vapours sorbed are in proportion to their molecular weights if the doubled molecules of the acetic acid are taken into account. When solutions of toluene and acetic acid are employed, the results agree with the conception that the two substances can replace each other in the adsorbed film. These absolute determinations of sorption agree with the ordinary relative measurements in which "positive sorption" of acetic acid is shown.

G. M. B.

**"Weighting" of Silk with Stannic Chloride.** F. FICHTER and F. REICHART (*Helv. Chim. Acta*, 1924, 7, 1078—1082).—Fichter and Müller (*Färber-Ztg.*, 1915, 26, 253, 274, 289) expressed the opinion that in "weighting" silk with stannic chloride the process begins with the formation of an additive compound of the silk and the stannic chloride. Elöd (*Chem.-Ztg.*, 1922, 46, 597; *Koll.-Chem. Beih.*, 1924, 19, 298) doubts this. New experimental data, however, have confirmed the previous conclusions. Silk (Japanese, Chinese, Turkish, and Italian) was treated at 100° with a solution of anhydrous stannic chloride in anhydrous toluene; the increase in weight was 2.91 to 4.81%, according to the provenance of the silk, but in each case the proportion of stannic oxide in the ash agreed fairly with that calculated on the assumption that the increase in weight was due simply to addition of stannic chloride (51.3 to 65.2% found, against 57.85% calculated).

The esters of amino-acids form additive compounds with stannic and titanic chlorides. Ethyl aminoacetate, for example, affords, when treated with stannic chloride in benzene solution, a resinous compound,  $(C_4H_9O_2N)_2 \cdot SnCl_4$ , easily decomposed by water.

Titanic and stannic chlorides combine with acetic acid to form *titanium dichloride diacetate*,  $\text{TiCl}_2\text{Ac}_2$ , pale yellow crystals, and *tin dichloride diacetate*,  $\text{SnCl}_2\text{Ac}_2$ , colourless crystals, respectively. Both compounds are immediately decomposed by water. W. A. S.

**Dyeing Processes. IV. Influence of Particle Size on the Process of Dyeing.** P. RUGGLI and A. FISCHLI (*Helv. Chim. Acta*, 1924, 7, 1013—1018; cf. A., 1924, ii, 464).—The size of the particles in solutions of various dyes was measured by the rate of diffusion of the dyes into 4% gelatin jelly (cf. Traube and Shikata, A., 1923, ii, 385; Auerbach, A., 1921, ii, 680). The nine (two mono-, three di-, three tri-, and one tetra-) sulphonic acids of benzeneazo- $\beta$ -naphthol used in the preceding experiments (*loc. cit.*) were compared with crystal-violet, and with six substantive dyes. The acid and basic dyes all diffused at approximately the same rate, viz., 23—31 mm. in 84 hours, but the substantive dyes diffused much more slowly and at varying rates.

Certain "union" dyes give redder shades on wool than on cotton from a neutral bath. Their solutions also become somewhat redder on heating, the original colour returning more or less rapidly on cooling. Comparative experiments made with six dyes are described which show these phenomena. The colours of the dyed cotton and wool, the original dyebath and the exhausted bath (in each case) were all compared with one another by matching the solutions etc. against mixtures of standard solutions of water-blue and naphthol-red O. In general, the exhausted bath was redder than the cotton dyed in it, but bluer than the wool. Conflicting results were obtained in other tests. The conclusion reached, however, is that the redder shades are produced by absorption of the smaller particles, and, indeed, are associated with the passage of the dyestuff into a more highly disperse form, this being also the explanation of the redder solution produced on heating (cf. Haller, *Kolloid-Z.*, 1922, 30, 249). W. A. S.

**Theory of Adsorption and Allied Phenomena.** J. FRENKEL (*Z. Physik*, 1924, 26, 117—138).—Langmuir's qualitative treatment of adsorption (*Physical Rev.*, 1916, 8, 149) is now placed on a quantitative basis and an exponential formula is deduced for the mean time during which a gas atom remains adsorbed at a solid surface. From this, other relations are obtained for the layer density, "critical reflexion temperature," diffusion coefficient, etc. The theory is extended to the sublimation and dissociation of solid substances. S. K. T.

**Surface Tension of Sodium and Potassium Amalgams at the Amalgam-Benzene Interface.** S. S. BHATNAGAR, M. PRASAD, and D. M. MUKERJI (*J. Indian Chem. Soc.*, 1924, 1, 81—89).—The interfacial tensions between benzene and sodium and potassium amalgams of various concentrations have been determined at 30° by a drop-weight method. Within the range examined the interfacial tension varies in a linear manner with the concentration of the alkali metals, except for two sharp dis-

continuities in the case of each metal (at 0.06 and 0.27% Na and 0.08 and 0.16% K) which are attributed to the formation of definite compounds. (Cf. Hine, A., 1917, ii, 287.) G. M. B.

**Structure of Surface Films on Water.** N. K. ADAMS (*J. Physical Chem.*, 1925, 29, 87—101).—A summary is given of previous work done by the author (cf. A., 1921, ii, 488; 1922, ii, 687; 1923, ii, 539). The forces exerted by unimolecular films of substances on water indicate a strong tendency of long chain molecules to pack closely together, side by side. This lateral adhesion is overcome when a suitable temperature is reached, which is higher, the longer the chains. There is a strong attraction between such groups as OH, CO<sub>2</sub>H, CO<sub>2</sub>, CH<sub>3</sub>, CN, etc., and water. M. B. D.

**Molecular Orientation of the Fatty Acids.** J. J. TRILLAT (*Compt. rend.*, 1925, 180, 280—281; cf. preceding abstract).—Compounds such as the fatty acids orient themselves when melted on a plate of glass and assume the smectic condition in which the molecules are parallel to one another and their extremities parallel to the surface of the glass. Under these conditions excellent X-ray reflection can be obtained. Powdered palmitic acid gives rise to large concentric circles corresponding with a microcrystalline structure (distances 3.5—4 Å.). The smectic state gives small circles corresponding with distances of 36 Å. measured both by transmission and reflexion. The latter method also discloses diffuse effects due to larger rings (3.5—4 Å.). As the thickness is increased the influence of orientation grows less and the diffuse rays become more intense. The external layer is thus removed from the oriented part and shows the microcrystalline structure. The photographs resemble those of Friedel for oleates, which should possess not only the smectic structure but also microcrystalline structure in thicker layers. R. A. M.

**Phototropism in Solution. II. Optical Activity as an Aid to the Study of Phototrophy.** B. K. SINGH (*J. Indian Chem. Soc.*, 1924, 1, 45—50).—A phototropic change in solutions of  $\alpha$ -naththylaminocamphor in chloroform (cf. A., 1921, i, 351) has been followed by polarimetric observations during the exposure of the solution to direct sunlight. A large increase of rotation was found to accompany the development of green colour. The reverse change in the dark was much slower. Orange or red light had practically no effect. The change did not occur in any solvent other than chloroform, and it was prevented in chloroform solutions by the addition of a trace of sodium ethoxide. The results are tentatively attributed to the formation of a compound of the keto and enol modifications of the "quinhydrone" type. G. M. B.

**Osmotic Pressure of Electrolytes of High Molecular Weight.** E. HAMMARSTEN (*Biochem. Z.*, 1924, 151, 177—180).—The freez-

ing-point depression shown by crystallised egg-albumin chloride prepared by dialysis (*a*) at the isoelectric point, (*b*) in the presence of hydrochloric acid followed by alkali, and (*c*) in the presence of acid at  $p_H$  3, shows that a certain number of the chloride ions are osmotically inactive, a fact which is attributed to the large difference in the ionic volumes of the two constituents of the protein salt (cf. A., 1924, i, 1139). J. P.

**Properties of Phosgene [Carbonyl Chloride] Solutions: Vapour Tension Curves of Aluminium Chloride Solution at 0° and 25°.** A. F. O. GERMANN and G. H. MCINTYRE (*J. Physical Chem.*, 1925, 29, 102—105; cf. A., 1924, ii, 674).—The vapour pressure of solutions of aluminium chloride in carbonyl chloride has been determined by a volumetric method (cf. Germann and Gagos, A., 1924, ii, 861) at 0° and 25° over a range of concentration of 0—50% aluminium chloride. M. B. D.

**Uric Acid. II. Hydrotropic Action on Uric Acid.** R. STERN (*Biochem. Z.*, 1924, 151, 268—273).—Sodium salicylate and sodium 2-phenylquinoline-4-carboxylate ("Atophan") have a marked hydrotropic action on uric acid, a 0.1% solution of "Atophan" dissolving three times as much uric acid as the same volume of distilled water under parallel conditions. The hydrotropic effect is a permanent one and is not due to a change in  $p_H$ . J. P.

**Recent Advances in the Field of Colloids.** T. SVEDBERG (*Chem. Reviews*, 1924, 1, 249—275).

**Metachemistry and Metachemical Processes (A Nomenclature and System of Colloids).** P. D. ZACHARIAS (*Kolloid-Z.*, 1925, 36, 39—42).—It is suggested that terms such as colloid or dispersoid chemistry should be replaced by "metachemistry," in order to avoid initial assumptions as to the nature of the materials studied. The term "tile" is suggested for all particles between  $0.1\mu$  and  $1\mu$ . E. M. C.

**Dispersoid Synthesis of Gold. II. (Preliminary Communication.)** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, 36, 1—12; cf. A., 1923, ii, 645, 869).—Gold sols prepared by the author's modification of the "formol" method with ordinary distilled water have remained stable for many months. Many failures in the formaldehyde method have been due not to the quality of the water, but to impurities in the formaldehyde solutions. The phosphorus, glycerol, tartrate, or citrate methods give stable sols, although moulds may remove the gold. Temperature control and the use of freshly-prepared solutions are necessary to secure reproducible dispersoid synthesis. The factors influencing the size of the colloidal particles are discussed. Increased concentration of the reacting solutions leads to an increase in the mean size of the crystalline aggregates, accompanied by a decrease in the size of the individual crystals. E. M. C.

**Influence of Excess of Reagents on the Formation of Dispersoid Solutions of Mercuric Sulphide.** N. I. MOROSOV (*Kolloid-Z.*, 1925, 36, 21—23).—The addition of sodium sulphide solution to an excess of mercuric chloride gives a white precipitate. With an excess of sodium sulphide, brown stable dispersoid solutions are formed.  
E. M. C.

**Preparation of Colloidal Elements by Photochemical Decomposition of their Gaseous Hydrides. I. Preparation of Colloidal Arsenic.** L. DEDE and T. WALTHER (*Ber.*, 1925, 58, [B], 99—102).—Colloidal solutions of arsenic are readily prepared by bubbling purified arsine through water which is exposed to light of short wave-lengths. According to the dilution, these solutions are yellow to bluish-violet in colour. Only the most concentrated solutions show any tendency towards coagulation; more dilute solutions slowly become colourless owing to the gradual oxidation of arsenic to arsenious oxide. They are very insensitive towards electrolytes. The particles are negatively charged. The behaviour of the solutions towards ammoniacal silver solution, mercuric chloride, and alkaline copper solution proves the particles to be arsenic and not solid arsenic hydride. It has been observed incidentally that arsine reacts with antimony sulphide (*e.g.*, of red rubber tube) to yield arsenic sulphide and stibine which decomposes into antimony and hydrogen; the latter unites with the sulphur in the rubber to give hydrogen sulphide.  
H. W.

**Electric Synthesis of Colloids.** G. BÖRJESON (*Diss.*, *Upsala*, 1921).—Although metallic sols produced by electrical spattering consist usually of (a) metallic globules of microscopic or sub-microscopic size, and (b) a truly colloidal portion, produced by condensation of gaseous metal, it is possible to eliminate the former. Gold alcossols may remain uncoagulated for a year. Most individual particles are secondary particles, *i. e.*, they possess a structure. Increased viscosity of the medium causes the formation of larger particles.  
CHEMICAL ABSTRACTS.

**Metal Sols in Non-dissociating Liquids. II. Composition of the Disperse Phase of Nickel Sols in Benzene and Toluene.** E. HATSCHKE and P. C. L. THORNE (*Kolloid-Z.*, 1925, 36, 12—16; cf. A., 1923, ii; 390).—The nickel sols in benzene and toluene, previously described, contained both positively and negatively charged particles. The decomposition of nickel carbonyl in boiling toluene in an atmosphere of hydrogen gives sols containing particles with negative charges and a high metallic nickel content. Solutions of nickel carbonyl in benzene or toluene often give a pale green precipitate of a hydrated basic nickel carbonate which is dispersed in the presence of  $\frac{1}{6}\%$  caoutchouc to give a positively charged colloid. It is believed that the nickel sols described previously consist of the oxidation products of nickel carbonyl, held on caoutchouc particles and carrying charges only in the outermost layers, with a corresponding difference of composition which is too small to be detected by analysis. The behaviour of organosols is not neces-

sarily simpler than that of hydrosols. An apparatus is described by means of which it is possible to maintain a steady stream of nickel carbonyl for several hours without attention. E. M. C.

**Electrolyte-free, Water-soluble Proteins. III. Salt-Protein Compounds ( $\text{ZnCl}_2$ ).** I. W. PAULI and M. SCHÖN (*Biochem. Z.*, 1924, 153, 253—284).—The authors have examined the compounds which are formed when a solution of pure zinc chloride is added to solutions of serum-albumin, gelatin, and ovalbumin freed from alkali- and acid-protein compounds by prolonged electro-dialysis. All three proteins form reversible compounds with zinc chloride. In the case of serum-albumin, electrometric determinations of free chloride ions show that about twice as much chlorine is bound to the protein as would be inferred from the conductivity measurements, indicating that complex ions containing bound chlorine assist in carrying the current. Serum-albumin and gelatin behave, on the whole, similarly towards zinc chloride, both in the conductivity changes following the addition of varying quantities of this salt and in the mobility of the ions in the mixed solutions. In such solutions serum-albumin and gelatin migrate chiefly toward the cathode. Over a certain range of zinc chloride concentration, which range increases with the dilution of the serum-albumin, heat coagulation of this protein is prevented. Ovalbumin, in presence of this salt, differs from the other two proteins examined, both in its conductivity relations and in the changes found in the ionic mobility. In an electric field it moves in the opposite direction to serum-albumin, and shows no zone of insusceptibility to heat coagulation. H. D. K.

**Quantitative Filtration as a Method for the Analysis of Dispersoids.** WO. OSTWALD (*Kolloid-Z.*, 1925, 36, 46—55).—Curves which show the connexion between the volume of filtrate and the time of filtration under constant pressure, serve to characterise suspensions of clays, soils, precipitates, etc., and to illustrate the changes in the structure of precipitates produced by different methods of preparation, by flocculation and ageing.

E. M. C.

**Action of Silver Sol on Arsenious Sulphide Sol.** H. FREUNDLICH and F. MOOR (*Kolloid-Z.*, 1925, 36, 17—21; cf. A., 1921, ii, 494).—A mixture of silver and arsenious sulphide sols undergoes in the dark a change of colour from golden-brown through greenish-brown to lilac, and, with exposure to light, through green to a golden-yellow. Both changes are prevented in the presence of a gelatin gel. The reaction in the dark is regarded as a direct interaction between the particles of the two sols. The secondary change under the action of light is purely chemical and involves oxygen, with the probable formation of a silver thioarsenite.

E. M. C.

**Stability of Dispersoid Silver Solutions.** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, 36, 55; cf. A., 1923, ii, 645; this vol., ii, 196).—Dispersoid silver solutions prepared by the author's modifi-

ation of the formaldehyde method have remained stable for a year.  
E. M. C.

**Physical Chemistry of the Globulins. VI. Alteration of Globulin by Heat.** M. ADOLF (*Koll.-Chem. Beihefte*, 1925, 20, 288—318; cf. A., 1923, i, 396; 1924, i, 101; ii, 728, 831).—By heating globulin suspensions in water at 100°, the solubility in alkali was reduced to  $\frac{1}{5}$ , in hydrochloric acid to  $\frac{1}{40}$ , and in neutral salt solutions to  $\frac{1}{100}$  of that of the unheated globulin. The combination of heated globulin with base increased with the concentration of the latter. The heated globulin combined with 27 times as much acid as the unheated, and observations on cataphoresis showed that the acid was really in molecular combination. The solubility in salt solutions was greatest for salts with tervalent ions. Solutions containing an excess of globulin in acid or alkali showed, after heating, no change in combining power or in solubility. Globulin in neutral salt solutions coagulated on heating, with no essential change in conductivity or hydrogen-ion concentration. Solutions in salts of tervalent ions underwent no change on heating.  
E. M. C.

**Vanadium Pentoxide Sol. I. Streaming Anisotropy.** H. FREUNDLICH, F. STAPELFELDT, and H. ZOCHER (*Z. physikal. Chem.*, 1924, 114, 161—189; cf. A., 1922, ii, 102; 1923, ii, 514).—The double refraction and dichroism (together called streaming anisotropy), which occur on the streaming of vanadium pentoxide sol, have been quantitatively studied, and the influence of age and concentration of sol, of the velocity of flow, and the temperature has been determined. The sol flowed through a tube with rectangular cross-section, and a polarisation spectrometer with a half-shadow apparatus was employed for the measurements. The source of illumination was the green light of the mercury lamp. It was found that the anisotropy is strongly influenced by the age of the sol. In a freshly-prepared sol it is zero; it increases continuously with time, and finally reaches a maximum. The velocity of ageing, at constant streaming velocity and temperature, is given by the equations  $d\Delta/dt = k_{\Delta}(\Delta_{\infty} - \Delta)^2$  and  $d\Gamma/dt = k_{\Gamma}(\Gamma_{\infty} - \Gamma)^2$ , where  $\Delta$  is double refraction and  $\Gamma$  dichroism. The magnitude of the velocity of ageing is very sensitive to the presence of impurities, arising from the ammonium vanadate used for the preparation of the sol. The influence of arsenic acid is specially marked. The relation between the velocity coefficients and the temperature is given by the Arrhenius equation  $\log_e k = -A/T + B$  in which the constants  $A$  have values of over 10,000, and the temperature coefficient for 10° is about 4. If a sol which has reached the limiting value is diluted, the anisotropy at first decreases in proportion to the dilution. The rate of decrease then slowly diminishes, and finally a new limiting value is reached. This behaviour probably depends on the fact that some of the colloid particles, which cause the double refraction, are in a state of true solution. The anisotropy increases with the velocity of flow. With fresh sols, the increase is regular, but with old sols, a limiting value is reached. For the same sol



at different ages, a series of curves is obtained. A similar series is obtained if the ageing is followed at a different temperature and concentration, or with another sample of the starting material (ammonium vanadate), or even with a different method of preparation of the sol. With rising temperature, the anisotropy diminishes, the influence of temperature being practically linear, and greater for fresh sols than for old. It is found that the double refraction of the sol corresponds, within the limits of error, to that of the vanadium pentoxide contained in it. The absolute value of the double refraction is 1.7.

L. L. B.

**Vanadium Pentoxide Sol. II. The Vortex Cross.** H. FREUNDLICH, F. STAPELFELDT, and H. ZOCHER (*Z. physikal. Chem.*, 1924, 114, 190—207; cf. preceding abstract).—An investigation of the so-called vortex cross of vanadium pentoxide sol, which is formed when the sol is rotated between two cylindrical walls and observed between crossed Nicols. Four minima of brightness are to be seen, giving the appearance of a dark cross, of which the arms form with the direction of polarisation an angle depending on the experimental conditions. The angle has been measured, and found to be independent of the thickness of the liquid layer and the concentration of the sol. It increases rapidly with increasing velocity gradient and increasing age of the sol, and decreases with rise of temperature. The increase of the vortex angle  $\psi$  with age has been followed, and it is found that the velocity of ageing is given by the equation  $d\psi/dt = k_\psi(\psi_\infty - \psi)^2$ . The angle measured in the slowly changing fresh sol has the value  $45^\circ$ , whilst  $\psi_\infty$  approximates to  $90^\circ$ . If the increase of  $\psi_0$  with temperature is considered, the influence of temperature on the growth of the angle with age is given by the Arrhenius equation. The temperature coefficient for  $10^\circ$  is about 2.3. The behaviour of the vortex cross is best explained in terms of the elasticity of the sol. The elastic deformation of the sol elements is small in fresh solutions and with small velocity gradient (cf. Schwedoff, *J. Physique*, 1892, [3], 1, 49). It behaves like that of a rigid body, and the cross angle is  $45^\circ$ . When the velocity gradient is great, and as the sol ages, it approaches  $90^\circ$ . According to this, the cross angle is identical with the angle of maximum deformation; and the direction of maximum deformation corresponds with the direction of the velocity gradient. The colloid particles do not, therefore, arrange themselves along the stream lines, owing to the friction between adjacent liquid layers of different velocities, but place themselves in the direction of maximum deformation. Only in old sols and with high velocity gradients does this direction practically coincide with the direction of flow.

L. L. B.

**Birefringency in Colloids.** A. FREY (*Koll.-Chem. Beih.*, 1925, 20, 209—243; cf. Wiener, A., 1911, ii, 557).—Lyophilic colloids in which the particles, themselves isotropic, are of elongated shape show positive birefringency, whilst with tabular particles the birefringency is negative, in accordance with Wiener's theory. The same principle applies when elongation or flattening is mechanic.

ally imparted to spherical particles such as those of gelatin. With lyophobic colloids, on the other hand, birefringency is due to orientation of the anisotropic (crystalline) particles, as in vanadium pentoxide sols; here Nägeli's theory satisfactorily accounts for the phenomena. Colloids which form gels but not sols, *e.g.*, animal tissues, starch, and cellulose, stand in an intermediate position: their particles are anisotropic, so that small deformations have little effect on the birefringency.

W. A. C.

**Birefringency and Dichroism in Dyed Gels.** H. NEUBERT (*Koll.-Chem. Beih.*, 1925, 20, 244—272).—Thin strips of collodion and denitrated collodion and threads of cellulose acetate were dyed, and thereby made dichroic, with (a) Congo-red, which increases the birefringency of the colloid, and (b) methylene-blue, which decreases it. For a given wave-length the same change in birefringency is brought about by equal amounts of dye, independent of the intrinsic birefringency of the colloid. Exactly the same change is brought about when an equal thickness of the dye itself, *e.g.*, on a glass plate, is rendered dichroic by mechanical stress. Colloids dyed with Prussian-blue show no dichroism and no change in birefringency.

W. A. C.

**Permeability of the Copper Ferrocyanide Membrane to Acids, and the Action of Protoplasm as an Ultrafilter.** R. COLLANDER (*Koll.-Chem. Beih.*, 1925, 20, 273—287; cf. A., 1924, ii, 154).—The rapidity of diffusion of organic acids through a copper ferrocyanide membrane is approximately inversely proportional to the molecular volume of the acid. The diffusion of strong mineral acids is largely determined by the volume of the anion. Earlier workers (*e.g.*, Walden, A., 1892, ii, 203) confused an exchange of hydrogen ions with rapidly diffusing cations for a true diffusion of acid. Thus a potassium ferrocyanide solution becomes strongly acid when in contact with a copper sulphate solution containing citric acid, but a copper sulphate solution becomes only slightly acid when the citric acid is added to the potassium ferrocyanide. Only traces of citric acid diffuse in both cases, but the potassium ion diffuses through the membrane more rapidly than the copper ion. The high permeability of protoplasm for water and oxygen, the more rapid diffusion of formamide compared with acetamide, and the relative permeability for ions suggest that the permeability of protoplasm for lipid-insoluble substances is determined by an ultra-filtration process.

E. M. C.

**Absorbent Power of Agar-Agar.** J. EFFRONT (*Compt. rend.*, 1925, 180, 29—33).—The absorptive power of agar-agar in contact with 0.1N-hydrochloric acid depends on the mineral content, and when all mineral matter is removed no absorption of acid takes place. The absorption of alkali is not so greatly affected by the presence of mineral matter; the absorption is due to the formation of a neutral salt which is stable only in the presence of excess of alkali. In the absorption of acid only the hydrogen ion enters the agar pulp. Agar-agar containing mineral matter will absorb copper

sulphate from solution owing to double decomposition between the latter and the alkali metal of the organic acid. Similar absorptive properties are shown by pulps of beetroots, turnips, and apples.

W. H.-R.

**Adsorption and Osmotic Phenomena in Gels.** T. TOMITA (*Biochem. Z.*, 1924, 153, 335—357).—The adsorption of various fatty acids and alcohols, of urethane and of diethylamine from their aqueous solutions by certain gels, and the swelling produced by the action of these solutions on such gels were studied. Gelatin, egg-albumin, agar, sodium cholate and silicic acid gels, and mixed gels containing gelatin and lecithin, egg-albumin and egg-yolk, were used. Comparative experiments on these gels, with and without the addition of lecithin, point to the conclusion that substances with a relatively small effect on the surface tension (acetic acid, urethane, or even butyric acid) enter the gels almost entirely through the aqueous phase, whilst substances with greater effect on surface tension (octyl alcohol, *n*-octoic acid) enter mixed gels both by the aqueous and the lipid phase. If certain colloids, such as peptone, albumin, and acid dyes, are added to the solutions of fatty acids, and the mixed solutions brought into contact with gels, a surface membrane is produced which does not prevent the entry of fatty acids but which interferes markedly with the swelling of the gel.

H. D. K.

**Density and Hydration in Gelatin Sols and Gels.** T. SVEDBERG (*J. Amer. Chem. Soc.*, 1924, 46, 2673—2676).—The contraction which always accompanies the hydration of gelatin, as measured in a dilatometer, amounts to 54 cub. mm. per gram of dry gelatin in water at 35°. The contraction is diminished considerably in presence of strong acids and alkalis, the first traces of these having relatively the most marked effect. Weak acids and alkalis, and salts or non-electrolytes have no effect. The contraction increases with falling temperature, no discontinuity occurring when the temperature passes into the region of gel formation.

G. M. B.

**Determination of Distribution of Size of Particles in Emulsions.** E. O. KRAEMER and A. J. STAMM (*J. Amer. Chem. Soc.*, 1924, 46, 2709—2718).—The rate of accumulation of a rising disperse phase in the upper layer of an emulsion is determined by observing the movement of the level of liquid in a slanting capillary side-tube due to the fall of density in the upper layer by which it is balanced (cf. Ostwald and Hahn, A., 1922, ii, 205). Distribution curves are derived from the accumulation curves, and the results with two emulsions prepared under the same conditions are shown to be similar. The positions of the maxima in the distribution curves are little affected by changes in the concentration of the emulsions. Potassium oleate tends to give larger drops in a benzene-water emulsion than does potassium palmitate, in accordance with the wedge theory of emulsification. The effect of a "homogeniser" on the degree of dispersion of benzene-in-water emulsions is described.

G. M. B.

**Slow Coagulation of Colloids of the First Order.** K. JABŁCZYŃSKI (*Roczniki Chemji*, 1924, 4, 251—264).—Spectrophotometric investigation of the kinetics of the slow coagulation of colloidal solutions of ferric hydroxide and arsenious sulphide by means of potassium chloride gives results which confirm the accuracy of Smoluchowski's equation,  $n=n_0/(1+\epsilon a n_0 t)$  (A., 1917, ii, 297) and of the author's equation,  $\log \tan \alpha - \log \tan \alpha_0 = K$  (this vol., ii, 35). For ferric hydroxide the relation between  $K$  and the concentration,  $c$ , of the potassium chloride is expressed approximately by the empirical equation,  $K=k_1 c^{7.5}$ ; the speed of the coagulation is not influenced by agitation of the liquid. The coefficient of coagulation of arsenious sulphide depends largely on the amount of hydrogen sulphide present in excess; this coagulation may be completely prevented by addition of a stabilising colloid, such as gum arabic.

The author considers that the coagulation of colloids, whether rapid or slow, and whether of the first or of the second order, proceeds according to the two equations mentioned. T. H. P.

**Rate of Crystallisation of Undercooled Aqueous Sols.** H. FREUNDLICH and F. OPPENHEIMER (*Ber.*, 1925, 58, [B], 143—148; cf. Brann, A., 1918, ii, 393).—The rates of crystallisation of water and twenty-two aqueous sols, emulsions, or suspensions have been measured between  $-3^\circ$  and  $-7^\circ$ . They may be arranged in two groups, in the first of which the particles diminish the rate of crystallisation as dissolved substances invariably do (sols of gold, platinum, arsenic trisulphide, mastic, sulphur, and silicic acid, oil and rubber emulsions, starch and gelatin solutions). In the second group the particles increase the rate of crystallisation (sols of iron oxide, vanadium pentoxide, copper oxide, osmium dioxide, Prussian-blue, benzopurpurin, cotton-yellow, setocyanine, chrysophenin, aniline-blue, soap solution, kaolin suspension). The particles of the substances of the second group are non-spherical (either rodlets or leaflets), whereas those of the first group do not differ greatly from the spherical form. H. W.

**Oxydase-like Actions of Colloidal Silicates.** H. OTA and M. NODA (*J. Sci. Agr. Soc. Japan*, 1924, No. 258, 287—290).—The activity of the colloidal silicates of silver, copper, cobalt, titanium, aluminium, manganese, zinc, magnesium, and ferrous iron, prepared by adding dilute sodium silicate solution to dilute solutions of the respective salts and examined by the indophenol reaction, decreases in the order given by the above series. Powdered kaolin, talc, and serpentine are inactive. Natural earths obtained from seven different areas in Japan exhibit activity, but the action is very weak compared with that of the above artificial colloidal silicates. K. K.

**Ionisation of Proteins.** K. LINDERSTRØM-LANG (*Compt. rend. Trav. Lab. Carlsberg*, 1924, 15, 1—29).—It is shown that the theory of Debye and Hückel (A., 1923, ii, 459) leads to similar expressions for the adsorption of hydrogen ions by protein as are obtained from mass law considerations. The equations are applied to

Sørensen's data for the acid-binding power of egg-albumin and lead to the conclusion that the diameter of the protein molecule is  $3.8 \times 10^{-7}$  cm., as compared with  $2.21 \times 10^{-7}$  cm. from osmotic measurements. The results suggest that the valency varies from 0 to 9 over the range of hydrogen-ion concentration considered. The original paper should be consulted for details. E. M. C.

**Measurements of the Mobility of Egg-albumin at Different Acidities.** N. D. SCOTT and T. SVEDBERG (*J. Amer. Chem. Soc.*, 1924, 46, 2700—2707).—The method previously described (A., 1923, i, 614) has been applied to the study of cataphoresis in sols of egg-albumin. The acidities were varied from  $p_H$  7 down to 2.5 by means of buffer mixtures of sodium acetate with acetic acid and disodium hydrogen phosphate with citric acid. The results with the two buffer mixtures are generally similar, but the acetate-acetic acid mixture gives a broader region of minimum mobility, in which definite indication was obtained of simultaneous movement towards both electrodes. The maximum mobility observed was at  $p_H$  2.93 of  $21.79 \times 10^{-5}$  cm./sec. towards the cathode.

G. M. B.

**Determination of the Mobility of Colloid Particles by the Method of Cataphoresis.** A. F. GERASIMOV (*J. Russ. Phys. Chem. Soc.*, 1924, 54, 818—828).—The experiments were conducted in a specially designed apparatus, consisting of a U-tube with limbs of unequal diameter to overcome the disturbing effects of the products of electrolysis; the electrode of opposite sign to that of the colloid was placed in the wider limb. "Collargol" was the colloid used, solutions of electrolytes of conductivity equal to that of the colloid being placed above the colloid in each limb. From measurements at small velocities (1 cm. per hour) it is possible to calculate the velocity corresponding with the initial potential gradient in the system and from this the mobility of the particles. It was found that the mobility of the particles in the limb containing the cathode is only affected by cations and in that containing the anode by anions; the mobility appears to increase with concentration.

G. A. R. K.

**Dissociation Constants of Dibasic Carboxylic Acids and the Normal Potential of the Quinhydrone Electrode in Absolute Methyl Alcohol.** L. EBERT.—(See i, 230.)

**Relation between the Equilibrium Constants in the Gaseous and Liquid Phases.** W. ŚWIĘTOSŁAWSKI (*Roczniki Chemji*, 1924, 4, 240—250).—Theoretical.

T. H. P.

**Studies in the Aluminium-Zinc System.** T. TANABE (*J. Inst. Metals*, 1924, 32, 415—452).—The equilibrium diagram based on measurements of conductivity and thermal expansion agrees with Hanson and Gayler's results, except in the  $\gamma$ -area (cf. *ibid.*, 1922, 27, 267). The eutectoid change, which occurs with all alloys containing 0.5—75% of aluminium, takes place at  $270^\circ$ . A study of the age-hardening of the alloys confirms Hanson and Gayler's

results in the main; the maximum hardness is explained on a colloidal basis. An abnormal change of hardness takes place at  $270^{\circ}$  with all alloys containing eutectoid; no evidence was found for the existence of  $\text{Al}_2\text{Zn}_3$ . S. K. T.

**Equilibrium in the System Gold-Zinc.** P. SALDAU (*Z. anorg. Chem.*, 1925, **141**, 325—362).—The system gold-zinc has been investigated by thermal and microscopic analysis, and by measurements of electrical conductivity, the theory of the last-named being developed. Solid phases of variable composition are divided into three classes: (1) those in which the conductivity isotherms show no maximum; these are simple solid solutions; (2) those in which the conductivity isotherms show a maximum which remains well-defined and unchanged in position as the temperature rises; such phases contain a definite compound which is stable at the temperatures concerned; (3) those in which the conductivity isotherms show a maximum which, with rising temperature, becomes flatter and slightly displaced; such phases contain a definite compound which gradually decomposes on heating. In the gold-zinc system, alloys containing less than 30 at.-% of zinc deposit on cooling a solid solution ( $\alpha$ ) which, if the alloy contains more than 13 at.-% of zinc, undergoes a transformation at about  $400^{\circ}$ , with the formation of a phase of variable composition ( $\alpha_1$ ) containing the stable compound  $\text{Au}_3\text{Zn}$ . At about  $250^{\circ}$ , the  $\alpha_1$  phase is transformed into a second form ( $\alpha_2$ ), which also contains the compound  $\text{Au}_3\text{Zn}$ , but in this modification the compound is slightly decomposed on heating. Alloys containing more zinc deposit on cooling a solid solution ( $\beta$ ), containing the stable compound  $\text{AuZn}$ , which forms a maximum on the freezing-point curve at  $725^{\circ}$ , the limits of the  $\beta$  solid solution being between 38 and 58 at.-% of zinc. Alloys containing still more zinc deposit on cooling a  $\gamma$  series of solid solutions, which, on cooling, undergo transformations like those of the  $\alpha$  solid solutions;  $\gamma_1$  and  $\gamma_2$  phases are formed which contain the compound  $\text{AuZn}_3$ . At the zinc end of the series, a  $\delta$  phase of very slightly variable composition is formed, the composition corresponding closely with the formula  $\text{AuZn}_8$ , but the existence of a definite compound is not confirmed by the conductivity measurements. Finally,  $\epsilon$  and  $\epsilon_1$  series of zinc-rich solid solutions are formed at the extreme zinc end of the series. It is not possible to detect the changes  $\alpha_1 \rightarrow \alpha_2$  or  $\gamma_1 \rightarrow \gamma_2$  by thermal means. W. H.-R.

**Solidification of Ternary Alloys of Aluminium, Magnesium, and Cadmium.** J. VALENTIN and G. CHAUDRON (*Compt. rend.*, 1925, **180**, 61—63).—The ternary system aluminium-magnesium-cadmium has been examined. The triangular equilibrium diagram is characterised by six freezing-point surfaces, three lines corresponding with binary eutectics, and a ternary eutectic at  $395^{\circ}$ . Aluminium and cadmium are almost completely immiscible in the liquid state, and this region of immiscibility extends for a considerable distance into the ternary alloys. The remaining five surfaces correspond with the primary deposition (on cooling) of

(1) the pure compound  $\text{MgCd}$ , (2) a solid solution in which the compound  $\text{Al}_2\text{Mg}_3$  is the chief constituent, and (3) solid solutions rich in aluminium, cadmium, and magnesium, respectively.

W. H.-R.

**Application of the Ideal Solubility Curve to the Interpretation of Equilibrium Diagrams in Metal Systems.** D. H. ANDREWS and J. JOHNSTON (*J. Inst. Metals*, 1924, **32**, 385—404).—The graph of  $\log c$  against  $1000/T$  for metal solutions, where  $c$  is the molar concentration of the solution in equilibrium with solid at temperature  $T$ , is linear for ideal solutions, the slope being determined by the latent heat of fusion of the solid. Regular divergence from this curve indicates compound formation in the fused mass. The use of the curve in investigating systems not far from ideal is described; in these cases it can be used for interpolation purposes, since it can be plotted for a pure solid phase from a knowledge of the m. p. and the latent heat of fusion. Systems showing limited solid solution give a curve which is linear over a certain range of concentration; outside this range deviation from linearity is found.

S. K. T.

**Stepwise Dissociation of Magnesium Carbonate.** M. CENTNERSZWER and B. BRUŽS (*Z. physikal. Chem.*, 1924, **114**, 237—250).—The method described by Centnerszwer and Andrusow (*A.*, 1924, ii, 655) has been used for the investigation of the dissociation of magnesium carbonate.

For pure, anhydrous magnesium carbonate, the following dissociation steps have been established: (a)  $2\text{MgCO}_3 \rightleftharpoons \text{MgO}, \text{MgCO}_3 + \text{CO}_2$ ; (b)  $2[\text{MgO}, \text{MgCO}_3] \rightleftharpoons 3\text{MgO}, \text{MgCO}_3 + \text{CO}_2$ ; (c)  $3\text{MgO}, \text{MgCO}_3 \rightleftharpoons 4\text{MgO} + \text{CO}_2$ ; control experiments have been performed with natural rhombic magnesite, which is found to decompose by the following stages: (a)  $4\text{MgCO}_3 \rightleftharpoons \text{MgO}, 3\text{MgCO}_3 + \text{CO}_2$ ; (b)  $\text{MgO}, 3\text{MgCO}_3 \rightleftharpoons 2[\text{MgO}, \text{MgCO}_3] + \text{CO}_2$ , or  $2\text{MgCO}_3 \rightleftharpoons \text{MgO}, \text{MgCO}_3 + \text{CO}_2$ ; (c)  $\text{MgO}, \text{MgCO}_3 \rightleftharpoons 2\text{MgO} + \text{CO}_2$ . The first of the dissociation products of magnesite, the monoxycarbonate, is metastable, and passes into the monoxymonocarbonate.

L. L. B.

**Action of Sulphuric Acid on Calcium Oxalate.** E. CARRIÈRE and E. VILON (*Compt. rend.*, 1924, **179**, 1402—1404).—A definite equilibrium is established in the reaction  $\text{CaC}_2\text{O}_4 + \text{H}_2\text{SO}_4 \rightleftharpoons \text{CaSO}_4 + \text{H}_2\text{C}_2\text{O}_4$ . Increase of the concentration of the reagents results in a displacement of the equilibrium to the left. Excess of sulphuric acid leads to an almost proportional increase in the oxalic acid formed. With rise in temperature the yield of oxalic acid at first increases, is maximal at  $30^\circ$  and minimal at  $35^\circ$ , and afterwards increases. This minimum is connected with the maximum solubility of calcium sulphate at this temperature.

H. T.

**Double Decomposition,  $(\text{NH}_4)_2\text{B}_4\text{O}_7 + \text{Na}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{B}_4\text{O}_7 + (\text{NH}_4)_2\text{SO}_4$ , in Aqueous Solution.** V. U. SBORGI and E. BOVALINI (*Gazzetta*, 1924, **54**, 919—933; cf. *A.*, 1924, ii, 477, 478).—Solubility data are recorded for temperatures between the

eutectic point and the temperature at which double salt is formed.  
T. H. P.

**Double Decomposition,  $(\text{NH}_4)_2\text{B}_4\text{O}_7 + \text{Na}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{B}_4\text{O}_7 + (\text{NH}_4)_2\text{SO}_4$ , in Aqueous Solution. VI.** U. SBORGI, E. BOVALINI, and M. MEDICI (*Gazzetta*, 1924, 54, 934—945).—Solubility data are recorded for temperatures between  $-11.02^\circ$  and  $38.7^\circ$ ; over this range double salt formation occurs.  
T. H. P.

**Double Decomposition,  $(\text{NH}_4)_2\text{B}_4\text{O}_7 + \text{Na}_2\text{SO}_4 \rightleftharpoons \text{Na}_2\text{B}_4\text{O}_7 + (\text{NH}_4)_2\text{SO}_4$ , in Aqueous Solution. VII.** U. SBORGI and E. BURICHETTI. **VIII.** U. SBORGI (*Gazzetta*, 1924, 54, 946—964).—Solubility data are recorded for the region  $38.7$ — $55.7^\circ$  in which the salts  $\text{Na}_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{B}_4\text{O}_7$  are stable; at higher temperatures, loss of ammonia creates complications.

These and previous results are shown in diagrams which serve to indicate a method for the preparation of borax from ammonium borate and sodium sulphate, which exhibits certain advantages over the method using sodium chloride (cf. A., 1921, ii, 580).

The diagram given by Meyerhoffer and Saunders (A., 1899, ii, 410; 1900, ii, 198) is confirmed and extended, but it remains undecided whether, in a double decomposition complicated by the formation of a double salt, such a diagram is the only one possible.  
T. H. P.

**Influence of Salts on Solubility.** H. VON EULER and K. RUDBERG (*Z. physiol. Chem.*, 1924, 140, 113—127).—According to Bjerrum (A., 1923, i, 445), the solubility of amino-acids should be greater in salt solutions than in water. This is shown not to be invariably the case. The decreases which occur may be due to a salting-out action on the undissociated molecule, the solubility of which possibly determines the total solubility of the amino-acid. In comparing the solubilities of ampholytes in different salt solutions the  $p_{\text{H}}$  of the solution should be defined. The solubilities of amino-acids are usually greater in mixtures than when alone; the reverse is found with mixtures of leucine and tyrosine.  
E. S.

**Heats of Fusion of Trinitrotoluene, "Tetryl," and Picric Acid.** W. H. RINKENBACH and R. E. HALL (*J. Amer. Chem. Soc.*, 1924, 46, 2637—2639).—From data obtained in the study of the binary systems trinitrotoluene—"tetryl," trinitrotoluene-picric acid, and "tetryl"—picric acid (e.g., A., 1923, i, 909, 1193) the following mean values of the heats of fusion are calculated: trinitrotoluene 20.2, picric acid 20.4, "tetryl" 22.2 g.-cal./g.

G. M. B.

**Heats of Dissociation of the Oxygen and Nitrogen Molecules.** A. EUCKEN (*Annalen*, 1924, 440, 111—121).—The heats of dissociation of oxygen and nitrogen are shown to be much larger than the values usually accepted, viz. 150 Cal. (cf. A., 1920, ii, 210; *Z. Physik*, 1921, 5, 440). A simple thermochemical calculation, which assumes Kohn's value for the heat of vaporisation of carbon (cf. this vol., ii, 100), gives 352 Cal. as the lower limit in



the case of oxygen; calculation of the work of separation of the atoms in the molecule gives an upper limit of 440 Cal. for nitrogen and 425 Cal. for oxygen. The value of this quantity for other di- and tri-atomic gases is also calculated; it is approximately proportional to the number of pairs of electrons concerned in the union of the atoms, each pair corresponding with a work of separation of approximately 80 Cal. The results agree fairly well with those calculated from thermochemical data. S. K. T.

**Re-determination of the Heats of Oxidation of Certain Metals.** J. E. MOOSE and S. W. PARR (*J. Amer. Chem. Soc.*, 1924, 46, 2656—2661).—The heats of oxidation of a number of pure metals have been determined by direct measurement in a bomb calorimeter, the completeness of oxidation being 99% in all cases except that of beryllium. The mean values obtained are as follows: aluminium 6970, beryllium 14,879, cadmium 580, cerium 1661, lanthanum 1641, magnesium 5996, molybdenum 1829, tantalum 1373, tin 1164, tungsten 1059, and zinc 1298 cal./g.

G. M. B.

**Thermochemical Studies on the Oximes. III. Stereoisomeric Dioximes.** A. DORABIALSKA (*Roczniki Chemji*, 1924, 4, 265—286).—The heats of formation of the sodium salts of glyoxime and methylglyoxime suggest the possibility of stereoisomerisation, three stereoisomeric forms being distinguished for glyoxime and four for methylglyoxime. In aqueous solution each of these two oximes forms a mixture of stereoisomerides. Electronic formulæ are suggested for the stereoisomeric oximes.

T. H. P.

**Conductivity of Salt Vapours in the Chlorhydrogen Flame.** S. KALANDYK (*J. Phys. Radium*, 1924, [vi], 5, 345—352).—Alkali halides diluted with sand to varying concentrations are introduced in finely powdered condition into the oxy- and chlorhydrogen flames, and the electrical conductivity measured, using a hot cathode and a hot anode alternately. In general, the conductivity increases with concentration to a maximum, which is very pronounced with a hot cathode in the oxyhydrogen flame. With the chlorhydrogen flame, the conductivity is greater with a hot anode than with a hot cathode for the same concentration of salt. This may be due to greater mobility of the positive ions, but may result from the thermionic emission of positive ions from the anode, and experimental evidence is adduced in favour of the latter view.

C. H. D. C.

**Electrical Conductivity Measurements in Dilute Methyl- and Ethyl-alcoholic Solution at 0°, 25°, and 56°.** P. WALDEN, H. ULICH, and F. LAUN (*Z. physikal. Chem.*, 1924, 114, 275—296; cf. A., 1923, ii, 723).—The conductivities of tetraethylammonium picrate, tetramethylammonium chloride, diethylamine hydrochloride, isobutylamine hydrochloride, and the tetraethylammonium salt of trinitroresorcinol have been measured at 0°, 25°, and 56° in methyl- and ethyl-alcoholic solutions, down to

very great dilutions—in one case, to 60,000 litres per mol. The authors describe a new form of conductivity cell, and methods for the purification of the alcohols, for which the values of  $\kappa_{25}$  were found to be 0.15 and  $0.22 \cdot 10^{-6}$  respectively. Tables are given of the conductivities at round dilutions, the values of  $\Lambda_{\infty}$  being obtained graphically by the square-root law. L. L. B.

**Conductivity Determinations in Non-aqueous Salt Solutions.** P. WALDEN and H. ULICH (*Z. physikal. Chem.*, 1924, **114**, 297—319; cf. preceding abstract).—Conductivity data for solutions of neutral uni-univalent salts in methyl and ethyl alcohol, aqueous ammonia, nitromethane, and acetophenone, are considered with reference to (1) the relation between conductivity and concentration, (2) the change of limiting conductivity with temperature, and (3) the mobilities of the ions (in the case of methyl- and ethyl-alcoholic solutions). The conclusion is reached that in non-aqueous salt solutions, as in aqueous, the region of dilute solutions is characterised by the validity of the cube-root formula at medium dilutions, and of the square-root formula at high dilutions, but that, as with aqueous solutions, the law of mass action is not applicable. The region of dilute solutions in the solvents here considered begins at some hundred litres per mol., whereas with water it begins at from 20 to 50 litres per mol.

It is shown that the numerous earlier measurements giving evidence for the validity of Ostwald's dilution law in non-aqueous solutions cannot be regarded as trustworthy. It is pointed out that the Hertz theory of ionic mobility, although it does not appear to agree with that developed by Debye and Hückel (cf. A., 1923, ii, 724), nevertheless gives almost identical values of  $\Lambda_{\infty}$ . It does not appear possible to decide experimentally between these two theories at the present time, and further theoretical investigation is necessary. New experimental data are advanced in support of the law  $\Lambda_{\infty} \cdot \eta = \text{constant}$ .

Ionic mobilities in methyl and ethyl alcohol are calculated for temperatures between  $0^{\circ}$  and  $56^{\circ}$ . It is found that although the simple ions, *e.g.*,  $\text{Cl}^{-}$  and  $\text{Na}^{+}$ , have a much higher speed in water than the polyatomic picric acid and tetraethylammonium ions, in organic media the mobility of these simple ions rapidly falls off, ultimately becoming smaller than that of the complex ions. This effect can probably be explained by increasing solvation with decreasing dissociation constant of the medium. It is also shown that isomeric organic cations do not move with equal speeds, and that the number, nature, and symmetry of the substituents in the ammonium radical exercise a marked influence. L. L. B.

**Cobalt Chloride Solutions.** I. C. MAZZETTI (*Gazzetta*, 1924, **54**, 891—907).—The mobility of the cobalt ion at various temperatures shows that the ratio of the mobility to the fluidity of water at the same temperature increases with the temperature from  $10^{\circ}$  to about  $30^{\circ}$  and then diminishes regularly with further rise of temperature. This divergence from the behaviour observed by Johnston (A., 1909, ii, 854) with all ions except calcium and

lanthanum probably depends on an independent increase in the value of  $\Lambda$  owing to dehydration of the cobalt ion.

The curves which show the relation between the equivalent conductivity (corrected for viscosity) and the concentration of cobalt chloride solutions exhibit, at all temperatures, a point of inflexion, suggesting that two distinct curves are involved. This behaviour is also explainable in terms of a change in the degree of hydration.

The values of  $C^{-1/3} \cdot \log 1/\alpha$  (cf. Ghosh, T., 1918, 113, 449, 627, 707, 790) differ but little from the theoretical values at high, but considerably at low, concentrations; as the temperature is raised, the agreement becomes perfect at the higher concentrations. The deviations are attributed to diminution of the hydration of the ions with increase in the concentration; hence the equivalent conductivity falls less rapidly than would be expected from the diminution in  $\alpha$ . It seems probable that complex ions are partly responsible for the observed effects, increase of the transport numbers of the anion with increase of the concentration being thus explained. T. H. P.

**Cobalt Chloride Solutions. II. Solutions of Barium Chloride and of Barium and Cobalt Chlorides.** C. MAZZETTI (*Gazzetta*, 1924, 54, 908—918; cf. preceding abstract).—Contrary to what was found for cobalt chloride solutions, the values of  $C^{-1/3} \cdot \log 1/\alpha$  for barium chloride solutions at 20° and 50° are in all cases less than the theoretical values. The observations point to hydration of the ions, the extent of which diminishes as the concentration increases.

Data obtained for the conductivity and viscosity of solutions containing both cobalt and barium chlorides afford evidence of the formation of complex ions. T. H. P.

**The Electron in the Chemistry of Solutions and in Electrochemistry. V. Ionic Reactions, the Ionisation of Metals, and the Osmotic Theory of the Galvanic Current. VI. Electrical Nature of Catalytic Phenomena.** L. PISARSHEVSKI (*J. Russ. Phys. Chem. Soc.*, 1924, 54, 777—797, 798—804).—V.—The processes of electrolysis and osmosis are discussed in the light of the author's views (A., 1923, ii, 729, 730). The atoms in a metal are ionised to a certain extent, depending on the more or less pronounced electropositive character of the metal. When the latter is immersed in water or an aqueous solution, an equilibrium is established between the ions which pass into solution, the electrons liberated in the process, and the "undissociated" atoms. The electrolytic solution pressure therefore depends on two factors: the internal ionisation of the metal, and the electrostatic attraction between the ions so produced and the solvent. The laws of osmosis are also readily interpreted on the basis of these considerations. The electrolytic potential of non-metals in contact with solutions containing their ions depends not only on their chemical nature, that is the tendency of the atoms to

acquire electrons, but also on the degree of ionisation of the electrode immersed in the solution.

VI.—The accelerating action of ferric ions on the oxidation of hydrogen iodide by chlorates is explained by the fact that the ferric ion is positive and therefore comes more readily into contact with both the negative ions taking part in the reaction, thus facilitating the transference of an electron which constitutes the process of oxidation (cf. A., 1923, ii, 730). Hydrogen ions act in a somewhat similar manner in accelerating the interaction between ferric and stannous ions on account of their great mobility (due to absence of solvate formation). The catalytic action of platinum on the union of hydrogen and oxygen is also discussed and it is suggested that the activity of the metal depends on its capacity to adsorb the gases on the one hand and to ionise on the other; the electrons formed act on the adsorbed gases and cause combination. Oxidation of the surface in such metals as zinc prevents their activity.

G. A. R. K.

**Significance of the Electrode Potential.** J. HEYROVSKY (*Chem. News*, 1924, 129, 379—380).—It is contended that Butler (*ibid.*, 128, 357), in criticising the author's thermodynamic treatment of electrode potentials, wrongly identifies the pressure of the metallic ions over the dry metal with the concentration of ions in the vapour over the moist interface, and that this leads to an erroneous step in the cycle.

C. H. D. C.

**Commutator Measurements on Polarised Electrodes.** M. KNOBEL (*J. Amer. Chem. Soc.*, 1924, 46, 2613—2621).—Over-voltage-time curves have been obtained both for increasing and decreasing overvoltage, using a special form of commutator. It is shown that the usual commutator method of measuring over-voltage (cf. Newbery, T., 1914, 105, 2419) is incorrect owing to the fact that the overvoltage falls in a few thousandths of a second when the polarising current is cut off. With platinised platinum electrodes the hydrogen is, however, retained on the surface and maintains the overvoltage. By a graphical method approximate values for the gas concentrations on the polarised electrodes have been deduced. On smooth electrodes, the adsorbed hydrogen is present as about 0.01 of a molecular layer at low polarisations, approaching a molecular layer at high polarisations.

G. M. B.

**Two Types of Overvoltage and the Temperature Effect.** J. L. BIRCHER, W. D. HARKINS, and G. DIETRICHSON (*J. Amer. Chem. Soc.*, 1924, 46, 2622—2631).—Two types of overvoltage are distinguished which have hitherto been confused. That of type A has a negative temperature coefficient which has the same value for several metals, thus indicating that this is not a property of the cathode material, but rather of the electrolyte. Over-voltage of type B, on the other hand, is more stable, tends to appear at low current densities, and is peculiar to active metals. It has a positive temperature coefficient and corresponds closely with the single potential of the metal. The effect of stirring the

electrolyte, of the solubility of the cathode, and of the roughness of its surface are discussed, and it is pointed out that variations in the latter make the values of true current density impossible to determine.

G. M. B.

**Effect of Pressure on Overvoltage.** M. KNOBEL (*J. Amer. Chem. Soc.*, 1924, 46, 2751—2753).—Measurements of the influence of pressure on the hydrogen overvoltage on platinum, lead, copper, and nickel confirm the results of Bircher and Harkins (*A.*, 1924, ii, 88) even when the stirring is violent owing to larger current density and low pressure.

G. M. B.

**Behaviour of Silver Iodide in the Photo-voltaic Cell. II. New Type of Silver Iodide Photo-voltaic Cell.** A. GARRISON (*J. Physical Chem.*, 1925, 29, 58—67; cf. *A.*, 1924, ii, 401).—A thin, transparent film of silver iodide is allowed to solidify on a gold plate and is immersed in a 0.1N-ammonium nitrate solution. The rate of rise of photo-potential is proportional to the light intensity at the beginning of the illumination. For a fixed intensity of light, the rate of chemical change decreases as the light is made more nearly monochromatic for any part of the visible spectrum. A freshly-prepared electrode is more sensitive in the blue region, but after exposure in this region it becomes much more sensitive to red light. The author assumes that the greater the degree of polarity of silver iodide, the longer the wave-length of the light which the valency electrons absorb. A molecule having absorbed a quantum of energy and become polar may return to a less polar state by giving up part of its energy to other molecules. The absorption of a quantum of blue light thus increases the number of molecules capable of absorbing green or red light and accounts for the fact that previous illumination intensifies the effect of long wave-lengths and that the parts of the spectrum taken separately are not additive in their chemical effect. M. B. D.

**Nitric Acid. I. Behaviour as a Nitrating Agent.** A. KLEMENC and R. SCHÖLLER (*Z. anorg. Chem.*, 1924, 141, 231—283).—The nitration of organic substances in solution in water and ether by nitric acid in presence of nitrous acid has been further examined. Nitration proceeds only in presence of oxides of nitrogen in which the nitrogen has a valency lower than five, and is accompanied by oxidation, being therefore autocatalytic. The experimental results indicate that the velocity of nitration varies with the 2.5 power of nitric acid concentration; a tentative assumption of an intermediate compound, *E*-acid,  $\text{H}_2\text{N}_3\text{O}_8$  [ $2\text{HNO}_3 + \text{NO}_2 \rightleftharpoons \text{H}_2\text{N}_3\text{O}_8$ ] leads to the equation

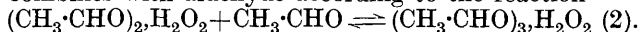
$$-d[\text{HNO}_3]/dt = Kk_1[\text{HNO}_3]^{5/2}[\text{HNO}_2]^{1/2}[\text{RH}]^2/k_2k''^{1/2}[\text{H}_2\text{O}]^{1/2}$$

for the nitration velocity, RH being the material nitrated. The oxidising action under the same conditions is also examined on the basis of the formation and decomposition of *E*-acid; the oxidation of arsenious acid is represented by the cycle  $\text{H}_3\text{AsO}_3 + \text{H}_2\text{N}_3\text{O}_8 \rightleftharpoons \text{H}_3\text{AsO}_4 + \text{H}_2\text{N}_3\text{O}_7$ ;  $\text{H}_2\text{N}_3\text{O}_7 + \text{HNO}_3 \rightleftharpoons \text{H}_2\text{N}_3\text{O}_8 + \text{HNO}_2$ , the latter reaction being strongly catalysed by mercury ions. The

velocity equations deduced from these assumptions are tested by observations on the nitration of methyl *p*-hydroxybenzoate in ether solution and of phenol in water; the values obtained for the constants are not uniform, but are held to indicate the general truth of the assumptions. Nitrosophenol is not an intermediate product in the nitration of phenol in water. Experiments on the partition of nitric and nitrous acids between ether and water, and on the conductivity of solutions of nitric acid containing nitrous acid, undertaken to obtain evidence of the existence of *E*-acid, gave no definite results.

Nitration in presence of sulphuric acid, using 2:4-dinitro-*m*-xylene, *p*-chloronitrobenzene, and 4:6-*m*-xylenedisulphonic acid, gave excellent constants for bimolecular reactions, the constants not being appreciably altered by the presence of nitrous acid and lower oxides of nitrogen. In this solvent, therefore, there is no formation of the intermediate *E*-acid. Nitric anhydride,  $\text{N}_2\text{O}_5$ , reacts as  $\text{N}_2\text{O}_5/2$ , giving the same constants as nitric acid. S. I. L.

**Oxidation of Acetaldehyde. II.** L. REINER (*Z. anorg. Chem.*, 1925, **141**, 363—374; cf. A., 1923, i, 1176).—When solutions of acetaldehyde and hydrogen peroxide are mixed, heat is evolved owing to the formation of diacetaldehyde hydroperoxide:  $2\text{CH}_3\cdot\text{CHO} + \text{H}_2\text{O}_2 \rightleftharpoons (\text{CH}_3\cdot\text{CHO})_2\cdot\text{H}_2\text{O}_2$  (1). At  $0^\circ$  this compound is fairly stable, but dissociates rapidly on heating the solution. The velocity of oxidation of acetaldehyde by hydrogen peroxide increases with increasing concentration of aldehyde, but is little affected by the amount of hydrogen peroxide, provided that the ratio hydrogen peroxide/aldehyde is greater than 0.25:1; a large excess of hydrogen peroxide slightly retards the oxidation. The amount of acetic acid produced is usually greater than that corresponding with the hydrogen peroxide used up, and the amount of this excess increases with the absolute concentration, but is unaffected by the ratio hydrogen peroxide/aldehyde. These results are accounted for if the diacetaldehyde hydroperoxide produced in (1) combines with aldehyde according to the reaction



This second additive product is then oxidised directly by molecular oxygen to acetic acid:  $(\text{CH}_3\cdot\text{CHO})_3\cdot\text{H}_2\text{O}_2 + \text{O}_2 \rightarrow 3\text{CH}_3\cdot\text{CO}_2\text{H} + \text{H}_2\text{O}$  (3). The molecular oxygen required in (3) may be obtained either from decomposition of the hydrogen peroxide or from the air, and the excess of acetic acid referred to above is greatly reduced if oxygen is excluded from the reaction vessel. The retarding effect of a large excess of hydrogen peroxide is due to its reducing the concentration of free aldehyde owing to the mass-action effect in equation (1). The oxidation may be regarded as an auto-oxidation of diacetaldehyde hydroperoxide, acetaldehyde being the acceptor; on the basis of the theory of Goard (A., 1924, ii, 161), the oxidation potentials are in the order  $(\text{CH}_3\cdot\text{CHO})_3\cdot\text{H}_2\text{O}_2 > \text{CH}_3\cdot\text{CHO} > (\text{CH}_3\cdot\text{CHO})_2\cdot\text{H}_2\text{O}_2$ . The autocatalytic effect of acetic acid previously reported (Reiner, *loc. cit.*) is incorrect.

W. H.-R.

**Molecular Attraction and Velocity of Reactions at Low Temperatures of Unsaturated Hydrocarbons.** O. MAASS and C. H. WRIGHT (*J. Amer. Chem. Soc.*, 1924, **46**, 2664—2673; cf. A., 1921, i, 761).—The freezing-point diagrams of the systems ethylene–hydrogen bromide and propylene–hydrogen bromide show that propylene molecules have a greater attraction for hydrogen bromide than have ethylene molecules, there being definite indication of compound formation in the case of propylene only. The fact that propylene combines in the liquid state with hydrogen bromide, whilst ethylene does not, is attributed to this difference in the respective attractions of the molecules. The velocity and the course of the reaction between propylene and hydrogen bromide have been determined at  $-78.2^{\circ}$  and at  $0^{\circ}$ , isopropyl bromide being the main product together with a small amount of a secondary hexyl bromide.  
G. M. B.

**Activation of Atoms and Molecules and Mechanism of Chemical Change.** N. R. DHAR (*Z. anorg. Chem.*, 1924, **141**, 1—22).—The well-known fundamental concepts of the activation of molecules and the radiation theory of chemical change are reviewed. Stress is laid on the fact that ionic reactions are very rapid compared with non-ionic. The similarity in mechanism between rise of temperature, light absorption, and catalysis is emphasised. Experimental observations support the view that if a sufficient quantity of catalyst could be added to change a large number of molecules from the inactive to the active form, or conversely, then the temperature coefficient would be smaller (in the case of positive catalysis), or greater (for negative catalysis), than for the uncatalysed reaction. The opinion is expressed that active nitrogen, ozone, active hydrogen, active chlorine, etc. are activated by light or electric discharge, and can be charged to a certain potential. Their activity is conditioned by the ease with which they can give up their charge as energy. The luminescence of active gases, such as nitrogen, hydrogen, oxygen, etc., and the appearance of radioactive excited phosphorescence, can probably be traced to the conversion of the active form of these substances into the inactive form by loss of energy.

All slow oxidations seem to yield ions and electrons, which could activate the oxygen molecule. This active oxygen would show all the characteristics of ozone. A part would revert spontaneously to the inactive form, with production of luminescence. This is the probable cause of the luminescence caused by the slow oxidation of phosphorus, the organic sulphur compounds, etc.

L. L. B.

**Perchlorate Ion as Catalyst in the Electrolytic Preparation of Persulphuric Acid.** A. MAZZUCHELLI (*Gazzetta*, 1924, **54**, 1010—1013).—The yields of persulphuric acid prepared by the anodic oxidation of sulphuric acid are markedly improved by addition to the solution used of a small proportion of perchloric acid or its ammonium or potassium salt. No hydrochloric acid is formed under these conditions.  
T. H. P.

**Autocatalytic Reaction: Ferric Chloride-Sodium Thio-sulphate.** J. HOLLUTA and A. MARTINI (*Z. anorg. Chem.*, 1924, **141**, 23—37; cf. *ibid.*, 1924, **140**, 206).—An unsuccessful attempt has been made to trace the initial acceleration of the reaction ferric chloride-sodium thiosulphate to the autocatalytic action of the end products, *i.e.*, the ferrous or tetrathionate ion. Addition of both ferrous and tetrathionate salts retards the reaction. The influence of the ferrous ion on the reaction velocity may be represented by the equation,

$$dx/dt = [k_2 - k'_2 \sqrt{x} \cdot (1301 - 21563x)] \cdot (a-x)(b-x).$$

It was thought that the phenomenon might be due to the catalytic action of sulphur formed by the reaction between hydrogen ions and sodium thiosulphate, or to the means adopted to stop the reaction at the required point. Both these explanations were, however, found to be incorrect. Investigations with the addition of foreign, complex anions (phosphate), and with a higher acidity, showed that the acceleration is probably due to a negative catalyst which is removed during the reaction; it is assumed to be the reacting ferrithiosulphate complex. L. L. B.

**Method of Producing Chemical Reactions.** M. BRUTZKUS (*Compt. rend.*, 1925, **180**, 199—201; cf. Brit. Pat. 155776, 217747).—A chemical reaction may be directed or accelerated by means of continuous and simultaneous variations of pressure, temperature, and concentration opposite to those resulting from the desired reaction, whereby a series of impulses is given to the reaction. Metals and metal oxides which catalyse gaseous reactions probably alter the conditions of pressure and concentration by differential absorption of the reacting gases, and temperature by rapid conduction of the heat liberated, thus preventing the reversible reaction from setting in. Internal-combustion engines provide the best means of studying chemical reactions under such conditions. J. W. B.

**Synthesis of Ammonia at High Pressures.** II. W. MOLDENHAUER (*Chem.-Ztg.*, 1925, **49**, 65—66; cf. A., 1924, ii, 404).—The author compares the results obtained by Larson and Dodge (A., 1924, ii, 104) and by Larson (A., 1924, ii, 331) on the ammonia equilibrium at high pressures with those of Claude and with Haber's equation. M. B. D.

**Mechanism of the Inhibition of the Catalytic Action of Platinum Black and Partly Reduced Nickel Oxide by Chlorine.** M. C. BOSWELL and C. H. BAYLEY (*J. Physical Chem.*, 1925, **29**, 11—19).—Nickel oxide on asbestos is reduced by hydrogen at 275° to a constant oxygen content (cf. A., 1923, ii, 231). After chlorine has been introduced, the oxide content can be decreased by passing more hydrogen over the catalyst. When hydrogen and oxygen are passed alternately over platinum black at 150°, an equilibrium is reached when the amounts of the two gases converted into water each time remain constant (cf. *Proc. Roy.*



*Soc. Canada*, 1923, **17**, 1). After poisoning the catalyst with chlorine, hydrogen accumulates after each successive gas treatment until it is suddenly evolved in a large amount as water. The poisoning is accomplished by the destruction of the surface film of the catalyst, thus rendering the interior oxygen accessible to free hydrogen. This interior oxygen is vital to the maintenance of the active surface film and hence of the catalytic action of the normal catalyst.

M. B. D.

### Theory of Catalytic Hydrogenation by Means of Platinum.

M. BODENSTEIN (*Annalen*, 1924, **440**, 177—185).—The hydrogen layer formed on platinum immersed in a mixture of hydrogen and oxygen is found by electro-potential measurements to be replaced by a layer of oxygen when the ratio of oxygen to hydrogen in the gas is 3.6 : 2 by volume, or greater. Other evidence supports this conclusion. A theory of heterogeneous catalysis is proposed in which the valency force emerging from the surface of a catalyst is supposed to deform the gaseous molecules adsorbed by a surface in such a way that they are in a specially active state. Thus, hydrogen may become atomic on platinum surfaces, the nucleus of the atom adhering to the surface of the catalyst by virtue of its electron, which is held between two slightly vibrating electrons in the metal. It is very improbable that a peroxide of platinum is formed in the catalysis of electrolytic gas (cf. A., 1921, ii, 185; 1924, ii, 724).

S. K. T.

### Catalytic Action of Alumina containing Other Substances.

A. CHARRIOU (*Compt. rend.*, 1925, **180**, 213—215).—The effect of foreign substances on the activity of alumina used as catalyst in the decomposition of ethyl ether (cf. Sabatier and Mailhe, A., 1910, i, 606) has been investigated. The least active sample of alumina contained 15% of calcium oxide. A sample containing 4.5% of the same impurity was slightly more active, and samples containing 2.5% of cobaltous oxide, 7.7% of cupric oxide, or 15% of phosphoric oxide were still more active. Other catalysts submitted to examination contained 6.5%  $\text{WO}_3$ , 8%  $\text{SO}_3$ , and 1%  $\text{SO}_3$ , whilst a fourth was prepared by the oxidation of aluminium in presence of mercury. The activity of these was found to increase in the order given. When pure alumina is heated at a red heat for  $\frac{1}{2}$  hour the activity falls to less than half its original value. The only admixture having a beneficial effect is that of blue tungsten oxide,  $\text{W}_2\text{O}_5$ ; a sample, prepared by treating alumina containing the trioxide with hydrogen at  $250^\circ$ , was considerably more active than the pure alumina.

W. A. S.

### Reduction of Nickelous and Ferric Oxides by Hydrogen.

A. F. BENTON and P. H. EMMETT (*J. Amer. Chem. Soc.*, 1924, **46**, 2728—2737).—The kinetics of the reduction by hydrogen of various specimens of nickel and ferric oxides have been examined. Reduction of nickel oxide is auto-catalytic, proceeding mainly at the interface between the solid phases, whilst no autocatalysis is

observed in the reduction of ferric to ferro-ferric oxide, the reaction velocity being greatest at the start and diminishing continuously. These results are in agreement with Langmuir's theory that heterogeneous reactions involving a solid substance on each side of the equation should be "interfacial" when the solids remain separate, but "non-interfacial" when solid solution occurs. Reduction of the nickel oxide is less rapid the higher the temperature of preparation of the sample. At higher reduction temperatures, the maximum rate of reduction is greater and occurs earlier in the process. Water vapour retards the reaction, as does oxygen in the hydrogen used. The mechanism of the hydrogen-oxygen catalysis over nickelous oxide appears to be that of activation of the oxygen by adsorption or by superficial conversion into a higher oxide of nickel.

G. M. B.

**Behaviour as Salts of Alkali Alkyls Dissolved in Metal Alkyls.** F. HEIN [with E. PETZCHNER, K. WAGLER, and F. A. SEGITZ] (*Z. anorg. Chem.*, 1924, **141**, 161—227).—The alkali alkyls, LiEt, NaEt, KEt, LiMe, LiPh, and LiCH<sub>2</sub>Ph, dissolve in zinc ethyl to form solutions which conduct electricity; with increasing electro-positive character of the alkali metal, the molecular conductivity and m. p. of the alkyl compound rise, and its miscibility with the solvent falls. Since lithium ethyl does not act as a conductor either in the fused state or in solution in benzene, and since the molar conductivities fall sharply with dilution in some cases, it appears that association with the solvent and formation of complex ions are necessary conditions, absence of which may cause the solution to remain non-conducting. Thus lithium phenyl conducts very little, sodium phenyl not at all, whilst *lithium benzyl*, LiCH<sub>2</sub>Ph, a yellow, amorphous precipitate obtained by the reaction between lithium ethyl and mercury dibenzyl in benzene solution, has the highest conductivity of the lithium alkyls examined. Aluminium ethyl and zinc propyl are also solvents giving conducting solvates; the associated compounds of the alkali alkyls with the former have higher m. p. and conductivities, with the latter lower, than the compounds with zinc ethyl. Dilute solutions of the alkali methyls in zinc methyl and aluminium methyl, and concentrated solutions of sodium and lithium ethyl in cadmium ethyl, do not conduct.

Electrolysis of sodium ethyl dissolved in zinc ethyl gives at the anode a mixture of gases containing about 40% of ethylene, about 40% of ethane, and the remainder butane, propane, and methane, justifying the assumption that the ethyl radical is liberated by the electrode. Zinc is deposited quantitatively at the cathode, Faraday's law being strictly obeyed. The conductivity temperature coefficient is positive. The potential required is less than 0.1 volt. With a lead anode, lead tetraethyl is obtained quantitatively; after passing a current of 0.02 amp. for 7 hours, the lead electrode had lost almost the theoretical weight, and the tetraethyl compound separated as an oil at the bottom of the electrolyte.

S. I. L.

[Corrosion of Copper, Brass, and Zinc in Sea-water.] **Seventh Report to the Corrosion Research Committee of the Institute of Metals.** G. D. BENGOUGH and R. MAY (*J. Inst. Metals*, 1924, 32, 81—256).—The chief initial corrosion product of copper in chloride solutions is cuprous chloride which, in both distilled and sea-water at the ordinary temperature, is oxidised to cupric chloride and cuprous oxide; in presence of sufficient oxygen, these are further oxidised to a basic chloride,  $\text{Cu}_4(\text{OH})_6\text{Cl}_2 \cdot \text{H}_2\text{O}$ . Cupric chloride does not accumulate in the water; it may attack the copper, causing an electrolytic corrosion in which metal is transferred from one part of the copper to another. The scales on copper exposed to sea-water were found to consist of calcium sulphate, cupric hydroxide (both probably forming protective layers), cupric oxychloride, and a basic copper carbonate. The scales have a much lower protective value in rapidly moving than in stagnant water. The corrosion of zinc in sea-water results mainly in the formation of carbonate, hydroxide, and oxychloride; the two last form protective layers, which, however, are greatly impaired by the presence of carbon dioxide. When brass corrodes in cupric chloride solution, zinc chloride and copper are first produced; the latter then redissolves to form cuprous chloride, which is then oxidised, in presence of sufficient oxygen, to the above-mentioned basic chloride. If the reaction is stopped at the first stage, no further corrosion takes place and copper is deposited on the zinc beneath the scales ("dezincification"); 0.02% of arsenic in the brass prevents this, but iron and manganese accelerate it. Brass in still water is cathodic with respect to a similar specimen in unaërated moving water and is anodic to one in slowly moving aërated water, but it becomes cathodic again in rapidly moving aërated water. The corrosion of brass condenser tubes is also investigated; it is very sensitive to the presence of "entangled" air in the water. [Cf. *B.*, 1924, 833.] S. K. T.

**Anodic Oxidation of Gold. II. Properties of Auric Sulphate.** F. JIRSA and H. JELINEK (*Chem. Listy*, 1924, 18, 251—252; see *A.*, 1924, ii, 692). W. A. S.

**Photochemical Formation of Hydrogen Bromide and Velocity of Formation of the Bromine Molecule from the Atoms.** M. BODENSTEIN and H. LÜTKEMEYER (*Z. physikal. Chem.*, 1924, 114, 208—236).—The velocity of combination of hydrogen and bromine in moderately intense light has been investigated. The views which have been put forward to explain the phenomena of the reaction are recapitulated, and a method is described which allows a decision to be made between the various possibilities. The method consists of subjecting bromine vapour and hydrogen, contained in suitable concentration in a silica vessel with plane parallel walls, to illumination from a tungsten arc lamp. The vessel is kept at a constant temperature over the range 160—218°. After each illumination, the absorption of bromine is measured with a spectrophotometer, from which the reaction velocity can be determined. The energy absorbed from the light is measured in

the cold vessel by means of a thermopile. It is shown that the measurement of the absorbed radiation (of wave-length 525, 516, and 504  $\mu\mu$ ) is not affected by temperature over the range investigated. It is found that the combination of hydrogen and bromine takes place with a velocity which is about three hundred times as great as that of the reaction in the dark at the same temperature, and according to a law which follows from that of the dark reaction. By this, the velocity is determined by that of the combination of hydrogen with bromine atoms, existing according to the equilibrium  $\text{Br}_2 \rightleftharpoons 2\text{Br}$ . In light, there is in place of the velocity of spontaneous decomposition, that of the decomposition of the bromine molecule by absorbed light quanta. The equation for the light reaction therefore has the form

$$+d[\text{HBr}]/dt = k\sqrt{\text{light absorbed}} \cdot [\text{H}_2]/(1 + [\text{HBr}]/10[\text{Br}_2])$$

This is derived in all particulars from the theory of the reaction in the dark. A measurement of the absorbed light quanta allows the velocity with which bromine atoms are formed and recombine to be ascertained. A comparison of the velocities in light and in the dark is supplied by associating the known dissociation equilibrium of bromine vapour with the concentration of bromine atoms. From this, the number of collisions can be calculated, and a comparison of this with the number of combinations to form molecules leads to the conclusion that only 1.25% of the collisions result in combination, independent of the total pressure of the gas, and of the temperature (within the narrow range investigated). This result contradicts that expected from theoretical considerations.

L. L. B.

**Photochemical Studies. IV. Properties of the Silver Gelatino-halides.** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1924, **33**, 550—558).—Aqueous colloidal solutions of silver chloride or bromide are rapidly reduced by “metol”—quinol developer in daylight. Colloidal solutions of these salts in 1% gelatin solution prepared in the dark slowly become rose-coloured, then grey, and finally black and flocculent on exposure to daylight. The developer has no action in the dark, but after a short period of incubation rapidly reduces the solutions on exposure to daylight. If the gelatin solution is prepared in the light, the reducing action of the developer is more rapid the greater the age of the solution, bromide solutions in all cases being more slowly reduced. Colloidal silver iodide solutions are practically unaffected by light and only very slowly and incompletely reduced by the developer, yielding yellow to brown translucent liquids. It is suggested that the action of the light in promoting the reducing action of the developer may be explained by assuming that the reduction is due to electrochemical action; the light reduces photochemically part of the silver halide to metal and this metal then becomes an anode and the unchanged halide a cathode, the anode being constantly depolarised by the developer and the cathode progressively reduced to metallic silver by the hydrogen ions discharged on its surface.

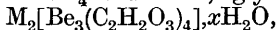
A. R. P.

**Photochemical Decomposition of Chromium Salts in the Presence of Organic Matter.** A. POPOVICKI (*J. Russ. Phys. Chem. Soc.*, 1924, 55, 1—6).—It is suggested that the substance obtained when gelatin treated with a dichromate is exposed to sunlight is the compound,  $4\text{Cr}_2\text{O}_3 \cdot 3\text{CrO}_3$ ; the tanning action on gelatin is attributed to this compound. G. A. R. K.

**Alleged Influence of Light on Electrophoresis.** K. SCHAUM and P. FRIEDERICH (*Z. wiss. Phot.*, 1924, 23, 98—101).—Sols of metals in water and organic media, prepared according to the methods of Bredig and of Svedberg, and of sulphur and arsenious sulphide in water, and suspensions of anthracene in pure hexane were investigated. Practically all the sols and suspensions examined showed no difference in the migration velocity in ultra-violet light and in light of long wave-length. Zinc hydrosol alone showed a small decrease in the velocity on exposure to ultra-violet radiation. The effect was not observed with zinc sols in alcohol, and is probably due to some chemical action. Electrophoresis of hydrosols of the silver halides is appreciably affected by light, which can bring about reversal of the direction of migration. The presence of silver oxide particles in a silver sol in water prepared by Bredig's method can be investigated by adding gelatin and observing a thin preparation in the microscope with dark-ground illumination. If acetic acid is allowed to diffuse in, any silver oxide particles are rapidly dissolved. The influence of positive particles of silver oxide on the direction of migration in a negative silver sol is briefly discussed. W. C.

**Photochlorination of Aliphatic Compounds in Carbon Tetrachloride.** J. PLOTNIKOV (*Z. wiss. Phot.*, 1924, 23, 79—80).—Some of the results obtained by Benrath and Hertel (*A.*, 1924, i, 821) indicate a tendency for periodicity in the photochlorination, an effect which would undoubtedly be more pronounced if longer times of exposure were employed. The results, however, are of little value, since monochromatic light was not used, and the source of light was not specified. W. C.

**Internally Complex Beryllates.** A. ROSENHEIM and F. LEHMANN (*Annalen*, 1924, 440, 153—166).—The following crystalline metallic salts of internally complex beryllates of some organic acids were prepared by dissolving beryllium carbonate or freshly-precipitated hydroxide in boiling solutions of alkali salts of the acid: salicylic acid,  $\text{M}_2[\text{Be}(\text{C}_6\text{H}_4\text{O} \cdot \text{CO}_2)_2] \cdot x\text{H}_2\text{O}$ , where  $\text{M}=\text{K}$ ,  $\text{Na}$ , or  $0.5\text{Ba}$  and  $x=3$ ,  $\text{M}=\text{NH}_4$  and  $x=2$ ; glycollic acid,



where  $\text{M}=\text{K}$  and  $x=8.5$ ,  $\text{M}=\text{Na}$  and  $x=4.5$ , and the ammonium salt,  $(\text{NH}_4)_4\text{H}_2[\text{Be}_5(\text{C}_2\text{H}_2\text{O}_3)_8] \cdot 3\text{H}_2\text{O}$ . With *o*-hydroxytoluic acid, two series of compounds were obtained, one,  $\text{M}_2[\text{Be}(\text{C}_8\text{H}_6\text{O}_3)_2] \cdot x\text{H}_2\text{O}$ , where  $\text{M}=\text{Na}$  and  $x=0$ ,  $\text{M}=\text{NH}_4$  and  $x=1$ , when freshly-precipitated hydroxide was used, and the other,  $\text{M}_2[\text{Be}_2\text{O}(\text{C}_8\text{H}_6\text{O}_3)_2] \cdot \text{H}_2\text{O}$ , where  $\text{M}=\text{NH}_4$  or  $\text{K}$ , when the hydroxide was stale. Boiling, strongly alkaline solutions of pyrocatechol dissolved beryllium

hydroxide and gave a series of normal salts,  $M_2[Be(C_6H_4O_6)_2] \cdot xH_2O$ , where  $M=NH_4$ , Na, K, 0.5Ba, and  $x=1, 5, 2, 1.5$ , respectively. By warming together known amounts of pyrocatechol with excess of hydroxide and gradually adding alkali the following polyberyllates were obtained:  $(NH_4)_2[Be_2O(C_6H_4O_2)_2] \cdot 5H_2O$ ;

$(NH_4)_4[Be_3(C_6H_4O_2)_5] \cdot 2H_2O$ ;  $(NH_4)_4[(Be_2O)_3(C_6H_4O_2)_5] \cdot 13H_2O$ ;  $M_8[Be_6O(C_6H_4O_2)_9] \cdot xH_2O$ , where  $M=Na$  and  $x=20$ ,  $M=K$  and  $x=9$ . A crystalline salt,  $(NH_4)_6[Be_3(C_6H_3O_2SO_3)_4] \cdot 8H_2O$ , and an amorphous product, probably a mixture, corresponding with  $Ba[Be_2(C_6H_3O_2SO_3)_2]$ , were also prepared. Vitreous metallic salts of internally complex beryllates of citric acid were obtained, but are not described. Similar compounds are formed with polyphenols, but not with polyalcohols. Boiling ethyl salicylate dissolves beryllium carbonate to form a complex beryllium compound.

The beryllium in the compounds derived from salicylic and *o*-hydroxytoluic acids is scarcely precipitated at all by ammonia or alkali hydroxide, showing that it is present in an exceedingly complex state. This is probably not caused by adsorption of beryllium hydroxide by the salt, since the compounds are reproducible. The glycollic acid compounds are readily, and the pyrocatechol compounds partly, decomposed by ammonia. The complex beryllium tartrate and the basic acetate are considered to be internally complex salts of the sexavalent radical,  $Be_4O$ .

S. K. T.

**Silicate Compounds of Cadmium.** A. DUBON (*Compt. rend.*, 1924, 179, 769—771; cf. A., 1921, ii, 403, and previous papers).—Addition of silica, followed by cadmium oxide, to fused potassium fluoride yields a semi-crystalline product which, when heated with excess of potassium chloride, yields a mixture of well-crystallised compounds. The latter, on separation by flotation methods, proved to contain (a) long prismatic *crystals*,  $K_2O, CdO, 4SiO_2$ ; (b) *crystals* of  $2CdO, SiO_2$  containing potassium, probably as impurity, and (c) yellow flattened prismatic *crystals* of  $3CdO, SiO_2$ . H. J. E.

**Absorption of Halogens by Mercurous Salts. I. Formation and Properties of some Complex Compounds of Mercury.** K. G. NAIK and M. D. AVASARE (*J. Indian Chem. Soc.*, 1924, 1, 75—80; cf. A., 1924, ii, 48).—Mercurous chloride, sulphate, and nitrate combine with bromine and iodine in alcoholic solution to yield crystalline substances which are not double salts, but complex compounds. *Mercuric chloriodide*,  $HgClI$ , red crystals becoming yellow at  $125^\circ$ , m. p.  $153^\circ$ . *Mercuric chlorobromide*,  $HgClBr$ , white crystals, subliming without melting. *Di-iodomercuric sulphate*,  $SO_4(HgI)_2$ , red crystals turning yellow at  $143^\circ$ , m. p.  $248^\circ$ . *Tetrabromodimercuric sulphate*,  $[SO_4(HgBr)_2]_2$ , white crystals, decomp.  $125^\circ$ , and m. p.  $235^\circ$  (decomp.). *Dichlorodimercuric sulphate*,  $SO_4(HgCl)_2$ , m. p.  $270^\circ$ . *Tetraiododimercuric nitrate*,  $(HgNO_3I)_2I_2$ , red crystals turning yellow at  $145$ — $146^\circ$ , m. p.  $250^\circ$ . *Tetrabromodimercuric nitrate*,  $(HgNO_3Br)_2Br_2$  (decomp.). *Tetrachlorodimercuric nitrate*,  $(HgNO_3Cl)_2Cl_2$ , decomp.  $100^\circ$ .

G. M. B.

**Direct Formation of Mercuric Oxychlorides.** H. PÉLABON (*Compt. rend.*, 1925, 180, 143—145; cf. A., 1924, ii, 762).—Determinations of the concentrations of mercuric chloride in solution in equilibrium with the solid phases obtained from mercuric chloride and red mercuric oxide demonstrate the existence of three oxychlorides,  $\text{HgO} \cdot 2\text{HgCl}_2$ ,  $2\text{HgO} \cdot \text{HgCl}_2$ , and  $4\text{HgO} \cdot \text{HgCl}_2$ . The same products are obtained more rapidly in presence of ethyl alcohol. The compound  $\text{HgO} \cdot 2\text{HgCl}_2$  is a white solid which is not produced if the temperature is above  $30^\circ$ , but once formed it is stable at  $100^\circ$ . G. M. B.

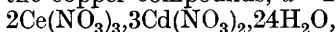
**Double Sulphates of Rare Earth and Alkali Metals. I. Lanthanum and Potassium.** F. ZAMBONINI and G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], 33, 301—308; cf. A., 1911, ii, 42).—The equilibrium between an aqueous lanthanum sulphate solution and solid potassium sulphate at  $25^\circ$  has been studied, and the results are represented graphically by plotting the values of  $\text{K}_2\text{SO}_4/\text{H}_2\text{O}$  in the liquid phase as abscissæ against those of  $\text{La}_2(\text{SO}_4)_3/\text{K}_2\text{SO}_4$  in the solid phase. Interpreted according to the phase rule (cf. A., 1903, ii, 473), this diagram indicates the formation of the following new (microcrystalline) double salts:  $2\text{La}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  (monoclinic);  $\text{La}_2(\text{SO}_4)_3 \cdot 4\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (spherical);  $\text{La}_2(\text{SO}_4)_3 \cdot 4 \cdot 5\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (globular);  $\text{La}_2(\text{SO}_4)_3 \cdot 5\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  (globular). W. E. E.

**Double Sulphates of Rare Earth and Alkali Metals. II. Neodymium and Potassium.** F. ZAMBONINI and V. CAGLIOTI (*Atti R. Accad. Lincei*, 1924, [v], 33, 308—313).—An examination of the system neodymium sulphate–potassium sulphate–water (cf. preceding abstract) shows that, at  $25^\circ$ , the following double salts are formed:  $\text{Nd}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{Nd}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{Nd}_2(\text{SO}_4)_3 \cdot 4\text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ ;  $\text{Nd}_2(\text{SO}_4)_3 \cdot 4\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ;  $\text{Nd}_2(\text{SO}_4)_3 \cdot 5\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ;  $2\text{Nd}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$  (microcrystalline: rosettes of pink monoclinic tablets,  $d^{15}$  3.026). W. E. E.

**Silicic Acids. II.** R. SCHWARZ and E. MENNER (*Ber.*, 1925, 58, [B], 73—77; cf. A., 1924, ii, 753).—The silicic acids described previously (*loc. cit.*) have been subjected to desiccation by means of acetone (cf. Willstätter and Kraut, A., 1924, ii, 615). Meta-silicic acid loses combined water at  $15^\circ$ , but can be freed from adsorbed water by acetone at  $0^\circ$ . Granatic acid,  $\text{H}_4\text{Si}_3\text{O}_8$ , which has now been prepared from the corresponding sodium salt, is also unstable at the atmospheric temperature. Di- and tri-silicic acids are easily desiccated by means of acetone under widely varied conditions. The dehydration curves of granatic acid and of meta-silicic acid at  $0^\circ$  are given; the existence of two further hydrates,  $12\text{SiO}_2 \cdot 10\text{H}_2\text{O}$  and  $12\text{SiO}_2 \cdot 9\text{H}_2\text{O}$ , is rendered probable. H. W.

**Double Nitrates of Metals of the Cerium Group with Copper and Cadmium.** G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], 33, 322—326; cf. this vol., ii, 145).—The following new compounds are described:  $2\text{Nd}(\text{NO}_3)_3 \cdot 3\text{Cu}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , lilac crystals,

$d^{15}$  2.248; of the same form and obtained in the same way as the corresponding cerium compound;  $2\text{Pr}(\text{NO}_3)_3 \cdot 3\text{Cu}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , minute, green crystals, and  $2\text{Sm}(\text{NO}_3)_3 \cdot 3\text{Cu}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , both of the same type as the preceding, were obtained similarly. The double nitrates of cadmium with cerium, lanthanum, and neodymium were prepared by evaporating the mixed solutions of the nitrates over sulphuric acid, at reduced pressure, below  $12^\circ$ . The following were obtained:  $2\text{La}(\text{NO}_3)_3 \cdot 3\text{Cd}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , colourless tablets like those of the copper compounds,  $d^{12}$  2.226;



$d^{12}$  2.294;  $2\text{Nd}(\text{NO}_3)_3 \cdot 3\text{Cd}(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$ , minute rose-coloured crystals of the same crystalline form as that of the lanthanum salt. Jantsch has observed a parallelism among the molecular volume curves of the double salts obtained from elements of the cerium group and certain members of the magnesium series of isomorphous elements; this is now shown to be shared by the curves of the double nitrates of copper and cadmium with elements of the cerium group. When the double salts given by the elements of the magnesium family with any other single metal are placed in order of decreasing molecular volumes, the succession, which has always been observed previously, is: cadmium, manganese, iron, copper, cobalt, magnesium, zinc, nickel. The double salts given by the members of this family with any one metal of the cerium group, however, fall into the following sequence: cadmium, manganese, magnesium, cobalt, zinc, nickel, copper. The copper double nitrates afford an excellent means of separating lanthanum from praseodymium. W. E. E.

**Reduction of Azoimide.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 213—220; from *Chem. Zentr.*, 1924, ii, 602—603).—Acid reducing agents such as stannous chloride and hydriodic acid reduce azoimide to ammonia and nitrogen. The reaction of azoimide with sodium hydrogen sulphite may be represented thus:  $\text{NaHSO}_3 + \text{NaN}_3 + \text{H}_2\text{O} = \text{NH}_2 \cdot \text{SO}_3\text{Na} + \text{N}_2 + \text{NaOH}$ , together with a subsidiary reaction:  $2\text{NaHSO}_3 + \text{NaN}_3 + \text{H}_2\text{O} = \text{Na}_2\text{S}_2\text{O}_6 + \text{NH}_3 + \text{NaOH}$ . In the reduction of azoimide by aluminium in alkaline solution, hydrazine and ammonia are formed: (i)  $\text{N}_3\text{H} + \text{H}_2 = \text{N}_2 + \text{NH}_3$ ; (ii)  $\text{N}_3\text{H} + 3\text{H}_2 = \text{NH}_3 + \text{N}_2\text{H}_4$ . G. W. R.

**Oxidation of Azoimide.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, ii, 602; from *Chem. Zentr.*, 1924, ii, 602; cf. A., 1906, ii, 98).—Azoimide is unattacked by potassium permanganate in neutral or alkaline solution. In sulphuric acid solution, a slow oxidation takes place:  $\text{HN}_3 + \text{O} = \text{N}_3\text{OH}$ . In addition, a portion of the azoimide appears to be oxidised to triatomic nitrogen, which then decomposes, yielding ordinary nitrogen molecules. Hydrogen hypoazide,  $\text{N}_3\text{OH}$ , resembles hypochlorous acid in its properties. It decomposes, yielding oxygen and, probably, azoimide. By oxidation of azoimide in sulphuric acid or boric acid solution in the presence of sodium nitride, nitric acid is produced, the first stage being the compound  $\text{N} \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix} > \text{N} \begin{smallmatrix} \text{OH} \\ \diagup \\ \text{O} \end{smallmatrix}$ , which then takes up more



oxygen, yielding the compound,  $\overset{\text{N}}{\underset{\text{N}}{\text{N}}} > \text{N}(\text{OH}) < \overset{\text{O}}{\underset{\text{O}}{\text{O}}}$ , which by loss of nitrogen yields nitric acid.

G. W. R.

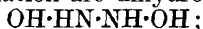
**Combustion of Ammonia to Hydrazine and Di-imide.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 221—224; from *Chem. Zentr.*, 1924, 95, ii, 1068).—The primary reaction in the combustion of ammonia in oxygen is:  $2\text{NH}_3 + \text{O}_2 = \text{N}_2\text{H}_2 + 2\text{H}_2\text{O}$ , the di-imide at once decomposing into its elements. A small part of the ammonia is oxidised to hydrazine, which can be detected with benzaldehyde.

R. B.

**Oxidation of Hydrazine and its Sulphonic Acids.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 188—200; from *Chem. Zentr.*, 1924, ii, 601—602).—Hydrazine may be used for standardisation in acidimetry and iodometry. When a standard solution of hydrazine sulphate is titrated with sodium hydroxide solution, the following reaction occurs:  $2\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 + 2\text{NaOH} = (\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$ . After addition of sodium hydrogen carbonate and starch solution, 0.1*N*-iodine solution is added. The blue coloration is obtained when four times as much 0.1*N*-iodine solution has been added as 0.1*N*-sodium hydroxide required for the first reaction. In the oxidation of hydrazine by iodine and by most other oxidising agents nitrogen is set free. Oxidation with potassium permanganate in hot sulphuric acid solution yields ammonium sulphate. The oxidation of hydrazinemonosulphonic acid and of hydrazinedisulphonic acid is also discussed.

G. W. R.

**Oxidation of Hydroxylamine.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 163—187; from *Chem. Zentr.*, 1924, ii, 600—601).—When hydroxylamine is oxidised by adding it together with dilute sulphuric acid to potassium permanganate solution, the successive stages of oxidation are dihydroxyhydrazine,



dihydroxydi-imide,  $\text{OH} \cdot \text{N} \cdot \text{N} \cdot \text{OH}$ ; nitric oxide,  $\text{O} \cdot \text{N} \cdot \text{N} \cdot \text{O}$ , and a nitrogen tetroxide having the constitution  $\overset{\text{O}}{\underset{\text{O}}{\text{O}}} > \text{N} \cdot \text{N} < \overset{\text{O}}{\underset{\text{O}}{\text{O}}}$ , called by

the author ortho-nitrogen tetroxide. The last compound yields nitric acid and nitrogen:  $5\text{N}_2\text{O}_4 + 4\text{H}_2\text{O} = 8\text{HNO}_3 + \text{N}_2$ . Some nitrous oxide is also formed. Complete oxidation to nitric acid cannot be effected with permanganate. Hypochlorous acid can oxidise hydroxylamine completely to nitric acid. The oxidation of hydroxylamine by iodine and other oxidising agents is also discussed. The views of Kurtenacker and Neusser (*A.*, 1924, ii, 249) are criticised.

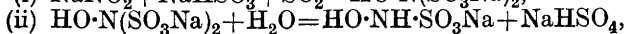
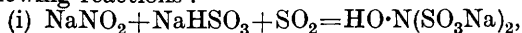
G. W. R.

**Oxidation of Hydroxylamine. II.** A. KURTENACKER and F. WENGEFELD (*Z. anorg. Chem.*, 1924, 141, 119—130; cf. *A.*, 1924, ii, 249).—The results of a number of studies of the oxidation of hydroxylamine by different investigators are reviewed. The authors' hypothesis is preferred to that of Angeli and of Raschig, since the intermediate compound postulated by both these in-

vestigators is not known to exist. Experiments are described on the oxidation of hydroxylamine by potassium dichromate in both acid and alkaline solution. In weak acid solution, half the hydroxylamine is oxidised to nitric acid, the percentage of nitric oxide increasing, and of nitrous oxide decreasing, with decreasing acidity of the solution. In strong acid solution, the percentage of hydroxylamine oxidised to nitric acid sinks to about 25, the gas produced at the same time being pure nitrous oxide. In alkaline solution, the formation of nitric acid is still further reduced, the gaseous products being nitrous oxide and nitrogen. The oxidation of the hydroxylamine is complete only in weak acid solution; in alkaline solution it varied from 47 to 64%, and in strong acid solution was about 78%. Oxidation experiments were also made with mercuric chloride in alkaline solution.

L. L. B.

**Hydroxylaminemonosulphonic Acid.** F. RASCHIG (*Schwefel-u. Stickstoffstudien*, 1924, 154—162; from *Chem. Zentr.*, 1924, ii, 448—449).—Hydroxylaminemonosulphonic acid, formed according to the following reactions:



is in some respects similar to, but is more readily oxidised than, the disulphonic acid. Its reducing properties are associated with the hydrogen atom which is directly linked with the nitrogen and not with the hydroxyl hydrogen. It can be determined titrimetrically by the reaction  $2\text{HO}\cdot\text{NH}\cdot\text{SO}_3\text{Na} + 4\text{I} + \text{H}_2\text{O} = \text{N}_2\text{O} + 4\text{HI} + 2\text{NaHSO}_4$ . The primary product of alkaline oxidation is the residue  $-(\text{OH})\text{N}\cdot\text{SO}_3\text{K}$ , which associates, yielding potassium dihydroxyhydrazinedisulphonate. This yields by loss of 1 mol.

of water an azoxy compound,  $\text{O} \begin{smallmatrix} \text{N}-\text{SO}_3\text{K} \\ \diagup \quad \diagdown \\ \text{N}-\text{SO}_3\text{K} \end{smallmatrix}$ , which, being unstable, decomposes, giving half of its sulphur as a sulphite and the remainder as the compound  $\text{K}_2\text{N}_2\text{O}_2\cdot\text{SO}_3$  (potassium dinitrosulphonate).

G. W. R.

**Hydroxylaminedisulphonic Acid.** F. RASCHIG (*Schwefel-u. Stickstoffstudien*, 1924, 147—153; from *Chem. Zentr.*, 1924, ii, 448; cf. preceding abstracts).—Hydroxylaminedisulphonic acid yields in the cold in acid solution hydroxylaminemonosulphonic acid. The sodium disulphonate gives, on oxidation with alkaline permanganate, sodium sulphazalinate,  $\text{O}:\text{N}:(\text{SO}_3\text{K})_2$ , a compound of quadrivalent nitrogen, which by hydrolysis with potassium hydroxide yields potassium hydroxylaminetrisulphonate and potassium hydroxylaminedisulphonate according to the equation  $4\text{ON}(\text{SO}_3\text{K})_2 + \text{KOH} = \text{HON}(\text{SO}_3\text{K})_2 + 2\text{ON}(\text{SO}_3\text{K})_3 + \text{KNO}_2$ . The mechanism of this reaction is discussed.

G. W. R.

**Hydroxylamineisodisulphonic Acid.** F. RASCHIG (*Schwefel-u. Stickstoffstudien*, 1924, 132—146; from *Chem. Zentr.*, 1924, ii, 447; cf. preceding abstracts and A., 1906, ii, 159).—Directions are given for the preparation of potassium hydroxylamineisodisulphonate from the corresponding trisulphonate by hydrolysis with

a weak acid. It has the constitution  $\text{NH}(\text{SO}_3\text{K})\cdot\text{O}\cdot\text{SO}_3\text{K}$ . In the presence of hydrochloric acid, the  $-\text{SO}_3\text{K}$  group attached to the nitrogen atom may be eliminated, whereby hydroxylamine-isomonosulphonic acid,  $\text{NH}_2\cdot\text{O}\cdot\text{SO}_3\text{H}$ , is produced. The oxidation of hydroxylamineisodisulphonic acid by sodium hypochlorite is discussed.

G. W. R.

**Hydroxylaminetrisulphonic Acid.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 128—131; from *Chem. Zentr.*, 1924, ii, 446—447; cf. preceding abstracts).—Potassium hydroxylamine-trisulphonate has the constitution  $(\text{KSO}_3)_2\cdot\text{N}\cdot\text{O}\cdot\text{SO}_3\text{K}$  (cf. Haga, T., 1904, 85, 78), which corresponds with its formation from potassium sulphite and potassium nitrosodisulphonate (obtained from the oxidation of potassium hydroxylaminedisulphonate) according to the equation  $2\text{O}\cdot\text{N}(\text{SO}_3\text{K})_2 + \text{H}\cdot\text{SO}_3\text{K} = \text{OH}\cdot\text{N}(\text{SO}_3\text{K})_2 + \text{KSO}_3\cdot\text{O}\cdot\text{N}(\text{SO}_3\text{K})_2$ . Directions are given for its preparation, starting from sodium nitrite and sodium hydrogen sulphite, using lead peroxide as an oxidising reagent in the preparation of the intermediate nitrosodisulphonate.

G. W. R.

**Action of Sulphite, Hydrogen Sulphite, and Sulphurous Acid on Hydroxylamine.** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 225—240; from *Chem. Zentr.*, 1924, ii, 1069).—The author regards the reaction,  $\text{NH}_2\cdot\text{OH}\cdot\text{HCl} + \text{H}\cdot\text{SO}_2\cdot\text{ONa} = \text{NH}_2\cdot\text{SO}_2\cdot\text{ONa} + \text{H}_2\text{O} + \text{HCl}$ , as proof of the asymmetrical constitution of sodium hydrogen sulphite. In the presence of sulphurous acid, the reaction with hydroxylamine gives, besides amidosulphonic acid, a considerable amount of ammonium sulphate, and nitrogen is evolved. It is assumed that the sulphurous acid is mainly present in the tautomeric form,  $\text{H}_2\cdot\text{SO}_2\cdot\text{O}$ , which by replacement of the hydrogen atoms may yield the diamide of a persulphuric acid,  $(\text{NH}_2)_2\text{SO}_2\cdot\text{O}$ , and this oxidises a further 2 mols. of hydroxylamine, yielding nitrogen and sulphamide,  $(\text{NH}_2)_2\text{SO}_2\cdot\text{O} + 2\text{NH}_2\cdot\text{OH} = (\text{NH}_2)_2\text{SO}_2 + \text{N}_2 + 3\text{H}_2\text{O}$ ; the latter substance in aqueous solution decomposes into ammonia and amidosulphonic acid. It is calculated that in aqueous solution two-thirds of the sulphurous acid is present in the normal asymmetric form and one-third in the tautomeric form. The difference in constitution between hydrogen sulphites and monosulphites is also shown in the reaction with chloroamide, which in the former case yields sodium chlorosulphonate, whilst in the latter case amidosulphonic acid is formed. (Cf. also Schäfer and Köhler, A., 1919, ii, 38.)

R. B.

**Potassium "Nitrososulphite" [Dinitrososulphonate].** F. RASCHIG (*Schwefel- u. Stickstoffstudien*, 1924, 108—127; from *Chem. Zentr.*, 1924, ii, 445—446).—The preparation of potassium nitrososulphite,  $\text{K}_2\text{N}_2\text{SO}_5$ , by the action of nitric oxide on 40% potassium sulphite solution is described. Its properties agree with the constitutional formula of Hantzsch (A., 1895, ii, 75). It is unattacked by potassium permanganate in acid solution. It is oxidised by sodium hypochlorite in the presence of small amounts of water. The usual products of decomposition are nitrous oxide and potassium

sulphate. Nitric oxide and potassium sulphite may be obtained from it by boiling with potassium hydroxide solution or by fusion. Hydrazinesulphonic acid may be obtained from it by alkaline reduction. The formation of potassium nitrososulphite can be explained by assuming, with Hantzsch, that nitric oxide before combination forms double molecules and also that both potassium atoms in potassium sulphite are joined to the sulphur atom. When nitric oxide reacts with potassium hydrogen sulphite the first product probably has the constitution  $\text{NO}\cdot\text{N}(\text{OK})\text{SO}_3\text{K}$ , which then undergoes rearrangement. When nitric oxide is passed into potassium hydrogen sulphite solution, potassium nitrilosulphonate,  $\text{N}(\text{SO}_3\text{K})_3\cdot 2\text{H}_2\text{O}$ , is formed, which decomposes on boiling, yielding potassium hydrogen sulphate and potassium amidosulphonate. The reaction between nitric oxide and potassium hydrogen sulphite may be explained by assuming the formation of potassium nitroxylsulphonate,  $\text{OH}\cdot\text{N}\cdot\text{SO}_3\text{K}$ , which combines further with nitric oxide, yielding potassium nitrosohydroxylaminesulphonate,  $\text{ON}\cdot\text{N}(\text{OH})\text{SO}_3\text{K}$ , from which the potassium nitrososulphite,  $\text{ON}\cdot\text{N}(\text{OK})\text{SO}_3\text{K}$ , is formed in alkaline solution. In the absence of alkali, potassium nitrosoaminedisulphonate is formed. In the decomposition of potassium nitroxylsulphonate,  $\text{OH}\cdot\text{N}\cdot\text{SO}_3\text{K}$ , hyponitrous acid and the residue,  $-\text{SO}_3\text{K}$ , are first formed. From the latter by simple association potassium dithionate is formed.

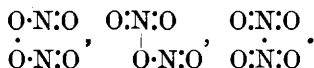
G. W. R.

**Reduction of Oxides of Nitrogen in Presence of Sulphuric and Sulphurous Acids.** A. GRAIRE (*Compt. rend.*, 1925, 180, 292—294).—A quantitative investigation of the reduction of oxides of nitrogen with a view to elucidate the mechanism of loss of nitrogen in the "lead chamber" process. Impure nitrosulphuric acid under normal conditions is not reduced further than nitric oxide by agitation over mercury, so that ferrous sulphate can effect a complete recovery of the nitrogen products. Addition of sulphur dioxide and other changed conditions result in loss of nitrogen through reduction to nitrous oxide in the liquid phase. Mixtures of nitric and sulphuric acids in presence of ferrous sulphate and sodium sulphite have been studied. Nitrous oxide is formed by the slow interaction of sulphur dioxide and nitric oxide (as  $\text{FeSO}_4\cdot\text{NO}$ ) in the liquid phase. Dilution increases the reduction; it is feeble in 35% sulphuric acid, but takes place readily at 25%. The product of the reaction is always nitrous oxide, nitrogen having been observed only in traces.

R. A. M.

**Nitrogen Peroxide.** A. SCHAARSCHMIDT (*Z. angew. Chem.*, 1924, 37, 933—938).—Saturated aliphatic hydrocarbons are but slowly attacked by nitrogen peroxide, fatty acids being first formed and then further oxidised to oxalic acid and carbon dioxide, whilst the peroxide is reduced to nitric and nitrous oxides and ultimately to nitrogen. Branched-chain paraffins are less resistant than straight-chain paraffins. An apparatus is described for conveniently observing the reaction in a closed glass tube (which ultimately bursts) at temperatures up to  $150^\circ$ ; there was no spontaneous

evolution of heat, but, even after the appearance of nitrogen trioxide in the tube, the mixture cooled as soon as the source of external heat was removed. With olefinic hydrocarbons (*e.g.*, amylene, cyclohexene), there is immediate formation of extremely unstable isomeric nitrosates and  $\psi$ -nitrosites, accompanied, in some cases, by polymerisation products. Nitrogen peroxide, in the cold, converts benzene very slowly into picric acid, and toluene more readily into trinitrotoluene (*cf.* this vol., i, 123). At the same time, nitro-nitrite compounds are formed, which are decomposed by alkalis (*e.g.*, to dinitrocresol). The various ways in which nitrogen peroxide reacts lead to the assumption that it occurs as an equilibrium mixture of three forms, *viz.*,



W. T. K. B.

**Action of Nitrogen Peroxide on Metallic Copper and its Adsorption by Cuprous Oxide.** A. KLEMENC and A. SCHROTH (*Ber.*, 1925, 58, [B], 168—175; *cf.* Sabatier and Senderens, A., 1893, ii, 374; Tartar and Semon, A., 1921, ii, 336; Park and Partington, A., 1924, ii, 183).—The action of nitrogen peroxide on specially prepared copper at the atmospheric or somewhat reduced pressure gives a product in which the value of the atomic ratio O:N is about 3. If the gas is used under increased pressure, an entirely different product is obtained in which the ratio O:N is 6.5. If nitrogen peroxide is passed several times over the same specimen of copper from which the adsorbed gas is removed after each passage, the quantity of adsorbed gas diminishes at the second passage and subsequently becomes approximately constant. It is therefore suggested that two actions occur simultaneously consisting in the adsorption of nitrogen peroxide by metallic copper and the oxidation of copper to cuprous oxide which also adsorbs nitrogen peroxide. The adsorptive capacity of the element for nitrogen peroxide appears to be greater than that of its oxide. "Nitro-copper" as postulated by Sabatier and Senderens (*loc. cit.*) does not appear to exist and the other "nitrometals" cannot be regarded as chemical individuals. The adsorption isotherm of the system  $\text{Cu}_2\text{O}-\text{NO}_2$ , passes through a maximum at about 1.6 atm.

H. W.

**Hydrogen Persulphide.** O. VON DIENES (*Annalen*, 1924, 440, 213—214).—Hypophosphorous acid solution reduces sulphur dioxide, both as a gas and in aqueous solution, to a product from which hydrogen persulphide may be extracted with ether, a solution of large quantities of sulphur in the persulphide remaining undissolved. Before the persulphide separates from the ether solution, crystals of monoclinic monosymmetric  $\beta$ -sulphur form as small, transparent, nacreous plates, which rapidly form tufts of monoclinic needles and change to pseudomonoclinic rhombic sulphur. The sulphur henceforth separates in rhombic form on the edges of these crystals (*cf.* A., 1885, 1037).

S. K. T.

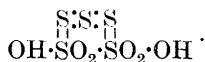
**Formation and Decomposition of Polythionates.** F. FOERSTER (*Z. anorg. Chem.*, 1924, **141**, 228—230; cf. *ibid.*, 1924, **139**, 246; Foerster and Hornig, A., 1923, ii, 23).—Besides the course indicated by the equation  $2\text{SO} + \text{H}_2\text{O} \rightleftharpoons \text{S}_2\text{O}_3'' + 2\text{H}^+$ , *i.e.*, by the formation of thiosulphuric acid, the intermediate product SO may lead to the production of polythionic acids by other changes, *e.g.*,  $\text{SO} + 2\text{S}_2\text{O}_3'' + 2\text{H}^+ \rightarrow \text{S}_5\text{O}_6'' + \text{H}_2\text{O}$ , and  $\text{SO} + 2\text{HSO}_3 \rightarrow \text{S}_3\text{O}_6'' + \text{H}_2\text{O}$ , analogous to those known in the case of selenium oxide,  $\text{SeO}$ .

S. I. L.

**Formation and Decomposition of Polythionates.** E. H. RIESENFELD (*Z. anorg. Chem.*, 1924, **141**, 109—110).—A reply to Foerster's criticism (this vol., ii, 148) of Josephy's paper (A., 1924, ii, 470). The constitution of the intermediate compounds in the formation and decomposition of polythionates is discussed.

L. L. B.

**Preparation and Properties of Polythionic Acids.** F. RASCHIG (*Schwefel- u. Stickstoff-studien*, 1924, 273—304; from *Chem. Zentr.*, 1924, ii, 1065—1068).—Pentathionic acid is prepared by the action of hydrochloric acid on cooled aqueous sodium thiosulphate in the presence of sodium arsenite; sodium pentathionate gradually separates on concentration of the filtrate at 35°. The filtrate, which still contains 12% of the sodium salt, contains 60% of pentathionic acid,  $\text{H}_2\text{S}_5\text{O}_6$ , free from tetrathionic or trithionic acids, and is practically unchanged after 2 months. The potassium salt has been obtained. Pentathionic acid is oxidised to sulphuric acid, quantitatively by potassium chlorate and hydrochloric acid, slowly by acidified potassium permanganate. With sodium carbonate, the pentathionate slowly deposits sulphur; under suitable conditions, the reaction,  $\text{K}_2\text{S}_5\text{O}_6 \rightarrow \text{K}_2\text{S}_4\text{O}_6 + \text{S}$ , is quantitative. Antimony and tin, like arsenic, prevent the separation of sulphur on acidifying sodium thiosulphate solutions. In the presence of sodium dihydrogen arsenite, the decomposition  $\text{Na}_2\text{S}_5\text{O}_6 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{SO}_2 + \text{S}$  was reduced from 88.8 to 13% of the reaction, pentathionic acid being formed to the extent of 85—90%. The intermediate formation of a dipentathionic acid,  $\text{H}_4\text{S}_{10}\text{O}_{12}$ , is assumed. The author represents the formation of pentathionic acid in Wackenroder's solution as being due to the condensation of five SO groups (cf. following abstract) arising from the reaction:  $\text{SO}_2 + \text{H}_2\text{S} = \text{SO} + \text{S} + \text{H}_2\text{O}$ , addition of water yielding pentathionic acid of the structure



The alternative reaction,  $2\text{SO}_2 + \text{H}_2\text{S} = 3\text{SO} + \text{H}_2\text{O}$ , is excluded, whilst with excess of hydrogen sulphide the reaction proceeds smoothly according to the equation,  $2\text{H}_2\text{S} + \text{SO}_2 = 3\text{S} + 2\text{H}_2\text{O}$ . Hyposulphurous acid is not formed, and the author accounts for the formation of pentathionic acid from sodium thiosulphate by suggesting decomposition to the group  $\text{S}:\text{SO}_2$ , which polymerises to  $\text{S}_{10}\text{O}_{10}$ .

Potassium tetrathionate is obtained by the oxidation of sodium thiosulphate with cupric sulphate:  $3\text{Na}_2\text{S}_2\text{O}_3 + 2\text{CuSO}_4 = \text{Cu}_2\text{S}_2\text{O}_3 + 2\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_4\text{O}_6$ , and treatment of the concentrated filtrate with potassium acetate. The potassium tetrathionate which separates is washed with alcohol. With sodium carbonate, the first reaction is:  $4\text{Na}_2\text{S}_4\text{O}_6 + 4\text{Na}_2\text{CO}_3 = 6\text{Na}_2\text{S}_2\text{O}_3 + \text{Na}_2\text{S}_3\text{O}_6 + \text{Na}_2\text{SO}_4 + 4\text{CO}_2$ . Tetrathionate is the first stage in the preparation of sodium trithionate by Willstätter's method (A., 1903, i, 543). Better yields are, however, obtained by the reaction  $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaHSO}_3 + 2\text{SO}_2 = 2\text{Na}_2\text{S}_3\text{O}_6 + \text{H}_2\text{O}$  in the presence of sodium arsenite. Acid potassium permanganate oxidises two-thirds of the trithionate sulphur to sulphate, the remainder forming dithionic acid. Alkaline permanganate oxidises thiosulphate to sulphate, whilst sodium hypochlorite in acid solution gives partly sulphate and partly tetrathionate. The action of sodium sulphide on sodium hydrogen sulphite is in accordance with the equation  $6\text{NaHSO}_3 + 2\text{Na}_2\text{S} = 2\text{Na}_2\text{SO}_3 + 3\text{Na}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$ . R. B.

**Constitution of Polythionic Acids.** F. RASCHIG (*Schwefel-u. Stickstoffstudien*, 1924, 305—310; from *Chem. Zentr.*, 1924, ii, 1068).—The following structural formulæ are proposed for sodium tetra-,  $\text{NaO} \cdot \overset{\text{S}}{\underset{|}{\text{O}}} \cdot \overset{\text{S}}{\underset{|}{\text{O}}} \cdot \overset{\text{S}}{\underset{|}{\text{O}}} \cdot \text{Na}$ , tri-,  $\text{NaO} \cdot \overset{\text{S}}{\underset{|}{\text{O}}} \cdot \overset{\text{S}}{\underset{|}{\text{O}}} \cdot \text{Na}$ , and penta-thionate,  $\text{NaO} \cdot \overset{\text{S}}{\underset{|}{\text{O}}} \cdot \overset{\text{S}}{\underset{|}{\text{O}}} \cdot \overset{\text{S}}{\underset{|}{\text{O}}} \cdot \text{Na}$ , and dithionic acid,  $\text{HO} \cdot \overset{\text{S}}{\underset{|}{\text{O}}} \cdot \overset{\text{S}}{\underset{|}{\text{O}}} \cdot \text{OH}$ . R. B.

**Complex Chromium Ammonium Compounds.** P. RAY and P. B. SARKAR (*J. Indian Chem. Soc.*, 1924, 1, 91—99).—By the action of ammonium thiosulphate and ammonia on chromium hydroxide, two compounds have been prepared which are the first examples to be described of trinuclear chromium ammonium compounds: *Decamminemonoaquotrihydroxydioltrichromium thiosulphate*,  $[\text{Cr}(\text{OH})_3 \cdot 2\text{CrOH}(\text{NH}_3)_5 \cdot \text{H}_2\text{O}](\text{S}_2\text{O}_3)_2 \cdot x\text{H}_2\text{O}$ , reddish-violet crystals and *enneamminediapotrihydroxydioltrichromium thiosulphate*,  $[\text{Cr}(\text{OH})_3 \cdot \text{CrOH}(\text{NH}_3)_5 \cdot \text{CrOH}(\text{NH}_3)_4 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}](\text{S}_2\text{O}_3)_2 \cdot 2\text{H}_2\text{O}$ , pinkish-violet crystals. The behaviour of these substances with a number of reagents is described and the arguments for the constitutions proposed are discussed. G. M. B.

**Sulphates of Quadrivalent Uranium.** R. J. MEYER and H. NACHOD (*Annalen*, 1924, 440, 186—199).—Uranous sulphate octahydrate,  $\text{U}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ , is obtained by reducing a saturated solution of uranyl sulphate containing 2 mols. of concentrated sulphuric acid per mol. of crystalline salt, by Rosenheim and Lobel's electrolytic method (A., 1908, ii, 294) and either precipitating the solution with alcohol or evaporating at  $75^\circ$  or over sulphuric acid. Evaporation at  $93$ — $95^\circ$  gives the tetrahydrate, which is also obtained by gradually adding concentrated sulphuric acid to the reduced solution between  $0^\circ$  and  $70^\circ$  until precipitation ceases. The precipitation of the two salts from solution depends only on the acidity of the latter.

The octahydrate is converted irreversibly into the tetrahydrate

at 68° (cf. A., 1905, ii, 827). It is less soluble in 0.1*N*-sulphuric acid than in water; the tetrahydrate below 55° is more soluble, indicating the presence of complex ions. The solubility curves for the two salts in sulphuric acid solution intersect at 26°, but this is not a transition point. Both hydrates are stable in solution between 15° and 92°. Freezing-point depression measurements show that the tetrahydrate has twice the molecular weight of the octahydrate in  $N/8-N/32$ -solutions in 0.1*N*-sulphuric acid.

S. K. T.

**Iron Carbonyls.** H. FREUNDLICH and W. MALCHOW (*Z. anorg. Chem.*, 1924, **141**, 317—324).—All three carbonyl compounds,  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_2(\text{CO})_9$ , and  $\text{Fe}(\text{CO})_4$ , when treated with sodium ethoxide in alcoholic solution, give red compounds soluble in water, and apparently hydrates; that from iron pentacarbonyl is thought to have the composition  $\text{Fe}(\text{CO})_5 \cdot 2\text{H}_2\text{O}$ . The tetracarbonyl is the most stable, and is readily prepared from the red compounds. No other derivatives of the carbonyls could be obtained. Resemblances between the carbonyls and the chlorides of bivalent molybdenum and ruthenium are pointed out.

S. I. L.

**Reaction between Potassamide and Salts of Cobalt and Iron in Liquid Ammonia.** F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1924, **46**, 2631—2636).—Potassamide acts on cobaltous thiocyanate in liquid ammonia to give *cobaltous amide*,  $\text{Co}(\text{NH}_2)_2$ , which loses ammonia when heated above 120° to yield *cobaltous nitride*,  $\text{Co}_3\text{N}_2$ , a black solid almost unaffected by water. *Ferrous tetraamminethiocyanate*,  $\text{Fe}(\text{SCN})_2 \cdot 4\text{NH}_3$ , is obtained by the action of iron wire on mercuric thiocyanate in liquid ammonia solution. Potassamide converts this salt into a slightly impure *ferrous nitride*,  $\text{Fe}_3\text{N}_2$ , which is also obtainable by treating ferrous bromide with potassamide and then with a solution of ammonium thiocyanate. The action of potassamide on a number of other salts of cobalt and iron has been examined, but no definite products were isolated.

G. M. B.

**Solubility of Nickel in Water containing Carbon Dioxide.** R. ROBL (*Z. angew. Chem.*, 1924, **37**, 938—939).—Commercially pure nickel (Fe 0.8%, Cu 0.4%) is appreciably attacked by water containing carbon dioxide, nickel carbonate being formed.

W. T. K. B.

**Isomeric Potassium Pentachlororuthenites.** A. GUTBIER and W. NIEMANN (*Z. anorg. Chem.*, 1924, **141**, 312—316; cf. Aoyama, A., 1924, ii, 771).—There is no ground for supposing the existence of a new  $\gamma$ -form; material prepared by the method of Howe (A., 1902, ii, 86) is found to have the properties ascribed by Aoyama to the  $\gamma$ -form, though Howe's product was named by Aoyama the  $\beta$ -form.

S. I. L.

**Osmium Tetroxide.** H. VON WARTENBERG (*Annalen*, 1924, **440**, 97—110).—Osmium may be obtained from alkaline solutions containing the tetroxide by heating with alcohol, mixing the pre-



precipitated hydrated osmium dioxide with sodium chloride (to prevent explosions) and vaporising at  $150^{\circ}$ , finally reducing in hydrogen for  $\frac{1}{2}$  hour at red heat. The latter operation is then repeated after washing. By burning hydrogen in oxygen containing osmium tetroxide, the dioxide is formed and may then be reduced to the metal.

One hundred g. of water dissolve 6.47 g. of osmium tetroxide at  $18^{\circ}$ ; 100 g. of carbon tetrachloride dissolve about 250 g. at  $20^{\circ}$ . Hence the oxide may be extracted from slightly acid solutions by shaking with carbon tetrachloride; it may be completely removed from the latter solution by shaking with sodium hydroxide. Osmium is precipitated from the alkaline solution, which probably contains  $\text{HOsO}_5$  ions, by platinum saturated with adsorbed hydrogen. The yellow colour given with alkali solution will detect 0.001% of the tetroxide in aqueous solution. Water does not wet the oxide.

The vapour-pressure curves of the solid and liquid oxide, which are given by  $\log p(\text{atm.}) = -13500/4.57T + 7.83$  and  $\log p(\text{atm.}) = -10100/4.57T + 5.49$ , respectively, run parallel with the corresponding curves for water up to the critical temperature. The interpolated m. p. is  $40.1^{\circ}$  and b. p.  $129^{\circ}$ . The critical data are:  $t_c = 404.8^{\circ}$  (surface tension data, assuming linear dependence on the temperature, gave  $390^{\circ}$ );  $v_c = 0.007$  and  $p_c$ , calculated from van der Waals' vapour-pressure equation by assuming the constant for water (an associated liquid) to hold for osmium tetroxide, 170 atm. Application of the Eötvös rule shows the fused oxide to be non-associated.

The molecular latent heat of fusion, determined by Schottky's method (*Physikal. Z.*, 1909, 10, 634), is  $3.41 (\pm 2\%)$  Cals. in agreement with the vapour-pressure measurements. The characteristic odour of the oxide first becomes apparent when its concentration is  $2 \times 10^{-5}$  mg. per c.c. Other physical constants are:  $n_D^{45}$  1.56;  $\kappa$  (specific conductivity) for liquid  $< 1 \times 10^{-11}$  rec.-ohms;  $d^{42}$  4.44 and  $d^{22}$  4.91; coefficient of expansion 0.00102. The heat of formation from the elements is  $93.37 (\pm 1.5\%)$  Cal.; the vapour is quite stable up to  $1500^{\circ}$ .

S. K. T.

### Compounds of Carbon Monoxide with Osmium Chloride.

W. MANCHOT and J. KÖNIG (*Ber.*, 1925, 58, [B], 229—232).—Osmium trichloride reacts with moist or dry carbon monoxide at  $270^{\circ}$ , giving a crystalline sublimate which is separated by boiling carbon tetrachloride into a compound, (?)  $\text{Os}(\text{CO})_3\text{Cl}_2$ , m. p.  $269\text{--}273^{\circ}$ , and a more soluble substance, m. p.  $252^{\circ}$ , which has not been fully investigated. The main product,  $\text{Os}(\text{CO})_3\text{Cl}_2$ , is characterised by unusual stability.

H. W.

**Metal-Carbon Monoxide Salts. IX. Compound of Carbon Monoxide with Iridium Chloride.** W. MANCHOT and H. GALL (*Ber.*, 1925, 58, [B], 232—234).—Iridium trichloride is converted by carbon monoxide at  $150^{\circ}$  into the compound,  $\text{IrCl}_2(\text{CO})_2$ , m. p.  $140^{\circ}$ , which differs from the other compounds of the metals of the platinum group (cf. this vol., ii, 149 and preceding abstract) in its instability particularly towards moisture, by which it is hydrolysed

to iridium oxide or hydrate, hydrochloric acid, and carbon monoxide.  
H. W.

**Preparation of Pure Hydrogen.** V. BAYERLE and M. TAMELE (*Chem. Listy*, 1924, **18**, 389—390).—Amalgamated zinc does not dissolve in dilute acids owing to the high overvoltage of the hydrogen; contact with a platinum sheet, however, immediately induces a rapid evolution of hydrogen from the platinum. An apparatus is described and illustrated which allows a continuous supply of pure hydrogen under considerable pressure to be obtained by making use of this reaction.  
A. R. P.

**Displacement of Alkali Metals by Iron.** L. HACKSPILL and R. GRANDADAM (*Compt. rend.*, 1925, **180**, 68—70).—When heated in a vacuum, iron can displace the alkali metals from their salts or hydroxide. With the chlorides, bromides, and iodides of sodium or potassium, the reaction is slight owing to the volatility of the halides, but, with the less volatile fluorides, a copious yield of alkali metal can be obtained. The sulphates are attacked by iron at 1000°, the first reaction being according to the scheme  $M_2SO_4 + Fe = FeSO_4 + 2M$ , followed by the decomposition of the ferrous sulphate to give ferric oxide. Potassium carbonate reacts with iron at 800—900° according to the equation  $2K_2CO_3 + 2Fe = Fe_2O_3 + CO + CO_2 + 4K$ , whilst, with the hydroxide, a yield of 70—80% of the theoretical can be obtained at 600—650°.  
W. H.-R.

**Hafnium Oxide in Tungsten Filaments.** J. A. M. VAN LIEMPT (*Nature*, 1925, **115**, 194).—A mixture of tungstic oxide with a solution of hafnium nitrate, when dried, heated, and reduced with hydrogen, yields tungsten powder of definite hafnium oxide content. On sintering in hydrogen, a portion of the hafnium oxide is reduced; the hafnium combines with the tungsten and influences recrystallisation.  
A. A. E.

**Ultra-centrifuge.** T. SVEDBERG and H. RINDE (*J. Amer. Chem. Soc.*, 1924, **46**, 2677—2693; cf. A., 1924, ii, 97).—The “ultra-centrifuge” here described is an apparatus designed for the study of the changes taking place in fine-grained sols during centrifuging. By direct or photographic observation of the changes of concentration of the sol, or of the boundary between clear dispersion medium and sol, with time, data are obtained from which, by means of a modified Stokes’ law, the size and distribution of size of particles can be calculated. The results of measurements with a fine-grained gold sol are given, the radius values obtained being from 11 to 38% higher than those arrived at by means of Zsigmondy’s nuclear method. The ultra-centrifuge has also been used to study the protective action of gelatin on a gold sol, and maximum and minimum values for the thickness of the adsorbed gelatin layer are calculated.  
G. M. B.

**Method of Determining the Solubility of Gases in Liquids.** W. MANCHOT (*Z. anorg. Chem.*, 1924, **141**, 38—44).—An apparatus is described for the determination of gas solubilities in salt solutions,

which consists of a modification of Ostwald's arrangement. A device is introduced to avoid the error arising from the difference of vapour pressure in the apparatus before and after the experiment.

L. L. B.

**Experimental Technique of Photochemistry. I. The Quartz Mercury Lamp as a Photo-chemical Light Source.**

L. REEVE (*J. Physical Chem.*, 1925, 29, 39—57).—The total radiation of a quartz mercury lamp grows rapidly with increase of voltage and depends greatly on the degree of cooling of the lamp. The intensities of various portions of the spectrum do not grow with wattage at the same rate, and, on the whole, the infra-red and extreme ultra-violet grow the fastest. The radiation is affected by adsorption by the luminous mercury vapour inside the lamp and therefore the dimensions of a lamp will affect its energy characteristics. The falling off in efficiency with age, due to devitrification and discoloration of the quartz, is most marked in the extreme ultra-violet.

M. B. D.

**Extraction Apparatus for Solid Substances at a Raised Temperature.**

H. SCHMALFUSS and H. WERNER (*J. pr. Chem.*, 1924, [ii], 108, 355—357).—A simple apparatus is described in which a solid is extracted by circulation of a small amount of solvent. As this acts at its b. p., it is claimed that the extractor is more efficient than that of Soxhlet. [Cf. *B.*, 1925, 115.]

F. M. H.

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## Mineralogical Chemistry.

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**Radial Distribution of certain Elements in the Earth.**  
H. S. WASHINGTON (*J. Washington Acad. Sci.*, 1924, **14**, 435—442).—The central core of the earth is composed of nickel-iron which gradually merges into a shell of silicates. Orthosilicates lie nearest the centre, but silication increases towards the surface so that metasilicates, alkali polysilicates, and pure silica are obtained. Progressions in other constituents may also be observed. Iron and magnesium as silicates increase at first from the border of the nickel-iron core until they reach a maximum in the metal-free shell composed chiefly of olivine and pyroxene. Above this, they decrease steadily until they are almost negligible in the granitic upper part of the crust. As regards the relative progression of calcium, sodium, and potassium, calcium begins to appear near the core with very little sodium and no potassium. It reaches a maximum and then falls off towards the surface, whilst sodium becomes more important, and potassium finally appears about the middle of the crustal shell and gradually becomes more abundant than sodium. The elements in the order of abundance which make up 98.6% of the earth's crust are: oxygen, silicon, aluminium,

iron, calcium, sodium, potassium, and magnesium. The earth as a whole is composed chiefly of seven elements. These are in order of abundance iron, oxygen, silicon, magnesium, nickel, calcium, and aluminium. M. S. B.

**Radioactivity of Gases Emitted from Vesuvius and the Solfataras of Campania and their Influence on the Development of Bacteria and Higher Plants.** J. STOKLASA and J. PENKAVA (*Compt. rend.*, 1924, 179, 819—822).—The conductivity of the atmosphere varies from point to point, reaching a maximum in volcanic districts; this maximum is nearly equalled by the values given by air taken from the neighbourhood of potash mines. The  $\beta$ - and  $\gamma$ -rays derived from radioactive substances of volcanic origin and also from potassium accelerate photosynthesis in cells containing chlorophyll. The mechanism is based on the decomposition of potassium hydrogen carbonate, under the influence of light and radioactivity, into formic acid, oxygen, and potassium carbonate with subsequent decomposition of the formic acid into formaldehyde and oxygen. Radioactivity in soil or atmosphere favours development of *Leguminosæ* and of nitrogen-fixing bacteria. H. J. E.

**New Mineral: Dussertite.** J. BARTHOUX (*Compt. rend.*, 1925, 180, 299—301).—Dussertite, an arsenical mineral from Djebel Debar mountain (Algeria), exists as minute rhombohedral or hexagonal green crystals,  $d$  3.75, hardness 3.5. A typical analysis is:  $\text{As}_2\text{O}_3$ , 31.90%;  $\text{Fe}_2\text{O}_3$ , 31.24%;  $\text{CaO}$ , 22.03%;  $\text{H}_2\text{O}$ , 10.61%, with smaller quantities of ferrous iron, magnesia, alumina, and sulphate; the mineral is regarded as similar to arseniosiderite,  $[\text{AsO}_4]_2(\text{FeAl})_3(\text{CaMg})_3[\text{OH}]_9$ . The other properties with the exception of birefringence (0.012) confirm this view. R. A. M.

**Crystal Structure, Chemical Analysis, and Dehydration of Becquerelite and Schoepite.** A. SCHOEP (*Bull. Soc. chim. Belg.*, 1924, 33, 578—587).—The axial ratios of becquerelite are  $a : b : c = 0.5537 : 1 : 0.5938$ ; characteristic faces are (101), (102), (021), (110), (001), (305); the cleavage is perfect parallel to (001) and nearly perfect parallel to (101). Characteristic faces of schoepite are (001), (100), (111), (124), (122), (110), (021). Both minerals contain uranium trioxide, lead oxide, and water, together with small amounts of tellurium trioxide, sulphur trioxide, ferric oxide, and silica; becquerelite contains more than 5% of lead oxide, whilst schoepite rarely contains as much as 1%. The former mineral loses half its water at  $150^\circ$  and the remainder at  $500^\circ$ , whilst the latter loses half at  $110^\circ$  and the remainder at  $325^\circ$ . Neglecting impurities, the composition of each mineral agrees with the formula  $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ; the minerals therefore represent dimorphous forms of the dihydrate of uranium trioxide. A. R. P.

**Sklodowskite, a New Uranium Mineral and its Relation to Uranotile.** A. SCHOEP (*Bull. Soc. chim. Belg.*, 1924, 33, 562—570).—The fibrous radiated nodules of sklodowskite previously described (A., 1924, ii, 868) have  $d$  3.54 and contain 13.33%  $\text{H}_2\text{O}$ , 13.49%  $\text{SiO}_2$ , 67.25%  $\text{UO}_3$ , 1.91%  $\text{MgO}$ , 2.57%  $\text{CaO}$ , and 1.27%

CoO. The compact form of the mineral is of a pale yellow colour, opaque and hard; it has no cleavage; in thin splinters it has  $n$  1.64 and  $d$  3.74. This form contains nearly 4% MgO and 2.64% TeO<sub>3</sub> but no calcium or cobalt. A citron-yellow, translucent, crystalline variety has also been found; the crystals are long, slender, orthorhombic prisms terminated by pyramids and contain 3.74% MgO, 1.08% TeO<sub>3</sub>, and 1.97% of alkali oxides together with a little nickel. The mineral loses about half its water at 110°, but the remainder is not expelled completely below 500°. Its composition agrees most closely with the formula  $\text{MgO}, 2\text{UO}_3, 2\text{SiO}_2, 7\text{H}_2\text{O}$ , and it is, therefore, the magnesium analogue of uranotile. A. R. P.

**Chemical Composition of Fourmarierite.** A. SCHOEP (*Bull. Soc. chim. Belg.*, 1924, **33**, 558—562).—Fourmarierite is a reddish-brown mineral found associated with other uranium minerals in the Belgian Congo. It crystallises in the orthorhombic system, exhibits dichroism, and has a perfect cleavage perpendicular to the inclined axis. Its chemical constitution is most nearly represented by the formula  $\text{PbO}, 4\text{UO}_3, 5\text{H}_2\text{O}$ , but, as the proportion of lead varies somewhat, the author prefers to formulate it as  $(\text{Pb}, \text{UO}_2)\text{O}, \text{H}_2\text{O}$ . No water is lost at 100°, but all the water and some oxygen are expelled at 350°. Some specimens contain as much as 0.67% of tellurium trioxide, and there is always a small quantity of ferric oxide present. A. R. P.

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### Analytical Chemistry.

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**Universal Commutator for Potentiometric Measurements by the Compensation Method.** A. ERNEST (*Chem. Listy*, 1924, 18, 250—251).  
W. A. S.

**Hydrogen Electrode Technique.** J. P. BAUMBERGER (*J. Lab. Clin. Med.*, 1924, 9, 720—722).—As the hydrogen electrode, a platinum wire spiral flattened while hot is recommended. Potassium chloride agar (2%) solution is preferred to saturated potassium chloride solution as a contact liquid. A device for rocking a Clark hydrogen electrode is described. CHEMICAL ABSTRACTS.

**Scrubber for Ammonia Distillates.** A. G. MURRAY (*J. Amer. Pharm. Assoc.*, 1924, 13, 423).—The apparatus is designed to fit in the neck of a Kjeldahl flask. The steam enters the scrubber through an opening near the top, passes down to the bottom and up through the neck to the condenser. The pocket of water is maintained by an outlet tube a short distance from the bottom, which ends in a fish-hook-shaped bend below. CHEMICAL ABSTRACTS.

**Apparatus for the Precipitation of Barium Sulphate.** A. G. MURRAY (*J. Amer. Pharm. Assoc.*, 1924, 13, 424).—The apparatus consists of a cup drawn to a capillary tube at the lower

end to permit a discharge of 2—3 drops per sec. The cup has a broad rim to rest in the neck of a capacious Erlenmeyer flask. The sulphate solution is boiled and the dilute barium chloride solution placed in the cup from which it is delivered hot.

CHEMICAL ABSTRACTS.

**Apparatus for the Determination of Urea by the Urease Method.** A. A. HORVATH (*J. Lab. Clin. Med.*, 1924, 9, 722—723).—The modification consists of a device for regulating the pressure.

CHEMICAL ABSTRACTS.

**Röntgen Spectroscopic Method of Quantitative Analysis.** P. GÜNTHER and G. WILCKE (*Annalen*, 1924, 440, 203—212).—A simple X-ray spectroscopic method of quantitative analysis is described in which a small induction coil is used as the generator of energy. The spectrum lines are photographed and their relative intensities measured by counting the silver particles per unit area. The results agree to about 2% with those obtained gravimetrically.

S. K. T.

**Possibility of Determining Spectrophotometrically Substances Oxidisable by Permanganate.** H. GOMBOS (*Biochem. Z.*, 1924, 151, 1—6).—A spectrophotometric examination of solutions of potassium permanganate with the view of utilising the method as a quantitative measure of oxidisable substances.

**Influence of Alcohol, Salts, and Temperature on the Change Point of some Indicators and Means of Avoiding Errors in Acidimetric Titrations.** A. RICHTER (*Z. anal. Chem.*, 1924, 65, 209—245).—The dissociation constant of dimethyl-yellow in pure water is  $1.22 \times 10^{-11}$  and is increased by the addition of sodium chloride to  $2.61 \times 10^{-11}$  in *N*-solution. The temperature factor is considerable, the dissociation constant increasing to  $12.0 \times 10^{-11}$  at 75° in water and to  $24.9 \times 10^{-11}$  in *N*-sodium chloride. With 0.1*N*-hydrochloric acid, the correction to be applied for the indicator increases from 0.15 c.c. at 20° to 0.34 c.c. at 80°; in the presence of sodium sulphate the correction increases from 0.23 c.c. to 2.0 c.c. in 0.1*N*-solution and to 4.8 c.c. in 0.5*N*-solution. Carbon dioxide has very little influence on the transition range of this indicator, the effect rarely amounting to the equivalent of 0.1 c.c. of 0.1*N*-acid. The dissociation constant of bromophenol-blue rises from  $0.85 \times 10^{-4}$  in pure water to  $1.9 \times 10^{-4}$  in *N*-sodium chloride and these figures are altered only slightly by increase of temperature or by the presence of alcohol. The smallest indicator correction is required when the solution contains half its volume of alcohol. The sensitivity of phenolphthalein to alkalis falls with increase of temperature, but this effect may be appreciably diminished by addition of sodium sulphate and increased by the presence of excessive amounts of alcohol. A theoretical discussion of the results is given together with tables of corrections for the three indicators examined.

A. R. P.



**Sodium Arsenite as a Reagent for Loosely-combined Halogen.** A. GUTMANN (*Z. anal. Chem.*, 1924, 65, 246—254).—Sodium arsenite in alkaline solution reacts with many organic compounds containing loosely-combined halogen atoms and with some non-metallic halides to form sodium arsenate, sodium halide, and derivatives of the compounds used containing less halogen. This reaction may be utilised as a test for the presence of loosely-combined halogen atoms and in some cases serves as a means of determining the compound tested. The following examples are described showing the action of alkaline arsenite: Iodoform is converted into methylene iodide, showing that only one of its iodine atoms is present in the labile, trivalent form. Similarly, di-iodophenol iodide is converted into di-iodophenol, but the isomeric tri-iodophenol is unattacked. Phenyl iododichloride is reduced to iodobenzene, dibromourethane to ethyl alcohol, ammonia, and carbon dioxide, and *p*-toluenesulphochloroamide to ammonia and the corresponding amine. Nitrogen halides are converted into ammonia, whilst halogen azides and cyanides yield salts of the corresponding acids. Sulphur monochloride converts sodium arsenite into sulphonylarsenate with the simultaneous formation of sulphite and chloride.

A. R. P.

**Universal Indicator for the Colorimetric Determination of  $p_H$  Values in Soil Experiments.** H. NIKLAS and A. HOCK.—(See i, 348.)

**Occurrence of Iodine in Nature. II. Determination of Minute Quantities of Iodine.** T. VON FELLENBERG.—(See i, 329.) **III. Iodine Determinations on Foodstuffs, Manures, and Swiss Mineral Waters.** T. VON FELLENBERG.—(See i, 347.)

**Mohr's Method for Determination of Silver and Halogens in other than Neutral Solutions.** H. W. DOUGHTY (*J. Amer. Chem. Soc.*, 1924, 46, 2707—2709).—Chlorides may be titrated accurately with silver nitrate in any acid solution using potassium chromate as indicator provided that the  $p_H$  value is first reduced to between 5 and 7 by addition of a sodium acetate-acetic acid (2 mol. : 1) buffer mixture.

G. M. B.

**Absorbent for Oxygen in Gas Analysis.** L. F. FIESER (*J. Amer. Chem. Soc.*, 1924, 46, 2639—2647).—The completeness and the rapidity of the action of an alkaline solution of sodium hyposulphite for absorbing oxygen are increased by the addition of 2% of sodium anthraquinone-2-sulphonate.

G. M. B.

**Sensitive, Qualitative Method for the Detection of Oxygen with Pyrogallol and Potassium Hydroxide.** H. SCHMALFUSS and H. WERNER (*Ber.*, 1925, 58, [B], 71—73; cf. Schmalfuss, A., 1923, ii, 783).—The gas under investigation is placed in a sealed glass bulb inside a bottle containing a few drops of water and a piece of filter-paper moistened with potassium hydroxide solution. The bottle is closed by a rubber stopper which holds an inverted glass

"mushroom," on the top of which a few grains of moistened pyrogallol are placed. The apparatus is evacuated at  $20^{\circ}$  until the air has been replaced completely by water vapour. It is then quickly shaken so that the pyrogallol falls on to the filter-paper, after which the bulb is broken. In the presence of 0.008% of oxygen, the paper acquires a pale pink tint within 2 minutes; with higher concentrations it becomes bluish-violet, pale brown, and dark brown. Accurate results are obtained in the presence of nitrogen, hydrogen, acetylene, carbon monoxide, nitrous oxide, nitric oxide, and ammonia, but not of carbon dioxide, sulphur dioxide, hydrogen sulphide, hydrogen cyanide, cyanogen, chlorine, or bromine.

H. W.

**Iodometric Analysis of a Mixture of Sulphide, Sulphite, and Thiosulphate.** A. KURTENACKER and K. BITTNER (*Z. anorg. Chem.*, 1924, **141**, 297—303).—A measured volume of the solution is allowed to flow into an excess of iodine solution in presence of acid, and the excess determined with thiosulphate. A second fraction is treated with zinc acetate and, without filtration, formaldehyde, and then added to excess of iodine solution; the back titration gives the iodine required by the sulphide and thiosulphate. If the zinc sulphide precipitate be filtered off, formaldehyde added to the filtrate, and the determination repeated, only the thiosulphate reacts.

S. I. L.

**Electrometric Titration of Hydrazine and its Salts.** E. C. GILBERT (*J. Amer. Chem. Soc.*, 1924, **46**, 2648—2655).—From the absence of any second point of inflexion in the titration curves of hydrazine in various concentrations with acids the conclusion is reached that the second dissociation constant of hydrazine hydrate is less than  $1 \times 10^{-12}$ , as compared with the value  $2.8 \times 10^{-13}$  calculated by Kolthoff (*A.*, 1924, ii, 871). Curves for the titration of hydrazine salts with bases are very similar to that obtained with ammonium hydrogen sulphate. Curves were also obtained for the titration of hydrazine with iodine and with potassium bromate, and the incidental discovery is recorded that hydroxylamine is completely oxidised by bromate either to nitrate or to nitrous oxide, depending solely on the order of mixing of the reagents.

G. M. B.

**Volumetric Determination of Sulphate in Minute Amounts.** K. KLINKE (*Biochem. Z.*, 1924, **154**, 171—175).—Andrews' volumetric method for determining sulphate (*A.*, 1890, 414) is modified and an attempt made to calculate the amount of sulphate with the help of the mass law. This failed and an empirical method is adopted. The author claims the limit of 0.01 mg. of sulphur.

P. W. C.

**Determination of Blood Urea-Nitrogen.** W. G. KARR.—(See i, 323.)

**Ammonia Content and Ammonia Formation of Blood.** J. K. PARNAS and J. HELLER.—(See i, 323.)

**Determination of Nitrates.** P. L. HIBBARD (*Ind. Eng. Chem.*, 1925, 17, 58).—Satisfactory results can be obtained with Scales' method only if any sodium carbonate present in the magnesium oxide is neutralised; Devarda's method is more trustworthy. [Cf. *B.*, 1925, 154.]  
C. I.

**Detection of Nitrates and Perchlorates.** C. S. MARVEL and V. DU VIGNEAUD (*J. Amer. Chem. Soc.*, 1924, 46, 2661—2663).— $\alpha$ -Phenyl- $\beta$ -diethylaminoethyl *p*-nitrobenzoate may be used in the form of its hydrochloride for detecting nitrates in 0.005*N*-solution and perchlorates in 0.0025*N*-solution. The only other common anions which interfere are iodides, oxalates, thiocyanates, and dichromates. The solubilities of the perchlorate, m. p. 144°, and of the nitrate are too great for their use in an accurate gravimetric determination.  
G. M. B.

**Determination of Arsenic in "Salvarsan" and its Congeners.** A. KIRCHER and F. VON RUPPERT (*Arch. Pharm.*, 1924, 262, 613—614).—The earlier method (A., 1921, ii, 130) is improved by using potassium bromate instead of iodine in titrating the arsenious acid produced when the substance is decomposed by boiling with sulphuric acid and potassium sulphate. [Cf. *B.*, 1925, 188.]  
W. A. S.

**Chromic Acid Method for Determining Organic Carbon** J. W. WHITE and F. J. HOLBEN (*Ind. Eng. Chem.*, 1925, 17, 83—85).—Organic carbon either in the dry state or in solution can be accurately determined by chromic acid oxidation, provided that the acid mixture is boiled. The sulphur trioxide fumes produced are absorbed in a U-tube placed at the beginning of the absorption train and containing glass wool moistened with 98.3% sulphuric acid. The oxidation is carried out in a Knorr's apparatus with 10 c.c. of 34% chromium trioxide solution and 50 c.c. of sulphuric acid (*d* 1.84). The method is especially suitable for the analysis of soils and soil extracts which need not be evaporated. [Cf. *B.*, 1925, 156.]  
C. I.

**[Analysis of Coal.] Three Point Method with Rapid Cooling.** D. J. W. KREULEN (*Chem. Weekblad*, 1925, 22, 28—29).—The method of determining volatile matter in coal by fixing three points on the curve showing loss of weight plotted against time under specified conditions (Delmarcel and Mertens, *Bull. Féd. Ind. Chim. Belg.*, Oct. and Nov., 1921) is modified by cooling the crucible in water, when fixing the first point, to arrest the decomposition suddenly.  
S. I. L.

**Polarimetric Determination of Inactive Substances: Potassium.** A. WRÓBEL (*Roczniki Chemji*, 1924, 4, 287—294).—When a solution containing sodium hydrogen tartrate and ammonium molybdate is treated with a potassium salt, the reaction of the latter with the tartrate results in depression of the optical rotation of the liquid, the extent of this depression serving as a means of determining the amount of potassium used. [Cf. *B.*, 1925, 192.]  
T. H. P.

**Determination of Sodium in Aluminium.** D. M. FAIRLIE and G. B. BROOK (*J. Inst. Metals*, 1924, 32, 283—289).—The aluminium is removed as crystals of nitrate from a strong nitric acid solution of the metal containing mercuric chloride; the sodium in the mother-liquor is converted into impure sulphate by ignition with sulphuric acid, the amounts of impurities present being determined by a separate analysis and deducted from the weight of the sodium salt. Ninety % of the sodium is extracted by this method; a further 5% is extracted by repeating the process on the aluminium nitrate crystals. The percentage error is large when the sodium content is very low. S. K. T.

**Simple Clinical Micro-method for Determining Sodium in Blood-serum.** F. LEBERMANN.—(See i, 324.)

**Determination of Radium in Uranium Minerals Containing Tantalum, Niobium, and Titanium.** (MME.) P. CURIE (*Compt. rend.*, 1925, 180, 208—211).—Generally the extraction of radium with the barium sulphate is the most certain of action. A mixture of the mineral with barium sulphate is fused with potassium hydrogen sulphate, the mass is extracted with water, and the residue treated with dilute hydrofluoric acid which leaves the barium sulphate containing the radium, the small portion of the latter which passes into solution being precipitated by the addition of sulphuric acid and barium chloride. The barium sulphate is converted into chloride by way of the carbonate, and its radium content is determined by transferring the emanation produced in a given time to an ionisation chamber by means of a current of air (cf. A., 1910, ii, 476). The accuracy of the method is 1% for radium contents of  $10^{-6}$ — $10^{-8}$  g. per g. of mineral, and slightly less for those of  $10^{-8}$ — $10^{-9}$  g. The residue obtained by the evaporation of the hydrofluoric acid solution may contain protoactinium accounting for 1% of the radioactivity of the mineral. J. W. B.

**Electrolytic Determination of Zinc [in the Presence of Copper].** J. W. SPRINGER (*Z. anal. Chem.*, 1924, 65, 315—317).—The nitric acid solution of the two metals is neutralised with ammonia, sulphuric acid is added, and the copper deposited on a rotating cathode from the boiling solution. The electrolyte, freed from copper, is then neutralised with sodium hydroxide, treated with a further 10 g. of the alkali, and electrolysed for 20 minutes, using a rotating cathode of amalgamated brass gauze. [Cf. B., 1925, 175.] A. R. P.

**Determination of Copper by Rapid Electrolysis in the Presence of Tin, Antimony, and Lead.** J. LUKAS and A. JILEK (*Chem. Listy*, 1924, 18, 378—383).—For the separation of copper from tin by rapid electrolysis, the sample is dissolved in a mixture of nitric and tartaric acids and the solution electrolysed in a platinum dish, which serves as cathode, using a rotating anode. If antimony is present hydrofluoric and phosphoric acids must also be added; in neither case does the presence of lead affect the

results. The first copper deposit should be redissolved in nitric acid and the solution filtered and electrolysed again in order to remove traces of carbon and antimony. [Cf. *B.*, 1925, 192.]

A. R. P.

**Detection of Copper in Distilled Water.** G. POIROT (*J. Pharm. Chim.*, 1924, [vii], 30, 393—399).—When a solution of alcohol-soluble guaiacum resin in pyridine is added to a mixture of alcohol and the water to be tested in the presence of a few drops of dilute hydrogen peroxide solution, a characteristic blue coloration is produced if copper is present, the limit of sensitiveness being 1 in  $10^8$ . The colour is soluble in alcohol, chloroform, and ethyl acetate, sparingly soluble in ether, benzene, and toluene, and insoluble in xylene, carbon disulphide, and light petroleum. It is destroyed by acids and by ammonia. The presence of pyridine, however, intensifies the colour and stabilises the resin solution, which is unchanged in activity after 50 days if kept in a yellow bottle with a ground-in stopper.

W. T. K. B.

**Systematic Detection of the Rarer Chemical Elements.** A. A. NOYES and W. C. BRAY (*Chem. Reviews*, 1924, 1, 277—291).

**Qualitative Separation of Cobalt, Nickel, Zinc, and Manganese.** LEMARCHANDS (*Bull. Soc. chim.*, 1924, [iv], 35, 1666—1668).—Potassium hydroxide is added to the solution containing the chlorides of the metals; the lower oxides of nickel, cobalt, and manganese are precipitated and are converted into higher oxides by addition of sodium perborate. The precipitate is collected and treated with warm dilute nitric acid; the cobalt and nickel oxides dissolve and are recognised in the solution by the potassium cobaltinitrite and dimethylglyoxime tests, respectively. Manganese dioxide is insoluble and its presence may be confirmed by conversion into potassium manganate. Zinc is detected by passing hydrogen sulphide into the first filtrate.

S. K. T.

**Detection of Cobalt, Alone or in Presence of Nickel and Other Salts, in Neutral Solution.** S. J. TINDAL (*Chem. News*, 1925, 130, 34—35).—Neutral solutions of cobalt salts yield a blue precipitate with solutions of sodium silicate soluble in excess of the precipitant; nickel salts under the same conditions give a pale green precipitate insoluble in excess of sodium silicate. The bright blue sodium cobalto-silicate solution is decolorised by mineral acids, rendered greenish-yellow by addition of bromine water in the cold, and black on boiling, owing to separation of cobaltic hydroxide, and turned a greenish-yellow colour both at the ordinary and elevated temperatures by addition of hydrogen peroxide. Nickel and the alkaline-earth metals do not interfere with the test, which will detect 0.00004 g. of cobalt in 5 c.c. of solution.

A. R. P.

**Rapid Separation of Tin and Tungsten by Electroanalysis.** A. JILEK and J. LUKAS (*Chem. Listy*, 1924, 18, 205—210).—To a solution containing tin and tungsten with an excess of an alkali

sulphide, Rochelle-salt and potassium hydroxide are added, followed by hydrogen peroxide. The solution is boiled, potassium phosphate added, and the electrolysis carried out at 60—70°. The method is superior to that of Treadwell, jun. ("Elektroanalytische Methoden"). It is not applicable to mixtures of tin and molybdenum or vanadium. [Cf. *B.*, 1925, 155.] W. A. S.

**Electrometric Titration of Antimony and Tin by Potassium Dichromate.** M. H. FLEYSHER (*J. Amer. Chem. Soc.*, 1924, **46**, 2725—2727).—Stannous and antimonious chlorides may be titrated by potassium dichromate in hydrochloric acid solutions, using the oxidation-reduction electrode to indicate the end-point. For the analysis of mixtures of the two, both are titrated together, and the antimony is then titrated separately, after addition of mercuric chloride in excess. G. M. B.

**Use of Titanous Chloride in Potentiometric Titrations.** O. TOMIČEK (*Chem. Listy*, 1924, **18**, 210—220; 233—241).—The reducing power of titanous chloride is the greater the lower the hydrogen-ion concentration of the solution, so much so that when Rochelle-salt is present, copper, bismuth, and lead salts are reduced to the metallic state. If titanous chloride titrations are followed potentiometrically, the method can be applied to determining vanadium, antimony, uranium, molybdenum, selenium, and copper. In the last three cases, the usefulness of the reagent has been questioned and in the others it has hitherto not been used. By similar means, chromates and vanadates may be determined in presence of ferric salts, chromates in presence of ferric salts and vanadates, and ferric in presence of cupric or uranyl salts.

W. A. S.

**Separation of Zirconium and Hafnium by Crystallisation of the Double Ammonium Fluorides.** J. H. DE BOER and A. E. VAN ARKEL (*Z. anorg. Chem.*, 1924, **141**, 284—288; cf. Hevesy and Jantzen, *A.*, 1924, ii, 53).—The action of fused sodium hydrogen sulphate on alvite and zirkite effects some separation, the soluble sulphates having a higher hafnium : zirconium ratio than the original mineral. The double fluorides,  $(\text{NH}_4)_3\text{ZrF}_7$  and  $(\text{NH}_4)_3\text{HfF}_7$ , are less suitable for the separation than the compounds  $(\text{NH}_4)_2\text{ZrF}_6$  and  $(\text{NH}_4)_2\text{HfF}_6$ . Two methods of fractionation were followed; the first fractions of the second series in each case were free from hafnium; about 150 crystallisations in 23 series gave end fractions containing 50% of hafnium, calculated on the zirconium present. S. I. L.

**Separation of Zirconium from other Metals, including Hafnium, by Fractional Distillation.** A. E. VAN ARKEL and J. H. DE BOER (*Z. anorg. Chem.*, 1924, **141**, 289—296).—The existence of the compound  $2\text{ZrCl}_4 \cdot \text{PCl}_5$  (Payküll, *Ber.*, 1879, **12**, 1719) has been confirmed; it is a white, crystalline solid, m. p. 164.5°, b. p. 416°. Traces of moisture hydrolyse it to the compound

$2\text{ZrCl}_4 \cdot \text{POCl}_3$ , a vitreous solid, b. p.  $363\text{--}364^\circ$ , readily converted into the first by the action of phosphorus pentachloride. Titanium and silicon if present distil readily in the form of the chlorides or additive compounds of these; iron and aluminium form much less readily volatile additive compounds, and remain in the residue. Hafnium forms compounds analogous to but slightly more volatile than those of zirconium, and can be concentrated by repeated distillation of the earlier fractions. S. I. L.

**Determination of Antimony in Stibnite and in Antimony Pentasulphide.** E. RUPP, G. SIEBLER, and W. BRACHMANN (*Pharm. Zentr.*, 1925, 66, 33—36).—Digestion of finely-divided stibnite with 15% sodium hydroxide solution at  $100^\circ$  results in complete dissolution of the antimony sulphide and its separation from iron sulphide and silicious impurities. The solution after being boiled with sufficient hydrochloric acid to convert the antimony into trichloride may be titrated directly with bromate or "chloramine," or after oxidation with hydrogen peroxide, the amount of pentachloride present may be determined iodometrically. For the determination of antimony in the pentasulphide, the sample may be dissolved directly to trichloride by heating with concentrated hydrochloric acid and the antimony determined as indicated above. A. R. P.

**Micro-method for Determining Organic Substances.** M. BALINT and P. RUSZCZYNSKI.—(See i, 323.)

**Analysis of Mixtures of Sugars.** E. HILDT (*Ann. Chim. anal.*, 1925, [ii], 7, 4—8).—The applications of fractional inversion methods are discussed and it is shown that at  $75^\circ$  1% solutions of lactose remain practically unaltered. The source of some strobopolarimetric errors due to mutarotation, particularly in connexion with lævulose, are detailed, and a comparative table is given showing the differences of coefficients of inversion of sucrose for a series of times, measured polarimetrically and by the copper method. [Cf. B., 1925, 142.] D. G. H.

**Micro-determination of Blood Sugar.** E. DINGEMANSE.—(See i, 323.)

**Reducing Power of Organic Compounds in Alkaline Solution and the Determination of Sugar by Analysis in Stages and with Separation of Colloidal Cuprous Oxide.** H. RUOSS (*Biochem. Z.*, 1924, 151, 337—356).—An investigation of the reduction by sugars of copper salts and dyes (orange II and fast red C) in alkaline solutions. A simple method of analysis in stages is described. The general conclusions reached are, that if 100 c.c. of the alkaline solution are reduced by  $z$  c.c. of the solution of reducing substance, the latter contains  $(A/z + B + Cz)\%$ . Or, if 100 c.c. of the alkaline solution are diluted until the alkalinity is  $nN$ , they require for complete reduction  $D + E/n + F/n^2$  mg. of the reducing substance.  $A$ ,  $B$ ,  $C$ ,  $D$ ,  $E$ , and  $F$  are constants. J. P.

**Determination of Invert Sugar.** C. J. DE WOLFF (*Chem. Weekblad*, 1925, 22, 78—79).—The work of van den Hout, Neeteson, and van Scherpenberg (this vol., ii, 74) is criticised. No effect could be observed as a result of washing out the vessels with sodium hydroxide, neither does distilled water cause any measurable inversion. The quantity of starch used does not influence the result. The diminution of the extent of the reduction of Fehling's solution by sucrose with increasing quantities of the latter is confirmed. S. I. L.

**Determination of Free Phenol and Cresol in Small Amounts of Blood.** G. HAAS and E. F. SCHLESINGER.—(See i, 334.)

**Colorimetric Picric Acid Method for Determining Lactose.** H. R. BIERMAN and F. J. DOAN (*J. Dairy Sci.*, 1924, 7, 381—392).—A modification of the method of Folin and Denis for the removal of fat and protein. CHEMICAL ABSTRACTS.

**Determination of the Reducing Power of Cellulose Products.** K. HESS [with W. WELTZIEN and H. NAKAMURA] (*Annalen*, 1924, 440, 290—304).—"Copper numbers" obtained from alkali-soluble celluloses by Schwalbe's method ("Die Chemie der Cellulose," 1911, 625) are not comparable with data similarly obtained from alkali-insoluble celluloses, on account of the sensitiveness of the alkali-soluble materials to the action of hot alkali. This is circumvented by precipitating the cellulose from its solution in alkali as the insoluble copper-cellulose compound by means of cold Fehling's solution (cf. A., 1924, i, 142) prior to completing the reaction at the boiling point of the solution. Consistent results are obtained if temperature and duration of reaction, as well as concentrations of all reactants, are standardised, and optimum conditions are described in detail. Reaction is complete after 5 minutes' boiling (cf. Bang, *Biochem. Z.*, 1907, 2, 284). The copper number yielded by a given sample is lower the higher the concentration of cellulose, alkali, or copper in the reaction mixture, variation of alkali content having the greatest effect. The effect is ascribed to the variation of solubility, in accordance with the law of mass action, of the copper-cellulose-alkali compound, the production of which is formulated  $2[\text{C}_6\text{H}_9\text{O}_5]^- + [\text{Cu}_4\text{H}_3\text{O}_6]^- + 2\text{Na}^+ \rightleftharpoons [\text{Cu}_{12}\text{H}_{16}\text{O}_{10}]\text{Na}_2 \downarrow + [\text{C}_4\text{H}_5\text{O}_6]^-$ . The reduction takes place at the surface of the precipitate, and not in the solution. Its completion in one operation indicates absence of attack on the cellulose molecule, whilst with Schwalbe's method, complete oxidation requires several treatments, a fraction of the cellulose, depending on its original purity, being attacked each time. The decrease in copper number with increasing copper content of the reagent emphasises the difference between cellulose and sugar with respect to this reaction, the effect being reversed in the case of the latter. Comparison of copper numbers obtained in this way with the specific rotations of the respective samples in cuprammonium solutions indicates that the copper number provides an exact criterion of purity. [Cf. B., 1925, 94.]

F. G. W.



**Determination of Acetone in Presence of Alcohol by a Vapour Pressure Method.** E. A. VUILLEUMIER (*Ind. Eng. Chem.*, 1925, 17, 174).—Since the difference in vapour pressure between an aqueous alcohol and an alcohol containing acetone of the same specific gravity is very marked, increasing with rise of temperature, this denaturant can be conveniently determined by comparing at the same temperature the vapour pressure of the unknown sample with that of a sample containing a known proportion of acetone and diluted to the same specific gravity.

D. G. H.

**Detection of Citric Acid.** RODILLON (*Répert. Pharm.*, 1924, 35, 233—234).—The solution to be tested is boiled with a little potassium dichromate solution, and a mixture of acetic acid and sodium nitroprusside is added after cooling. Ammonium hydroxide solution free from acetone is added without mixing, when acetone produced from the citric acid generates a violet-red colour at the surface of contact. Alternatively, the acetone may be detected by the iodoform reaction.

CHEMICAL ABSTRACTS.

**[Determination of Citric Acid.]** A. F. CAMP (*Ann. Missouri Bot. Garden*, 1923, 10, 213—298).—A dilute aqueous solution of citric and sulphuric acids is distilled, the first distillate being discarded, and that obtained after addition of potassium permanganate is collected and redistilled after addition of sodium hydroxide and hydrogen peroxide. The distillate so obtained, after being shaken with iodine and sodium hydroxide solutions, is acidified and the mixture titrated with standard thiosulphate solution. A percentage correction, depending on the amount of citric acid found, is applied. In certain circumstances, it is necessary first to separate the citric acid as the calcium or barium salt.

CHEMICAL ABSTRACTS.

**Determination of Phenolsulphonephthalein in the Urine of Jaundice.** H. A. ABRAMSON.—(See i, 329.)

**Winkler's Method for Determining the Iodine-Bromine Number without Potassium Bromide.** O. KÖPKE (*Z. Unters. Nahr. Genussm.*, 1924, 48, 364—370; cf. A., 1922, ii, 534).—In the revised method, standard potassium bromate solution, dilute hydrochloric acid, and a small quantity of powdered potassium bromide are added to a solution of the oil or fat in carbon tetrachloride solution. After keeping for some hours in a dark place, an excess of standard sodium arsenite solution is added, the liquid is acidified with hydrochloric acid, and titrated with standard potassium bromate solution. In unsuitable illumination, indigo-carmin may be used as an indicator.

G. S. W.

**Detection of Nitroaminophenols in Urine.** L. DESVERGNES.—(See i, 328.)

**Urea Oxalates and their Determination as Secondary Oxalate in Fertilisers.** T. SABALITSCHKA and G. KUBISCH.—(See i, 347.)

**Indicator Method for the Determination of Urea and Arginase.** A. HUNTER and J. A. DAUPHINEE (*Proc. Physiol. Soc.; J. Physiol.*, 1924, 59, xxxiv).—Urea in concentrations up to 0.15% can be determined by decomposing it with urease in the presence of 0.05*M*-phosphate at a  $p_H$  of 6.9 and determining colorimetrically the resulting change in  $p_H$ . For the detection and determination of arginase the extract is allowed to act under specified conditions of temperature and  $p_H$  on a standard solution of arginine, and the urea produced in a given time is determined as above.

CHEMICAL ABSTRACTS.

**Determination of Small Amounts of Glycogen in Solution.** S. E. DE JONGH and J. PLANELLES.—(See i, 325.)

**Titration of Alkaloids.** H. B. RASMUSSEN and S. A. SCHOU (*Pharm. Zentr.*, 1924, 65, 729—730).—A solution of the alkaloid in dilute hydrochloric acid was titrated with 0.1*N*-sodium hydroxide. The potential, relative to a quinhydrone electrode (cf. Veibel, T., 1923, 123, 2203), and hence the  $p_H$ , was determined after each addition of alkali. The results are represented in graphs, which show a point of inversion, and the corresponding values for  $p_H$ , as found directly and as interpolated from the titrimetric curves, are given. The values found by interpolation are as follows: strychnine, 4.96—5.09; brucine, 4.65—4.83; morphine, 4.77—4.90; codeine, 4.93—4.94; narcotine, 4.29—4.32; nicotine, 6.41—6.58; hydrastine, 4.92—5.01; cinchonine, 5.93—5.96; quinine, 6.39—6.42; atropine, 4.75—4.90. Methyl-red is recommended as indicator for all the above (for cinchonine with buffer solution of  $p_H$  5.9), except narcotine (methyl-orange, buffer solution of  $p_H$  4.2), and quinine (*p*-nitrophenol, buffer solution of  $p_H$  6.2).

W. T. K. B.

**Colorimetric Determination of Solutions of Novocaine.** P. CHERAMY (*J. Pharm. Chim.*, 1924, 30, 408—411).—The colour formed on mixing solutions of novocaine, sodium nitrite, hydrochloric acid, and sodium carbonate containing 0.5% of potassium guaiacolsulphonate varies from red to yellow, according to dilution, and is suitable for colorimetric comparison with a standard novocaine solution at a dilution of 1:20,000 of novocaine. The colour reaction is unaffected by the presence of methyl *m*-amino-*p*-hydroxybenzoate, *p*-aminobenzoic acid, cocaine, stovaine, or of small amounts of adrenaline, although more concentrated solutions of the last-named also give a red coloration due to oxidation. Sodium hydrogen sulphite, however, exerts a markedly depressant action on the colour formation, and should be removed, before diazotising, by addition of 1 drop of 0.1*N*-iodine solution. Solutions of novocaine may be sterilised, without change, in slightly alkaline glass vessels at 100°, but at 120° the alkali causes appreciable change and sterilisation should be effected in vessels of superior glass or in the presence of a solution of benzoic acid.

W. T. K. B.

**Colour Reactions of Eserine.** L. EKKERT (*Pharm. Zentr.*, 1925, 66, 53).—Eserine and its salts, when left in the air, are trans-

formed into rubreserine (Ehrenberg, A., 1895, i, 436) which, when warmed with sodium hydroxide solution, yields various colour changes, and finally an emerald-green solution (A) is obtained: When acidified with mineral acids, this solution becomes ruby-red and, on the addition of dilute sodium thiosulphate solution, carmine-red with a blue fluorescence, or of ammonium sulphide, green. On acidification of solution A with acetic acid, an indigo-blue or, if more dilute, a garnet colour is produced which is extractable with chloroform. If a salt of eserine be dissolved in chloroform and heated to the b. p. with sodium hydroxide, these colour reactions are not obtained, but the aqueous layer becomes gradually golden-yellow, whilst the chloroform assumes a pale rose tint. This is cited as further evidence of the presence in eserine of an hydroxyl group.  
L. F. H.

**Analysis of Adrenaline.** D. ECHAVE (*Anal. Asoc. Quím., Argentina*, 1924, 12, 234—257).—A discussion from the analytical point of view of the physical and chemical properties of different samples of commercial adrenaline.  
G. W. R.

**Application of the Denigès-Grimbert-Leclère Reaction to the Characterisation and Determination of Adrenaline in Suprarenal Powders.** O. BAILLY (*J. Pharm. Chim.*, 1924, [vii], 30, 404—405).—When an aqueous sulphuric acid maceration extract of suprarenal powder is filtered and mixed with solutions of sodium acetate and mercuric chloride, the presence of adrenaline produces a red coloration, which attains its maximum intensity after 3 minutes and can serve for the determination by colorimetric comparison with a standard solution of adrenaline.  
W. T. K. B.

**Bitter Principles in Hops and Beer.** L. KLEIN (*Chem. Listy*, 1924, 18, 221—226; 242—244).—Siller's method (A., 1909, i, 728) for determining humulone in hops is improved by substituting potassium iodide for potassium sulphide in detecting the excess of lead salt used as the precipitating agent.

The "iodine-number" of the resinous extract from beer or wort made from fresh hops is about 200, but that of the extract from beer made from old hops is only 150 to 170. The longer the wort is boiled with the hops, the higher is the "iodine-number" of the resin extracted from it.  
W. A. S.

**Extraction of Proteins.** G. PINESS, H. MILLER, and G. A. ALLES.—(See i, 331.)

**Determination of Colloid Material in Soils.** G. J. BOUYOCOS.—(See i, 348.)

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## General, Physical, and Inorganic Chemistry.

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**Apparent Tripling of certain Lines in Arc Spectra.** T. ROYDS (*Proc. Roy. Soc.*, 1925, **A**, 107, 360—367).—As many spectra as possible have been searched through the visible region for instances of lines becoming complex when the amount of material in the arc is increased. Only seven such lines have been found, these being lithium 6708, 6103; thallium 5350; strontium 4876.2, 4872, 4832; manganese pair 4235. The thallium line 5350 has been specially studied; it is shown that it is essentially a doublet and that the different phases can be simply explained as different stages in the self-reversal of the two lines of the doublet. The resolution by interatomic fields suggested by King is considered unnecessary to the explanation. N. H. H.

**Fine Structure of the Helium Line 5876 Å.** R. BRUNETTI (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 413—415).—The  $D_3$  helium line appears to be undecomposable and endowed with only a single satellite. Both retain their separate structures in even intense magnetic fields and are, therefore, not lines of a multiple series in the ordinary sense of the term. The origin of the structure of the helium line 5876 Å. is thus still unexplained. T. H. P.

**Comet Tail Spectrum and Deslandres' First Negative Group.** H. B. LEMON (*Proc. Nat. Acad. Sci.*, 1925, **11**, 41—43).—A long vacuum tube of the Wood type filled with helium pumped by circulation through activated carbon furnishes an extremely brilliant comet tail spectrum provided the partial pressure of the carbon compounds is of the order  $10^{-4}$  mm. The composition of the residual carbon compounds is quantitatively unknown, although carbon dioxide and certain hydrocarbons are present. The helium plays only a secondary rôle in the excitation of these spectra, but nevertheless is necessary for their production with great intensity. J. S. C.

**Auroral Green Line.** J. C. McLENNAN (*Nature*, 1925, **115**, 382).—Under conditions which indicate its identity with the auroral green line, a line at  $5577.35 \pm 0.15$  Å. has been observed in the spectrum of a mixture of air with excess of helium. A. A. E.

**"Dashed" and Displaced Spectral Terms.** A. LANDÉ (*Z. Physik*, 1924, **27**, 149—156).—An alternative allocation of quantum numbers to certain terms in the spectra of the alkaline-earth metals is suggested. S. B.

**Spark-spectra of Indium and Gallium in the Extreme Ultra-violet Region.** M. WEINBERG (*Proc. Roy. Soc.*, 1925, **A**, 107, 138—156).—By means of the quartz spectrograph 80 gallium lines between 1855 and 2364 Å. have been examined and

107 indium lines between 1855 and 2337 Å. Using a vacuum grating spectrograph, 828 lines which could be attributed to gallium were found and measured between 157 and 2059 Å., and 464 indium lines in the range 161—2082 Å. For the examination of the quartz region, the spark chamber was filled with hydrogen. M. S. B.

**Structure of the Line Spectra of Ionised Oxygen.** F. CROZE (*Compt. rend.*, 1925, **180**, 432—433; cf. this vol., ii, 166).—In addition to the six multiplets in the spectra of ionised oxygen, resulting from combinations between two systems of quadruple terms, there are also combinations between double terms, the more important of which are given. J. S. C.

**Structure of Spectrum of Ionised Nitrogen.** A. FOWLER (*Proc. Roy. Soc.*, 1925, **A**, **107**, 31—42).—The second line spectrum of nitrogen, between  $\lambda$  6650 and 2200, due to singly-ionised nitrogen, has been examined in vacuum tubes with gas at various pressures, and under varying conditions of electrical discharge. The terms identified belong to singlet and triplet systems, and combine with each other in agreement with the selection rules applicable to other spectra in which  $p'$  and  $d'$  terms appear. The value 70,000 has been provisionally assigned to  $2p$ . The series electron in singly-ionised nitrogen,  $N^+$ , probably occupies, normally, a  $2s$  orbit, so that it has two electrons in  $1s$  orbits, two in  $2s$ , and two in  $2p$ . From the spectroscopic displacement law it may be inferred that this is also the probable arrangement of orbits in the neutral atom of carbon. Three groups of lines involving one of the  $p$  terms show large displacements ( $>0.5$  Å.) to the red in vacuum tubes at relatively high pressures. M. S. B.

**Scattered Radiation due to X-Rays from Molybdenum and Tungsten.** S. K. ALLISON and W. DUANE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 25—27).—Using an improved form of the apparatus previously described (*ibid.*, 1924, **10**, 381) and employing a modified technique, previous work has been repeated and it is found that the equation of Compton, deduced from his theory of single electron scattering, represents the wave-lengths of a large part of the secondary radiation due to primary rays in the  $K$ -series spectra of molybdenum and tungsten. J. S. C.

**Short Wave X-Ray Spectrograph and some  $K$ -Series Emission Wave-lengths.** J. M. CORK (*Physical Rev.*, 1925, [ii], **25**, 197—200).—A transmission type of spectrograph for short X-rays is described. The results of measurements of wave-lengths (in  $X$ -units) of  $K$ -series lines  $\alpha'$ ,  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively, are as follows:—barium, 389.45, 384.83, 340.66, 332.62; lanthanum, 375.18, 370.29, 327.99, 319.57; cerium, 361.24, 356.73, 315.75, 307.32; praseodymium, 348.66, 343.84, 304.12, 296.55; neodymium, 336.40, 331.51, 293.33, 286.15; samarium, 313.46, 308.75, 273.55, 265.72; gadolinium, 293.01, 287.71, 254.28, 248.01; dysprosium, 274.14, 269.28, 238.08, 231.53; erbium, 256.95, 251.90, 222.74, 216.93; tungsten, 213.69, 208.84, 184.56, 179.07.

A. A. E.

**Complex Structure of Röntgen-spark Spectra.** G. WENTZEL (*Z. Physik*, 1925, **31**, 445—452; cf. A., 1924, ii, 638).—A provisional attempt to predict complex spark spectra from the theories of Röntgen-arc and optical spectra. R. A. M.

**Influence of Velocity-Dependence of Electron Mass on the Zeeman Effect.** W. PAULI, jun. (*Z. Physik*, 1925, **31**, 373—385).—Mathematical. The Zeeman effect in a homologous series of elements, especially the alkali metals, would depend on the atomic number if the relativity mass change exerted any influence. This would imply a contribution by the electrons of the *K*-shell to the impulse moment and to the magnetic moment. The absence of such effects supports other arguments against the participation of the inner closed shell in the form of core-impulses in the origin of complex optical spectra and Zeeman effects. R. A. M.

**Atomic Rays.** G. C. SCHMIDT (*Ann. Physik*, 1924, [iv], **75**, 337—368; cf. A., 1924, ii, 727).—The nature of the charged particles emitted on heating a series of salts has been examined. The halogen salts of iron, magnesium, zinc, ammonium, etc. emit positively charged particles which *e/m* measurements prove to be charged atoms of the metals. The chlorides of lead and barium emit both positively and negatively charged particles. The nitrates of barium etc. decompose, and the residual oxides emit electrons (by the Wehnelt effects). It is suggested that fused or solid salts which conduct electrolytically emit their more mobile ionic constituents in the form of these charged particles. The emission of electrons is taken to indicate "metallic" conduction. S. B.

**Positive Rays produced by Ultra-violet Light.** L. A. DU BRIDGE (*Physical Rev.*, 1925, [ii], **25**, 201—207).—When precautions are taken against scattered light effects, no positive current can be observed from gold, copper or aluminium surfaces exposed to ultra-violet light (cf. Demer, *Ann. Physik*, 1909, **30**, 137). A. A. E.

**Cathode Rays.** A. BECKER (*Ann. Physik*, 1924, [iv], **75**, 435—447).—The advantages of the hot electrode tube over the older methods for the production of moderately fast cathode rays are discussed. S. B.

**Intensities of Multiplet-lines.** L. S. ORNSTEIN and H. C. BURGER (*Z. Physik*, 1925, **31**, 355).—The view advanced by Burger and Dorgelo (A., 1924, ii, 361) that the sum of the intensities of the components of multiple spectral lines with common end or initial levels was proportional to the statistical weight of these levels, is regarded as inadequate and a new theoretical treatment based on the work of Sommerfeld and Heisenberg (*Z. Physik*, 1922, **11**, 131) is advanced. The measurement of intensities is troublesome, but preliminary work on a *df* multiplet of iron discloses three weak lines the intensities of which are in excellent agreement with the newer theoretical considerations. A discussion of the summation rule follows. R. A. M.

**Series Spectra of Two-valency-electron Systems and of Three-valency-electron Systems.** I. S. BOWEN and R. A. MILLIKAN (*Nature*, 1925, **115**, 422—423).—Tabulated data are given for the comparison of term-values of series of atoms constituting a two-electron system (Mg I, Al II, Si III, P IV, S V) and a three-electron system (Al I, Si II, P III, S IV). A. A. E.

**Harmonic Analysis of Electron Orbits.** F. C. HOYT (*Physical Rev.*, 1925, [ii], **25**, 174—186).

**Momentum Imparted to Electrons by Radiation.** E. O. HULBURT and G. BREIT (*Physical Rev.*, 1925, [ii], **25**, 193—196).—Theoretical. Only experiments of the "fish track" type are likely to permit of the observation of the deflexion of a part of a beam of electrons by electromagnetic radiation. A. A. E.

**Magnetic Field of a Moving Electron.** F. GUÉRY (*Compt. rend.*, 1924, **179**, 895—897).—The application of Maxwell's theory leads to a value for the magnetic field of a moving electron which is not in accordance with the first law of Laplace. There results from this expression an action between elements of current which is half that observed, but it is not an admissible hypothesis to attribute half the action to modifications of the electric field due to the movement. The conclusion is reached that the magnetic field of an electron is a mathematical expression without physical reality. H. J. E.

**Photographic and Ionisation Effect of X-Rays of Different Wave-lengths.** R. BERTHOLD (*Ann. Physik*, 1925, [iv], **76**, 409—438).—The relation between the darkening of a photographic plate and the amount of ionisation produced by a homogeneous beam of X-rays was determined for a range of four octaves, using K-radiation from selected anti-cathodes. Both effects diminish with increasing frequency, the relation being linear, viz.  $S/I = m(47.5 - \nu)$ , where  $S$  is the darkening,  $I$  the ionisation, and  $\nu$  the frequency  $\times 10^{18}$ ;  $m$  is a constant which can have any value. E. B. L.

**Number of Free Electrons with a Metal.** E. H. HALL (*Proc. Nat. Acad. Sci.*, 1925, **11**, 36—38).—The relations existing between the atoms, the free electrons, and the positive ions within a metal are essentially those of dissociation equilibrium, there being certain essential mechanical differences between the condition of the ions within a solid metal and those in a liquid solution which render the third law of thermodynamics inapplicable. The number of free electrons may be as great as 2 or 3% of the number of atoms at the ordinary temperature and the alteration of the number of free electrons with rise of temperature need not be in accord with the reaction isochore equation. The "ionising potential" of metals varies from 0.125 volt in cobalt to 0.33 volt in iron at 0°, a much smaller quantity than the ionising potential of the corresponding metal vapour. J. S. C.

**Heat of Evaporation of Electrons.** J. J. WEIGLE (*Physical Rev.*, 1925, [ii], **25**, 187—192).—Values (volts/electron) equivalent to the heat of evaporation of 1 g.-mol. of electrons at 0° Abs. are calculated on the assumption that the electrons form a space lattice, and compared with values measured experimentally by thermionic emission or by the photoelectric effect. The respective results, preceded by the heat of evaporation (in kg.-cal./mol.), are : sodium, 42.3, 1.83, 1.82; potassium, 35.3, 1.53, 1.55; rubidium, 35.6, 1.54, 1.45; caesium, 30.6, 1.34, 1.36. The assumption of electronic space lattices is thus supported. A. A. E.

**Diffusion of Electrons against an Electric Field in the Non-oscillatory Abnormal Low-voltage Arc.** K. T. COMPTON and C. ECKART (*Physical Rev.*, 1925, [ii], **25**, 139—146).

**Atomic Fields of Helium and Neon.** J. E. JONES (*Proc. Roy. Soc.*, 1925, **A**, **107**, 157—170).—Theoretical. Experimental data on the viscosity and the equation of state of helium indicate that the atomic field can be represented by a repulsive force equal to  $5.74 \cdot 10^{-113} r^{-14}$ , where  $r$  is the distance between the centres of the atoms and an attractive force  $1.930 \cdot 10^{-45} r^{-5}$ . The atomic field of neon has been calculated from thermal conductivity and viscosity data, and also from X-ray measurements of the interatomic distances in crystals of sodium fluoride and magnesium oxide, the ions of which are assumed to have the same outer field as neon, plus that due to their electrostatic charges. The repulsive force is  $3.892 \cdot 10^{-165} r^{-21}$ . The value of the attractive force has not been determined, but is shown to be very small. M. S. B.

**Influence of Ionic Diffusion on Almost Saturated Currents.** G. JAFFÉ (*Ann. Physik*, 1924, [iv], **75**, 391—402).—A theoretical discussion of the effect of the diffusion of gaseous ions upon the current-voltage curves of condensers, near the saturation point. Expressions are developed for the characteristics of plate, cylindrical, and spherical condensers. S. B.

**Determination of Elementary Charge  $E$  from Measurements of Shot-effect.** A. W. HULL and N. H. WILLIAMS (*Physical Rev.*, 1925, [ii], **25**, 147—173).

**Precise Measurement of the Critical Potentials of Gases.** E. G. DYMOND (*Proc. Roy. Soc.*, 1925, **A**, **107**, 291—309; cf. this vol., ii, 6).—The author describes the application of an apparatus giving automatic differentiation of the characteristic current-voltage curves with a view to increase the sharpness of the bends. The reasons for the divergence of the value found for the first excitation potential of helium, 20.9 volts, from that calculated from the optical data are discussed. The problem of interpretation of the characteristic curves taking into account the variation in the probability of effective collision and the velocity distribution of the electrons is attacked. N. H. H.



**Abnormal Low-voltage Arcs in Mercury Vapour, Argon, and Helium.** R. BÄR (*Z. Physik*, 1925, **31**, 430—438; cf. Eckart and Compton, *Physical Rev.*, 1924, [ii], **24**, 97; Bär, Laue, and Meyer, *Z. Physik*, 1923, **20**, 83).—The low-voltage arcs obtained by a potential difference of a few volts in neon, argon, and mercury vapour are not caused merely by oscillations, but correspond with true abnormal arcs. In helium such an oscillation-free, low-voltage arc can only be obtained after the strongest heating of a filament, and a potential difference of 16.5 volts (which is not far from the excitation potential of helium) is required. The average voltage required for a helium arc caused by oscillations is 8. R. A. M.

**Influence of Radiation on Ionisation Equilibrium.** M. SAHA and R. K. SWE (*Nature*, 1925, **115**, 377—378).

**Thermionic Effects Caused by Vapours of Alkali Metals.** I. LANGMUIR and K. H. KINGDON (*Proc. Roy. Soc.*, 1925, **A**, **107**, 61—79; cf. A., 1923, ii, 367).—When a tungsten filament is heated at 1200° Abs., or above, in saturated caesium vapour, and surrounded by a negatively charged cylinder, a positive ion current flows from the filament, because all the caesium atoms striking the filament are converted into ions. Since at high filament temperatures and low pressures of alkali metal vapour the electron emission is the same as in the absence of vapour, the positive ion emission can be determined and the thermal ionisation of caesium vapour calculated. These experimental results are in good agreement with Saha's equation (Fowler and Milne, *Mon. Not. Roy. Astr. Soc.*, 1923, **83**, 403). At high filament temperatures, for example, 1500° Abs., at which all the atoms striking the filament are converted into ions, the vapour pressure may be calculated from the positive ion current. The pressure  $p$  (in bars) of caesium vapour is given accurately by the equation  $\log_{10} p = 10.65 - 3992/T$ , where  $T$  is the absolute temperature.

If the tungsten filament be covered with a monatomic layer of thorium, the electron emission is greatly increased, but the positive ion emission becomes practically negligible.

At lower filament temperatures, the pure tungsten surface is covered by a layer of adsorbed ions, which share electrons with the tungsten, and electron emission is increased, whilst positive ion emission is decreased. There is qualitative evidence of the existence of two phases in the adsorbed films, since the positive ion emission increases discontinuously with rise of temperature. From a consideration of dilute adsorbed films the equation of state for the film is found to correspond to the ideal gas laws. The heat of evaporation of adsorbed caesium from tungsten, in the form of ions, corresponds with 4.0 volts for dilute and 4.3 volts for concentrated films, and 5.1 volts for an oxygenated filament. Curves have been drawn showing the variation of electron emission with temperature for different pressures of caesium vapour, both from pure tungsten and from a filament covered with a film of oxygen from which the electron emission is greatly increased.

M. S. B.

**Halogen Isotopes and Infra-red Reflexion Spectra.** A. H. PFUND (*Proc. Nat. Acad. Sci.*, 1925, **11**, 53—55).—On the assumption that the resonating mechanism responsible for bands of selective reflexion is localised in the negative ion, each halogen salt of potassium should have as many bands of selective reflexions as there are isotopes (potassium chloride, 2; potassium bromide, 2; and potassium iodide, 1). Associating the lighter isotopes with the band of shorter wave-length, parallel lines are obtained on plotting atomic weight against the wave number ( $1/\lambda$ ). These are discussed and support is advanced for the view that the isotope  $\text{Cl}^{37}$  is most abundant in rock-salt, whilst  $\text{Cl}^{35}$  is most abundant in sylvite.

J. S. C.

**Atomic Weight of Carbon and Silver.** G. DEAN (*J. Chem. Soc.*, 1924, **125**, 2656—2672).—The atomic weight of carbon has been determined from the ratio  $\text{AgCN} : \text{Ag}$ , a known weight of carefully purified silver cyanide being reduced to silver by heating in a current of hydrogen. From 21 experiments a mean value of  $12.002 \pm 0.001$  was obtained, if  $\text{Ag}$  be 107.88 and  $\text{N}$  14.008. By reducing silver cyanate to silver by heating in a current of purified moist air, the ratio  $\text{AgCNO} : \text{Ag}$  has been determined. The mean of 16 experiments gave  $\text{C} = 12.003 \pm 0.001$ . By combining the results of the cyanide and cyanate series, new independent values for the atomic weight of silver,  $\text{Ag} = 107.871$ , and the equivalent of cyanogen,  $(\text{CN}) = 26.008$ , involving no other assumption than  $\text{O} = 16$ , have been deduced. From the equivalent of cyanogen, assuming the atomic weight of nitrogen, that of carbon is found to be 12.000. The densities of metallic silver, silver cyanide, and cyanate have been determined.

M. S. B.

**Atomic Weight of Hafnium.** O. HÖNIGSCHMID and E. ZINTL (*Z. anorg. Chem.*, 1924, **140**, 335—336).—The atomic weight of hafnium was determined by analysis of a sample of the bromide containing according to X-ray spectroscopic measurements about 6% zirconium. The mean value found was 171.88; correction for the zirconium content yields the value 180.8.

S. K. T.

**Atomic Weights of Zirconium and Hafnium.** G. HEVESY (*Nature*, 1925, **115**, 335—336).—The zirconium samples used by Venable and Bell (*A.*, 1917, ii, 479) contained from 0.7 to 1% of hafnium; these authors' corrected value for the atomic weight of zirconium is 91.3, in close agreement with that obtained by Hönigschmid and Zintl (see preceding abstract) and that predicted by Aston from positive-ray data. The figure  $91.3 \pm 0.1$  should be adopted.

Hönigschmid and Zintl's figures for the atomic weight of hafnium have been corrected for zirconium content of the material (0.16 and 0.57%), yielding a value of  $178.6 \pm 0.1$ .

A. A. E.

**Long-range Particles from Polonium.** N. YAMADA (*Compt. rend.*, 1925, **180**, 436—439).—The ratios of the number of long-range particles to the number of  $\alpha$ -particles of ordinary range, from polonium deposited on copper, nickel, and silver, have been deter-

mined. The values obtained are much smaller than those of Bates and Rogers (A., 1924, ii, 296), especially after removing occluded gases and water vapour from the metals, metallic screens, etc. The majority of the long-range particles observed by Bates and Rogers are to be traced to the copper on which the polonium was deposited and to the mica screens used. The particles which persist after removal of occluded gas, water, etc., are present to the extent of three or four in  $10^7$   $\alpha$ -particles of ordinary range, and their range is about 10–14 cm. in air. J. S. C.

**Ionisation by  $\alpha$ -Particles in Monatomic and Diatomic Gases.** R. W. GURNEY (*Proc. Roy. Soc.*, 1925, A, 107, 332–340).—To throw light on the discrepancy between the ionisation produced by  $\alpha$ -particles in certain substances and that to be expected from current theories, measurements have been made of the total ionisation produced by definite beams of  $\alpha$ -particles in xenon, krypton, argon, neon, helium, oxygen, hydrogen, and nitrogen. In the five monatomic gases the ionisation increases with increasing atomic number, which would be expected from their decreasing ionisation potentials. But in the diatomic gases the ionisation is less than in any of the monatomic gases, indicating that energy has been expended in other ways. The ratio of the value of the ionisation in air to that in the other gases is found to vary with the velocity of the  $\alpha$ -particles. N. H. H.

**Stopping-power of Gases for  $\alpha$ -Particles of Different Velocities.** R. W. GURNEY (*Proc. Roy. Soc.*, 1925, A, 107, 340–349).—By selecting small portions of the range the relative stopping power of the five rare gases and of hydrogen and oxygen has been measured for  $\alpha$ -particles of high, intermediate, and low velocities, separately. The values of the relative stopping powers tend to converge at the end of the range. The values for high velocities are in good agreement with the relative atomic stopping powers calculated by Fowler. The measurements of ionisation described in a previous paper (see preceding abstract) are discussed in the light of this result. N. H. H.

**Ejection of Protons from Nitrogen Nuclei, Photographed by the Wilson Method.** P. M. S. BLACKETT (*Proc. Roy. Soc.*, 1925, A, 107, 349–369).—By means of a modified and automatic form of Wilson's condensation apparatus about 23,000 photographs of the tracks of  $\alpha$ -particles in nitrogen have been taken from two directions at right angles. These have shown the tracks of about 270,000  $\alpha$ -particles of 8.6 cm. range and 145,000  $\alpha$ -particles of 5.0 cm. range. In addition to a large number of forks corresponding with elastic collisions between  $\alpha$ -particles and nitrogen atoms, eight have been found which undoubtedly represent the ejection of a proton from a nitrogen nucleus. From measurement and from the fact that these eight forks are doubly and not trebly branched, it is inferred that the  $\alpha$ -particle takes the place of the ejected proton in the nitrogen nucleus resulting in a particle of mass 17 and atomic number 8; that is, an isotope of oxygen. Since it has not been

detected by Aston's mass spectrograph, it is probably of rare occurrence or else possessed of a short life. Its life must, however, be greater than the time of effective supersaturation in the condensation chamber, which is about  $1/1000$  second. N. H. H.

**Recoil Effect in Scattering of  $\gamma$ -Rays.** D. SKOBELZYN (*Z. physik*, 1924, **28**, 278—286).—The Wilson cloud-track method has been applied to the electrons emitted during the passage of  $\gamma$ -rays through matter, and the velocities of the electrons have been determined by the application of a magnetic field. The Compton theory of scattering was verified in the following particulars. (1) The energy imparted to the electron by radiation of frequency  $\nu$  is very often only a small fraction of the value  $h\nu$ . (2) The velocity of the electron has always a forward component. (3) The velocities of the electrons diminish with increase of the angle between their path and that of the exciting radiation. S. B.

**Absorption and Diffusion of  $\gamma$ -Radiation of Great Energy in Light Elements.** J. THIBAUD (*Compt. rend.*, 1924, **179**, 815—818; cf. A., 1924, ii, 515, 717).—For a single element the number of electrons dislodged on the  $K$  level is much greater than that on the  $L$  level; as in the case of  $X$ -rays, a  $\gamma$ -ray is more readily absorbed by an electronic level of greater energy. Although a study of the comparative emissive intensities of different elements leads to the inference that only the heavy elements are capable of yielding photo-electric spectra, photographs show that the photo-electric phenomenon may be excited in lighter elements. The fluorescence absorption of  $\gamma$ -rays seems to decrease less rapidly with  $N$  than Bragg's law would indicate; the suggestion is made that it may be proportional to  $N^2$  rather than  $N^4$ . A fraction of the  $\gamma$ -radiation is diffused in the mass of the radiator; in a "corpuscular  $\gamma$ -ray spectrum" derived from a light element this effect is shown by the emission of two types of electrons. The first corresponds with the rays which have undergone change of wave-length, the others are "resonance electrons" (cf. Compton, A., 1923, ii, 280). The diffusion of  $\gamma$ -rays is difficult of observation. As with  $X$ -rays, diffusion by quanta appears to be of little importance in the case of  $\gamma$ -rays. The continuous base observed in the spectra of secondary  $\beta$ -radiation may be due to the degradation of these quanta. H. J. E.

**Absorption of  $X$ -Rays.** E. C. STONER and L. H. MARTIN (*Proc. Roy. Soc.*, 1925, **A**, **107**, 312—331).—By the use of a balance method, the absolute absorption coefficient of aluminium has been determined for the three wave-lengths 0.45, 0.631, and 0.708 Å. Primarily comparative to aluminium the absorption of copper, palladium, silver, and tin and the relative absorption of uranium oxide have also been investigated over a range of 0.3 to 0.71 Å. and the results compared with those of previous observers. The measurements are discussed in relation to current theories of  $X$ -ray absorption, notably the  $\lambda^3$  ( $\lambda = X$ -ray wave-length) and  $Z^4$  laws and the magnitude of the  $K$  and  $L$  absorption discontinuities.

N. H. H.

**Statistical-mathematical Inquiry into the Sub-electron.** H. DAECKE (*Physikal. Z.*, 1924, **23**, 624—631).—Mathematical. Owing to the failure of purely physical methods to decide the question as to the existence of a sub-electron, the author has applied a cyclic error method to an examination of published data, and concludes that values of  $e$  less than  $4.77 \times 10^{-10}$  are most probably integral sub-multiples of it. D. M. E.

**Periodic Structural Regularities in Spectra as Related to the Periodic Law of the Chemical Elements.** W. F. MEGGERS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 43—47).—The periodicity of structural regularities in spectra as related to the periodic law of the chemical elements is revealed in the verification of the displacement law of Kossel and Sommerfeld and the extension of Rydberg's alternation law. The structures are in accord with the quantum theory of spectral line emission as developed by Bohr and others. J. S. C.

**Magnetic Atom Moments and Directional Quantisation.** W. GERLACH (*Physikal. Z.*, 1924, **23**, 618—620).—An improved apparatus is described for studying the Debye-Sommerfeld quantisation in a magnetic field and for determining the magnetic moment of atoms. For silver, the value  $M=5690$  gauss/cm. was obtained. Gold and copper behaved similarly to silver. Tin, lead, and antimony were unaffected by the magnetic field. In the case of nickel, the atomic stream was diffused, and it would appear that the atom has a magnetic moment of several magnetons. D. M. E.

**Absorption Spectra of Pyrrole and its Derivatives. III. Influence of Amino and Carbamido Groups on the Absorption Spectra of Pyrrole Derivatives.** G. KORSCHUN and (MME.) C. ROLL (*Bull. Soc. chim.*, 1925, [iv], **37**, 130—140; cf. A., 1923, ii, 107).—The absorption spectra of the ethyl esters of the following pyrrolicarboxylic acids were examined: 1-amino-2:5-dimethyl-, 1-carbamido-2:5-dimethyl-, 1-amino-2:3:5-trimethyl-, 1-carbamido-2:3:5-trimethyl-pyrrole-4-carboxylic acids, 1-amino-2:5-dimethyl- and 1-carbamido-2:5-dimethyl-pyrrole-3:4-dicarboxylic acids. The general conclusions reached are that auxochrome groups in the 1-position alter the distribution of residual valency in the pyrrole nucleus, and lose their auxochromic influence. Methyl and carbamido groups in the 1-position cause displacement of the absorption spectra towards the ultra-violet, whilst the amino group causes practically no displacement. A decrease in the degree of saturation of the substituent in the 1-position, for example by the formation of an enolic modification of the carbamido group under the influence of alkalis, displaces the absorption towards the red, whilst an increase in the degree of saturation, for example by salt-formation from the amino derivatives, causes a displacement in the opposite direction. F. G. W.

**Spectrum of Chlorophyll in the Living Leaf.** J. WLODEK (*Bull. Internat. Acad. Pol. Sci. Lettres*, 1924, **B**, 407—423).—The displacement of the chlorophyll spectrum of the living leaf

towards the infra-red region in comparison with that of a solution of chlorophyll appears to be attributable to the optical system of the tissue of the leaf, as also is the effacement of the boundaries of the absorption bands. The spectrum of the leaf chlorophyll is probably a mixed spectrum composed of a common with a reflected spectrum intermixed with unabsorbed light. The duality of the first absorption band of chlorophyll, observed with both the living and the killed leaf, is explainable by assuming that the spectrum of the chlorophyll is not that of a mixture of green pigments, but is composed of two distinct superposed spectra of neo- and allo- (*a*- and *b*-)chlorophylls. Under the influence of light, the spectra of leaf chlorophyll undergo change; the stripes of the first absorption band corresponding with both chlorophylls alter in width, this indicating either a change in the relative amounts of the two chlorophylls or the appearance of new spectra of unstable compounds of chlorophyll with carbon dioxide. T. H. P.

**Neodymium Oxide.** E. L. NICHOLS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 47—52).—The spectrum of the glowing oxide studied with the spectrophotometer reveals ten or more crests on the brightness curve of the visible spectrum which are assumed to be the envelopes of groups in a much more complicated but almost wholly submerged structure. The crests fall into two sets such that the frequency differences between neighbours in a given set are multiples of 18.5, the Tanaka interval for neodymium. The luminescence of the oxide has been investigated over the temperature range 600—1000°. Comparison of the bulk and bead spectra shows that the various lines of neodymium are all parts of a single structure. The absorption spectrum of neodymium in aqueous solution shows no obvious sign of identity with either emission spectra. J. S. C.

**Theory of Band Spectra.** R. MECKE (*Z. physik*, 1924, **28**, 261—277).—It is shown that a formal analogy can be drawn between the representations of line and band spectra, both comprising three quantum numbers. Further, there is evidence of a regular alternation of odd and even multiplets from element to element in the periods of the periodic table, in band spectra as well as in line spectra. The positive nitrogen bands may be regarded as the “arc” spectrum of the nitrogen molecule and contain a quintet system. The negative bands, or “spark” spectrum, contain a doublet system. S. B.

**Isotope Effect in Band Spectra.** I. R. S. MULLIKEN (*Physical Rev.*, 1925, [ii], **25**, 119—138; cf. A., 1924, ii, 3, 294, 295, 446, 640; Jevons, A., 1915, ii, 33; 1924, ii, 640; Loomis, A., 1921, ii, 530).—In a theoretical discussion of the isotope effect in band spectra of diatomic molecules, definitions are obtained of the origin of a band-system and of the origin of a band. The incidence of the vibrational and the rotational isotope effects is considered, and an explicit equation for band-heads is obtained. The quantum theory of band spectra is supported by confirmatory

evidence in the case of BO, SiN, CuH, CuCl, CuBr, and CuI. Applications of the isotope effect to the study of isotopy and the interpretation of band spectra, and its relation to the positive ray method, are examined.

A. A. E.

**Application of the Quantum Theory of Band Spectra to the First Negative Deslandres Group of Carbon.** C. M. BLACKBURN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 28—34).—A discussion of the structure of the lines studied by Lemon from the point of view of the quantum theory of band spectra. Owing to the simplicity of the structure, the radiator of the bands probably approximates very closely to the dipole molecule. The molecule in question is in simple rotation about a non-precessing axis perpendicular to the line joining the nuclei. The moments of inertia of the molecule in the vibrationless state before and after emission are  $8.07 \times 10^{-40}$  and  $6.78 \times 10^{-40}$  g./cm.<sup>2</sup>, respectively. J. S. C.

**Fluorescence and its Applications.** E. BAYLE, R. FABRE, and H. GEORGE (*Bull. Soc. chim.*, 1925, [iv], **37**, 89—115).—A self-starting, gas-filled, direct current, quartz mercury arc-lamp is described (cf. George, *Revue d'optique*, 1925, 1), and photographs are shown comparing its spectrum with those of the ordinary mercury arc-lamp and a high-frequency lamp (cf. George, *Compt. rend.*, 1920, **170**, 458). The above direct-current lamp gives the highest output of ultra-violet rays of wave-length around 3650, which is most suitable for use with a nickel oxide screen (cf. *U.S. Bur. Standards, Tech. Papers*, 1920, **148**). Various substances, chiefly in the solid state, were submitted to the action of the ultra-violet rays produced by the above lamp and screen. The fluorescence spectra were compared photometrically, over the range  $\lambda = 4000$ —7600, at intervals of 200 Å., with rays of the same wave-length obtained from white light, to determine the distribution of luminous intensity in the spectrum under examination, and hence, using Gibson and Tyndall's coefficients of visibility (*U.S. Bur. Standards, Tech. Papers*, 1923), to calculate the total luminous intensity of the fluorescence spectrum. Solid sodium salicylate gives a violet fluorescence the intensity of which, taken as 20 units, forms a convenient standard of comparison. The fluorescence persists in aqueous solution, is perceptible in solutions of 1 : 25,000, and can be used for the detection of salicylic acid in milk. Salicylates show stronger fluorescence than *m*- and *p*-hydroxybenzoates. Etherification of the hydroxyl group destroys the fluorescence, and the latter is much more intense with the aryl than with the alkyl salicylates. Coumarin and its derivatives show only weak fluorescence, with the exception of æsculin. Novocaine hydrochloride shows a bluish-violet fluorescence, intensity 32, whilst stovaine and cocaine hydrochlorides remain dark. The colours and intensities of the following isoquinoline derivatives are tabulated: papaverine, bluish-white, 6; hydrastine, greenish-white, 55; narcotine, violet, very dark; narceine, violet-blue, 7; veratric acid, pale blue, 5; opianic acid, similar, 10; potassium opianate,

blue, 5; hydrastinine and cotarnine, nil; hydrastine hydrochloride, blue, 36; hydrastine salicylate, greenish-white, 55; hydrastinine hydrochloride, 4; and cotarnine hydrochloride, yellow, 35. Freshly-prepared hydrastine sulphate solution shows no fluorescence, the latter developing slowly in the cold, rapidly in the hot, and instantaneously on the addition of a few drops of hydrogen peroxide.

F. G. W.

**Colour and Chemical Constitution. XIX. Organic Fluorescence.** J. MOIR (*Trans. Roy. Soc. S. Africa*, 1924, 12, 45—50).—All organic substances which are known to exhibit fluorescence contain an aromatic ring, although the presence of such a ring is not essential to the production of colour and the majority of aromatic substances do not fluoresce. For the production of fluorescence further factors are required in the nature and arrangement of the groups attached to the ring, and one of the groups must apparently be an auxochrome. The arrangement of the groups appears to be less important than their nature, when only one aromatic ring is present. Two ortho-groups alone do not cause fluorescence; it is apparently necessary that, in addition to the auxochrome, a second group attached to the ring by an atom having a double linking to another atom should be present. The fluorescence of  $\alpha$ -naphthol, sodium salicylate, and sodium coumarate can be explained in this way. The non-fluorescence of *o*-nitrophenol and the fluorescence of *m*-nitrodimethylaniline present difficulties, and it is possible that spatial differences come into play. The striking fluorescence of the quinol derivatives previously described (A., 1923, ii, 108) and of umbelliferone is probably to be attributed to the co-operation of two pairs of factors. Substances which contain two aromatic rings doubly linked exhibit fluorescence without any auxochromes being present. The fluorescence is sometimes shown only in sulphuric acid solution, sometimes only in the solid state. Since it is impossible to assign a quinonoid structure to the solution of xanthene in sulphuric acid it is evident that fluorescence does not depend on unsaturation outside the ring, but wholly on the rings as such with the presence of two groups holding them in a rigid position, *i.e.*, on purely spatial factors. It is suggested that fluorescence is merely the reflexion of light from such rigid molecules acting as mirrors, and that only such molecules as are devoid of rigidity do not fluoresce.

The following data are given for the position of absorption-bands by transmitted light in solutions of the substances in concentrated sulphuric acid: xanthene,  $\lambda$  360 (strong) and 425 (weak); dihydroanthracene, 352 and 400; dihydroacridine, 430 and 408 (narrow) and 340 (broad); dihydrophenazine, 398 (broad); phenoxazine, 417; xanthhydrol, 450 and 470 (weak); anthracene, 330 (broad); acridine, 355 (narrow); phenazine, 510 and 550 (weak); phenoxazonium salts, 460; anthraquinone, 403 (broad); acridone, 336 and 358 (both narrow); phenazine oxide, 501 and 544; xanthone, 340 and 405. The green solution of anthracene and dihydroanthracene has 701, whilst the corresponding quinhydrone of



dihydrophenazine probably has an absorption band above 760. The quinhydrone of phenoxazine has a band at 537 in sulphuric acid.

R. B.

**Absorption of Fluorescent Light by the Emitting Substance.** T. DUSEBERG (*Physikal. Z.*, 1925, **26**, 157—166).—A narrow beam of light was sent vertically through a rectangular trough and the fluorescent light which was emitted horizontally was examined in a spectrophotometer after passing through a layer of the fluorescent solution. Light of wave-length of the maximum intensity was transmitted better than that on either side of it. The fluorescent light can again excite fluorescence in the second solution, the shorter wave-lengths being the more active. This furnishes the explanation of the fact that the maximum intensity of the fluorescent light is displaced towards longer wave-lengths by passage through a considerable layer or a concentrated solution of the substance.

E. B. L.

**Excitation of Phosphorescence by High-frequency Radiation.** E. RUPP (*Ann. Physik*, 1924, [iv], **75**, 369—390).—On Lenard's photoelectric theory of phosphorescence, a conductivity change should accompany the excitation of a phosphorescent body. In the present paper, the conductivity changes in zinc sulphide induced by excitation by X-rays and  $\gamma$ -rays are described, and are correlated with the light emission from the sulphide. The problem is discussed whether such high-frequency radiations excite the "phosphor" by direct photoelectric action, or indirectly by the secondary action of high-velocity electrons ejected from the body of the material.

S. B.

**Effect of Heat Treatment upon the Cathode Luminescence of Fluorite.** F. G. WICK and J. M. GLEASON (*J. Opt. Soc. Amer.*, 1924, **9**, 639—648).—The effect of preliminary heating on the rate of decrease of the intensity of the luminescence from fluorite has been examined; when excited by continuous bombardment by cathode rays. Heating at 600° increased the duration of phosphorescence and decreased the rate of its decay. Fluorite subjected to surface fusion, however, had a shortened period of phosphorescence.

S. B.

**Critical Potential of Methane and its Absorption in the Ultra-violet.** G. GLOCKER (*Proc. Nat. Acad. Sci.*, 1925, **11**, 74—77; cf. A., 1924, ii, 374).—No part of the maximum in the current potential curve obtained in three- or four-electrode tubes filled with methane can be due to a resonance potential. Absorption measurements fail to detect any absorption in the required region (for 5 volts, 2400 Å.) and further proof is afforded by Lenard photoelectric experiments. The various theoretical possibilities are discussed.

J. S. C.

**Exact Magnitude of the Electric Moment of Dipolar Molecules, and the Chemical Significance of Orientation Polarisation.** L. EBERT (*Z. physikal. Chem.*, 1925, **114**, 430—440).—The uncertainty in the value of the electric moment,  $\mu$ , is discussed.

Different values are obtained for  $\mu$  by applying the classical gas theory and the quantum theory, respectively, to molecular rotation. For diatomic molecules,  $\mu_{\text{quantum}}$  = about 0.5  $\mu_{\text{class}}$ . The values calculated from Gans' orientation-polarisation theory by Smyth (cf. A., 1924, ii, 810) are uncertain on account of the incompleteness of the polarisation balance. The question of the deformation of atoms and ions is discussed. The different deformabilities of the halogens are clearly reflected in the values of  $P_0 + P_A$  for their compounds, which in general diminish in the series  $\text{Cl} \rightarrow \text{Br} \rightarrow \text{I}$ .

It is assumed that a central atom surrounded by similar atoms forms an electrically symmetrical complex, if co-ordination-saturation is attained. If saturation is not reached, then  $P_0 + P_A$ , or the moment, decreases with the approach of that symmetry which corresponds with the maximal co-ordination number. The dipolar character of a molecule is to be regarded as an indication of an association tendency.

L. L. B.

**Dielectric Constants of Liquid Mixtures.** M. GRÜTZMACHER (*Z. Physik*, 1924, 28, 342—354).—The dielectric constants of chloroform, carbon tetrachloride, carbon disulphide, toluene, benzene, and of binary mixtures of these, have been measured. The constants for the mixtures cannot be calculated satisfactorily by any formula so far proposed.

S. B.

**Method of Measuring the Dielectric Constants of Liquids.** L. A. SAYCE and H. V. A. BRISCOE (*J. Chem. Soc.*, 1925, 127, 315—322).—The apparatus consists of a container shaped like an elongated Dewar flask, in which the liquid fills the annular space, the inner walls being silvered so as to form the plates of a condenser. For the measurement of the capacity a variable condenser ( $C_3$ ) is connected in parallel with an inductance ( $L_3$ ). To this circuit is loosely coupled an oscillatory circuit ( $L_1C_2$ ) in which oscillatory currents are maintained by means of a triode valve. Resonance between the two circuits is then indicated by a sudden drop in the anode current of the triode circuit. The dielectric container of unknown capacity ( $C_4$ ) is then coupled in parallel with  $C_3$ , and the reduction that has to be made in  $C_3$  in order to restore resonance is a measure of the capacity of  $C_4$ . Details are given of the construction of a suitable wide-range condenser capable of very accurate adjustment. The method is tested for benzene, for which the dielectric constant is 2.2389 at 25°, using a frequency of  $65 \times 10^3$  cycles per sec.

W. H.-R.

**Dielectric Constant of Water in [the presence of] Strong Electrolytes.** H. ZAHN (*Z. Physik*, 1925, 31, 362—372).—By a development of the work of Schaefer the difference in  $\epsilon$  between two different electrolytes of the same conductivity can be measured by measuring the change of intensity of a field in passing through a cylinder of the dielectric. It is claimed confidently that the dielectric constant of water in a saturated lithium chloride solution is smaller than that in a dilute sodium chloride solution of the same conductivity. Exact numerical values are not yet possible;

$\epsilon$  is certainly  $<57$ , probably  $<42$ , and may even be considerably less.

R. A. M.

**Magneto-chemical Phenomena.** A. SCHÜKAREW (*Z. physikal. Chem.*, 1925, **114**, 500; cf. this vol., ii, 47).—Further observations on the magneto effect are recorded.

L. L. B.

**Effect of Pressure on Refractive Index of Organic Liquids.** I. EISELE (*Ann. Physik*, 1925, [iv], **76**, 396—402).—Two hollow prisms were employed, in one of which the liquid was submitted to pressure. Monochromatic light traversing the prisms was examined by an interferometer and the shift in the bands on increasing the pressure was measured. The relationship found does not agree with any formula connecting refractive index and compressibility, but the results lie between the values calculated from the Beer and Lorentz formulas.

E. B. L.

**Rotation Dispersion. II.** J. LIFSCHITZ (*Z. physikal. Chem.*, 1925, **114**, 485—499; cf. A., 1923, ii, 525).—A further investigation of the relation between rotation dispersion, light absorption, and stereo-constitutive structure. A series of metallic complexes of active *d*-alanine, *l*-propylenediamine, and *l*-aspartic acid has been studied polarimetrically, and the effect of different modes of linking on the rotatory power is discussed. It is shown that homopolar and heteropolar principal valencies have characteristically different optical effects, and that secondary valencies are different from both. For internal complex salts (characterised by containing a metal atom connected by both primary and secondary valencies) there are special rules. It is concluded that primary and secondary valencies are not optically similar in character, and that Werner's evidence as to their identity is unacceptable. By isolation of the partial antipodes of the *d*-alanine complex of cobalt, direct evidence seems to be given of a relative asymmetric synthesis by formation of cleavable metal complexes from inactive metallic salts and active co-ordinated molecules, and at the same time a new method seems to be found for the preparation of active internal complex salts. It is pointed out that the investigation of rotation dispersion represents a crucial method for the exploration of stereo-constitutive questions.

L. L. B.

**Rotatory Dispersion of certain Normal Alkyl Hexahydro-mandelates.** C. E. WOOD and M. A. COMLEY (*J. Chem. Soc.*, 1924, **125**, 2630—2646).—To determine the effect on rotatory dispersion of the substitution of the *cyclohexyl* group for the methyl group of lactic acid (cf. T., 1923, **123**, 600) the optical rotations of the nine esters, from methyl to *n*-nonyl, of hexahydromandelic acid have been studied over as wide a temperature range as possible. All the esters exhibit complex rotatory dispersion which, in the higher members, approaches the condition for anomaly. The esters in general retain the sign of rotation of the acid from which they are derived. Molecular dispersion is shown to be chiefly dependent on the groups immediately surrounding the asymmetric centre, temperature and lengthening of the chain producing only secondary

effects. The molecular dispersion of the lactates is not very different from that of the hexahydromandelates. Large differences, however, are observable in the molecular rotation. The temperature coefficient of the latter is negative for the hexahydromandelates and positive for the lactates, and the numerical value of the first is decidedly greater than that of the second. In general, the molecular rotation appears to decrease to an approximately constant value on ascending the series, irregularities being observed in the *n*-butyl and *n*-octyl esters. Experimental details of the preparation and resolution of hexahydromandelic acid and of the preparation of the different esters have been given. M. S. B.

**Rotatory Dispersive Power of Organic Compounds. XIII. Significance of Simple Rotatory Dispersion. Rotatory Dispersion of Camphorquinone and of Sucrose.** T. M. LOWRY and E. M. RICHARDS (*J. Chem. Soc.*, 1924, 125, 2511—2524).—In view of recent criticism, the utility of the simple dispersion formula  $\alpha = k/(\lambda^2 - \lambda_0^2)$  (T., 1913, 103, 1067; Lowry and Dickson, A., 1914, ii, 786) has been explained. The graphical and numerical methods of testing it have been described, and the casual and systematic errors and limits of application discussed. A complex dispersion may appear to be simple if the partial rotations are all controlled by identical or closely similar dispersion constants. A new method has been described for distinguishing between simple and complex rotatory dispersion, depending on Drude's postulate that the wave-lengths of his dispersion equations coincide with the wave-lengths of maximum absorption of light. The genuine hyperbolic curve of the simple dispersion formula can be distinguished from the false hyperbola of the complex dispersion, controlled by two natural frequencies, because the latter, in the region of longer wave-lengths, will be directed towards an imaginary asymptote lying between the real asymptotes of the component partial rotations, whilst the former will have as its asymptote the central line of a real absorption band. The method is limited to equations in which the value of the dispersion constant is not less than about  $\lambda_0^2 = 0.055$  by the difficulty of making exact measurements of selective absorption beyond  $\lambda = 2327 \text{ \AA}$ . Measurements have been made of the rotatory dispersion of camphorquinone and sucrose, and the results discussed from the point of view of the new method of testing. M. S. B.

**Diffusion of Light in Fluids.** Y. ROCARD (*Compt. rend.*, 1925, 180, 52—53).—In the preparation of optically pure liquids by filtration, the size of the filter-pores is of little importance, but the filtration must be very slow. If a parallel beam of light traverses a liquid in the direction *Ox*, and is observed from a distant point on *Oy*, depolarisation ( $\rho$ ) is defined as the ratio of the intensity of the light vibrating along *Ox* to that vibrating along *Oz*. For optically pure water,  $\rho = 0.11$  for green light, and for freshly-prepared water the value of  $\rho$  is little affected by wave-length. A slight fluorescence is produced owing to gradual solution of the glass of the containing vessel, as a result of which  $\rho$  may rise to

0.18 in violet light. For benzonitrile  $\rho=0.65$  for red light, whilst for nitrobenzene  $\rho=0.68, 0.67, 0.68,$  and  $0.74$  for red, yellow, green, and blue light, respectively. Theoretical reasoning shows that  $\rho$  should be little affected by a high magnetic field in agreement with the results of Martin (this vol., ii, 90). W. H. R.

**Electrical Double Refraction of Gases.** N. LYON (*Z. Physik*, 1924, 28, 287—298).—According to the Born dipole theory, the Kerr constant of a gas should increase more rapidly than its density at high pressures. The electrical double refraction of carbon dioxide has accordingly been measured in the pressure interval 10—50 atm. using a potential difference of 30,000 volts, but the double refraction was found to be closely proportional to the density of the gas throughout the range. S. B.

**Pyrrole and Melanins. Spectrophotometric Studies.** G. GALLERANI (*Arch. ital. Biol.*, 1924, 72, 189—207; from *Chem. Zentr.*, 1924, ii, 2168).—Studies on the absorption spectra of pyrrole and of melanins and on the effect of chemical changes on these spectra confirm the relationship between these substances. The absorption curve of ozonised pyrrole resembles that of oxyhæmoglobin. Pyrrole-black obtained by oxidation in the presence of adrenaline is similar to the melanins. After injection of pyrrole or of 2:5-dimethylpyrrole, the urine of dogs shows the melanin curve. Pyrrole-black is regarded as an intermediate stage between pyrrole and the melanins. G. W. R.

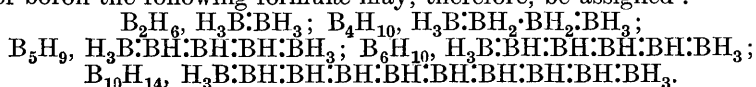
**Quantum Theory and Molecule Formation.** M. BORN and J. FRANCK (*Z. Physik*, 1925, 31, 411—429).—Triple collisions are required for a quantum mechanism of additive reactions, but not for reactions involving displacement or adsorption. This fact throws light on the phenomena of catalysis and particularly on surface effects. The impact of a quantum of light and two atoms may be regarded as a triple collision. The formation of molecules is considered in detail, first from the point of view of classical mechanics and, secondly, from that of the quantum theory. The conception of a "quasi-molecule" is introduced. Two atoms behave as a loosely bound unit for a finite period after collision without either rotations or vibrations becoming quantised, the entity having a life-period of  $10^{-12}$  to  $10^{-13}$  sec. The evidence for the real existence of such molecules is discussed theoretically and various optical phenomena are quoted in support.

The conception of quasi-molecules leads in the extreme case to a condition whereby an equilibrium between attractions and repulsions follows from classical mechanics. No alternative quantum state could exist, so that any disturbance would disrupt the quasi-molecule, which must therefore be regarded as labile from the point of view of quantum mechanics. A quantum-theory criterion of stability will therefore require that a stable molecule shall show a neighbouring energy state greater than the initial state by at least one quantum number.

The idea of chemical affinity is thus meaningless unless the

criterion of energy levels is fulfilled. From these considerations the notion of a true molecule gains in precision. R. A. M.

**Valency of Boron.** R. C. RÂY (*J. Indian Chem. Soc.*, 1925, **1**, 133—139).—From its position in the periodic classification, boron should possess a positive valency of three and a negative valency of five, the latter being apparent in the case of its hydrides and their related compounds. The stability of the complex  $\text{B} \cdot \text{B}$  has previously been shown (T., 1922, **121**, 1088) and to the hydrides of boron the following formulæ may, therefore, be assigned :



The borohydrate,  $\text{H}_4\text{B}_2(\text{OH})_2$ , and the halogen derivatives,  $\text{B}_2\text{H}_5\text{X}$  and  $\text{B}_2\text{H}_4\text{X}_2$ , would be represented by  $\text{H}_2\text{B}(\text{OH}) \cdot \text{BH}_2(\text{OH})$ ,  $\text{H}_3\text{B} \cdot \text{BH}_2\text{X}$ , and  $\text{XH}_2\text{B} \cdot \text{BH}_2\text{X}$ , respectively. The possibility of boron functioning as a quinquevalent element on the Lewis-Langmuir theory has been discussed (Böeseken, A., 1923, ii, 406); on Bohr's theory, the boron atom consists of the helium structure of two electrons revolving in one-quantum orbits and three electrons in two-quantum orbits. These three electrons can each share the outer ring of three halogen atoms, thus completing their octets, or five additional electrons can gather round the boron atom to complete its octet. The non-existence of  $\text{BH}_5$  has been explained by Rankine (A., 1922, ii, 635). Further examples of quinquevalent boron are cited from the literature. J. W. B.

**Valency Problem of Sulphur. VIII.** H. LECHER.—(See i, 390.)

**Electronic Theory of Valency and the Electrolytic Oxidation of Formaldehyde.** C. DEL FRESNO (*Anal. Fis. Quim.*, 1924, **22**, 545—550; cf. A., 1924, i, 612).—The electrolytic oxidation of formaldehyde is further discussed and a scheme is suggested in accordance with the Langmuir theory of atomic structure.

G. W. R.

**Complexity of the Solid State. I. Behaviour of Pure Sulphur Trioxide.** I. A. SMITS and P. SCHOENMAKER (*J. Chem. Soc.*, 1924, **125**, 2554—2573).—The irregular behaviour of sulphur trioxide with regard to melting point and vapour pressure indicates a remarkable complexity. This has been studied by examination of the intensively dried ice-form, obtained by distillation and drying over phosphorus pentoxide so that the velocity of inner transformation becomes very small. After keeping for 56 hrs. at  $18^\circ$ , the vapour pressure at  $0^\circ$  had diminished by 71.4 mm., and by distillation the vapour pressure could be changed continuously from an initial value of 207 mm. to a final value of 22 mm. at  $0^\circ$ . As the vapour pressure diminished the initial melting point first rose and then fell. All these different solid phases belong to the ice-form, since they give melting ranges falling on the continuous three-phase line corresponding with the equilibrium, solid-liquid-vapour, for a dissociable compound. This can be explained

on the theory of allotropy by assuming that the system, sulphur trioxide, is composed of at least two different kinds of molecules,  $\alpha$  and  $\beta$ , which not only change each into the other, but also form a dissociable compound  $\alpha\beta$ . After intensive drying, equilibrium is reached only slowly. When behaving as a unary system, the ice-form of sulphur trioxide is a little richer in the more volatile pseudo-component than the dissociable compound. A second metastable form, the low-melting asbestos form, and the stable or high-melting asbestos form have also been investigated and show similar phenomena. M. S. B.

**Composition of Simple Substances as Revealed by Intensive Drying.** A. SMITS (*Chem. Weekblad*, 1924, 21, 594—600; cf. *B.*, 1924, 855).—The vapour pressure of the high-melting form of sulphur trioxide, m. p.  $\pm 60^\circ$ , has been determined, after intensive drying and partial distillation, at  $50^\circ$ . The vapour pressures were 59.1 cm. mercury before distillation, 3.7 cm. one hour after distilling off part of the material, 29.1 cm. 43 hrs. after distillation, and 49.4 cm. 761 hrs. after distillation. These results are compared with those obtained with mixtures of chlorine and bromine at  $-80^\circ$ , and are held to indicate that this form of sulphur trioxide is a mixture of two different modifications and of a compound of the two. S. I. L.

**Complexity of the Solid State. II. Behaviour of Phosphorus Pentoxide.** I. A. SMITS and A. J. RUTGERS (*J. Chem. Soc.*, 1924, 125, 2573—2579).—Determinations have been made of the vapour pressure of the crystalline sublimate of intensively dried phosphorus pentoxide. This was shown to vary with the velocity of distillation. Above  $400^\circ$ , the very volatile metastable forms are transformed into a more stable modification, and the vapour pressure falls continuously to 0.02 cm. of mercury, but, as before, the values depend on the previous history. According to the old views on phase equilibria, the stable modification should melt at a higher vapour pressure than the highest exhibited by the metastable form. On the contrary, however, it shows an initial melting point with a much lower vapour pressure, namely, 0.59 atm. at  $563^\circ$ , whilst the metastable modification gives about 2 atm. at  $370^\circ$ . It also melts over a large temperature range. In this respect, phosphorus pentoxide resembles sulphur trioxide (cf. preceding abstracts). The crystalline state evidently consists of mixed crystals built up from molecules of different kinds, and the pure substance behaves as a unary system only when inner equilibrium is established. M. S. B.

**Systematic Doctrine of Affinity. XXX. Heats of Formation of Intermetallic Compounds. VI. Tin Alloys.** W. BILTZ and W. HOLVERSCHUIT (*Z. anorg. Chem.*, 1924, 140, 261—276).—The heats of formation of alloys of tin with calcium, magnesium, and sodium were measured by the method previously described (cf. *A.*, 1924, ii, 482), a solvent of ferric chloride in hydrochloric acid being used. The results, in Cal. per g.-mol.,

together with the densities of the alloys at 25°, were:  $\text{CaSn}_3$ , 43 ( $d$  5.989);  $\text{Mg}_2\text{Sn}$ , 49 ( $d$  3.625);  $\text{NaSn}_2$ , 15 ( $d$  4.725);  $\text{NaSn}$ , 11 ( $d$  3.990);  $\text{Na}_4\text{Sn}_3$ , 36 ( $d$  3.570);  $\text{Na}_2\text{Sn}$ , 12 ( $d$  3.111);  $\text{Na}_4\text{Sn}$ , 21 ( $d$  2.315). The alloy with the highest heat of formation ( $\text{Mg}_2\text{Sn}$ ) is the only one of the above which is formed from its components with an increase in volume; the sodium alloys are formed with a percentage contraction which increases with increasing sodium content. The curve of the heats of formation of the sodium alloys against the valency numbers exhibits a change in gradient (cf. *ibid.*); this supports the complex theory of intermetallic compounds.

S. K. T.

**Theoretical Stoichiometry of the Intermolecular Forces and the Space Occupied by the Molecules of Organic Compounds.** I—II. E. WÖHLISCH (*Physikal. Z.*, 1925, 26, 170—176, 177—184).—A study of the molecular volumes of isomerides and the diameters of the molecules as calculated by several different methods. The volumes of the molecule calculated from van der Waals' equation and from the viscosity of the vapour show a dependence on constitution, as also do the values for the volume at the critical temperature and the b. p. in certain cases; values obtained from the molecular refraction and the surface tension and heat of vaporisation were useless for the purpose. Rise in b. p. accompanies diminution in the space between the molecules, even when an increase in the total molecular volume produces a rise in b. p. Acids have larger volumes than the isomeric esters and smaller spaces between; similarly, the molecules of the alcohols are larger than those of the isomeric ethers; branched hydrocarbons have smaller volumes than simple chains; addition of chlorine to a carbon atom reduces the volume of the molecule.

E. B. L.

**X-Ray Investigation of the Lower Members of the Fatty Acid Series.** R. E. GIBBS (*J. Chem. Soc.*, 1924, 125, 2622—2625).—X-Ray measurements of the  $d_1$ ,  $d_2$ ,  $d_3$ , and also  $d_4$  spacings have been extended to the lowest members of the fatty acid series (cf. Müller, T., 1923, 123, 2043; Piper and Grindley, A., 1923, i, 1056). For the higher members,  $d_1$  varies directly with the number of carbon atoms and is evidently related to the length of the chain. At hexoic acid deviations from the linear law appear and increase gradually down to propionic acid. An abrupt change occurs at acetic acid. This corresponds with the change observed in the freezing points (Massol, A., 1896, i, 408). The side spacings for the even acids,  $d_2$ ,  $d_3$ , and  $d_4$ , change only to a small extent, but the odd acids show less regularity. The results are discussed from the point of view of the three possible types of chain suggested by Müller and Shearer (T., 1923, 123, 3156). Mention is made of further work which demonstrates the true crystalline nature of stearic acid.

M. S. B.

**Compton Effect with no Box Around the Tube.** P. A. ROSS and D. L. WEBSTER (*Proc. Nat. Acad. Sci.*, 1925, 11, 56—61; cf. following abstract).—Observations of the spectra of scattered



X-rays, the scattering occurring in a compartment large enough to make the inverse square law alone suppress the scattered rays from light elements beyond detection, fail to detect the peak reported by Duane. The position of the Compton line agrees with the computed position within the limits of experimental error. The photographs with aluminium as scatterer are better defined than those obtained with sulphur. The present status of the tertiary-ray hypothesis is reviewed. J. S. C.

**Compton Effect : its Relation to Duane's Box Effect.** P. A. ROSS and D. L. WEBSTER (*Proc. Nat. Acad. Sci.*, 1925, **11**, 61—64; cf. Duane and collaborators, *ibid.*, 1924, **10**, 374—379).—Evidence is reviewed definitely contrary to Duane's box-effect theory as an explanation of the Compton peaks, and leaves Compton's theory of the scattering of quanta by single electrons as the only hypothesis yet advanced capable of explaining their existence. J. S. C.

**Röntgenographic Measurement of Absolute Dimensions of a Single Crystal in Bodies of Fine Crystalline Structure.** N. SELJAKOW (*Z. Physik*, 1925, **31**, 439—444).—Mathematical. An expression is deduced similar in form to one published without proof by Scherrer. The results given by the expressions differ by about 2% only. R. A. M.

**Röntgen-Spectroscopic Determination of the Proportion by Weight of an Element in Mixtures and Compounds.** R. GLOCKER and W. FROHNMEYER (*Ann. Physik*, 1925, [iv], **76**, 369—395).—A photograph of the absorption spectrum of the material for X-rays is obtained and the ratio of the density at the edge of the band to the density just outside it measured. Crystals, powders, solutions, sheets, etc. can be used. The method is particularly applicable when an element of high atomic weight has to be determined in the presence of elements of low atomic weight; also when only a small quantity of the material is available or when ordinary analytical methods are tedious. The degree of accuracy is about  $\pm 5\%$  of the correct weight. Thus, barium in a glass gave 5.45% as against 5.8% by chemical analysis; the exposure necessary was 90 mins., using a water-cooled Coolidge tube fed with 5 milliamps. at 55,000 volts. E. B. L.

**Orientation of Ammonium Iodide by Muscovite Mica.** L. ROYER (*Compt. rend.*, 1925, **180**, 448—450; cf. this vol., ii, 110).—The orientation of ammonium iodide on the two surfaces of a cleaved crystal of muscovite mica has been investigated. Each of the two planes separated by cleavage gives rise to one or the other of two possible orientations. The layers of molecules are individually deprived of a plane of symmetry but are symmetrical one to the other by reference to the plane (010). The addition of ammonium iodide permits of the exact determination of the lattice structure of mica and of the molecular magnitudes of its mesh. J. S. C.

**Molecular Symmetry in Crystal Structure.** J. H. SMITH (*Nature*, 1925, **115**, 334—335).—Sodium and potassium chlorate, bromate, and iodate exhibit structural relations similar to those known to exist among the alkali polyhalides, and falling into two groups, the cæsium chloride and the sodium chloride group, respectively. Sodium chlorate and bromate and potassium chlorate belong to the latter, potassium bromate and iodate, and probably sodium iodate, to the former. The half-molecule parallelepipedon of potassium chlorate has edges 3.56, 3.69, 3.69 Å. Potassium bromate is ditrigonal pyramidal (pseudocubic), with edge of one molecule pseudocube 4.46 Å. The edges of the one molecule parallelepipedon of monoclinic (pseudocubic) potassium iodate are 4.57, 4.50, 4.50 Å. It is inferred that the complex radicals act as single units and the molecule behaves as an electric doublet. Since the symmetry is independent of the constituent atoms in the radical, it is probable that the crystal-forming forces are electrostatic attractions independent of any structural axes the radicals may possess. A. A. E.

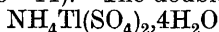
**Relationship between the Fine Structures of the Two Crystalline Forms of Carbon and Zinc Sulphide.** J. BECKENKAMP (*Z. anorg. Chem.*, 1924, **140**, 277—291).—A comparison of the crystal forms of diamond and zinc blende and of graphite and wurtzite, based on the considerations previously put forward by the author (cf. this vol., ii, 90), supports Bragg's atomic arrangement for graphite. The observed axial ratios of the molecule are in agreement with both the Bragg and the Debye-Scherrer structures. It is shown that diamond and zinc blende must be considered chain compounds, whereas graphite represents a typical ring compound; the structures of these molecules are described in detail. S. K. T.

**Symmetry between Growth and Diminution in Size of Crystals.** G. FRIEDEL (*Compt. rend.*, **179**, 1924, 796—799).—A cylindrical cavity, 2 mm. in diameter and 5 mm. deep, ending in a roughly hemispherical surface was made in a crystal of alum. The whole crystal, including the sides but not the bottom of the cavity, was then varnished, and an alum solution, not quite saturated, allowed to flow through the cavity. Subsequent examination showed octahedral, cubic, and dodecahedral facets arranged in the form of a "negative crystal" at the bottom of the cavity. The dominant faces were octahedral, the cubic and dodecahedral faces occurring principally on the edges and summits. It is concluded that crystal growth from a saturated solution and the diminution in size undergone in a solution which is not quite saturated are approximately symmetrical processes as regards ratios of increase and decrease between the various faces of the crystal. H. J. E.

**Modification of Crystal Faces owing to their Syncrystallisation with Foreign Matter Dissolved in the Mother-liquor.** P. GAUBERT (*Compt. rend.*, 1925, **180**, 378—380).—Discussion of hypotheses. The production of cubes, instead of octahedra, of lead nitrate by its crystallisation from a saturated solution of methylene-

blue is attributed to orientation of crystals of the former on those of the latter, and it is stated that all other cases of modification by syncrystallisation can be similarly explained; the faces are not modified by the presence of isomorphous substances. F. M. H.

**Isomorphism between Tervalent Thallium and Rare Earth Metals.** F. ZAMBONINI and G. CAROBBI (*Atti R. Accad. Lincei*, 1925, [vi], 1, i, 8—14).—The double sulphates



and  $\text{NH}_4\text{La}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  form monoclinic crystals, the crystallographic constants being, respectively,  $a:b:c = 1.080:1:1.017$ ,  $\beta = 104^\circ 26'$ , and  $a:b:c = 0.3509:1:0.9145$ ,  $\beta = 97^\circ 36'$ ; the respective molecular volumes of the two salts are 152.4 and 151.5. The salts form mixed crystals, the limiting solubility of the latter in the former being about 11.7%. The double sulphate,  $\text{NH}_4\text{Nd}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , also dissolves to the extent of 11% in  $\text{NH}_4\text{Tl}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . Unsuccessful attempts have been made to replace metals of the rare earths in the double nitrates



by tervalent thallium. The ammonium in ammonium thallic sulphate,  $(\text{NH}_4)_3\text{Tl}(\text{SO}_4)_3$  (cf. Marshall, A., 1903, ii, 21), is capable of partial isomorphous substitution by univalent thallium.

T. H. P.

### Deformation- and Recrystallisation-structure of Metals.

R. GLOCKER (*Z. Physik*, 1925, 31, 386—410; cf. A., 1924, ii, 518).—A röntgenographic investigation of the effect of rolling and subsequent heat treatment on the surface of metallic silver. Photographs are given showing the interference patterns obtained with a plate of rolled silver before and after heating for various periods at temperatures up to  $850^\circ$ . Short heat treatment has little effect, but 10 mins. at  $140$ — $150^\circ$  causes a definite change in the photograph, black spots being superposed on the original X-ray diagram. Recrystallisation is indicated by the disappearance of some of the intensity maxima. A graphical method of interpretation is given and the experiments are discussed fully and the orientation of the crystals under various conditions is worked out in detail.

In the rolled surface the [112] direction is parallel to the direction of rolling and the [011] plane occurs on the rolled plane of the metal. If the heating is continued long enough or is at a high temperature, complete recrystallisation occurs when the regular orientation of the rolled surface disappears entirely. By less drastic heating an intermediate stage occurs, in which the [112] direction is still parallel to the direction of rolling, but instead of a [011] plane in the surface a [113] plane is found, i.e., the cube edge is shifted to a position symmetrical to both direction and plane of rolling. The new surface structure disappears with further heating. R. A. M.

### Fatty Acids.

G. FRIEDEL (*Compt. rend.*, 1925, 180, 409—411).

—Smectic structure is intermediate between amorphous structure and crystalline structure. A smectic substance is characterised by the possession of a single direction, perpendicular to which its molecules

are arranged in equidistant planes, the distribution of the molecules in every plane being irregular. X-Ray or, more simply, microscopical examination shows that fatty acids, particularly palmitic acid (cf. Trillat, this vol., ii, 187), are crystalline and not smectic.

W. E. E.

**Molecular Weight of Cholesterol.** J. R. PARTINGTON and S. K. TWEEDY (*J. Chem. Soc.*, 1925, 127, 496—498).—The mean molecular weight of cholesterol determined from the elevation of the b. p. in benzene and in alcohol, and by the depression of the f. p. in benzene, is 423, showing that some association takes place in these solvents.

A. R. P.

**Cryoscopy in Sodium Sulphate Decahydrate.** E. E. TURNER and W. H. PATTERSON (*Trans. Faraday Soc.*, 1924, 20, 345—347).—The molecular weights of a number of salts have been determined using sodium sulphate as cryoscopic solvent (cf. Löwenherz, A., 1896, ii, 149). The most probable value of the depression constant,  $K$ , is 32.5, but for carbamide, which was used as a standard, the depression is not strictly proportional to the concentration. The molecular weight  $M$  is given by the relation  $M = 100Kw/W\Delta$ , where  $w$  is the weight of solute,  $W$  the combined weight of solute and sodium sulphate decahydrate, and  $\Delta$  the observed depression of the transition temperature. Sodium nitroprusside, ferrocyanide, aluminoxalate, ferrioxalate, and chromioxalate exist as simple molecules, in agreement with the work of Burrows (T., 1919, 115, 1429). Borax and sodium oxalate give abnormally low results.

W. H. R.

**Effects of certain Elements on the Electrical Resistivity of Copper.** A. L. NORBURY (*Inst. Metals*, Mar., 1925; advance copy, 4 pp.).—The effect of dissolved elements on the electrical resistivity of copper is small when the affinity of the element for copper is small, but the resistivity of the metal is increased greatly when the alloying element has a great affinity for copper. [Cf. B., 1925, 245.]

A. R. P.

**Thermal and Electrical Conductivities of some Pure Metals.** F. H. SCHOFIELD (*Proc. Roy. Soc.*, 1925, A, 107, 206—227).—The thermal and electrical conductivities of commercially pure aluminium, copper, magnesium, nickel, and zinc have been determined at temperatures of 100° and higher. In determining the thermal conductivity lateral heat loss was eliminated by use of the guard-ring principle. The thermal conductivity of aluminium was found to increase with rising temperature; that of nickel to decrease at first and then above 500° to show an increase. The other metals showed on the whole slight decreases of conductivity with temperature. The values of Lorenz's function  $K/\lambda T$  ( $K$  and  $\lambda$  being the thermal and electrical conductivities and  $T$  the absolute temperature) for copper, magnesium, and zinc were practically constant at all temperatures; that for aluminium showed a rise with increasing temperature; that for nickel a rise to 300°, above which temperature it remained nearly constant except for an

abnormal value at 400°. The results are compared with those of previous workers who, however, for the most part employed lower temperatures.

N. H. H.

**Effect of Changes in Total Carbon and in the Condition of Carbides on the Specific Resistance and on some Magnetic Properties of Steel.** E. D. CAMPBELL and G. W. WHITNEY (*J. Iron and Steel Inst.*, 1924, **110**, 291—311).—Two series of steel bars, one with and one without chromium, were prepared, the composition of the individual specimens of each series differing only with regard to the carbon; this was done by heating carburised bars with uncarburised in an atmosphere of moist hydrogen for several days at 950° and cooling in dry hydrogen. In this way, part of the carbon was removed from the bars rich in this element and re-deposited in those poor in carbon. In the pure iron-carbon series the specific resistance of the annealed metal is a linear function of the carbon content up to 0.9%, at which point there is an abrupt rise followed by a slightly more rapid linear rise than before. In the chromium-iron-carbon series, increase of carbon content at first decreases the resistance due to the precipitation of the chromium from solid solution as a double iron-chromium carbide, then, after passing the eutectoid point, increases the resistance linearly with the carbon content. In hardened alloys of both series, the specific resistance increases more rapidly than the carbon content, indicating a lowering of the molecular weight of the carbides with increase of atomic concentration, or a decrease in their stability. Experimental evidence is given in support of a new theory of the mechanism of remanent magnetism.

A. R. P.

**Optical Study of Indanyl Bases.** C. COURTOT and A. DONDELINGER (*Bull. Soc. chim.*, 1925, [iv], **37**, 115—130).—The following densities and refractive indices are recorded: indanylamine,  $d_4^{15}$  1.0380,  $n_D^{15}$  1.5619; *N*-methyl-, 0.9981, 1.5411; *N*-dimethyl-, 0.9803, 1.5357; *N*-ethyl-, 0.9846, 1.5342; *N*-diethyl-, 0.9542, 1.5218; *N*-phenyl-, 1.0910, 1.6215; *N*-o-tolyl-, solid  $[M]=72.79$  in benzene; *N*-*m*-tolyl-, 1.0742, 1.6122; *N*-*p*-tolyl-, solid,  $[M]=73.02$  in benzene; *N*-xylyl-, 1.0600, 1.6037; *N*-phenyl-*N*-methyl-, 1.0790, 1.6165; *N*-phenyl-*N*-ethyl-, 1.0647, 1.6065; and *N*-methyl-*N*-benzyl-indanylamine, 1.0438 and 1.5775, respectively. The  $\alpha$ -indanyl group behaves, refractometrically, as an aliphatic group, causing no anomaly in the molecular refractions of secondary or tertiary bases when the remaining groups attached to the nitrogen atom are aliphatic or alicyclic. In the indanyl-alkylarylamines, the molecular refractions agree with those calculated using Brühl's constants, but show an exaltation of 1.58—1.64 units above the value calculated using Eisenlohr's constants. Phenyl-, *o*-, *m*-, and *p*-tolyl- and xylyl-indanylamines show an exaltation of 0.67—0.88 (liquid) and 1.41—1.64 (in benzene), this being apparently characteristic of the phenylindanyl group, and independent of the positions of substituents in the phenyl group. The absorption spectra of the above bases are figured, as well as those of *o*-, *m*-, and *p*-nitrophenyl-, diphenyl-, and  $\beta$ -naphthyl-

indanylamines. The latter shows a bluish-violet fluorescence. The indanyl group is a stronger chromogen than the benzyl, but weaker than the phenyl group. F. G. W.

**Effect of Temperature on the Anomalous Reflexion of Silver.** M. DE SÉLINCOURT (*Proc. Roy. Soc.*, 1925, A, 107, 247—254).—On the assumption that the anomalous reflexion coefficient of silver which occurs at about 3200 Å. is, in terms of the classical electro-magnetic theory, due to the inability of the “free” electrons to vibrate with frequencies corresponding with this region, the effect of the temperature of the silver has been determined, since it is to be expected that if the restoring force on the vibrating electrons varies with the distance between them and neighbouring atoms and electrons, the limiting frequency on either side of this band will vary as the metal contracts or expands. At the temperatures measured ranging from  $-183^{\circ}$  to  $+150^{\circ}$ , the band was found to be shifted towards the longer wave-lengths with increasing temperature, which corresponds with the view that with increasing distance between the atoms the restoring force and hence the frequency is diminished. The width of the band was found to vary with temperature, from which it is inferred that the particles controlling the electrons have an amplitude of oscillation of the same order as the atom. To explain this, a restatement in terms of the quantum theory is considered probably necessary. N. H. H.

**Specific Heats.** S. WIESNER (*Ann. Physik*, 1925, [iv], 76, 439—443).—The author imagines the atoms of a substance in process of melting as forming aggregates, the rotation of which takes up the energy supplied—the latent heat of fusion. If  $d$  is the difference between the specific heats of the solid and liquid and  $r$  the atomic refraction, he shows that  $r\sqrt{d} = \text{const.} = 3$ . E. B. L.

**Specific Heat of Liquids.** R. N. GHOSH (*J. Indian Chem. Soc.*, 1925, 1, 123—124).—An empirical formula,  $E = 3NkT + N/2 \cdot x/(e^x - 1)$ , where  $x = h\nu/kT$ ,  $N$  = number of atoms per unit mass,  $v$  is Lindemann's constant,  $T$  the absolute temperature, and  $h$  and  $k$  are Planck and Boltzmann's constants, is proposed for the energy of a liquid per unit mass. From this equation  $C_v = 3Nk + \frac{1}{2}Nk \cdot e^x x^2 / (e^x - 1)^2$ , and the value of  $C_v$  is calculated for fourteen elements in the liquid state. J. W. B.

**Heats of Combustion of Decahydronaphthalenes and  $\beta$ -Decalones.** W. A. ROTH and R. LASSÉ (*Annalen*, 1924, 441, 48—53).—A thermal examination of Hückel's products (this vol., i, 258). Between *cis*- (1499.9) and *trans*-decalins (1496.9) there is a difference of 3 kg.-cal. per mol. in heat of combustion. The *cis*- and *trans*- $\beta$ -decalones ( $\beta$ -ketodecahydronaphthalenes) give equal values (1400.2 kg.-cal. per mol.). *cis*-Decalin is thermically identical with Willstätter and Hatt's preparation (A., 1912, i, 545; Roth and von Auwers, A., 1915, ii, 146). C. H.

**Recent Measurements of the Joule Effect for Carbon Dioxide.** F. G. KEYES and F. W. SEARS (*Proc. Nat. Acad. Sci.*, 1925, 11, 38—41).—The Joule effect for carbon dioxide is considered

from a thermodynamic point of view and theoretical equations are developed, the experimentally determined temperature changes being in fair agreement with those predicted. A convenient form of apparatus is described in which the fall in temperature is measured by means of a ten-junction copper-constantan thermocouple.

J. S. C.

**Pyrophoric Phenomenon in Iron.** A. SMITS and G. WALLACH (*Rec. trav. chim.*, 1925, **44**, 130—131).—By reducing ferrous oxide with hydrogen at temperatures varying between 575° and 800° and cooling in hydrogen, it is found that, on heating for 1 hour, the pyrophoric properties begin to decrease from 650° and rapidly disappear above 710°; this corresponds with the rapid alteration in the internal condition of iron at about 760°.

F. M. H.

**Osmium Tetroxide.** H. VON WARTENBERG (*Annalen*, 1925, **441**, 318; cf. this vol., ii, 231).—Ruff and Tschirsch (A., 1913, ii, 416) have already recorded the b. p. of osmium tetroxide as 130°, from vapour-pressure determinations by extrapolation.

R. B.

**Boiling Point Relations for Fused Salts.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1924, **141**, 131—132; cf. A., 1921, ii, 486; 1922, ii, 739).—The relation  $T_{(p=15)}/T_s = 0.765$  (where  $T$  is the absolute b. p. at 15 mm., and  $T_s$  the b. p. at 760 mm.), which has been shown to hold for fused salts, has now been verified from the experimental data of von Wartenberg and his collaborators for a large number of halides. Good agreement is obtained in nearly every case, the few deviations being probably due to experimental difficulties.

L. L. B.

**Melting Point and Vaporisation of Graphite.** E. RYSCHKEWITSCH (*Z. Elektrochem.*, 1925, **31**, 54—63).—Carbon rods containing less than 0.1% of impurity and narrowed in the middle were heated electrically in an atmosphere of argon. The course of the operation was followed by a kinematograph camera taking 25 pictures per sec. No gradual diminution of the cross-section of the rod occurred, but a bright line appeared at the narrowest part where, less than 1/10 sec. afterwards, the rod parted and formed an arc. Small globules of carbon having equal densities were found in the vicinity of the arc at the conclusion of the experiment. These observations show that the rod parted by fusion and not by sublimation. Simultaneous measurements were made of the current density, the pressure, and the temperature, the latter by means of a radiation pyrometer. The temperature of the rod taken just at the moment of parting was found to be independent of the pressure (0.21 to 0.935 atm.) and from it the m. p. was estimated to be  $3800 \pm 100^\circ$  Abs. Measurements were also made of the temperature of the arc formed when the rod parted. This was found to be independent of the current density but dependent on the pressure. It varied from 3450° Abs. at 0.005 atm. to 4330° Abs. at 1.5 atm. Those values above 3800° Abs. (about  $\frac{1}{3}$  atm.) are considered to be the b. p. of graphite at different pressures.

N. H. H.

**Melting and Heat of Vaporisation of Graphite.** K. FAJANS (*Z. Elektrochem.*, 1925, **31**, 63—70).—Theoretical. The presence of less than 0.1% of impurity in the graphite used by Ryschkewitsch (cf. preceding abstract) is shown to have a negligible effect. It must be assumed that the positive crater of the arc at pressures above about  $\frac{1}{3}$  atm. is covered with a very thin layer of liquid carbon and the temperature of the crater measured above this pressure is its boiling point. For determining the vapour-pressure curve and from it the heat of vaporisation the arc method is considered better at the present than measurements of the rate of vaporisation of carbon filaments. The heat of vaporisation obtained by Kohn and Guckel using the arc method is used to calculate the heat of sublimation of diamond, the value obtained being very near that previously given by the author (cf. A., 1920, ii, 469) namely 150 cal. at the ordinary temperature. N. H. H.

**Influence of Pressure on the Freezing Point of *p*-Nitrotoluene, *m*-Dinitrobenzene, and Guaiacol.** N. A. PUSHIN (*J. Chem. Soc.*, 1924, **125**, 2628—2630).—By the manometric method of Tammann ("Kristallisieren und Schmelzen," 1903, 192—194), the m. p. of *p*-nitrotoluene has been found to increase from 51.5° to 122.4° as the pressure increases from 1 to 3000 kg./cm.<sup>2</sup>, that of *m*-dinitrobenzene from 89.8° to 138.0° between 1 and 2000 kg./cm.<sup>2</sup>, and the m. p. of guaiacol from 28.3° to 60.5° for the same range of pressure. The values found for guaiacol are in close agreement with those calculated from Denecke's equation (A., 1920, ii, 10).

M. S. B.

**Numerical Values of Chemical Constants and Frequencies of Elements.** A. C. EGERTON (*Proc. Physical Soc.*, 1925, **37**, 75—83; cf. A., 1920, ii, 84).—The chemical constant  $C$  is given by the Sackur relation  $C = 3/2 \log M - C_0$ , where  $C_0 = \log 2\pi^{3/2} R^{5/2} / N^4 h^3$ . The value of  $C_0$  calculated from the accepted radiation constants is -1.589. The weighted mean of observations on 10 elements leads to an experimental value  $1.596 \pm 0.008$ . This value leads to figures for both Stephan's and Wien's constants, which agree with the latest experimental values. The data relating to the chemical constants of 61 elements have been collected and tabulated together with values of  $\beta\nu$  (characteristic temperature) based on (a) the Lindemann melting-point formula, (b) the coefficient of expansion, and (c) observations. Values based on specific heat data are given and the relative accuracies discussed. The Lindemann formula gives the closest approximation to experiment. If  $\beta\nu$  is plotted against  $\log M$  (atomic mass) for various similar elements a linear relation is generally applicable. The evidence is inadequate for a discussion of the relationships between the characteristic frequencies of the elements. R. A. M.

**Theoretical Stoichiometry of Molecular Volume, Inter-molecular Attraction, Viscosity, and Ionic Mobility of Liquid Organic Compounds.** E. WÖHLISCH (*Biochem. Z.*, 1924, **153**, 120—128).—A brief theoretical review from the point of view of the



kinetic theory of results published elsewhere. Acids have a larger specific molecular volume ( $\Phi$ ) and a smaller total volume ( $V$ ) than the isomeric esters, whilst for the alcohols  $\Phi$  is greater than and  $V$  is less than the corresponding values for the isomeric ethers. Addition of methyl groups or chlorine atoms lowers  $\Phi$  and increases  $V$ . The ratio  $\Phi/V$  is greater for isomerides of high than for those of low b. p., and increases in homologous series. Of two isomerides, that with the higher b. p. has the higher coefficient of internal friction, since it has a larger molecule and a lesser intermolecular volume ( $V-\Phi$ ). The internal friction of liquids increases in homologous series. Molecular association leads to an increase in  $\Phi$  and a diminution in ( $V-\Phi$ ). The non-applicability of the Stokes-Einstein equation to the ionic mobilities of certain isomeric ions is correlated with the intermolecular attraction between solvent and solute molecules, in the sense that the attractive forces affect the ionic mobility in the same way as an increase in molecular radius (cf. Lorenz, "Raumerfüllung und Ionenbeweglichkeit," Leipzig, 1922). J. P.

**Specific Volume of Steels.** J. H. ANDREW and A. J. K. HONEYMAN (*Iron and Steel Inst., Carnegie Schol. Mem.*, 1924, **13**, 253—266).—The effect of varying heat treatment on the specific volume of carbon- and nickel-chromium-steels was investigated. For annealed carbon steels the specific volume  $v=0.12712+0.00052a$ , where  $a$  is the percentage of carbon. That of  $\text{Fe}_3\text{C}$  is 0.1306. The effect of quenching both kinds of steel from various temperatures is recorded. The specific volume of fully tempered martensite is the same as that of the corresponding pearlite, indicating that in both conditions of the steel the cementite possesses the same crystalline form. CHEMICAL ABSTRACTS.

**Liquid Densities at Various Temperatures.** J. J. VAN LAAR (*Z. anorg. Chem.*, 1924, **140**, 52—60).—Polemical against Saslawsky (A., 1924, ii, 452). L. J. H.

**Density Determinations of Rock-salt Crystals.** W. GEISS (*Ann. Physik*, 1925, [iv], **76**, 403—408).—The density was determined by weighing in air and in benzene and also by flotation in a mixture of benzene and bromoform. The results obtained were:  $d_4^{18}=2.1644\pm0.5\%$ ; coefficient of linear expansion between  $0^\circ$  and  $50^\circ=40\times10^{-6}$ , from which the lattice constant= $2.81400[1+0.000040(t-18)]$ . E. B. L.

**Density of Rhodium.** T. K. ROSE (*Inst. Metals*, Mar., 1925; advance copy, 2 pp.).—Pure rhodium melted in the oxy-hydrogen flame and forged hot has  $d_4^{12} 12.472$  in a vacuum. An ingot forged up from sponge had  $d_4^{12} 12.222$ . A. R. P.

**Vapour Pressure of Tellurium.** J. J. DOOLAN and J. R. PARTINGTON (*Trans. Faraday Soc.*, 1924, **20**, 342—344).—The vapour pressure of tellurium has been determined by a modification of the method of von Wartenberg (A., 1913, ii, 670). The metal was heated in a stream of nitrogen and the loss in weight determined

at three fixed temperatures and at least three rates of flow at each temperature. Assuming that the molecule of tellurium is diatomic, the vapour pressure is calculated as  $1.86 \times 10^{-2}$ ,  $4.40 \times 10^{-3}$ , and  $6.10 \times 10^{-4}$  atmospheres at  $671^\circ$ ,  $578^\circ$ , and  $488^\circ$ , respectively. The mean value for the heat of volatilisation per gram-mol. is 26.5 cal.

W. H. R.

**Saturated Vapour Pressure of Hydrocyanic Acid.** R. HARA and H. SINOZARI (*Tech. Rep. Tohoku Imp. Univ.*, 1924, 4, 145—152).—Pure hydrocyanic acid, b. p.  $25.7^\circ$ , was obtained by the action of sulphuric acid ( $d$  1.39) on potassium cyanide, the vapour being passed over calcium carbonate and anhydrous calcium chloride before condensation; its polymerisation may be prevented by preserving it in contact with anhydrous calcium chloride. By a modification of the isoteniscopic method of Smith and Menzies (A., 1910, ii, 1036), the vapour pressure was determined within the limits  $0$ — $46^\circ$ . The observed values are in satisfactory agreement with those calculated from the formula  $\log P = -1836.63/T^{1.06} + 7.5030$ .

C. S.

**Vapour Pressure of Germanium Hydride.** R. SCHENK and A. IMKER (*Ber.*, 1925, 58, [B], 271—272).—Redetermination of the vapour pressure curve of germanium hydride indicates the b. p.  $-90^\circ$  to  $-91^\circ$ , which is in harmony with the value ( $-88.5^\circ$ ) given by Paneth, Haken, and Rabinovitsch (this vol., ii, 60). The lower value observed previously (A., 1922, ii, 855) is ascribed to the preservation of germanium hydride over-night in contact with mercury whereby partial decomposition is caused with liberation of hydrogen.

H. W.

**Determination of Surface Tension by the Ring Method (Torsion Balance).** P. L. DU NOÛY (*Biochem. Z.*, 1925, 155, 113—118).—The author describes the standardisation and use of his apparatus for reading off directly in dynes/cm. the surface tension of liquids. The instrument is based on the ring method, is worked like a torsion balance, and has been used for a large number of determinations of the surface tension of colloidal liquids, chiefly blood-serum. The figures obtained agree within 0.1 dyne/cm. with those of other authors.

P. W. C.

**Relation between the Hardness of Metals and Temperature.** F. SAUERWALD and K. KNEHANS (*Z. anorg. Chem.*, 1924, 140, 227—242).—The absolute hardness, in terms of the work of compression, of various metals was determined over a wide range of temperature. For copper, tin, antimony, lead, and aluminium, the hardness is a linear function of the temperature, but with nickel, magnesium, zinc, and iron the curves are irregular. For nickel and magnesium the curves are composed of straight lines, but with zinc and iron the relationship is more complicated. Provisionally the breaks are considered to indicate polymorphism, although this is not always clear. The recoil curves show a general similarity to those for the hardness for the latter group. With the former they decrease with

rising temperature except that for each metal there is a characteristic break during which the recoil is independent of temperature.

L. J. H.

**Piezoechemical Studies. XXVII. Relation between Diffusion-velocity, Viscosity, and External Pressure.** E. COHEN and H. R. BRUINS (*Z. physikal. Chem.*, 1925, **114**, 441—452; cf. A., 1924, ii, 521).—A method is described for the determination of viscosity at high pressures in an Ostwald viscosimeter, enclosed in a pressure chamber. It was found that the viscosity of mercury at 20° was raised by 4.8% by a pressure of 1500 atm., and since in similar circumstances the diffusion velocity of cadmium through mercury decreases by 5%, it is concluded that the product of diffusion-velocity and viscosity is constant, independent of the external pressure.

L. L. B.

**Viscosity of Binary Mixtures.** D. B. MACLEOD (*Trans. Faraday Soc.*, 1924, **20**, 348—369).—The viscosities of binary mixtures of liquids can be expressed by the equation  $\eta = \eta_1 m_1 x_1/x + \eta_2 m_2 x_2/x$ , where  $\eta_1$  and  $\eta_2$  are the viscosities of the constituents,  $m_1$  and  $m_2$  their molecular percentages,  $x_1$  and  $x_2$  their amounts of "free space" per c.c., and  $x$  the free space of the mixture. The values of  $x_1$  and  $x_2$  can be calculated from the densities and viscosities at two different temperatures, and the value of  $x$  is given by the equation  $x = x_1 v_1 + x_2 v_2 \pm C$ , where  $v_1$  and  $v_2$  are the volume percentages and  $C$  the change of volume per c.c. on mixing. In normal mixtures in which the volume change is small, the curve connecting viscosity and composition is a sagged one, the amount of the sagging depending on the relative viscosities. When contraction occurs on mixing, the curve rises to a maximum, the position and magnitude of which depend on the amount of contraction and on the viscosities, and consequently also on the temperature. When the constituents have almost equal viscosities the maximum occurs at almost equimolecular proportions, but otherwise the maximum tends to form near the viscous end of the curve, unless the constituents differ very markedly in viscosity, when the curve becomes S-shaped. Minima on the curve are usually accompanied by expansion on mixing. The formation of compounds causes a greater loss of free space than is indicated by the change in density, and the calculated results are therefore too low. The equations have been tested by means of existing data for a number of binary mixtures of organic liquids.

W. H.-R.

**Viscosity and Allotropy of Glass.** H. LE CHATELIER (*Ann. Physique*, 1925, [x], **3**, 5—21).—A critical discussion of the work of Washburn and Shelton (*Univ. of Illinois Bull.*, No. 140, 1924, **21**, 1) and of English (*J. Soc. Glass Tech.*, 1924, **8**, 205) on the viscosity of glasses. The relation between the temperature and the log. log. of the viscosity is given by a linear equation of the type  $\log. \log. \eta = M[(t-1000)/1000] + N$  ( $M$  being a constant and  $N$  the viscosity at 1000°). For the glasses examined by English and for certain of those examined by Washburn and Shelton, two such

linear expressions are required, one for the upper, and a second for the lower temperature zone, indicating a transformation point at a temperature in the region of  $1000^{\circ}$ . The results of English, for lime and magnesia series of the molecular type  $3\text{SiO}_2, x\text{RO}, (1-x)\text{Na}_2\text{O}$ , show a simple linear relationship between the parameters  $M$  and  $N$  and the proportion of lime or magnesia molecules present. [Cf. B., 1925, 242.] A. COUSEN.

**Solid Solutions of Compounds of Elements of Different Valencies.** G. BRUNI and G. R. LEVI (*Atti R. Accad. Lincei*, 1924, [v], 33, ii, 377—384).—The results of X-ray analysis confirm the conclusion reached from those of thermal analysis (cf. Tacchini, this vol., ii, 122) that lithium and magnesium fluorides form solid solutions, the mixed crystals undergoing decomposition at a low temperature. At the ordinary temperature, solid solutions of the lithium fluoride type containing up to 20%  $\text{MgF}_2$  may be prepared. The replacement of a certain number of magnesium fluoride molecules by a corresponding number of double lithium fluoride molecules causes neither appreciable change in the lithium fluoride space lattice nor the appearance of new lines in the corresponding X-ray photographs, but, just as in other similar cases, the formation of the mixed crystals is accompanied by a slight increase in the volume of the elementary cell. T. H. P.

**Measurement of the Change in Volume in Metals during Solidification.** H. ENDO (*Sci. Rep. Tōhoku Imp. Univ.*, 1924, 13, 193—218).—Measurements have been made of the change in volume on solidification for a number of metals of low m. p. In the method employed, the metal is suspended in an inactive liquid during solidification or melting and the change in buoyancy determined. Results are given for mercury, sodium, potassium, rubidium, tin, bismuth, thorium, cadmium, lead, gold, silver, copper, and aluminium. When the change in volume per unit mass is plotted against the atomic weight, a periodic curve similar to the curve for atomic volume is obtained. [Cf. B., 1925, 248.] C. S.

**Measurement of the Change in Volume in Alloys during Solidification.** H. ENDO (*Sci. Rep. Tōhoku Imp. Univ.*, 1924, 13, 219—227).—Using the method described in a previous paper (preceding abstract) measurements of the change in volume during solidification have been made for silumin, duralumin, copper-aluminium alloys, brass, and bronze. The mean coefficient of cubical expansion between  $20^{\circ}$  and  $500^{\circ}$  was also determined. [Cf. B., 1925, 248.] C. S.

**Modification of the Structure of Aluminium Alloys containing Large Proportions of Silicon.** N. PARRAVANO and A. SCORTECCI (*Atti Congr. Naz. Chim. Ind.*, 1924, 291—294).—Fusion of aluminium-silicon alloys with 1% of sodium or calcium modifies the structure of the metal so that, on cooling, the constituents are indistinguishable under the highest magnifications. Similar effects are produced in the same way in aluminium-silicon

alloys containing small proportions of other metals, the mechanical properties being improved at the same time. [Cf. *B.*, 1925, 247.]

T. H. P.

**Intermetallic Reactions in a Lead-base Bearing Metal.** O. W. ELLIS (*Nature*, 1925, 115, 382).—A study of the influence of pouring temperatures and mould temperatures on the micro-structure of a lead-base bearing metal. [Cf. *B.*, 1925, 286.]

A. A. E.

**Influence of Lead and Tin on the Brittle Ranges of Brass.** D. BUNTING (Inst. Metals, Mar., 1925; advance copy, 10 pp.).—The presence of lead in brass causes a general decrease of toughness and raises the upper limit of the brittle range. Addition of small quantities of tin to  $\alpha$ -brass increases its impact strength and reduces considerably the brittle range, but larger quantities cause the separation of the brittle  $\gamma$  or  $\delta$  constituent and a consequent great increase of brittleness. [Cf. *B.*, 1925, 246.]

A. R. P.

**Recrystallisation Phenomena [in Aluminium].** H. RÖHRIG (*Z. Metallk.*, 1925, 17, 63).—Annealing rolled sheets of aluminium at 220–350° results in rapid recrystallisation and the growth of very large crystals differently oriented from those produced by annealing at a higher temperature. This behaviour is similar to that previously observed in the case of silver. [Cf. *B.*, 1925, 246.]

A. R. P.

**Gas Solubility and Hydration.** W. MANCHOT [with M. JAHRSTORPER and H. ZEPTE] (*Z. anorg. Chem.*, 1924, 141, 45–81; cf. this vol., ii, 233).—The solubility of nitrous oxide and acetylene in aqueous solutions of electrolytes (including chlorides, bromides, nitrates, sulphates, phosphates, and iodates) has been determined at 25° over a wide range of concentration. The order of the effects of anions and cations is in agreement with the statements of previous investigators. The solubilities are always calculated for equal weights of water in the solutions, contrary to earlier investigations, where only the volume of the solution is considered. The present method has the advantage that a direct comparison is obtained with the value for the solubility in water, and it is possible to express in mols. of water the lowering of solubility caused by 1 mol. of dissolved substance. This value decreases with increasing concentration of salt.

The quantities of water "inactivated" by 1 mol. were found to be the same for nitrous oxide and acetylene, within the limits of error. Acetylene shows small variations with nitrates, which are probably due to chemical reaction. The quantity of water required by 1 mol. of salt is somewhat greater at 0° than at 25°. The influence of nitric, hydrochloric, and sulphuric acids on the solubility of nitrous oxide was studied, and found to be different from that of salts; with rising concentration, the solubility falls at first, reaches a minimum, and then increases. Some non-electrolytes produce a decrease in solubility, others an increase. An attempt has been made to calculate the number of mols. of water required by the

various ions, and satisfactory agreement obtained by several different methods.  
L. L. B.

**Solubility of Lead Chloride in Acetic Acid.** W. HERZ and E. MARTIN (*Z. anorg. Chem.*, 1924, **140**, 339—340).—The solubility of lead chloride in acetic acid solutions decreases at first slowly and then rapidly as the acid concentration approaches 14.9*N*. The solution in glacial acetic acid gives only a brown coloration with ammonium sulphide.  
S. K. T.

**Solubility of Mercury Halides in Mixtures of Glycerol and Water.** E. MOLES and M. MARQUINA (*Anal. Fís. Quím.*, 1924, **22**, 551—554).—The solubility of mercuric chloride in water at 25° is 0.26 g.-mol. per litre, whilst that of mercuric bromide at the same temperature is 0.0170 g.-mol. per litre. The solubilities of mercuric chloride and bromide in mixtures of glycerol and water are recorded. In both cases, the solubility increases with the proportion of glycerol.  
G. W. R.

**Solubility in Mixed Liquids.** G. PLEUGER (*Physikal. Z.*, 1925, **26**, 167—170).—The solubility of benzamide and aceto-*p*-toluidide has been measured in mixtures of alcohol-water, alcohol-carbon disulphide, alcohol-carbon tetrachloride.

In general, at temperatures well below the melting point of the substance, the solubility is greater than would be expected from the mixture rule, and in several cases a most decided maximum is observed. There appears to be no connexion between the change of solubility and the dielectric constants.  
E. B. L.

**Piezoechemical Studies. XXVIII. Solubility Determination at High Pressures by means of Conductivity Determination.** E. COHEN and J. C. VAN DER BOSCH (*Z. physikal. Chem.*, 1925, **114**, 453—499).—A conductivity method is described whereby the solubility of solids may be determined with great accuracy at high pressures. The principle of the method depends on the fact that the relation between the conductivity,  $\kappa$ , and the concentration  $C$ , of the solution may be expressed by the equation  $\kappa = a + bC + dC^2 + eC^3$ . Thallous sulphate was selected for experiment, on account of the marked influence of pressure on the solubility, and the resistances of a large number of solutions of different concentrations were determined at 30° and at pressures up to 1500 atm. For each pressure the equation  $\kappa = f(C)$  was calculated. It was found that the results could be expressed by the following curve:  $C = 5.831 + 0.003295p - 0.000000109p^2$ , and that at 1 atm.,  $(dC/dp)_{1\text{atm.}} = 0.003295\%$ . The agreement between the solubility found by the conductivity method and by the direct method (cf. A., 1923, ii, 386) is excellent. The disadvantages of the method are that it can only be applied to electrolytes, and that it is very tedious, owing to the long time taken to attain solution equilibrium.  
L. L. B.

**Salting-out.** E. A. HAFNER and L. VON KÜRTHY (*Arch. exp. Path. Pharm.*, 1924, **104**, 148—169).—The salting-out of phenol

from aqueous solution is selected as a typical example of the process under consideration. Interferometric measurements show that phenol solutions differ from solutions of other substances (*e.g.*, dextrose, potassium chloride) in that the displacement of the interference bands is not a linear function of the concentration of the solution. This is attributed to the aggregation of the phenol molecules, a view which is supported by the fact that departure from proportionality also appears with concentrated solutions of potassium chloride. A similar aggregation of phenol molecules occurs, according to interferometric measurements, when electrolytes are added to phenol solutions in amount insufficient to salt out the phenol, *i.e.*, the salting-out process commences before the actual separation of the phenol. This aggregation is considered to be a result of the polarisation of the molecules present in the solution, which is brought about by the introduction of an electric charge (electrolyte solution). The substance (phenol) with the smaller dielectric constant has the smaller polarisability and hence moves towards, and collects at, points where the strength of the electric field is small. Salting-out is thus a function of the dielectric constants of solvent and solute and will occur more readily the greater the difference between the values of these constants; other factors (such as hydration of ions) may, however, be present and obscure this relation. E. S.

**Sorption of Ammonia and Carbon Dioxide by Glass.** D. H. BANGHAM and F. P. BURT (*J. Physical Chem.*, 1925, 29, 113—129; cf. A., 1924, ii, 392).—Measurements of the rate of sorption of ammonia by glass wool of known surface area at 0° and different pressures are found to agree, over the experimental range investigated, with the equation,  $s^m = kp \int_0^t p_t dt$ , where  $s$  is the sorption value in c.c. of gas sorbed (reduced to n.t.p.) and  $p_t$  the momentary pressure, both at the time  $t$ , and  $m$  is a constant of about 12. With carbon dioxide, the value of  $m$  varies with the pressure. M. B. D.

**Adsorption from the Standpoint of Capillarity.** W. A. PATRICK and N. F. EBERMAN (*J. Physical Chem.*, 1925, 29, 220—228; cf. this vol., ii, 193).—The adsorption of water from its solution in *n*-butyl alcohol by silica gel has been determined at 1°, 26.2°, and 50° for concentrations of water up to the solubility limit. The adsorption can be represented by the formula  $V = K(S\sigma/S_0)^{1/n}$  (cf. A., 1920, ii, 417), in which  $V$  is the volume of liquid solute adsorbed per gram of gel,  $S$  the equilibrium concentration of the solute in the solution,  $K$  and  $1/n$  are constants,  $\sigma$  is interfacial tension, and  $S_0$  a constant, which has a value, in general, less than the actual solubility of the solute. The equation can be deduced theoretically, using Rayleigh's equation connecting the vapour pressure of a liquid with the radius of curvature of its surface. M. B. D.

**Anomalous Adsorption of Dyes by Wool and Cotton.** J. B. SPEAKMAN and A. E. BATTYE (*J. Text. Inst.*, 1925, 16, 53—60 T).—The anomalous adsorption by wool of basic dyes such as night-blue

and Victoria-blue described by Biltz and Steiner (A., 1910, ii, 830) is associated with the observation of Gee and Harrison (*Trans. Faraday Soc.*, 1910, 6, 42) that untreated wool has a negative charge and acid-treated wool a positive charge when immersed in water. The process of dyeing is regarded as due to adsorption of dye by a neutralisation of the charge on the adsorbent and also to those unknown forces which are responsible for normal adsorption. Increasing the concentration of a solution of night-blue increases its acidity, and since this represses the negative charge on the wool, the latter has a decreasing adsorptive power for the dye. The adsorption of the dye is therefore dependent on the relation between the rate of increase of the normal adsorption and the rate of decrease of the adsorption due to the electrical charge of the fibre. The anomalous adsorption described by Biltz and Steiner is an instance where the adsorption due to the electrical charge has a dominating influence. In buffered solutions of night-blue, adsorption increases regularly with increase of concentration. A. J. H.

### Behaviour of Hydrated Aluminium Oxide towards Dyes.

J. K. WOOD and A. WOOLLER (*J. Soc. Dyers and Col.*, 1925, 41, 47—53).—Carefully purified samples of hydrated aluminium oxide prepared under varied conditions of temperature and concentration by addition of ammonia or sodium hydroxide to aqueous solutions of aluminium chloride or acetate are found to adsorb acid but not basic dyes. Hydrated aluminium oxide prepared from the acetate readily adsorbs basic dyes if a trace of alkali is added, but that prepared by means of sodium hydroxide strongly adsorbs basic dyes only when previously ignited; in each case the adsorbed dye is readily removed by washing with water. The adsorption of basic dyes from aqueous solution is not affected by the presence of sodium sulphate, but is favoured by the presence of potassium citrate and particularly by sodium phosphate. Quantitative measurements in the presence of sodium phosphate at a measured hydron concentration are described. Magenta is more strongly adsorbed than methylene-blue, the latter being more easily removed from the hydrated oxide by washing. Basic dyes adsorbed by hydrated aluminium oxide are removed by washing with water containing sodium chloride, sodium sulphate, or sodium acetate, but not by washing with water containing phosphate or free alkali. Hydrated aluminium oxide containing comparatively large amounts of chlorine decolorises aqueous solutions of methyl-orange and orange-IV, but with preparations containing less than 0.05% of chlorine a certain minimum concentration of dye was necessary before any adsorption occurred. Samples of hydrated aluminium oxide containing 0.56% of chlorine were shaken up with 5% solutions of sodium phosphate, potassium citrate, sodium sulphate, potassium dichromate, and sodium acetate, were then thoroughly washed with distilled water and dyed with ponceau-2R; the amount of dye adsorbed was found to increase in the order of the solutions named, those samples treated with phosphate and acetate having a white and an intense brick-red colour, respectively; in this behaviour



hydrated aluminium oxide resembles wool. Measurements of the adsorption of acid dyes such as picric acid, naphthol-yellow S, brilliant-crocein R, orange II, ponceau-2R, amaranth, and brilliant-crocein 9B are described. The mode of preparation of hydrated aluminium oxide has less influence on its dyeing properties than is the case with stannic and titanic acids (cf. Wood and Morley, A., 1923, ii, 425, 426). The behaviour to acid dyes is largely determined by the presence of acidic impurities (cf. Michaelis and Rona, A., 1919, ii, 496).

A. J. H.

**Theory of Dyeing.** G. ROSSI and A. BASINI (*Annali Chim. Appl.*, 1925, 15, 4—16).—The authors regard dyeing as a simple process of adsorption of the colouring matter by the fibre. Dyeing may occur when the adsorption compound is insoluble in water, that is, when the affinity of the secondary valencies of the fibre towards those of the colouring matter is greater than that of the latter for the secondary valencies of the solvent. If this is not the case, dyeing is possible only with the intervention of mordants which, behaving like substantive dyes towards the fibres, give absorption compounds with increased affinity of their secondary valencies towards those of the dye; the same effect is produced if the mordant and dye yield compounds the secondary valencies of which have a greater affinity for those of the fibre than for those of the solvent.

That the generation of heat during the dyeing process cannot be regarded as evidence in favour of the salt-formation theory of dyeing is shown by the observation that the coagulation of colloidal arsenic trisulphide is accompanied by thermal change. Other experimental results supporting the authors' theory are: (1) the quantity of dye adsorbed by fibres immersed in dye-baths containing stabilising emulsoids is less than that which the same fibres are able to adsorb in absence of stabilisers, and (2) the proportion of dye combining with the fibre varies, within certain limits, with the concentration of the bath.

T. H. P.

**Adsorption.** F. SCHELTE (*Z. physikal. Chem.*, 1925, 114, 394—412).—The isotherms representing the adsorption of methyl-violet, ethyl-violet, diamond-fuchsin, and methylene-blue by window and lead glass are found to be of the usual form. The surface of the glass powder was determined by the method of Schmidt and Durau (A., 1924, ii, 238), which involves the determination of the solubility of the glass in dilute alkali; it was found that this solubility depends, not only on the chemical composition, but also on the previous thermal history of the glass. The adsorption for the two glasses was found to be different. Expressed as percentage of surface covered, the values for methyl-violet, ethyl-violet, diamond-fuchsin, and methylene-blue on window glass are 196.6, 164.8, 198, and 136.4, respectively, whilst the corresponding values on the lead glass are 192, 140.3, 75.2, and 79.5, respectively. The extent of the adsorption does not depend only on the magnitude of the surface area, but on the chemical composition and physical properties of the adsorbent.

L. L. B.

**Adsorption Compounds. V.** R. HALLER (*Kolloid-Z.*, 1925, 36, 86—92; cf. A., 1924, ii, 93).—In a group of acid triphenylmethane dyes, the introduction into the benzaldehyde nucleus of a sulphonic group increases the dispersion, although this is diminished by the introduction of a halogen or nitro group. The aluminium, iron, and chromium lakes are polydisperse, the lower degree of dispersion giving a blue and the higher a reddish-violet. Wool is dyed in reddish colours and cotton in blue. E. M. C.

**Adsorption. IX. Adsorption by Soil.** P. N. PAVLOV (*Kolloid-Z.*, 1925, 36, 78—81).—The form of the curve representing the adsorption of ammonium chloride from aqueous solution by soil depends on the relative amounts of soil and solution. In accordance with the author's criteria (cf. A., 1924, ii, 833) the action is a complex chemical process, probably involving a series of reactions in which almost insoluble double salts are formed, each of which is stable over a definite range of concentration. E. M. C.

**Vapour Pressure-Water Content Diagram and Adsorptive Power of Aniline-black.** P. P. KASAKEVITSCH (*Kolloid-Z.*, 1925, 36, 82—85).—The vapour pressure-water content curves of aniline-black are quite smooth and show considerable hysteresis. At all stages of humidity the water content for drying is about twice that for wetting. The importance of the slowness of many adsorption reactions is emphasised and it is shown that the amount of hydrochloric acid removed from solution by aniline-black in one month is independent of the final concentration of acid. E. M. C.

**Capillarity, Evaporation, and Efflorescence.** K. SCHULTZE (*Kolloid-Z.*, 1925, 36, 65—78).—The rate of evaporation of water from circular capillaries is proportional to the area of the cross-section, and falls off rapidly with the depth below the mouth of the tube. The rate of evaporation is considerably greater from tubes of irregular cross-section, and it is suggested that the shapes of the capillaries are important factors in determining the course of evaporation from granular and porous materials. Efflorescences were obtained during the evaporation both of salt and of colloidal solutions. E. M. C.

**Behaviour of Oil and Oleic Acid with Water. IV.—VI.** J. F. CARRIÈRE (*Rec. trav. chim.*, 1925, 44, 121—129; cf. A., 1924, i, 461).—The behaviour of a pure oil with water is contrasted with that of an oil containing a trace of oleic acid. Anomalies in the behaviour of oil and water, which certain observers have attributed to hydrolysis, are now explained as due to the presence of impurities. The interfacial tensions of neutral oil/water, and of oleic acid/water, respectively, as given in the literature, require correction to about 26 and 10.5 dynes/cm. respectively at 20°. Traces of fatty acids in oil may be detected by the action of ammonia vapour after establishment of the oil/water equilibrium. [Cf. B., 1925, 250.]

F. M. H.

**Colours Due to Thin Films on Metals.** U. R. EVANS (*Proc. Roy. Soc.*, 1925, **A**, 107, 228—237).—Experiments are described which support the view that the colours of thin films on metals are due to interference. Mallock's objection (*Proc. Roy. Soc.*, 1918, **A**, 94, 566) that the temper colours on steel are not changed by polishing is countered by an experiment in which the colours are changed in the correct sequence by cathodic treatment in dilute hydrochloric acid. Raman's view (*Nature*, 1922, 109, 105) that the colours are due to a granular structure is shown to be untenable, since the colours on molten lead can be obtained as easily when the oxide is molten as when it is solid. The sequence of colours obtained on iron and lead as above and also by exposing silver to iodine vapour and copper to hydrogen sulphide corresponds fairly well with that expected from the interference theory. Furthermore on removing the lead oxide film the colours seen by transmitted light are complementary to those seen by reflected light. The author considers that Tammann and Köster (*A.*, 1922, ii, 831) were justified in using the interference principle to follow the velocity of the growth of films but that the principle may have been applied incorrectly.

N. H. H.

**Densities of certain Aqueous Potassium Chloride Solutions as Determined with a New Pycnometer.** H. C. PARKER and E. W. PARKER (*J. Physical Chem.*, 1925, 29, 130—137).—A modified type of Sprengel pycnometer is described. The capacity is about 100 c.c. and it has a calibrated capillary stem which obviates the filling of the pycnometer to an exact volume. The densities of 0.099271*N*, 0.1*N*, and 0.01*N* solutions of potassium chloride are 1.004840, 1.004881, and 1.000372 respectively, based on the value 0.9998406 for water at 0°. The accuracy is about 1 part in a million parts.

M. B. D.

**Densities of Solutions of Aluminium Chloride in Phosgene [Carbonyl Chloride].** A. F. O. GERMANN (*J. Physical Chem.*, 1925, 29, 138—141; cf. *A.*, 1924, ii, 674).—The density of pure carbonyl chloride at 0° and 25° is 1.4275 and 1.3685, respectively. The density of solutions of aluminium chloride in carbonyl chloride has been measured at these temperatures, and over the range investigated (0—50% aluminium chloride) varies linearly with the percentage of aluminium chloride present.

M. B. D.

**Alteration of the Volume Contraction on Solution.** J. N. RAKSHIT (*Z. Elektrochem.*, 1925, 31, 97—101).—The contraction which occurs when various substances are dissolved in water and ethyl alcohol has been measured at different concentrations. A summary of previous work is given and the theory of the alteration of contraction with dilution discussed. The present results agree in general with van Laar's hypothesis.

N. H. H.

**Neutralisation of Chloric Acid by Alkalis Studied by Viscosity Measurements.** L. J. SIMON (*Compt. rend.*, 1924, 179, 822—825).—Chloric acid, on neutralisation with sodium or potassium hydroxide, gives results similar to those previously

obtained with polybasic acids (A., 1923, ii, 219; 1924, ii, 335, 455). The differences previously observed between the two alkalis also apply to the present case.

H. J. E.

**Refractometric Studies of Neutralisation.** F. S. HAMMETT (*J. Franklin Inst.*, 1925, **199**, 91—98).—The refractive index of mixtures of strong and weak mono-, di-, and tri-basic acids (hydrochloric, acetic, sulphuric, oxalic, phosphoric, and citric) and strong mono-acidic bases (sodium and potassium hydroxides) is a linear function of the salt concentration when excess of base is present. The linear relation also holds for excess of acid when the acids are monobasic, but not when di- or tri-basic acids are involved. This is ascribed to the formation of acid salts.

L. F. G.

**Electrolyte-free, Water-soluble Proteins. II. Effect of Carbon Dioxide.** I. M. ADOLF and W. PAULI (*Biochem. Z.*, 1924, **152**, 360—372).—The preparation by electro-dialysis of highly purified serum-albumin, egg-albumin, and "glutin" (gelatin) is described. The conductivity of such pure proteins rises on contact with air, and is again lowered by electro-dialysis to a constant value corresponding with the hydrogen ions and negative protein ions present. It is suggested that the increase of conductivity, which does not affect the hydrogen-ion concentration, the isoelectric point, or the anodic migration of the protein, is due to the formation of equivalent amounts of negative and positive protein ions associated with positive hydrogen and negative hydrogen carbonate ions, respectively.

J. P.

**Distribution of Particles in Colloidal Suspensions.** W. W. BARKAS (*Trans. Faraday Soc.*, 1925; advance proof).—The constants in the equation given by Porter and Hedges (A., 1923, ii, 743), viz.  $\log_e n/(1 - bn) + 1/(1 - bn) = Ky + A$ , are empirical. These constants should have values which depend on the size and mass of the particles, and an attempt has been made to determine them for suspensions of gamboge, copper, and silver. Sols containing particles between certain narrow limits of size were used, the determination of the distribution being carried out in a specially constructed cell by the method of counting. Values of  $K$  were determined, and from the equation  $K = gNm(u - \gamma)/R_0Tu$  the values for the limiting radius of the gamboge, silver, and copper particles were found to be  $1.85 \times 10^{-5}$  cm. ( $K = 120$ ),  $4.32 \times 10^{-6}$  cm. ( $K = 80$ ), and  $6.47 \times 10^{-6}$  cm. ( $K = 220$ ), respectively. These values were checked by measurement of the rate of fall of thin cloud in uncentrifuged solution, and good agreement was obtained with gamboge and copper particles. In the derivation of the equation it is assumed (1) that the particles are spherical, (2) that Stokes' law is obeyed, and (3) that the particles exist in the pure state in the solution. With regard to (1), it was observed with the larger particles of gamboge that the diffraction rings are of irregular intensity, from which it is inferred that these particles are not spherical. The formula of Porter and Hedges appears to hold within the limits of experimental error.

L. L. B.

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**Law of Distribution of Particles in Colloidal Suspension. Specific Volume of a Gamboge Suspension.** J. R. H. COUTTS (*Trans. Faraday Soc.*, 1925; advance proof).—Measurements of the densities of gamboge suspensions by means of a pycnometer show that there is no measurable change in volume in the formation of these suspensions. L. L. B.

**Connexion between Osmotic Pressure, Swelling Pressure, and Adsorption.** M. PÓLÁNYI (*Z. physikal. Chem.*, 1925, **114**, 387—393; cf. A., 1914, ii, 720).—The author has derived the relation  $c' - c + (dc'/d \log_e C)_{c=\text{const.}} = c/RT \cdot dP/dc$ , where  $c'$  is the crystalloid concentration in the solution containing colloid,  $c$  the crystalloid concentration in the crystalloid solution,  $C$  the colloid concentration, and  $P$  the swelling pressure or osmotic pressure. Its validity is confirmed within the limits of error by Loeb's data for gelatin phosphate. L. L. B.

**Stability of Arsenious Sulphide Hydrosol and Velocity of Colloidal Particles Moving under the Influence of Gravity.** A. DUMANSKI (*Kolloid-Z.*, 1925, **36**, 98—99).—The particles of an arsenious sulphide sol, kept under observation for 4 years, fell at a constant rate of 0.031 cm. per day. E. M. C.

**Colloidal Lead Dioxide from Lead Tetra-acetate.** A. GUTBIER and H. O. MEYER (*Z. anorg. Chem.*, 1924, **141**, 95—100).—Perfectly dry lead tetra-acetate, prepared by the method of Dimroth and Schweizer (cf. A., 1923, ii, 744), was found to decompose immediately in presence of water, giving lead dioxide. To prepare colloidal lead dioxide from the acetate, the latter (1.5 g.) should be slowly added, at the ordinary temperature and with rapid stirring, to a 0.3% solution of gum arabic (250 c.c.) to which 0.2N-ammonia solution (30 c.c.) has been added. The sol is filtered from small quantities of brown precipitate, and dialysed as rapidly as possible. The pure preparation is dark brown. A white precipitate of hydrated lead dioxide separates slowly on long keeping. L. L. B.

**Colloidal Sugar. I.** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36**, 118—122).—When solutions of dextrose in commercial absolute alcohol or acetone are poured into a large excess of ether at the ordinary temperature, the crystallisation process passes through a marked colloidal stage, lasting about 2 hrs. The suspensions produced by pouring alcoholic dextrose solutions into benzene, toluene, or xylene are much more stable and show violet, deep blue, or green shades with a strong opalescence in the complementary colours. E. M. C.

**Cholesterol and its Esters.** E. KEESER (*Biochem. Z.*, 1924, **154**, 321—327).—Methods are described for preparing stable sols of cholesterol and lecithin. Both sols diminish the stability of negatively charged colloids. The activity of the sols of the fatty acid esters of cholesterol in diminishing the stability of negatively charged colloids is reduced as the length of the carbon chain in the homologous series is increased. A cholesterol sol has a considerably

lower surface tension than pure water. Its fatty acid esters are less active in lowering the surface tension of water, the activity again falling off as the molecular weight increases. The constant proportion existing in the organism between free cholesterol and its esters has an important bearing on the physical state of the body colloids.

H. D. K.

**Colloids and Mineral Waters.** E. HENRIJEAN and W. KOPACZEWSKI (*Compt. rend.*, 1924, 179, 909—912).—The surface tension of coloured negative colloid solutions is equal to, and that of positive colloid solutions is less than that of distilled water. A similar difference is found when distilled water is mixed with the colloid. On substituting mineral water for the distilled water, the effect is reversed; this is attributed to the presence of a positive colloid in the natural water. If a natural mineral water is replaced by an artificial preparation of identical chemical composition, no such reversal is observed. The conclusion is reached that the ferruginous mineral water used in the experiments (Spa, Source Pierre-le-Grand) contains an electropositive hydrosol of iron.

H. J. E.

**Colloids and Mineral Waters.** D'ARSONVAL and BORDAS (*Compt. rend.*, 1924, 179, 912—913; cf. preceding abstract).—Certain mineral waters deposit sediment after being bottled. The deposition of sediment may be avoided by adding carbon dioxide in order to avoid both oxidation and precipitation from acid carbonates. Certain cases of deposition, however, do not seem to be traceable to these two causes.

H. J. E.

**Velocity Function of the Viscosity of Disperse Systems.** I. W. OSTWALD (*Kolloid-Z.*, 1925, 36, 99—117).—It is suggested that the term "structural viscosity" should be used quite generally in referring to the deviations from Poiseuille's law which are shown by certain colloidal solutions. Such deviations are shown in the influence of change of pressure or rate of flow on the viscosity. Even for colloids exhibiting "structural viscosity," measurements with the Ostwald type of viscosimeter are trustworthy. A simple pressure-viscosimeter is described for measuring the effect of variations in the rate of flow. The capillary viscosimeter is modified by using a short, narrow capillary with an upper bulb in the form of a flat lens and by increasing the length of the arms to 20—50 cm. The filling tube is wide and is graduated throughout its length. The instrument is calibrated for water for different heights of filling. If  $t_w$  and  $t_k$  are the times of flow for water and for the colloidal solution, for the same height, and if  $k_1, k_2$ , etc., are constants, the results for a large number of colloidal solutions may be expressed by  $t_k = k_1 \cdot t_w^n$  with an accuracy of 1—2%. In some cases better agreement is given by  $t_k = t_w^n + k_2 \cdot t_w^n$  or  $t_k = k_3(t_k - t_w)^n$ . Similar equations hold for measurements with the Hess and the Couette apparatus. The exponent  $n$ , which measures the "structural viscosity," is greater than 1; the highest value found was 1.75 for

a 1% caoutchouc sol in benzene. The constant  $k$  is generally less than 1, but may be greater. For colloidal solutions, such as those of gelatin, reduction of concentration or heating causes both constants to approach the value 1. Since colloidal solutions, like their dispersive media, probably give values for  $k$  less than 1 for higher pressures and turbulent motion, the complete relationship between velocity of flow and pressure will be represented by a sigmoid curve.

E. M. C.

### Physico-chemical Properties of Gelatin. Rotatory Power.

F. VLÈS and E. VELLINGER (*Compt. rend.*, 1925, **180**, 439—442).—The mutarotation and rotatory power of gelatin gels at various  $p_H$  values have been investigated at 40° and at the ordinary temperature (12—15°). The diffusion of light by the gels and the resulting polarisation have also been studied in their relation to the  $p_H$  value of the gel. The light diffused is a maximum at the isoelectric point ( $p_H$  4.7) and passes through minima at  $p_H$  values 2.6 and 13. Freshly-prepared samples exhibit mutarotation at the ordinary temperature, but not at 40°. The phenomenon is most pronounced at the isoelectric point. The rotatory power (negative) at 12—15° plotted as a function of  $p_H$  exhibits a pronounced maximum at the isoelectric point and two minima, one at  $p_H$  3 and the other well on the alkaline side. The rotation is more pronounced for blue than for yellow light. At 40° there is a slight minimum at  $p_H$  4.7. The mutarotation is due to the slow conversion of a system stable at 40° into one stable at 12—15°, the rate of change being retarded by the viscosity of the medium. The development of a maximum value in the rotation is attended by the parallel development of an opalescence, showing the change to be accompanied by a modification of the physical structure. The interpretation of the  $p_H$ -rotatory power diagram is considered.

J. S. C.

### Osmotic Pressure of Hæmoglobin. Explanation of the Effect of Acetic Acid, based on Donnan's Theory of Membrane Equilibrium.

H. C. WILSON (*Biochem. J.*, 1925, **19**, 80—83).—When hæmoglobin is dialysed in an osmometer against acetic acid, there results a four- to six-fold increase in osmotic pressure above the value against distilled water. The hydrogen-ion concentration of the hæmoglobin solution is considerably less than that of the acetic acid solution. It is supposed that hæmoglobin acetate is formed.

S. S. Z.

### General Character and Electrical Properties of Gels.

F. MICHAUD (*J. Chim. physique*, 1924, **21**, 386—395; cf. *A.*, 1923, ii, 134; *Compt. rend.*, 1924, **178**, 993).—An electrical double layer exists at the surface of a gel which itself consists of a network of canals filled with liquid, the radii of the canals being less than that of the double layer. Adsorption occurs and is general; the negative charges only can penetrate the canals. Addition of alkali increases the charge on the double layer, the attraction between the charges is increased, and the canals expand to allow the positive charges to enter, as a result of which the gel expands. Conversely, acids produce contraction, but, if the acid is sufficiently strong, it may reverse

the sign of the double layer and expansion will then occur, as in the case of gelatin. The deformation of gels by electric currents is due to electrical osmosis, and prolonged passage of the current results in the drying of the gel at the anode, whilst liquid collects round the cathode. Conversely, a difference of potential is produced if the gel is pressed, owing to the liquid being forced along the canals. A complete explanation of the above phenomena must take account of both chemical and adsorption processes. Gels are an essential constituent of living matter, and certain muscular and nervous effects may be due to their properties. If a current is passed through a nerve, the latter is more excitable at the cathode, possibly owing to the production of liquid as in the case of gels. W. H.-R.

**Electro-dialysis of Agar.** E. H. HARVEY (*Amer. J. Pharm.*, 1925, 97, 66—70).—By subjecting agar sols to a preliminary treatment with 0.5% acetic acid and water and then to electro-dialysis for 12 hrs. at 50°, the ash content on a dry basis was reduced from 3.75% to 0.81%. E. M. C.

**Chemical Theory of the Protective Action of Sugars. II.** D. L. SHRIVASTAVA, R. S. GUPTA, M. PRASAD, and S. S. BHATNAGAR (*J. Physical Chem.*, 1925, 29, 166—177; cf. A., 1924, i, 942).—Adsorbed sugars (sucrose, arabinose, mannose, maltose, lævulose, and xylose) do not contribute to the rotation observed when the sugar is dissolved in a colloidal solution (cadmium, antimony, and arsenic sulphides, and selenium). Similar observations made with aluminium stearate and palmitate, zinc oleate, and magnesium oxide lead to the same conclusion. The change in optical activity is not due to mutarotation produced by the dissolving agents. M. B. D.

**Conditions of Precipitation, by Electrolytes, of Selenium Hydrosol and Other Hydrosols.** J. J. DOOLAN (*J. Physical Chem.*, 1925, 29, 178—187).—The coagulating powers of various electrolytes have been determined for selenium and tellurium hydrosols. The results are not in accord with Whetham's law (A., 1900, ii, 62). M. B. D.

**Ionic Conflict and its Relations with the Physico-chemical Constants of Plasma.** A. H. ROFFO and L. M. CORREA (*J. Chim. physique*, 1924, 21, 466—468).—Certain physiological properties of blood plasma depend on the value of the ratio  $(\text{Na} + \text{K})/(\text{Mg} + \text{Ca})$  formed by the four chief mineral elements. The value of this ratio is also responsible for the physical properties of some colloids. In determining the physical properties of plasma, it is necessary to add oxalate to prevent coagulation. Test portions of blood were treated with just sufficient oxalate to prevent coagulation and plasma was prepared by centrifuging. When this plasma was treated with quantities of sodium oxalate increasing from 1 to 10 mg., the surface tension gradually increased from 60.50 to 60.92 dynes, a more rapid increase to 70.4 dynes occurring when 12 mg. of sodium oxalate were added. The weights of the test portions are not stated. W. H.-R.



**Dissociation of Chlorine into Atoms.** M. TRAUTZ and F. GEISSLER (*Z. anorg. Chem.*, 1924, **140**, 116—148).—The amount of chlorine present in a porcelain vessel of known volume at atmospheric pressure was determined for temperatures between 1151 and 1264°, and compared with that calculated after making allowances for the departure of chlorine from the simple gas laws. From the temperature coefficient of the equilibrium constant the heat of decomposition is  $59500 \pm 200$  cal. The chemical constant calculated from the isochore lies between 0.54 and 2.27, which differs considerably from that calculated by Stern's formula. L. J. H.

**Equilibrium of Gases in the Reaction of Explosives.** N. YAMAGA (*J. Fac. Eng. Tokyo Imp. Univ.*, 1924, **15**, 207—271).—Calculations in the theory of explosives based on the analysis of the gaseous products are incorrect owing to the change of equilibrium constant during cooling. The equilibrium at the moment of explosion is that of the water-gas reaction. During cooling methane is formed by the reactions  $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ ,  $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$ , and  $4\text{CO} + 2\text{H}_2\text{O} = \text{CH}_4 + 3\text{CO}_2$ . These reactions occur only below 1500°, the stability temperature of methane. The equilibrium constants of the water-gas and methane reactions were calculated by the Nernst heat theorem, using the specific heat data of Piers and of Bjerrum. The constants given by these equations are compared with those given by the expressions of several other authors. All equations are satisfactory up to 2000° Abs. Above this, wide divergences occur except between the author's equations and that of Nernst. A consideration of the thermodynamic relations of gas mixtures based on van der Waals' equation shows that at high temperatures actual gas mixtures may be treated as ideal. On this basis a graphical method is developed by which the temperature and heat of explosion, and the equilibrium at the moment of explosion, may be derived from the analysis of the explosive and its heat of formation. F. G. T.

**Equation for the Haber Equilibrium.** L. J. GILLESPIE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 73—74).—The equations  $\log Kp = (2679.35 + 1.1184p)/T - (5.8833 + 0.001232p)$  and  $\log Kp = (2172.26 + 1.99082p)/T - (5.2405 + 0.002155p)$  represent the values of the equilibrium constant over the temperature range 325—500° at pressures up to, and greater than, 100 atm. respectively. Attempts to obtain a single equation for high and low pressure data failed because of certain discontinuities. Haber's data for 30 atm. do not agree with the above equation. An explanation of the discrepancy is offered. J. S. C.

**Electrolytic Dissociation of Dibasic Acids. II. Second Dissociation Constants.** E. LARSSON (*Z. anorg. Chem.*, 1924, **140**, 292—300).—The second dissociation constants at 18° of 14 organic acids measured by the author's electrometric method (cf. A., 1923, ii, 55) are shown to agree with values calculated from the formula previously given, and with those obtained by other methods. The values for oxalic acid,  $7.1 \times 10^{-5}$ , and maleic acid,  $5.1 \times 10^{-7}$ ,

are higher than those found by Chandler (cf. A., 1908, ii, 467), but are supported by other evidence. Bjerrum's  $n$  and  $r$  factors (A., 1923, i, 1059) are calculated for the acids investigated; those obtained for a series of dibasic  $\alpha$ -thio-fatty acids indicate that the carboxyl groups in racemic acids are about 0.8 Å. nearer than in the corresponding *meso*-compounds. The value of  $n$  tends to increase as ethylenic linkages are introduced into the molecule. S. K. T.

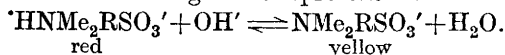
### Aqueous Solutions of Carbon Dioxide and Carbonic Acid.

C. FAURHOLT (*J. Chim. physique*, 1924, **21**, 400—455).—The equilibria between carbon dioxide, carbonic acid, and carbonate and hydrogen carbonate ions in aqueous solutions of different acidity were investigated in detail. Buffer solutions of formates, acetates, cacodylates, phosphates, borates, and carbonates with their respective acids were used to give solutions of known  $p_H$  value. To these were added solutions of carbonic acid, and, after a measured interval, excess of dimethylamine; the latter combines with carbonate or carbonic acid to form a carbonate, and with molecular carbon dioxide ( $\text{CO}_2$ ) to form a carbamate, the relative amounts of the two being determined. In some cases corrections have to be applied owing to variation of the  $p_H$  value during the experiment, but the original must be consulted for these. Carbon dioxide is hydrated in two ways, represented by the equations (1)  $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$ , and (2)  $\text{CO}_2 + \text{OH}' = \text{HCO}_3'$ . These reactions take place simultaneously, but for values of  $p_H < 8$  the hydration is almost entirely due to reaction (1), whilst for values of  $p_H > 10$  reaction (2) predominates. Between these limits the two reactions take place with comparable velocity, but the agreement between calculated and experimental values is not good, owing possibly to side reactions with the (borate) buffer solution. The velocity coefficients of the reactions (1) and (2) are respectively 0.0013 and 405 at 0° and 0.011 and 1740 at 18°. Dehydration occurs by the reversal of reactions (1) and (2), reaction (1) predominating in acid solutions. The values of the dehydration velocity coefficients at 0° and 18° are  $k_{\text{H}_2\text{CO}_3}$ , 1.16 and 7.1, and  $k_{\text{HCO}_3'}$ ,  $10^{-5.59}$  and  $10^{-4.52}$ , respectively. The total velocity of dehydration varies with the acidity and is a complex function, as the proportions of the initial carbonate existing as  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3'$ , and  $\text{CO}_3''$  vary greatly with the acidity. In strongly acid solution the time taken to reach equilibrium is about 1 sec. and 1/7 sec. at 0° and 18°; with decreasing acidity these times rise to a maximum at  $p_H$  8, being 700 secs. and 80 secs. at the same temperatures, whilst for  $p_H > 9$  the times decrease regularly. At equilibrium, in solutions from  $p_H$  0 to  $p_H$  4.5, less than 2% of the total dissolved carbon dioxide is in the form of carbonic acid or carbonate or hydrogen carbonate ion; in alkaline solutions ( $p_H$  12 to 15) almost the whole exists as carbonate ( $\text{CO}_3''$ ) ion. The values of the first and second dissociation constants of carbonic acid are determined as  $2 \times 10^{-4}$  and  $10^{-10.5}$  respectively at 0°. In reaction (1) above, the equilibrium constant  $K_{\text{hydrate}} = a_{\text{H}_2\text{CO}_3}/a_{\text{CO}_2}$  is 1/891 at 0°, and 1/646 at 18°. The solutions of carbon dioxide used varied from 0.2 to 0.5 M.

W. H.-R.

**Condition of Methyl-orange in its Transition Interval.**

I. M. KOLTHOFF (*Rec. trav. chim.*, 1925, **44**, 68—74).—Bjerrum's theory of salt-like double ions is applied to the case of methyl-orange, and the colour change thus represented:



Methyl-orange fulfils the criteria for a basic indicator (cf. A., 1922, ii, 156; 1923, ii, 330) and the dissociation constant of the base is of the same order as that of dimethylaminoazobenzene. The sulphonc acid group behaves as a very strong acid. F. M. H.

**Condition of Methyl-red in its Transition Interval.**

I. M. KOLTHOFF (*Rec. trav. chim.*, 1925, **44**, 75—81).—By means of partition experiments with the aqueous solution and light petroleum near the isoelectric point ( $p_H$  3.9) of *o*-methyl-red (dimethylaminoazobenzene-*o*-carboxylic acid), it is found that at 15°  $k_b = 2.5 \cdot 10^{-12}$  and  $k_a = 9 \cdot 10^{-6}$ . According to Bjerrum's theory (A., 1923, i, 444), the red double ion 'HNMe<sub>2</sub>RCO<sub>2</sub>' forms with acids 'HNMe<sub>2</sub>RCO<sub>2</sub>H and with bases NMe<sub>2</sub>RCO<sub>2</sub>'. At  $p_H$  4—6, *o*-methyl-red behaves as a base,  $k_b$   $7 \cdot 10^{-10}$ ,  $k_a$   $2.5 \cdot 10^{-3}$ . Similarly, the behaviour of *p*-methyl-red is best explained by the theory of double ions, and for it are found  $k_b$   $10^{-10.5}$  and  $k_a$   $10^{-3.3}$ . F. M. H.

**Cryoscopic Measurements with Nitrobenzene. III. Equilibrium in Nitrobenzene Solution.**

F. S. BROWN (*J. Chem. Soc.*, 1925, **127**, 345—348; cf. this vol., ii, 32).—The dissociation of naphthalene picrate and of naphthalene-trinitrotoluene have been investigated by cryoscopic measurements of their solutions in moist nitrobenzene in the presence of partially dehydrated Glauber's salt. The dissociation obeys the law of mass action. The free energy of formation of naphthalene picrate at 3° is calculated as 2083 cal. per mol. in agreement with values obtained by Brönsted (A., 1912, ii, 20) from *E.M.F.* measurements. W. H.-R.

**Deliquescence of Salts.** K. SCHERINGA (*Pharm. Weekblad*, 1925, **62**, 185—190).—A solid salt becomes liquid on exposure by attraction of water from the air when the vapour pressure of its saturated solution, at the temperature prevailing, is less than 65% of the vapour pressure of water at that temperature, but remains dry if this figure is over 70%, the relative humidity of the atmosphere being usually about 65%. Tables showing this percentage pressure for various salts at various temperatures and pressures are given.

S. I. L.

**Lithium. III. Lithium Hydride.**

G. F. HÜTTIG and A. KRAJEWSKI (*Z. anorg. Chem.*, 1925, **141**, 133—160; cf. A., 1924, ii, 756).—The dissociation pressure of lithium hydride has been measured at various temperatures. The hydride was prepared by a modification of Moers' method (A., 1921, ii, 200), the maximum yield being obtained at 750°. Hydrogen attacks the molten lithium at temperatures above 400°, yielding a product which contains 98.77%

of the hydrogen required for the formula  $\text{LiH}$ . Sublimation is accompanied by decomposition, the hydrogen not recombining with the lithium, and the hydride is extremely unstable in air. As the percentage of hydrogen in the sample increases so the pressure increases, an extremely rapid increase occurring as the hydrogen content approaches that required for the composition  $\text{LiH}$ ; this behaviour is similar to that observed with magnesium halide-ammonia systems investigated by Biltz and Hüttig (A., 1922, ii, 59), and is said to afford additional evidence that lithium hydride is a true compound. A difference of 0.02% in the hydrogen content doubles the pressure. The period required for the attainment of a constant pressure value varies very largely for different investigations and different temperatures and the experimental results are broadly represented by two typical curves, one for high temperatures and the other for low temperatures. The values for the dissociation pressure of a solid phase of composition  $\text{LiH}_{0.987}$  are, at temperatures of  $150^\circ$ ,  $170^\circ$ , and  $190^\circ$ ,  $p(\text{mm.})=0.05$ ,  $0.11$ , and  $0.34$ , respectively. At the ordinary temperature ( $23.5^\circ$ ) the observed pressure was  $0.023$  mm., which shows a large discrepancy from the value ( $4.57 \times 10^{-22}$  mm. at  $13^\circ$ ) calculated by Moers (*loc. cit.*) from the heat of formation and specific heat data. If a preparation which has been decomposed at high temperature is left for a time at the ordinary temperature and then again heated at the higher temperature the hydrogen pressure measured is greater than that recorded when the heating is uninterrupted. With a solid phase containing a large excess of metallic lithium no extremely small dissociation pressures are obtained such as are required on thermochemical grounds. In explanation, it is suggested that the hydrogen ion eliminated is freely mobile and diffuses throughout the system, producing a homogeneous phase. The calculated heat of the reaction is also in good agreement with the experimental value obtained by Gunz,  $2\text{Li} + 1.00\text{H}_2 = 2\text{LiH} + 43,200$  cals. Arbitrary extrapolation of the value of the dissociation pressure to that of pure lithium hydride yields a value greater than 1 atm. From the experimental  $p/t$  value the heat of reaction is calculated by use of the Nernst equation, and certain X-ray spectroscopic measurements are recorded. In pure lithium hydride, the arrangement of the lithium ion is a face-centred cubic lattice and the distance between the middle points of the lithium and hydrogen ions is calculated to be  $2.00 \times 10^{-8}$  cm. The energy liberated by the combination of metallic lithium with gaseous hydrogen ( $2\text{Li} + \text{H}_2 = 2\text{LiH}$ ) at absolute zero is calculated to be  $U_0 = 40,775$  cals., whilst that for the reaction of two atoms of lithium with 1 mol. of hydrogen to produce 2 mols. of lithium hydride is practically zero.

J. W. B.

**Alpha Phase Boundary in the Copper-Zinc System.** R. GENDERS and G. L. BAILEY (Inst. Metals, Mar., 1925; advance copy, 9 pp.).—The  $\alpha$  phase boundary in the copper-zinc system is a straight line perpendicular to the axis of composition up to  $450^\circ$  at 61% Cu; above this temperature it inclines in a slightly curved line to meet the solidus at about  $906^\circ$  and 67.5% Cu. Alloys containing 61—

63% Cu consist of pure  $\alpha$  at the ordinary temperature, but on heating above 450° this is progressively transformed into  $\beta$  until above 800° the change is complete. [Cf. *B.*, 1925, 246.] A. R. P.

### Equilibrium Diagram of the Aluminium-Zinc System.

T. ISIHARA (*Inst. Metals*, Mar., 1925; advance copy, 17 pp.).—According to measurements of the electrical conductivity the solubility of aluminium in solid zinc falls from 1% at the m. p. to 0.3% at 20°, whilst the solubility of zinc in solid aluminium is 22.5% at 20°, 30% at 280°, and 60% at 440°. The eutectic contains 5% Al and melts at 380°, the peritectic line at 440° extends from 13% to 41% Al and the eutectoid line at 280° from 0.3% to 65% Al. The eutectoid contains 21% Al and is formed by the decomposition of the unstable  $\beta$  phase, which appears to consist of a solid solution of an unknown compound in  $\alpha$ , into  $\beta + \gamma$ . In alloys containing  $\beta$  a transformation similar to the A2 transformation in iron takes place at 340–360°. [Cf. *B.*, 1925, 246.] A. R. P.

### Ternary System Molybdenum-Nickel-Silicon.

PFAUTSCH (*Z. Metallk.*, 1925, 17, 53–56).—Besides the binary compounds  $\text{MoSi}_3$ ,  $\text{MoSi}_2$ ,  $\text{MoNi}$ ,  $\text{Ni}_2\text{Si}$ ,  $\text{Ni}_3\text{Si}_2$ , and  $\text{NiSi}$ , the system molybdenum-nickel-silicon contains two ternary compounds  $\text{Ni}_3\text{Mo}_2\text{Si}$  and  $\text{Ni}_4\text{MoSi}_2$ . The former is stable at all temperatures below 2100°, when it melts unchanged, but the latter decomposes below 850° as follows:  $2\text{Ni}_4\text{MoSi}_2 = \text{Ni}_3\text{Mo}_2\text{Si} + \text{Ni}_3\text{Si}_2 + \text{Ni}_2\text{Si}$ . The silicide,  $\text{NiSi}$ , forms a eutectic with the stable ternary compound. All the alloys in this system with the exception of those rich in nickel and consisting of homogeneous mixed crystals are very hard and brittle. [Cf. *B.*, 1925, 247.] A. R. P.

### Ternary System Chromium-Nickel-Molybdenum.

E. SIEDSCHLAG (*Z. Metallk.*, 1925, 17, 53–56).—No ternary compounds are formed in this system, but there is evidence of the formation of a ternary eutectic containing between 5 and 10% Ni. The structure of the alloys rich in nickel consists of a homogeneous mixed crystal phase, but all other alloys contain two or three phases consisting of the compound  $\text{MoNi}$ , molybdenum containing small quantities of nickel and chromium in solid solution, and the homogeneous mixed crystal phase. The alloy containing 60% Ni, 20% Mo, and 20% Cr is only very slightly attacked by hot hydrochloric acid or by hot dilute sulphuric acid and unattacked by solutions of the alkali hydroxides. [Cf. *B.*, 1925, 247.] A. R. P.

### Dissociation Equilibria of Compounds of Ferrous Salts with Nitric Oxide.

W. MANCHOT [with H. HAUNSCHILD] (*Z. anorg. Chem.*, 1924, 140, 22–36).—Old data (A., 1907, ii, 93) and some from new determinations are combined to obtain the equilibrium constant for the dissociation of the substance  $\text{FeSO}_4 \cdot \text{NO}$ . This compound is exothermic (11,900 cal.), and its dissociation increases with rise of temperature. No relationship exists between the ionisation and complex formation, but it is believed that addition

takes place in the first instance to the undissociated molecule. At higher temperatures oxidation occurs. L. J. H.

**Equilibrium of the Reciprocal Salt System Sodium Chloride-Magnesium Sulphate with Reference to Natural Salt Solutions.** N. S. KURNAKOV and S. F. SHEMTSCHUSHNI (*Z. anorg. Chem.*, 1924, **140**, 149—182).—The quaternary system  $\text{H}_2\text{O}-(\text{Mg}^{++}\text{Na}_2^{++})-(\text{Cl}_2-\text{SO}_4^-)$  was studied at  $0^\circ$  and  $25^\circ$ . At the lower temperature there are four solid phases, viz.,  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ . At  $25^\circ$ , the solid phases  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , and astrakanite,  $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$  are formed. Tables of data and projections of the space models for both temperatures are given.

The paths of crystallisation are discussed.

L. J. H.

**Heats of Solution and of Decomposition of Chlorine Dioxide.** H. BOOTH and E. J. BOWEN (*J. Chem. Soc.*, 1925, **127**, 342—345).—Mixtures of chlorine dioxide and carbon dioxide were passed into water contained in a vacuum-jacketed calorimeter, and the rise in temperature was compared with that produced by the expenditure of a known amount of electrical energy. The heat of solution is  $6600 \pm 200$  cal./mol. independent of the concentration of the solution produced. The heat of decomposition is 23,500 cal./mol., and was determined by sparking a mixture of chlorine dioxide and carbon dioxide in a vacuum-jacketed vessel containing a small thermocouple, the rise in temperature being compared with that produced by the expenditure of a known amount of electrical energy through a heating coil. The heat of dissociation of a molecule of chlorine dioxide is then calculated as  $\text{ClO}_2 = \text{Cl} + \text{O}_2 - 4000$  cals., the small energy change corresponding with two vibrational quanta. Since the gas is stable thermally, the energy of vibration is not sufficient to activate a molecule chemically but electronic activation is required.

W. H.-R.

**Graphitic Conduction in Conjugated Chains of Carbon Atoms.** T. M. LOWRY (*Nature*, 1925, **115**, 376—377).—If the view is accepted that at each stage of an isomeric change involving migration of an atom the intermediate double bonds of the conjugated system are ionised, it is possible to explain the mechanism of such an action harmoniously with Armstrong's dictum that "chemical action is reversed electrolysis." The process, called "graphitic conduction," is analogous to metallic, and not to electrolytic conduction.

A. A. E.

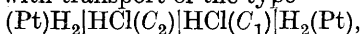
**Conductivity Measurements of Very Dilute Solutions.** H. REMY (*Z. Elektrochem.*, 1925, **31**, 88—95).—For conductivity measurements in very dilute solutions, the use of "ultra-pure" water can be avoided if the impurity in "conductivity water" be limited to the least practicable amount of carbonic acid the influence of which on the conductivity may be calculated on the basis of the law of mass action. A simple method is described for testing the compliance of a sample of water with this condition. The solubility

of a number of sparingly soluble oxides has been determined in this way by conductivity measurements and the results are in good agreement with those obtained by conductometric titration and (where possible) gravimetric analysis. N. H. H.

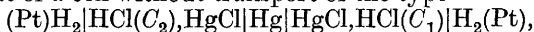
**Velocity of the Hydrogen Ion in Gels under the Action of the Electric Current.** N. ISGARISCHEV and A. POMERANZEVA (*Z. Elektrochem.*, 1925, **31**, 101).—An answer to the explanation offered by Liesegang (*ibid.*, 1924, **30**, 449) of the "inertia" of the hydrogen ion in gels, previously described by the authors (A., 1924, ii, 90). Experiment shows that there is no appreciable difference in the velocity of the hydrogen ion whether *N*- or 2*N*-sulphuric acid be used. N. H. H.

**Migration of Ions in Solid Electrolytes.** C. TUBANDT and H. REINHOLD (*Z. Elektrochem.*, 1925, **31**, 84—88).—A reply to the suggestion of Le Blanc and Kröger (this vol., ii, 41) that the unidirectional ion migration in solid electrolytes found previously by the authors is a consequence of the prevailing experimental conditions. For a given substance, it is always the same ion which moves by diffusion and current conductance, irrespective of the conditions. N. H. H.

**Diffusion Potential and Transport Number of Hydrochloric Acid in Concentrated Solution.** S. R. CARTER and F. M. LEA (*J. Chem. Soc.*, 1925, **127**, 487—494).—The diffusion potentials between *N*-hydrochloric acid and solutions of concentration from 1.0—11.5*N* have been investigated. The usual diffusion potential formula requires correction for the vapour pressure of the solutions, and for the variation of transport numbers between solutions of widely differing concentration. If  $\epsilon'$  is the observed potential of a cell with transport of the type



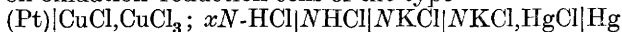
and  $E'$  that of a cell without transport of the type



the diffusion potential  $\pi$  can be expressed by the relation

$$\pi = E' - \epsilon' + RT/4F \cdot \log (b-c)/(b-c')$$

where  $b$  is the barometric pressure,  $c$  and  $c'$  are the vapour pressures of the dilute and concentrated solutions, respectively. By means of this formula the diffusion potentials between hydrochloric acid solutions have been calculated from observations on the above types of cells, and the results are satisfactorily confirmed by measurements on oxidation-reduction cells of the type



and a similar cell without transport. The values are, however, much higher than those calculated from conductivity-viscosity data assuming a constant transport number. The results confirm the equation of Dolezalek (A., 1898, ii, 421) for the calculation of the *E.M.F.* of a concentration cell from vapour-pressure measurements, and show that the calomel-mercury electrode is suitable as an anodically reversible electrode in concentrated hydrochloric acid.

W. H.-R.

**Measurements in Series with the Gas Cell.** E. WÖHLISCH (*Biochem. Z.*, 1924, 153, 129—130).—A simple arrangement is described for rapidly connecting any one of a series of gas electrodes with a potassium chloride-calomel electrode. J. P.

**Concentration Cells in Methyl Alcohol. II. Solutions containing Tetraethylammonium Iodide.** J. GRANT (*Trans. Faraday Soc.*, 1924, 20, 385—390; cf. A., 1924, i, 150).—Using silver-plated platinum electrodes immersed in a paste of precipitated silver iodide, concentration cells containing solutions of tetraethylammonium iodide of different dilutions were made, and the electromotive forces measured at 25°. The transport numbers of the cation calculated from these results by the equation of Nernst are appreciably lower than those obtained by Carrara (A., 1903, ii, 708), using the direct method, but like the latter they increase with the dilution, and reach an approximately constant value of 0.280 at very great dilutions, and this may be taken as the true transport number when complex ions no longer exist. The form of the curves indicates that the term  $n_c$  in the Nernst equation does not really represent the value of the transport number for the mean dilution of the two solutions used. W. H.-R.

**Overvoltage as a Function of Current Density and the Effects of Time, Temperature, Stirring, Pressure, Nature of Surface, and of a Superimposed Alternating Current.** W. D. HARKINS and H. S. ADAMS (*J. Physical Chem.*, 1925, 29, 205—219).—The overvoltage of hydrogen on mercury is proportional to the logarithm of the current density at 20°. No appreciable variation of the hydrogen overvoltage on mercury with the pressure (1/36—3 atm.) was found over a wide range of current density. For a range of temperature of 0—80°, the overvoltage is lowered about 2 millivolts per degree and all the curves exhibit considerable time hysteresis. The effect of rotating the cathode is to cause a decrease in the overvoltage on mercury, gold, polished and rough platinum. Stirring with gaseous hydrogen lowers the overvoltage on a tin cathode and subsequent rotation of the cathode has no further effect. When the current density is kept constant the overvoltage increases with time. Superposition of an alternating current (frequency 15—1800 and current density 1—200) lowers the overvoltage except on smooth or rough copper, on which the overvoltage is raised. The relation between the overvoltage and the current density was examined at 25° with cathodes of platinum, tungsten, molybdenum, monel metal, nickel, gold, silver, copper, tantalum, mercury, cadmium, and tin. A rough cathode gives a lower overvoltage than a smooth at the same apparent current density. Members of the same family of elements in the periodic system have nearly the same overvoltage. M. B. D.

**Overvoltage and Surface Forces at the Lead Cathode.** S. GLASTONE (*Trans. Faraday Soc.*, 1925; advance proof).—The minimum overvoltage is said to be a measure of the free energy of the reaction  $2\text{H} \longrightarrow \text{H}_2$ , when the total concentration of gas at the



electrode is sufficient to overcome the capillary forces at the electrode and so permit bubble formation. The influence of the surface tension of the electrolyte on overvoltage has been examined. Mixtures of water with ethyl alcohol, methyl alcohol, acetic acid, *iso*-butyl alcohol, *iso*amyl alcohol, and *isobutyric* acid were used containing sulphuric acid, also buffer solutions in ethyl alcohol and *N*-sodium hydroxide in ethyl alcohol. The addition of ethyl or methyl alcohol or acetic acid lowers the tension of the gas-electrolyte surface and also lowers the overvoltage. *iso*Amyl alcohol and *isobutyric* acid cause the overvoltage first to increase and then to decrease.

L. L. B.

**Electro-endosmosis.** III. F. FAIRBROTHER and H. MASTIN (*J. Chem. Soc.*, 1925, 127, 322—327; cf. *J.*, 1924, 125, 2319).—Using a diaphragm of carborundum powder, the influence of anions and cations on electro-endosmosis and on the difference of potential across the diaphragm have been investigated. Cations tend to annul the original negative charge of the carborundum in water; this effect increases with the valency of the cation, and, with ter- and quadri-valent ions the charge becomes positive and rises to a maximum at a concentration of about  $N/4000$ . In the case of  $Al^{+++}$  and  $Th^{++++}$  ions the sign of the charge is reversed at a concentration of a few micro-mols. per litre. With potassium salts in very low concentrations, the charge is slightly more negative than in water, but becomes less negative with increasing concentration. Anions have comparatively little effect. These results resemble those obtained by Kruyt (*A.*, 1918, ii, 289) for the effects of cations on stream potentials in capillary tubes.

W. H.-R.

**Effect of Superposed Alternating Current on the Anodic Solution of Gold in Hydrochloric Acid.** A. J. ALLMAND and V. S. PURI (*Trans. Faraday Soc.*, 1925; advance proof).—The experiments were made with a gold anode, a platinum cathode, and dilute hydrochloric acid as electrolyte. Without the alternating current the gold anode begins to dissolve at a certain potential, but on increasing the current density the anode becomes passive. By increasing the strength of hydrochloric acid, the potential range over which the gold remains active is increased. Further increase in anodic potential results in evolution of chlorine. Measurements were made of the effect of variation in the frequency, the A.C./D.C. ratio, the concentration of the electrolyte, and the temperature. Potential readings were first taken until chlorine was evolved. This gives the D.C. current density up to which gold remains active. Taking this current density as a standard, alternating currents in the ratio of 0.5, 1, and 2 were successively superposed, and potential readings with increasing D.C. were taken recording (a) anodic potentials, (b) D.C. current densities up to that at which gold is dissolved, (c) D.C. current densities at which chlorine is first evolved, and (d) cell voltages. The activity is defined as the limiting direct current density to which a gold cathode can be subjected without exhibiting passivity, and the percentage increase compared with the value when using direct current is found to increase with (1) increase in acid concentration,

(2) increase of temperature, (3) increase of the ratio A.C./D.C., and (4) decrease of frequency. The dissolution potential of gold is found to be lower (1) the higher the A.C./D.C. ratio, (2) the lower the frequency; and the potential of gold at current density at which dissolution ceases is lower the higher the frequency. Acid concentration and A.C./D.C. ratio have little effect on this value. The potential of initial chlorine evolution is lower (1) the greater the A.C./D.C. ratio, (2) the lower the acid concentration. The effect of frequency here is small. A theory is put forward to explain these results.

L. L. B.

**Effect of Superposed Alternating Current on the Polarizable Primary Cell Zinc-Sulphuric Acid-Carbon. I. Low Frequency Current.** A. J. ALLMAND and V. S. PURI (*Proc. Roy. Soc.*, 1925, A, 107, 126—137).—When an alternating current is superposed on the primary cell, amalgamated zinc-sulphuric acid-carbon, the delivery of direct current from the latter is increased. By studying the behaviour of each electrode separately, when an alternating current is passed through it alone by means of an auxiliary electrode, it has been shown that, contrary to Brown's conclusion (A., 1914, ii, 332), the influence of the alternating current, at least up to frequencies of about 400, is confined almost exclusively to the carbon electrode, a marked depolarisation of the hydrogen-ion discharge therefore taking place. The effect becomes relatively greater as the strength of the alternating current increases, but increase in periodicity reduces the influence. It is suggested that the oxygen discharged during the anodic pulse of the alternating current, by combining with or displacing the "active" hydrogen at the cathode, lowers the electrolytic solution pressure of the latter. The small effect on the zinc electrode is also in the direction of a depolarisation, indicating that, as the electrode behaves reversibly in the absence of an alternating current, the latter causes a dissolving zinc anode to act like a more electropositive metal.

M. S. B.

**Anodic Purification of Mercury.** E. BRUMMER and S. VON NÁRAY-SZABÓ (*Z. Elektrochem.*, 1925, 31, 95—97).—An apparatus is described in which mercury is purified electrolytically. A rotating cup containing the mercury forms the anode. It is constructed so as to stir the electrolyte, which is a solution of mercurous nitrate acidified with nitric acid. The cathode is of platinum. Base metals are thus dissolved out. The results of the purification are described.

N. H. H.

**Electrolytic Corrosion of Ferrous Metals.** W. M. THORNTON and J. A. HARLE (*Trans. Faraday Soc.*, 1925; advance proof).—"Forced electrolytic corrosion" tests are described, in which the specimen is used as anode in a bath of dilute sulphuric acid. During test the anode is kept covered with a film of molecular oxygen. No appreciable amount of gas is given off, except with the rustless metals. By plotting loss of weight against ampère-hours, straight lines are obtained which indicate that there is no skin effect. A

table is given which shows that the alloys investigated fall into two groups. It appears that every ferrous alloy has a definite rate of corrosion if the conditions are kept constant, but it is probable that resistance to air corrosion will always be less than to anodic corrosion.

L. L. B.

**Electrolysis of Nitrobenzene with the Mercury Dropping Cathode. I. Reduction Potential of Nitrobenzene. II. Influence of the Cathodic Potential on the Adsorption of Nitrobenzene.** M. SHIKATA (*Trans. Faraday Soc.*, 1925; advance proof).—I. Current-voltage curves for the reduction of nitrobenzene in hydrochloric acid, sodium hydroxide, and various salt solutions have been determined with the dropping mercury electrode. The concentration of the nitrobenzene was  $4.47 \times 10^{-4}$  and  $4.47 \times 10^{-5}$  mol./litre. The influence of hydrogen-ion concentration on the saturation current was investigated. In presence of nitrobenzene, deposition of hydrogen takes place at a much less negative cathodic polarisation. If the reduction proceeds according to the equation (1)  $R \cdot NO_2 + 2H \rightarrow R \cdot NO + H_2O$ , or (2)  $R \cdot NO_2 + 4H \rightarrow R \cdot NH \cdot OH + H_2O$ , the reduction potential from (1) is

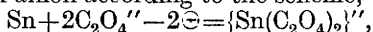
$$\pi = -RT/2F \log_e p_R/[H'] = -RT/2F \log_e k'/[H']^2 C_{R \cdot NO_2},$$

$C_{R \cdot NO_2}$  being a constant under the experimental conditions. In hydrochloric acid solution the observed reduction potentials are in agreement with this formula, but in sodium hydroxide solution the reduction potentials are more positive. A theory is advanced to explain these results, involving the adsorption of the nitrobenzene at the mercury interface according to the well-known adsorption isotherm  $C = aC_0^{1/m}$ . Neutral salts exert a salting-out effect.

II. The current-potential curves indicate that the occurrence of a minimum is due to a desorption effect of the nitrobenzene on the mercury surface. From a consideration of electro-adsorption, the conclusion is reached that reducibility is favoured by increase in adsorption. In alkaline solution the oxygen of the nitro group appears to be attached more closely to the mercury surface and less firmly held in the nitrobenzene molecule. The possible utilisation of the observed facts in micro-analysis is pointed out.

L. L. B.

**Electrolysis of Solutions of Potassium Oxalate with a Tin Anode and an Electrometric Determination of the Constitution of the Complex Anions Formed.** F. H. JEFFERY (*Trans. Faraday Soc.*, 1924, 20, 392—401).—The electrolysis of 0.5—3*N*. solutions of potassium oxalate has been examined at 14—18°, using a tin anode. For currents of 0.4—0.01 amp. the tin dissolves first to form a complex anion according to the scheme,



and the substance  $K_2Sn(C_2O_4)_2 \cdot H_2O$  has been isolated. At this stage no gas is evolved, but after a time, which depends on the current density and the concentration of the anolyte, the current suddenly drops. At this point, the anode is covered with a fine black deposit of tin, and if this is not removed, oxygen begins to be evolved; if the electrolysis is continued the whole of the stannous complex undergoes anodic oxidation with the production of stannic

complex ions of the type  $\{\text{Sn}(\text{C}_2\text{O}_4)_3\}''$ ; a solid substance derived from quadrivalent tin is formed which may be either  $\text{Sn}(\text{C}_2\text{O}_4)_2$  or  $\text{K}_2\text{Sn}(\text{C}_2\text{O}_4)_3$ . Up to this point, no tin is deposited on the cathode. The anode potential remains constant over a wide range of current densities if the surface is kept free from finely-divided metal and from products of electrolysis, but if these accumulate the potential may rise to 9 volts referred the hydrogen electrode as zero, the current being 0.1 amp. The change from complex stannous ion formation to that of anodic oxidation is very rapid. A method for the determination of the composition of complex ions by measurements of potential, viscosity, and resistance is described, for details of which the original must be consulted.

W. H.-R.

**Electro-deposition of Manganese. II.** A. J. ALLMAND and A. N. CAMPBELL (*Trans. Faraday Soc.*, 1924, 20, 379—384; cf. A., 1924, ii, 555).—The best conditions for the deposition of pure manganese consist in the electrolysis of a solution containing manganous and ammonium sulphates separated by a diaphragm from the anode solution, which contains ammonium sulphate. The hydrogen-ion concentration is kept at  $10^{-6}$  to  $10^{-8}$  by the addition of sulphuric acid or ammonia during the electrolysis. The temperature should be  $30^\circ$  and the current density at the cathode from 10 to 15 amp./dm.<sup>2</sup>; under these conditions a current efficiency of 30 to 35% can be obtained with a rotating cathode. If an ebonite burnisher is pressed very lightly against the rotating cathode, the character of the deposit is much improved whilst the efficiency may rise to as much as 54%. No advantage is gained by superposing an alternating current on the direct current, or by using the chloride instead of the sulphate. Electrolytic manganese contains considerable quantities of dissolved hydrogen, but is still brittle when the latter is removed.

W. H.-R.

**Potentiometric Investigation of the Reduction of Permanganate by Ferrous Ion and Iodine Ion.** E. MÜLLER and H. MÖLLERING (*Z. anorg. Chem.*, 1924, 141, 111—118).—The reactions between permanganate and ferrous sulphate, and permanganate and potassium iodide, in sulphuric and hydrochloric acid solutions, have been studied potentiometrically. For the former reaction in sulphuric acid solution,  $\text{MnO}_4' + 5\text{Fe}'' + 8\text{H}^+ = \text{Mn}'' + 5\text{Fe}''' + 4\text{H}_2\text{O}$ , the end-point potential  $e_u$  is +0.65 volt if the permanganate is added to the iron solution, and +0.76 volt if the ferrous salt is added to the permanganate solution. In hydrochloric acid solution,  $e_u$  is +0.67 volt (permanganate added to iron), or +0.66 volt (iron added to permanganate). In sulphuric acid solution the second reaction is complicated by a secondary reaction resulting in the formation of iodate, and in hydrochloric acid solution, by the formation of iodine chloride.

L. L. B.

**Kinetics and Mechanism of Reaction of the Reduction of Ferric Salts by Thiosulphate in Weakly Acid Solution.** J. HOLLUTA and A. MARTINI (*Z. anorg. Chem.*, 1924, 140, 206—226).—The velocity of reduction of ferric chloride by sodium thiosulphate

in the presence of dilute hydrochloric acid was studied. No consistent velocity constant could be obtained on any assumption as to the order of the reaction, principally owing to the accelerating influence of the iron in acid solution. In neutral solution, excess of ferric chloride retards the reaction, as does excess of thiosulphate in both neutral and acid solutions. Neutral salts retard the reaction. The facts are explained on the assumption that the reaction takes place in two stages, a preliminary (rapid) equilibrium  $\text{Fe}^{+++} + 2\text{HS}_2\text{O}_3' = [\text{Fe}(\text{S}_2\text{O}_3)_2]' + 2\text{H}^+$  being followed by the slow reaction  $[\text{Fe}(\text{S}_2\text{O}_3)_2]' + \text{Fe}^{+++} = 2\text{Fe}^{++} + \text{S}_4\text{O}_6''$ . The influence of neutral salts and the retarding influence of excess of ferric chloride in very low acid concentration are then in accord with Brönsted's theory (A., 1922, ii, 699).  
L. J. H.

**Occurrence of Iodine in Nature. IV. Evolution of Elementary Iodine from Sea Water.** T. VON FELLEBERG (*Biochem. Z.*, 1924, **152**, 132—134).—The rate of loss of iodine from sea-water (from Capri and Isle of Wight) has been determined. Lighting conditions have little effect on the rate of loss, which is chiefly dependent on the access of air, and surface exposed. J. P.

**Reactions between Solid Phases. IV.** J. A. HEDVALL and J. HEUBERGER (*Z. anorg. Chem.*, 1924, **140**, 243—252).—A reply to the criticism of Balareff (A., 1924, ii, 611). Further experiments are described showing that reaction does occur between substances that have been carefully dried, although the presence of water may slightly lower the temperature at which reaction begins and facilitates its completion. The suggestion that surface melting occurs is examined and rejected.  
L. J. H.

**Influence of Emulsoids on the Rate of Dissolution of Zinc in Solutions of Lead, Nickel, and Copper Salts.** J. N. FRIEND and J. S. TIMMUS (*Inst. Metals*, Mar., 1925; advance copy, 7 pp.).—Agar reduces the rate of dissolution of metallic zinc in solutions of lead acetate according to the logarithmic law; the rate is increased by an increase of temperature or by a rise in the concentration of the lead salt. The percentage retardation of dissolution of zinc in solutions of copper sulphate containing small quantities of agar is reduced by a rise in temperature above 15°, contrary to the usual behaviour. Sucrose retards the dissolution of zinc in nickel sulphate solutions considerably, but has little action in the case of copper sulphate or lead acetate solutions. [Cf. B., 1925, 246.]  
A. R. P.

**Some Metallic Couples Decomposing Water at the Ordinary Temperature.** E. S. HEDGES and J. E. MYERS (*J. Chem. Soc.*, 1925, **127**, 495—496).—Very active metallic couples are obtained by placing clean magnesium sheet in a 2% ammonium chloride solution containing 0.2% of crystallised nickel chloride, ferrous sulphate, or cobalt chloride. The resulting deposits of copper are of very fine texture and very adherent and the couples decompose water vigorously for a few minutes, then more slowly, the hydrogen

evolution continuing for several hours, especially in the presence of 0.1% of ammonium chloride. A. R. P.

**Kinetics of the Oxidation of Thiocarbamide by Charcoal.** H. FREUNDLICH and A. H. FISCHER (*Z. physikal. Chem.*, 1925, **114**, 413—429; cf. A., 1916, ii, 238).—The oxidation of thiocarbamide in solution by blood charcoal is similar to the oxidation of phenylthiocarbamide under the same conditions, and is regarded as following the equation  $2\text{CS}(\text{NH}_2)_2 + \text{O}_2 = \text{C}_2\text{H}_4\text{N}_4\text{S} + 2\text{H}_2\text{O} + \text{S}$ . The course of the reaction was followed by manometric measurement of the velocity of oxygen absorption, but in some cases the decrease of thiocarbamide concentration was followed by titration. In the first stages, the reaction is an adsorption catalysis. The velocity depends on the quantity of thiocarbamide adsorbed by the charcoal, and follows the equation (i)  $dz/dt = k(a/q + sa)$ , where  $dz$  is the amount of oxygen adsorbed in the time  $dt$ ,  $a$  the adsorbed quantity of thiocarbamide, and  $q$  and  $s$  are constants. The velocity also depends on the quantity of oxygen adsorbed on the surface, and the kinetics of the reaction can be explained by supposing that the two substances replace one another. If  $dz/dt = kab$ , where  $b$  is the adsorbed oxygen, and assuming that  $b = 1/q + sa$ , the equation (i) is obtained. The influence of oxygen pressure on the velocity of the reaction is given by the equation  $dz/dt = kp^{1/n}$ . The temperature coefficient is 1.62 for  $10^\circ$ , and is in keeping with the Arrhenius formula. The reaction products are preferentially adsorbed by the charcoal, owing to the fact that they drive out both the oxygen and the thiocarbamide. Urethane also checks the reaction, and the retardation increases with rise in the homologous series. Hydrocyanic acid has a retarding influence only at low concentrations of thiocarbamide, at which the hydrocyanic acid and thiocarbamide adsorption were of the same order of magnitude. L. L. B.

**Influence of some Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Mixtures of Inflammable Gases and Air.** III. W. P. JORISSEN and J. C. MEUWISSEN (*Rec. trav. chim.*, 1925, **44**, 132—140; cf. A., 1924, i, 253; this vol., ii, 53).—The effect of the vapours of carbon tetrachloride, di- and tri-chloroethylene, tetrachloroethylene, and tetra- and penta-chloroethane, on the explosion limits of pure methane, carbon monoxide, acetylene, and hydrogen has been investigated. In every instance, there is a fall in the lower explosion limit with di- and tri-chloroethylene, whilst in the case of hydrogen, a similar effect is also produced by tetrachloroethylene and tetra- and penta-chloroethane. [Cf. B., 1925, 234.] F. M. H.

**Catalysis and the Inversion of Sucrose by Acetic Acid.** E. SAILLARD (*Mon. Sci.*, 1925, **15**, 10—12).—The effect of the addition of organic and inorganic salts on the rate of inversion of sucrose by acetic acid is studied. Potassium acetate and sodium formate entirely prevent the inversion and sodium sulphate exerts a retarding influence. Sodium chloride and nitrate, magnesium chloride and sulphate accelerate the reaction. The non-inversion of the sucrose

precipitated from beet molasses by glacial acetic acid may hence be ascribed to the anticatalytic influence of the organic salts present.

W. E. E.

**[Negative] Catalysis.** H. W. UNDERWOOD, jun. (*Proc. Nat. Acad. Sci.*, 1925, **11**, 78—80).—The so-called stabilisers employed in the preservation of otherwise unstable substances form molecular compounds with the substance preserved and are thus true negative catalysts. Ether, phenol, resorcinol, and benzene are stabilisers for chloroform, and evidence of molecular compound formation is available for each of these substances. In examining 25 compounds, no serious contradiction to the molecular compound theory was found. Fugitive dyes may be protected against the action of light by treatment of the dyed wool or cotton with dilute solutions of phenol or resorcinol.

J. S. C.

**Catalysis of Hydroxylamine.** A. KURTENACKER and F. WENGEFELD (*Z. anorg. Chem.*, 1924, **140**, 301—319).—Investigations of the action of various substances on the decomposition of hydroxylamine are described. Molybdic acid has no action in alkaline solution; it acts catalytically in acid solution, ammonia, nitrogen, nitrous and nitric oxides being formed. The results with vanadic acid confirm those previously published (A., 1924, ii, 250). Copper sulphate in acid solutions yields mainly nitrous and nitric oxides, with small quantities of nitrogen; in strongly alkaline solutions nitrous oxide is the main product. Ferric hydroxide produces nitrous oxide and ammonia, catalytically, in alkaline solutions. The decomposition of hot alkaline hydroxylamine solutions yields nitrous oxide, ammonia, and nitrogen, but no nitric oxide. The results are explained by assuming a rapid oxidation and reduction of the catalyst by the hydroxylamine, which is itself reduced to ammonia in the former process. Quadrivalent vanadium, quinquivalent molybdenum, and bivalent iron are shown to reduce hydroxylamine to ammonia, in support of this explanation. The formation of nitric oxide is explained by assuming the reduced catalyst to be peroxidised and so able to oxidise some hydroxylamine more energetically. Previously published results of other workers are cited in support of the theory.

S. K. T.

**Reaction Velocity of Oxygen with Solutions of Inorganic Salts. I. Oxidation of Nitrites. II. Catalytic Oxidation of Arsenites.** W. REINDERS and S. I. VLES (*Rec. trav. chim.*, 1925, **44**, 1—28, 29—46).—I. Pure sodium nitrite (from which carbon dioxide must be excluded, since it gives rise to nitrous acid and nitrous oxide) is not oxidised in neutral or alkaline solution. Oxidation of a dilute solution by oxygen in presence of nitric acid is carried out in a closed thermostat, with stirring so rapid that a saturated solution of oxygen results; the initial relative reaction velocity is determined from measurements of the consumption of oxygen. When sodium nitrite is present in large excess, the velocity is independent of its concentration, but it increases with the quantity of nitric acid which is converted into nitrous acid,

and the reaction is bimolecular as regards the latter; no simple relationship exists between reaction velocity and oxygen concentration. The mechanism of the reaction is considered to consist in the oxidation of free nitrous acid to nitric oxide, nitrogen peroxide, and water, followed by oxidation of nitric oxide to nitrogen peroxide; this reacts with water to form nitric oxide and nitric acid, which yields sodium nitrate and nitrous acid. The detection of nitric oxide, the concentration of which is determined for various mixtures of sodium nitrite and nitric acid, confirms the theory, as also does the effect of temperature changes. Potassium nitrite behaves like sodium nitrite. All strong acids produce the same effect, and salts have no catalytic influence, the accelerating action of iron and aluminium salts being due to their hydrolysis.

II. Oxidation of pure sodium or potassium arsenite by free oxygen only occurs in alkaline solution in presence of a catalyst. If a copper salt is used for this purpose, a complex of unknown composition is formed and the order of the reaction with regard to it lies between 1 and 2. The reaction velocity is proportional to the arsenite-ion concentration and depends on the hydroxyl-ion concentration, reaching a maximum with a 0.5 *N*-solution of potassium hydroxide. It is unaffected by various inorganic salts, but retarded by glycerol and other substances which form complexes with copper salts in presence of alkalis. Since alteration of the oxygen pressure has little influence, the measured velocity cannot be that of direct oxidation of arsenite to arsenate. It is suggested that oxidation takes place in two stages: (a)  $\text{Cu}' \text{ complex} + \text{AsO}_2' \rightarrow \text{Cu}' \text{ complex} + \text{AsO}_3$ , which is shown to be a reaction of the same order of velocity as the measured oxidation of arsenites, (b)  $\text{Cu}' \text{ complex} + \text{O}_2 \rightarrow \text{Cu}'' \text{ complex}$ , which is a very rapid reaction. Certain other metallic salts do not behave like copper, since they do not form reducible complexes at such alkalinity that the arsenite is incompletely hydrolysed.

Carbon catalyses the oxidation of arsenite to arsenate. This reaction is proportional to the arsenite-ion concentration, to that of potassium hydroxide, and to the quantity of carbon, but is little influenced by the oxygen concentration. It is suggested that (a) the oxygen is adsorbed by the carbon and thus activated, this being a rapid reaction, and (b) the activated oxygen gradually converts the arsenite into arsenate.

F. M. H.

**Periodic Dissolution of Metals.** E. S. HEDGES and J. E. MYERS (*J. Chem. Soc.*, 1925, 127, 445—449; cf. A., 1924, ii, 325).—The dissolution of magnesium in acetic, sulphuric, nitric, or orthophosphoric acid in the presence of an activating agent shows periodicity. In these and the previously described periodic reactions activation can be produced by touching the dissolving metal with electrically deposited copper, or by first dipping the magnesium into solutions of copper or ferrous sulphate. Regularity in the periodicity is favoured by uniformity of the surface of the activating metal, whilst the frequency increases with decreasing amounts of the activating agents. Ordinary copper is inactive, but can be



activated by electrolytic or chemical deposition and also by cold-rolling; the activation is associated with an unstable, close-grained, and possibly amorphous structure. "Naturally active" vessels (*loc. cit.*) can be produced by leaving glass tubes to soak for long periods in a mixture of colloidal platinum and gelatin in hydrochloric acid.

W. H.-R.

**Union of Hydrogen and Oxygen in Presence of Silver and Gold.** D. L. CHAPMAN, J. E. RAMSBOTTOM, and C. G. TROTMAN (*Proc. Roy. Soc.*, 1925, **A**, **107**, 92—100).—The catalytic action of metallic gold and silver on the reaction between hydrogen and oxygen is prevented by the presence of a film of oxide on the surface of the metal. If this be removed the metal is as active as if previously heated in hydrogen. The Bone and Wheeler effect (*A.*, 1906, ii, 434), therefore, can apparently be simply explained by the removal of inhibiting oxygen by hydrogen instead of activation by adsorbed hydrogen. Hydrogen and oxygen will combine, even at ordinary temperature, in the presence of a condensed silver film.

M. S. B.

**Catalytic Decomposition of Hydrogen Peroxide Solution by Animal Charcoal: the Production of Highly Active Charcoals.** J. B. FIRTH and F. S. WATSON (*Trans. Faraday Soc.*, 1924, **20**, 370—377; cf. *A.*, 1924, ii, 542).—Crude animal charcoal dried at 120° is comparatively inactive towards hydrogen peroxide, but its activity can be slightly increased by heating in a vacuum or treatment with iodine. The catalytic activity of the charcoal purified with hydrochloric acid is greater than that of the crude material and can be greatly increased by heating in a vacuum at 600—900°, and still more so by sorption of iodine from solution followed by complete removal of the iodine and further heating in a vacuum. The increased activity is accompanied by an increase in bulk, although repeated treatment with iodine increases the volume but not the catalytic activity. On the other hand, after four treatments with iodine, the charcoal produces a vigorous oxidation of alcohol with the formation of aldehyde. Small quantities of mineral matter increase the activity owing to their action as a spacing agent, whilst larger quantities retard it, since the carbon particles tend to be covered and protected.

W. H.-R.

**Comparison between the Homogeneous Thermal Decomposition of Nitrous Oxide and its Heterogeneous Catalytic Decomposition on the Surface of Platinum.** C. N. HINSHELWOOD and C. R. PRICHARD (*J. Chem. Soc.*, 1925, **127**, 327—336).—The heterogeneous thermal decomposition of nitrous oxide on the surface of a heated platinum wire between 600° and 1200° is retarded by the presence of oxygen and proceeds at a relatively faster rate at low than at high pressures. The velocity of the reaction is represented by the equation  $-d[\text{N}_2\text{O}]/dt = k[\text{N}_2\text{O}]/(1 + b[\text{O}_2])$ , and the heat of activation in the catalytic reaction is 32,500 cal. per g.-mol. This reaction is unimolecular, whereas the homogeneous

thermal decomposition of nitrous oxide is bimolecular and its heat of activation is much greater; the platinum surface in the heterogeneous reaction acts as an acceptor for atomic oxygen, the nitrous oxide probably giving its oxygen atom to the platinum, thereby forming a retarding film of atomic oxygen. A. R. P.

**Catalytic Activity of Copper. V. Comparison of the Rates of Dehydrogenation of Various Alcohols.** W. G. PALMER and F. H. CONSTABLE (*Proc. Roy. Soc.*, 1925, A, 107, 255—269; cf. A., 1924, ii, 843).—Measurements of the rates of dehydrogenation of certain alcohols by supported copper films have led to the conclusion that the reaction is direct, as stated by Sabatier, and that there is no intermediate formation of ethylene and water, as suggested by Ipatiev. The primary alcohols, ethyl, propyl, butyl, *isobutyl*, and *isoamyl*, show equal rates of dehydrogenation and the same temperature coefficients. It is therefore inferred that reaction occurs in a unimolecular adsorption film covering the surface of the copper, the common radical  $\cdot\text{CH}_2\text{-OH}$  being in contact with the surface, whilst the hydrocarbon chains are perpendicular to it. With *isopropyl* alcohol, the velocity was five times that of the others. Rapid poisoning of the catalyst occurred with one sample of *isopropyl* alcohol and with *isobutyl* and *isoamyl* alcohols. From a study of the decay curves a theory of poisoning has been developed, and on the basis of this a poisoning correction has been applied to the results with *isobutyl* and *isoamyl* alcohols, which are then seen to be identical in activity with ethyl alcohol. N. H. H.

**Catalytic Action of Copper. VI. Reproducibility of the Catalyst, and of the Periodic Change in its Activity, and the Activation of the Catalyst by Alternate Oxidation and Reduction.** F. H. CONSTABLE (*Proc. Roy. Soc.*, 1925, A, 107, 270—279).—The reproducibility of the catalyst is attributed to the persistence of the granular structure throughout oxidation and reduction, assisted by the fireclay support and by standardising the conditions of oxidation. Chemical reaction occurs only when the alcohol molecule is adsorbed over a characteristic arrangement of copper atoms termed a reaction centre. The catalyst surface exposes many crystal faces as well as some amorphous material. There is a large variation in the number of atom centres lying beneath one adsorbed alcohol molecule on various faces of the crystal; it is thus probable that the density of reaction centres varies also. The periodic variation in activity may be explained as due to a periodic predomination of more active planes in the surface. The activity is controlled by at least two factors: the value of the heat of activation and the reaction centre density. If the latter is of the same order for all the types of faces exposed, then the heat of activation plays the greater part in deciding the activity of the surface. The variation of the temperature coefficient in the opposite sense to the activity is thus explained. N. H. H.

**Catalytic Action of Copper. VII. Effect of Pressure on the Rate of Dehydrogenation of Alcohols.** F. H. CONSTABLE (*Proc. Roy. Soc.*, 1925, A, 107, 279—286).—The validity of the

assumption that reaction occurs in a unimolecular film covering the surface of the copper has been demonstrated by measuring the rate of dehydrogenation of ethyl and butyl alcohols under pressures ranging from 10 to 140 cm. of mercury, when the velocity of reaction was found to be independent of the pressure. The observations show further that the mean life of a molecule in the activated layer does not alter appreciably under the conditions studied.

N. H. H.

**Mechanism of Kolbe's Electrosynthesis.** R. A. GIBSON (*J. Chem. Soc.*, 1925, 127, 475—486).—The production of trichloromethyl trichloroacetate by the electrolysis of a normal solution of trichloroacetic acid is independent of the current density at the anode within wide limits. No formation of ester occurs until the polished platinum or iridium anode acquires a potential of 2.35 volts, at which point a marked decrease occurs in the amount of free oxygen evolved, but this critical potential does not represent the discharging potential of the trichloroacetate ion. The reaction is not determined solely by the anode potential, but the nature and state of the anode are important factors; thus no ester formation takes place at anode potentials of 3 volts when anodes of gold or of platinum or glass are used. The synthesis is not due to the union of discharged anions, as suggested by Crum Brown and Walker (A., 1891, 1192, 1193), but to direct oxidation by the oxygen developed at the anode (cf. Kolbe, *Annalen*, 1849, 69, 279), according to the reactions (a)  $R\cdot CO_2H + R'\cdot CO_2H + O = RR' + 2CO_2 + H_2O$ , or (b)  $R\cdot CO_2H + R'\cdot CO_2H + O = R\cdot CO_2R' + CO_2 + H_2O$ , or (c)  $R\cdot CO_2H + O = R\cdot OH + CO_2$ . Peculiarities are noted in the behaviour of platinum anodes which have been polarised for many hours at a low potential. These are due to the existence of  $\alpha$ - and  $\beta$ -forms of platinum; the former has a limited oxidising power but accelerates the reaction  $O + O \rightarrow O_2$ , whilst the latter has high oxidising power and retards the same reaction. The  $\alpha$ -form is produced by prolonged polarisation.

W. H.-R.

**Reactions in the Lead Accumulator.** A. LOTTERMOSER and M. GRÜTZNER (*Z. anorg. Chem.*, 1924, 140, 93—115).—The potential of each plate separately has been determined during charge and discharge at varying current strengths and with acid of different density, and from this the separate capacities of the plates are considered. The theory of Dolezalek completely accounts for the observed results. The capacity of the accumulator is the less the more rapidly it is discharged, mainly owing to incomplete diffusion of acid into the porous layer. This effect is far more apparent at the peroxide than at the lead plate. The capacity is also greatest for the concentration of acid which has the greatest conductivity ( $d$  1.19). The recovery curves after charge and discharge are also given.

L. J. H.

**Electrolysis of some Tin Alloys.** R. KREMANN and P. G. VON REHENBURG (*Z. anorg. Chem.*, 1924, 140, 1—21).—In continuation of previous work (A., 1924, ii, 723, 724) the electrolytic conductivity

of fused lead-tin, tin-bismuth, and antimony-tin alloys was studied. In each case the electrolytic effect increases to a limit with increasing current density. The maximum electrolytic effect is obtained with equimolecular mixtures. In each case the tin goes to the cathode in accordance with its "conductance capacity" as defined by Benedicks (*Jahrb. Radioaktiv.*, 1916, 13, 381). [See *B.*, 1925, 211.]

L. J. H.

**Electrolysis of Molten Amalgams of Lead, Tin, and Bismuth.** R. KREMANN and A. KAPAUN [with BUDAN] (*Z. anorg. Chem.*, 1924, 140, 183—205; cf. preceding abstract).—In the electrolysis of amalgams of lead, tin, and bismuth, the lead, tin, and mercury, respectively, migrate to the cathode in agreement with the rule that the component having the greater conductance capacity should do so. In the case of the lead amalgam, considerable diffusion occurred after the alloy had become solid (at the ordinary temperature). The general rules previously reported were all followed, although the limiting value of the electrolysis effect (with increasing current density) was not quite reached. [See *B.*, 1925, 211.]

L. J. H.

**Photographic Reversal.** H. ARENS (*Z. physikal. Chem.*, 1925, 114, 337—386).—Three types of photographic reversal are described. The first type (solarisation) is caused by the continued action of the same kind of energy, and in place of the Lüppo-Cramer theory, which is shown to have little experimental support, another is advanced, involving the coagulation of the silver of the grain surface. By means of this theory, a number of phenomena are explained. The second type of reversal is that caused by the superposition of different kinds of energy. The Villard-effect (white light  $\rightarrow$  Röntgen rays) and the Clayden-effect (spark light  $\rightarrow$  white light) are closely similar, and can be traced to solarisation. The Herschel effect (red light  $\rightarrow$  white light) is shown to be dependent on the presence of potassium bromide, bromine ions or molecules, and is supposed to be due to the desensitising action of potassium bromide for red light. The third type of reversal is that due to addition of the image substance (desensitisation): This phenomenon is classed by the author with the Herschel effect, and regarded as being due to the oxidation by light of the silver of the grain surface, in presence of bromine molecules or ions. [Cf. *B.*, 1925, 266.]

L. L. B.

**Photocatalytic Effect of Neutral Salts.** G. BERGER (*Rec. trav. chim.*, 1925, 44, 47—67).—The decomposition of uranyl formate in formic acid solution,  $\text{U}^{\text{VI}}\text{O}_2(\text{HCO}_2)_2 + 3\text{H}\cdot\text{CO}_2\text{H} = \text{U}^{\text{IV}}(\text{HCO}_2)_4 + \text{CO}_2 + 2\text{H}_2\text{O}$ , was followed by determining the decrease in acidity, and for this ionic reaction the influence of neutral salts is large. The salt effect is small for the non-ionic transformation of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid, observed in dilute acetone solution. The magnitudes of the salt effects are in good agreement with the activity theory which Brönsted postulated for dark reactions (*A.*, 1922, ii, 699), whence it seems that these photocatalytic

reactions are identical. The influence of neutral salts is also studied in the case of the decomposition in light of a weakly acid solution of each of 9 complex cobalt salts. Here the matter is more complicated and the activity theory can be applied only qualitatively; with high salt concentrations, a secondary effect is superimposed, which, according to the positive or negative charge of the light-sensitive complex, is retarding or accelerating.

F. M. H.

**Realisation of Chemical Reactions in Compressors.** M. BRUTZKUS (*Compt. rend.*, 1925, **180**, 429—431; cf. this vol., ii, 215).—The conditions obtaining in Diesel gas engine cylinders are recommended as providing a general method for the promoting of chemical reaction in gaseous systems.

J. S. C.

**Mercury Helide.** J. J. MANLEY (*Nature*, 1925, **115**, 337; cf. this vol., ii, 57).—The simplest formula for mercury helide is  $\text{HgHe}$ .

A. A. E.

**Higher Oxides of Silver. I.  $\text{Ag}_2\text{O}_3$ .** F. JIRSA (*Chem. Listy*, 1925, **19**, 3—9).—Higher oxides of silver are formed by the energetic oxidation of metallic silver or of silver salts, and contain either the monoxide,  $\text{Ag}_2\text{O}$ , alone or the sesquioxide,  $\text{Ag}_2\text{O}_3$ , together with the monoxide and varying amounts of the silver salt from which they are prepared. The higher oxide does not appear to be capable of separate existence and is easily decomposed by heating the compounds containing it to temperatures just below  $100^\circ$ ; for example,  $\text{Ag}_7\text{NO}_{11} = 3\text{Ag}_2\text{O}_3 + \text{AgNO}_3 + \text{O}_2$ . By extracting the product of this reaction with boiling water the oxide,  $\text{Ag}_2\text{O}_3$ , remains insoluble in an almost pure state. This oxide catalytically accelerates the decomposition of the sesquioxide.

A. R. P.

**Beryllium. I. Beryllium Sulphate and its Hydrates.** F. KRAUSS and H. GERLACH (*Z. anorg. Chem.*, 1924, **140**, 61—80).—Beryllium sulphate tetrahydrate may be crystallised from slightly acid solution. On heating, any smaller proportion of water may be obtained, but vapour-pressure measurements indicate that only the tetra- and di-hydrates, and possibly the monohydrate, exist as pure substances. The anhydrous salt may be prepared either by dissolving beryllium oxide in concentrated sulphuric acid, and washing off the excess acid with absolute alcohol, or by heating the tetrahydrate at  $400^\circ$  for 1 hr. Loss of sulphur trioxide does not occur until the temperature is raised to  $580^\circ$ . The hexa- and hepta-hydrates, although frequently referred to in the literature, do not exist.

L. J. H.

**Kinetic Studies on Solid Metals. Decomposition of the Compound  $\text{Al}_2\text{Zn}_3$ .** W. FRAENKEL and W. GOEZ (*Z. Metallk.*, 1925, **17**, 12—21).—The compound  $\text{Al}_2\text{Zn}_3$  is stable only above  $256^\circ$ ; at lower temperatures it decomposes into its elements with evolution of heat and contraction in volume. A specimen quenched from  $400^\circ$  in water at  $0^\circ$  soon attains a temperature of  $40^\circ$  or more when removed from the water, whilst its volume is reduced by

0.33%. Calorimetric measurements of the rate of rise of temperature and dilatometric measurements of the volume change show that the decomposition is strictly a unimolecular action. [Cf. *B.*, 1925, 175.] A. R. P.

### Double Chromates of the Rare Earths and Alkali Metals.

**I. Double Chromates of Lanthanum and Potassium.** G. CAROBBI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 416—420).—Investigation of the isotherm for 25° of the system  $\text{La}_2(\text{CrO}_4)_3$ — $\text{K}_2\text{CrO}_4$ — $\text{H}_2\text{O}$  indicates the existence of hydrated *double chromates* with the components in the molecular proportions 1 : 1 : 2, 1 : 3 : 2, 1 : 4 : 2, 1 : 4.5 : 2, and 1 : 5 : 2. T. H. P.

**Double Sulphates of Rare Earth and Alkali Metals. II. Neodymium and Potassium Sulphates.** F. ZAMBONINI and V. CAGLIOTI (*Atti R. Accad. Lincei*, 1924, [v], **33**, ii, 385—389).—The various double neodymium potassium sulphates are described. [Cf. this vol., ii, 222.] T. H. P.

**Mechanism of the Reaction in the Reduction of Titanium Tetrachloride with Hydrogen and the Behaviour of the Reduction Products in a Vacuum.** R. SCHMIDT (*Ber.*, 1925, **58**, [B], 400—404; cf. *A.*, 1923, ii, 769).—Titanium dichloride, almost free from oxygen, is obtained by the thermal decomposition of titanium trichloride in a carbon tube at temperatures not greatly exceeding 600°; if glass or quartz tubes are used oxygen is abstracted from the silica with consequent production of oxygenated compounds. At 600°/0.02 mm., titanium dichloride is slowly volatile, but the volatilised dichloride is decomposed and deposited in the colder parts of the tube as the trichloride mixed with small amounts of the tetrachloride. The effect is due to decomposition of the dichloride into titanium and the tetrachloride and reaction of the latter with unchanged dichloride to give trichloride. Confirmation is afforded of the previous view (*loc. cit.*) that reduction of titanium tetrachloride by hydrogen is not direct, but that three reactions,  $\text{TiCl}_4 + \text{H}_2 = \text{TiCl}_2 + 2\text{HCl}$ ;  $\text{TiCl}_2 + \text{TiCl}_4 = 2\text{TiCl}_3$ ;  $2\text{TiCl}_3 + 2\text{HCl} = 2\text{TiCl}_4 + \text{H}_2$ , may proceed simultaneously. H. W.

### Acid Properties of Ammonium Salts in Liquid Ammonia.

F. W. BERGSTROM (*J. Physical Chem.*, 1925, **29**, 160—165).—Ammonium salts in liquid ammonia behave as acids and react with most of the elements above hydrogen in the electropotential series as it is known in water. By treating various elements with ammonium salts in liquid ammonia the following ammonates have been prepared :  $\text{LaI}_3 \cdot x\text{NH}_3$ ,  $\text{CeI}_3 \cdot 7.5-8\text{NH}_3$ ,  $\text{CeBr}_3 \cdot 7.5-8\text{NH}_3$ ,  $\text{Fe}(\text{NO}_3)_2 \cdot 0.6-0.4\text{NH}_3$ . M. B. D.

**Action of Nitric Acid on Metals.** N. R. DHAR (*J. Physical Chem.*, 1925, **29**, 142—159; cf. *A.*, 1922, ii, 756; 1924, ii, 486).—The action of nitric acid on copper, silver, mercury, and bismuth gives only nitrous acid and hyponitrous acid and not hydroxylamine, hydrazine, or ammonia, which are formed by hydrogenation of nitric acid. These four metals can only take oxygen away from nitric

acid and cannot add hydrogen to it. Nitrogen is formed by decomposition of hyponitrous acid and nitric oxide from the decomposition of nitrous acid.

M. B. D.

**Experiments with a Hot and Cold Quartz Tube.** H. STAUDINGER and W. KREIS (*Helv. Chim. Acta*, 1925, 8, 71—74).—A number of unsuccessful attempts were made to isolate unstable substances such as solid unimolecular  $\text{NO}_2$ , red tellurium,  $\text{S}_2$ , and SO by the sudden cooling of gases from  $1000^\circ$  to  $-190^\circ$ .

G. M. B.

**Hydrolytic Decomposition of Phosphorus Trichloride.** A. D. MITCHELL (*J. Chem. Soc.*, 1925, 127, 336—342).—When phosphorus trichloride is hydrolysed by water the solution produced has much stronger reducing properties when first formed than has a normally produced solution of phosphorous acid; its acidity is 98% of the theoretical at first and gradually increases during  $\frac{1}{2}$  hr. to the maximum, probably owing to the intermediate formation and gradual decomposition of an oxychloride. The duration of increased reducing power is greater than can be attributed to the formation of the oxychloride, and is most probably due to the presence of the active tautomeric form of phosphorous acid,  $\text{P}(\text{OH})_3$ , which is slowly converted into the normal form  $\text{HPO}(\text{OH})_2$ .

A. R. P.

**Oxidation of Tervalent Chromium by Silver Oxide in Alkaline Solution.** F. HANS (*Z. anorg. Chem.*, 1924, 140, 337—338).—The quantitative oxidation of chromic salts in alkaline solution by silver oxide is shown to proceed equally well when the latter is replaced by silver nitrate, chloride, carbonate, or thiocyanate. Silver bromide and iodide are too insoluble to react.

S. K. T.

**Tellurium Suboxide.** A. DAMIENS (*Compt. rend.*, 1924, 179, 829—831).—Attempts to repeat the preparation of tellurium suboxide as described by Divers and Shimoze (T., 1883, 43, 319) did not corroborate their results. The reactions  $\text{Te} + \text{SO}_3 \rightarrow \text{TeSO}_3$  and  $\text{TeSO}_3 \rightarrow \text{TeO} + \text{SO}_2$  are incomplete when pure tellurium is used, and the resulting substance, described as suboxide, was found to be a mixture of tellurium and tellurium dioxide.

H. J. E.

**Occurrence of Iodine in Nature. V. Iodine Content of Air.** T. VON FELLEBERG (*Biochem. Z.*, 1924, 152, 135—140).—Elementary iodine is present in dew, and is demonstrable in larger amounts just above the ground than at higher levels of the atmosphere as the dew evaporates.

J. P.

**Iron and Oxygen.** F. S. TRITTON and D. HANSON (*J. Iron and Steel Inst.*, 1924, 110, 90—121).—The purest electrolytic iron that could be obtained by electrolysis of ferrous sodium chloride solutions contained 0.08% of oxygen and melted at  $1535^\circ$ . Molten iron will retain oxide equivalent to 0.21% of oxygen in solution at  $1530^\circ$ ; further quantities of iron oxide simply float on the surface of the metal. At the ordinary temperature, the oxygen-iron solid solution contains 0.05% O. The oxide in equilibrium with molten

iron at high temperatures melts at  $1370^{\circ}$ . The chief effect of oxygen in iron is to increase the grain size, with a corresponding decrease in the resistance of the metal to shock, and to reduce its ductility. Oxygen has no influence on the temperatures of the transformation points.

A. R. P.

**Action of Iron on Copper at High Temperatures.** P. SIEBE (*Z. Metallk.*, 1925, 17, 19—21).—Iron has no action on pure electrolytic copper at any temperature below  $1100^{\circ}$ , but ordinary "tough pitch" copper which contains cuprous oxide is rendered brittle and porous by heating in contact with iron at temperatures above  $750^{\circ}$ . This is due to the reducing action of the hydrogen and carbon monoxide in the iron; the action of the hydrogen is the greater as it readily diffuses into hot copper, whereas carbon monoxide has only a superficial action. [Cf. *B.*, 1925, 175.]

A. R. P.

**Effects of Impurities on Copper. II. Effect of Iron on Copper.** D. HANSON and (MISS) G. W. FORD (*J. Inst. Metals*, 1924, 32, 335—361).—The solubility of iron in solid copper is 4% at  $1100^{\circ}$  and less than 0.2% at  $750^{\circ}$ , below which temperature the solubility changes only very slightly. The large change in solubility at about  $800^{\circ}$  is ascribed to the transition  $\gamma$ -iron  $\rightarrow$   $\alpha$ -iron. Addition of iron up to 0.2% rapidly lowers the electrical conductivity of copper; with higher percentages heat treatment has a large influence. The ductility of copper is unimpaired by the presence of iron, which also acts as a deoxidiser. [Cf. *B.*, 1924, 833.]

S. K. T.

**Preparation of Crystalline Compounds of Ferrous Salts and Nitric Oxide. III.** W. MANCHOT and E. LINCKH (*Z. anorg. Chem.*, 1924, 140, 37—46; cf. *A.*, 1914, ii, 567).—Ferrous selenate behaves like ferrous sulphate in absorbing nitric oxide and a similar ring test may be made with ferrous selenate and concentrated selenic acid. The combination is similar to that in the case of ferrous sulphate (cf. ii, 298), giving an equilibrium constant on the assumption that the combining ratio is 1 : 1. The crystalline compound may be prepared by saturating a concentrated aqueous solution of ferrous selenate ( $\text{FeSeO}_4 \cdot 5\text{H}_2\text{O}$ ) with nitric oxide in the presence of a little concentrated selenic acid. On adding a large excess of absolute alcohol, also saturated with nitric oxide, with cooling in a freezing mixture, brownish-black crystals appear after some hours. The crystals are unstable, losing nitric oxide when kept in air, but apparently the formula is  $\text{FeSeO}_4 \cdot \text{NO} \cdot 4\text{H}_2\text{O}$ .

L. J. H.

**Action of Ammonia on Aqueous Solutions of Ferrous Salts.** E. WEITZ and H. MÜLLER (*Ber.*, 1925, 58, [B], 363—375).—If gaseous ammonia is slowly passed into a sufficiently concentrated solution of a ferrous salt in the presence of a suitable quantity (2—5 mol.) of the corresponding ammonium salt in the absence of air, greenish-white ferrous hydroxide is precipitated initially; this slowly passes into solution and is replaced by the complex salt, which rapidly separates in the crystalline form as the passage



of the gas is continued. In this manner, ferrous chloride, bromide, iodide, nitrate, and perchlorate are converted into the corresponding hexammineferrous salts,  $[\text{Fe}(\text{NH}_3)_6]\text{X}_2$ . Ferrous sulphate does not give a hexammine compound, but, according to the quantity of ammonium sulphate, either *aquopentammineferrous sulphate*,  $[\text{Fe}(\text{NH}_3)_5\text{H}_2\text{O}]\text{SO}_4$ , or an additive compound of this substance and ammonium sulphate,  $[\text{Fe}(\text{NH}_3)_5\text{H}_2\text{O}]\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ . Ferrous acetate does not yield a crystalline hexammine by reason of its ready solubility and, on this account, solutions of ferrous acetate, ammonium acetate, and ammonia are well adapted to the preparation of sparingly soluble hexammine salts by double decomposition with potassium bromide or iodide or ammonium perchlorate. Since the hexammines lose ammonia readily and quantitatively when heated in a current of an indifferent gas, a means is provided of preparing anhydrous ferrous halides. The crystalline hexammines and their solutions have the pale green colour of the hexa-aquo salts. Like the salts prepared in the dry way, the white colour of which is due to their finer state of division, they are unstable towards air and moisture. In consequence of the ready oxidisability of ferrous iron the hexammineferrous salts of powerfully oxidising acids, such as chloric, bromic, chromic, and permanganic acids, are incapable of existence; the solution of hexammineferrous acetate gives a precipitate of ferric hydroxide with the alkali or ammonium salts of these acids. The nitrate and perchlorate are stable at the atmospheric temperature, but when warmed in solution or suspension give a black precipitate of ferrous-ferric oxide; the perchlorate ion is reduced to chloride, nitrate ion mainly to nitrous oxide. Hexammineferrous nitrite appears to exist in solution.

The inability of ferrous solutions containing ammonium salts to give a precipitate of ferrous hydroxide with ammonia is attributed to the depression of the concentration of ferrous ions in consequence of ammine formation and of hydroxyl ions by repression of the dissociation of ammonium hydroxide to such an extent that the solubility product of ferrous hydroxide is not attained. The precipitability of ferrous hydroxide depends to some extent on the anion present in the solution; its formation is most readily repressed in the case of the sulphate, whereas with perchlorate some separation occurs even when ammonium perchlorate and ferrous salt are present in the molecular ratio, 30 : 1.

Manganous salts behave very similarly to ferrous salts. Manganese salts yield crystalline ammines in strongly ammoniacal solution, whereas in more dilute solution complex formation is less in evidence.

H. W.

**Cuprous Hydroxide.** P. KLASON (*Svensk Kem. Tidskr.*, **36**, 202—203; from *Chem. Zentr.*, 1924, ii, 2741).—Cuprous hydroxide,  $\text{CuOH}$ , is obtained practically pure by the interaction of cuprous iodide with sodium hydroxide. The exclusion of air is not essential. The precipitate is insoluble in ammonia, and is oxidised to the blue cupric state only on prolonged keeping.

R. B.

**Crystalline Cuprous Bromide.** D. B. BRIGGS (*J. Chem. Soc.*, 1925, 127, 496).—The residual liquid in the distilling flask used for the preparation of ethyl bromide from ethyl alcohol, bromine, and red phosphorus, after filtration gave a dark green solution and, on boiling, a white, crystalline precipitate of cuprous bromide when treated with copper sulphate. Under the same conditions, the residual liquid from the preparation of ethyl iodide yielded cuprous iodide.

A. R. P.

**Preparation of Selenic Acid.** W. MANCHOT and A. WIRZ-MÜLLER (*Z. anorg. Chem.*, 1924, 140, 47—51).—Selenic acid may be prepared entirely free from selenious acid by the anodic oxidation of the latter. The best results were obtained with a cathode of platinum, an anode of platinum covered with lead peroxide and surrounded by a porous pot, 5*N*-nitric acid as catholyte and concentrated selenious acid as anolyte, low current density, and low temperature; 1.7 amp.-hrs. were required per g. of selenium dioxide (theoretical 0.48) and the yield was about 80% of the theoretical.

L. J. H.

**Ultra-balance.** F. HOLTZ and W. H. F. KUHLMANN (*Ber.*, 1925, 58, [B], 266—268).—By placing in front of the rider scale which carries the 5 mg. rider a second, short scale carrying a 0.5 mg. rider an ultra-balance is constructed which is sensitive to  $5 \times 10^{-8}$  g. with a maximal load of 20 g. The balance is figured in the original.

H. W.

**Ebullioscopic Apparatus.** W. SWIENTOSLAWSKI, and W. ROMER (*Bull. Internat. Acad. Pol. Sci. Lettres*, 1924, 59—62).—The modified apparatus previously described (A., 1924, ii, 469) is altered by the introduction of a short glass-tube sleeve to surround the thermometer bulb. This improved apparatus admits of the determination of the b. p. with an accuracy of  $\pm 0.0015^\circ$ . When making ebullioscopic measurements, two such instruments should be used, so that the b. p. of the solvent and solution may be determined simultaneously.

T. H. P.

**Electrolyte-free, Water-soluble Proteins. I. Electro-dialysis.** W. PAULI (*Biochem. Z.*, 1924, 152, 355—359).—The general principles of electro-dialysis are discussed, and an apparatus having parchment or collodion membranes, which may be used for the purification of water-insoluble proteins, is described.

J. P.

**Laboratory Apparatus for High-temperature Nitrations.** C. KRANZ and R. KOPECKY (*Z. ges. Schiess- u. Sprengstoffw.*, 1925, 20, 25—26).—A flask is fitted with a cap carrying three tubulures for, respectively, thermometer, stirrer, and reflux condenser. The joint between the flask and the cap is either packed with asbestos or sealed with an appropriate liquid. The other joints are made acid-proof in a similar manner.

W. A. S.

**Laboratory Apparatus.** F. A. WIGGERS (*Ind. Eng. Chem.*, 1925, 17, 141).—A device for saving supernatant fluids consists of a separating funnel, closed at the top, with a tap on its stem, and

having an inlet pipette for the liquid and an attachment for the vacuum pump. A distilling apparatus consists of a flask encased in an outer closed flask containing water, the latter provided with an inlet, a thermometer holder, and a safety valve. [Cf. *B.*, 1925, 268.] D. G. H.

**Apparatus for Concentrating Specially Sensitive Solutions.**

H. SCHMALFUSS and K. KALLE (*J. pr. Chem.*, 1925, [ii], 109, 153—157).—A modification of the Schulze-Tollens apparatus (A., 1892, 1386) is described, in which an automatic regulator allows of continuous evaporation for prolonged periods without attention. The solution to be evaporated is placed in a flask *A* and the whole apparatus is evacuated. From *A*, the solution is siphoned into a counterpoised flask, *B*, until the increased weight in *B* operates a regulating lever which shuts off the vacuum from *B*, closes the siphon, and admits carbon dioxide at atmospheric pressure to *B*. The solution is thereby lifted to the top of an evaporating coil down which it is allowed to drip slowly in a vacuum, the coil being maintained at a suitable temperature. The vapours pass off through a condenser and are collected. The concentrated liquid drips back into *A*. The operation continues until, owing to the diminished weight in *B*, the lever shuts off the carbon dioxide, opens the vacuum cock, and releases the siphon, when the cycle commences again. The whole apparatus can be placed in a thermostat and operated at constant temperature. The apparatus will evaporate 3 litres to 100 c.c. at 40° in two days. R. B.

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## Mineralogical Chemistry.

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### Radioactive Methods for the Age Determination of Minerals.

G. KIRSCH (*Tsch. Min. Mitt.*, 1924, **36**, 147—156).—The trustworthiness of the method of determining the age of minerals from the lead (radium-*G*)/uranium ratio is discussed. It is necessary to know the atomic weight of the lead present in order to distinguish between primary lead and radium-*G*; and further, it is found that in specimens for which this has been determined the composition varies from piece to piece. New estimates, in millions of years, are: for bröggerite from Moss, Norway, 895; pitchblende from Jáchymov, Bohemia, 207; uraninite from Morogoro, East Africa, 605; pitchblende from Katanga, Belgian Congo, 550. From the published data for thorianite from Ceylon, the half life-period for thorium is calculated as  $T = (1.65 \pm 0.05) \times 10^{10}$  years, and the age of the thorianite estimated at about 150 million years. The genetic relationship between uranium and thorium is discussed, and for thorium uranium is calculated  $T = 63.2 \times 10^6$  or  $62.6 \times 10^6$  years.

L. J. S.

**Occurrence of Iodine in Nature. VII. Iodine Content of Rocks, Geological Formations, and Minerals, and Conditions for the Accumulation of Iodine in Earths.** T. VON FELLEBERG (*Biochem. Z.*, 1924, 152, 153—171).—Iodine is present in rocks and sedimentary deposits in amounts considerably greater than in organic products. It occurs partly in acid-soluble and partly in acid-insoluble form, and is but slightly extracted by water. No relation between iodine content and given geological formations appears to exist. The same mineral from different sources generally contains the same amount of iodine, but chemically similar and mineralogically different specimens (*e.g.*, quartz) often contain very different amounts of iodine. The iodine present in weathered rocks, and still more so in the earths derived from these rocks, is greater than in the original unweathered rock. The accumulation of iodine is more evident in acid than in basic rocks and earths.

J. P.

**Occurrence of Iodine in Nature. VIII. Evolution of Elementary Iodine from Earths.** T. VON FELLEBERG, H. GEILINGER, and K. SCHWEIZER (*Biochem. Z.*, 1924, 152, 172—184).—In the presence of oxygen earths and rocks liberate elementary iodine from added alkali iodide. The action is catalytic and is specially marked if ferric oxide and alkaline-earth carbonates be present. Ferrous iron is much less catalytically active. Earth treated with manure liberates less iodine than untreated earth. The smaller the catalytic activity an earth possesses the greater is its power of accumulating iodine. Earths of low catalytic power are found in districts relatively free from goitre and *vice versa*.

J. P.

**Merrillite and Chlorapatite in Stony Meteorites.** E. V. SHANNON and E. S. LARSEN (*Amer. J. Sci.*, 1925, [v], 9, 250—260).—A calcium phosphate sparingly present (a few hundredths of 1%) in certain meteoric stones was provisionally referred to francolite by Merrill in 1917, and was called merrillite by Wherry in the same year. In order to isolate sufficient material for analysis, 0.5—1 kg. samples of the material were crushed and sieved and separated by means of an electromagnet and heavy liquids. From the Allegan meteorite 35 mg. of merrillite were isolated, and from the New Concord meteorite 58 mg. of merrillite (I) and 42 mg. of chlorapatite (II), which yielded:

	P <sub>2</sub> O <sub>5</sub> .	CaO.	Na <sub>2</sub> O.	Cl.	F.	CO <sub>2</sub> .	Insol.	Sp. gr.
I.	35.21	44.10	16.42	trace	nil	nil	4.27	3.10
II.	36.06	52.40	—	4.87	nil	—	5.29	3.20

This and two other analyses give for merrillite the formula  $3\text{CaO}, \text{Na}_2\text{O}, \text{P}_2\text{O}_5$ . It is distinct from any known terrestrial mineral, and it does not belong to the apatite group, although it is optically uniaxial and negative ( $\omega=1.623$ ,  $\epsilon=1.620$ ). A search for merrillite amongst the apatite isolated from 25 samples of rocks and iron ores was unsuccessful.

L. J. S.

**Cordierite from Madras, India.** M. S. KRISHNAN (*Min. Mag.*, 1924, **20**, 248—251).—Cordierite of a deep violet colour and  $d$  2.598 from a garnet-sillimanite-cordierite-gneiss in the Madura district, Madras, gave :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	MnO.	H <sub>2</sub> O.	Total.
48.37	29.22	2.20	7.07	9.54	1.92	0.42	1.84	100.58

It is unusual in often being optically positive. The optic axial angle in four crystals was  $2V=81^\circ$  to  $84^\circ$  over the positive bisectrix, whilst in another crystal  $2V=85^\circ$  over the negative bisectrix. This variation in the optic axial angle is probably due to the isomorphous replacement of magnesia by ferrous oxide. The violet colour of the mineral is to be attributed to manganese rather than to iron.

L. J. S.

**Calcio-Ancylite and accompanying Minerals from the Chibine Mountains [Russian Lapland].** G. P. TSCHERNIK (*Bull. Acad. Sci. Russie*, 1923, **17**, 81—94).—This mineral,  $d$  3.82, has the composition :

Ce <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	SrO.	CaO.	BaO.	Fe <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .
37.81	0.59	9.69	3.49	1.27	0.32	0.65
Na <sub>2</sub> O + K <sub>2</sub> O.	SiO <sub>2</sub> .	CO <sub>2</sub> .	H <sub>2</sub> O.	Impurities.	Total.	
0.39	1.15	22.70	4.44	17.8	100.32	

If the impurities, and the iron, aluminium, alkali metals, and silica, which appear to be derived from natrolite or other admixtures, are left out of account, the formula of the mineral is calculated to be  $5\{(Ce,Y)_2O_3,3CO_2\},7\{(Sr,Ca,Ba)O,CO_2\},10H_2O$ . The only other published analysis of ancylite was made by Mauzelius (*Z. Kryst.*, 1901, **34**, 649) on a specimen from Narsarsuk in Southern Greenland, and indicated the formula  $4Ce(OH)CO_3,3SrCO_3,3H_2O$ . The mineral investigated by the author has evidently been subjected to the action of an alkaline solution rich in calcium, barium, and iron.

The matrix containing the calcio-ancylite contained also (i) grains of violet-red yttrocerite,  $2\{(Ce,Y)_2F_6\},18CaF_2,3H_2O$ ,  $d$  3.61, hardness 4, and (ii) crusts of snow-white, porcelain-like material,  $d$  2.86, hardness above 5, and of composition corresponding with the formula  $2(Ce,Y,Al)_2O_3,2(Ca,Fe^+,K_2,Na_2)O,5(Si,Ti)O_2,8H_2O$ , which resembles that of the zeolites in structure. T. H. P.

**Manganese-bearing River Pebbles.** E. DITTLER (*Tsch. Min. Mitt.*, 1924, **36**, 164—169).—"Shiny pebbles" from the bed of the Vistula have a thin (1—2 mm.) black coating of iron and manganese hydroxides, the smooth surface having a metallic lustre. Analysis of a sandstone pebble gave : insoluble in hydrochloric acid (quartz grains) 90.84, Mn<sub>2</sub>O<sub>3</sub> (and MnO<sub>2</sub>) 1.14, Fe<sub>2</sub>O<sub>3</sub> 3.67, H<sub>2</sub>O 4.19% ; micro-sections show the presence of psilomelane and limonite as the cementing material of the sand grains. Pebbles of mangandolomite from the Enns in Upper Austria show a dull black skin 1—2 mm. in thickness. Analyses of the inner

and outer portions show that manganese hydroxide has accumulated on the exterior at the expense of manganese carbonate. Experiments were made on the adsorption of manganese from a solution of manganese hydrogen carbonate by quartz sand and other materials. Quartz sand took up 51.74% of the manganese from the solution, kaolin 68.73, compact limestone 72.90, marl 78.53, and precipitated chalk 96.53% (in the last case there being probably also chemical replacement). It is suggested that in the case of the "shiny pebbles" the manganese was taken up from the river water.

L. J. S.

**New Mineral Analyses.** E. DITTLER (*Tsch. Min. Mitt.*, 1924, 36, 213—216).—*Talc from Sirwan, Armenia*.—A compact, pale yellowish-green mineral, thought to be "agalmatolite" gave  $d$  2.832,  $n$  1.554, and, on material dried at  $110^\circ$ , the results under I. The molecular ratios  $H_2O : RO : SiO_2 = 1 : 2.5 : 3$  differ somewhat from those of talc.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	NiO.	MgO.	CaO.	H <sub>2</sub> O.	Total.
I.	59.44	0.24	trace	1.51	0.12	0.02	31.11	1.85	5.80	100.09

*Damourite from Mt. Lyell, Tasmania*.—Pale greenish material translucent at the edges and consisting of a compact aggregate of fine scales has  $d$  2.872; from analysis II (mean of two) is calculated: muscovite ( $KH_2Al_3Si_3O_{12}$ ) 98.07, fayalite ( $Fe_2SiO_4$ ) 1.93 mol.-%.

*Felspars from Lower Austria*.—These are from a felspar quarry in pegmatite between Krems and Gföhl. Microcline-perthite,  $d$  2.558, showing enclosed spindles of albite, gave III, corresponding with orthoclase 68.10, albite 31.90 mol.-%. Albite,  $d$  2.625, as bluish-white cleavages, gave IV, corresponding with albite 98.14, orthoclase 1.86 mol.-%.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O (-110°).	H <sub>2</sub> O (+110°).	Total.
II.	43.37	39.03	0.40	1.41	—	10.98	0.75	0.76	3.80	100.50
III.	64.20	20.55	0.14	—	trace	11.26	3.48	—	0.28	99.91
IV.	66.80	20.94	—	—	trace	0.34	11.91	—	0.10	100.09

L. J. S.

**Composition of the River and Lake Waters of the United States.** F. W. CLARKE (*U.S. Geol. Survey, Prof. Paper*, 135, 1924, 198 pp.).

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### Analytical Chemistry.

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**Logarithmic Tables for Volumetric Analysis.** E. J. KRAUS (*Chem.-Ztg.*, 1925, **49**, 145).—The author recommends the construction of special tables giving only the essential figures required, *e.g.*, the logarithms of numbers increasing by 0.05 corresponding with burette readings and the factors and their logarithms cor-



responding with different titres of a definite weight of the standard substance.

A. R. P.

**Qualitative "Drop-analysis" of the Elements in Groups I to III.** N. A. TANANAEV (*Z. anorg. Chem.*, 1924, **140**, 320—334).—A method is given for the qualitative analysis of solutions containing the nitrates of most of the metals occurring in the first three analytical groups. The reactions, which are carried out on one drop of solution, are arranged so that the tests for any one metal are, as a rule, not masked by the presence of the other metals. A modified scheme is also described in which a preliminary separation into groups is carried out by precipitating all the metals as sulphides and successively treating the precipitate with acids of different concentration.

S. K. T.

**Collodion Ultra-filtration Membrane for Physico-chemical Analysis of Solutions.** E. FOUARD (*Ann. Chim. Analyt.*, 1925, [ii], **7**, 33—34).—A diaphragm of collodion is capable of acting as a retainer not only of micro-organisms but also of colloidal, protein, pectic, cellulosic, starch, and tannic aggregates. It may be rendered rigid and resistant to a pressure of 40 atm. by being deposited on a framework of fine mesh wire (1—2 mm.) surrounding an artificial silk envelope, which in its turn covers an enamelled metal tube uniformly pierced by small holes. [Cf. *B.*, 1925, 268.]

D. G. H.

**Rapid Determination of Solid Matter in Liquids.** C. B. VON BÖRNEGG (*Chem.-Ztg.*, 1925, **49**, 185).—The evaporation of a small quantity of the liquid is accelerated by means of a filter-paper which is held vertical, with its lower edge in the liquid, by means of a wire passing through a hole pierced in the upper portion. The liquid must not ascend as high as the hole. The filter-paper is weighed in with the containing dish both before and after evaporation. [Cf. *B.*, 1925, May 1.]

S. K. T.

**Detection of Gaseous Poisons in Blood.** E. KOHN-ABREST.—(See i, 451.)

**Quantitative Chemical Analysis by Means of X-Ray Spectrum.** D. COSTER and Y. NISHINA (*Chem. News*, 1925, **130**, 149—152).—The method of determining the proportion of a metal in a mixture of oxides containing it by adding a known weight of another oxide until the intensity of one of its lines in the X-ray spectrum coincides with that of the corresponding line in the spectrum of the metal the proportion of which is required, sometimes gives false results owing to the presence of other elements. This defect in the process may be remedied by determining in an artificial mixture of the same substances in known proportions the concentration of added element necessary to make the intensity of any one of its lines equal to that of any near one of the lines of the element the proportion of which is sought. In this way a factor is obtained which is used in calculating the proportion of the desired element in the original mixture from the data obtained by testing this mixture in the same way as the standard. For

example, in the determination of hafnia in zirconium materials the intensity of the  $L\beta_1$  line of hafnium is compared with that of the  $L\beta_2$  line of lutecium, and in the determination of zirconium in hafnium compounds the  $L\alpha$  line of zirconium is compared with the  $L\beta_1$  line of yttrium.

A. R. P.

**Spectrophotometric Determination of Hydrogen-ion Concentrations and of the Apparent Dissociation Constants of Indicators. II. Thymol-blue. III. Bromocresol-green.**

W. C. HOLMES and E. F. SNYDER (*J. Amer. Chem. Soc.*, 1925, 47, 221—226, 226—229).—II. The dissociation curve of thymol-blue in alkaline solution conforms with the theoretical dissociation curve over a range of less than 10% and more than 90% dissociation. In the acid range the dissociation of the indicator remains normal up to the mid-point, beyond which dissociation is retarded. The average values obtained for the apparent dissociation constant,  $K$ , were 8.91 in the alkaline range and 1.5 in the acid range.

III. The apparent dissociation constant of bromocresol-green was found to be 4.68 in a relatively pure sample, 4.65 and 4.69 in commercial samples. The dissociation curve in the alkaline range conformed with the theoretical formula between 10% and 90% dissociation.

G. S. W.

**Rational Notation for the Expression of the Reaction of Solutions. D. GIRIBALDO** (*Anal. Fis. Quím.*, 1924, 22, 555—572).

—The disadvantages of the Sørensen ( $p_H$ ) method of expressing the reaction of solutions are discussed. The author proposes  $\log [H]/[OH]$  as an expression for reaction. By this means, neutrality is expressed by zero. Comparative figures are given for different acids and also for certain physiological fluids.

G. W. R.

**Antimony Electrode as an Indicator for Hydrogen Ions and its Application in Potentiometric Titrations of Acids and Bases. I. M. KOLTHOFF and B. D. HARTONG** (*Rec. trav. chim.*, 1925, 44, 113—120).

—The potential of the antimony electrode, as used in presence of a little antimony oxide, changes with  $p_H$ , but its rate of change at  $p_H$  1—5 differs from that at  $p_H > 9$ . The use of an antimony electrode in neutralisation reactions is described, whilst it may be employed where the hydrogen electrode cannot, in determining free acid in the presence of oxidising agents.

F. M. H.

**Colorimetric Determination of Hydrogen-ion Concentration in Soils. H. NIKLAS and A. HOCK** (*Z. angew. Chem.*, 1925, 38, 150—151).—Either Michaelis' nitrophenol series or Clark's series of indicators may be used for  $p_H$  determinations in soils. The results agree well with those obtained electrometrically.

W. A. S.

**Borax as a Standardising Agent for Acids and Bases.**

M. G. MELLON and V. N. MORRIS (*Ind. Eng. Chem.*, 1925, 17, 145—146).—Borax is shown to be a suitable standardising reagent for

both hydrochloric and sulphuric acids, and sodium, potassium, and barium hydroxides, and if suitably recrystallised appears to have no disadvantages. Indicators of suitable  $p_H$  range are methyl-orange for the acids and phenolphthalein for the bases. [Cf. *B.*, 1925, 269.]  
D. G. H.

**Determination of the Acidity of Mineral Soils.** G. HAGER.—(See i, 489.)

**Determination of Free Acid of Gastric Juice.** H. SAHLI.—(See i, 458.)

**Test for Chlorine in the Presence of Bromine, Iodine, etc.** M. DIMITROFF (*Z. anorg. Chem.*, 1924, **140**, 253—260).—The substance is oxidised by potassium permanganate in acid solution in a flask so fitted that air can be passed through the solution during the process and passed, together with the halogens evolved, out into a solution containing one or two drops of 0.1*N*-ammonium bromide in 10 c.c. of 2*N*-sulphuric acid. Here any chlorine from the original substance replaces bromine in the solution. One to two drops of sodium bromate are now added while air (now pure) is still passed through. The bromide is oxidised and the bromine passes off whilst the chloride remains unaffected; thus a precipitate with silver nitrate indicates chlorine in the original substance.

L. J. H.

**Determination of Chlorides in Blood.** C. BENGUEREL.—(See i, 455.)

**Determination of Chlorides and Sulphates in Expressed Plant Tissue Fluids.** R. A. GORTNER and W. F. HOFFMAN.—(See i, 455.)

**Sensitive Reaction for Copper and Bromine.** K. SCHERINGA (*Pharm. Weekblad*, 1925, **62**, 173—174).—The solution is evaporated to dryness and the residue damped with sulphuric acid containing a trace of a bromide or a copper salt. Formation of copper bromide occurs with a deep violet coloration. The test will detect 0.0005 mg. of sodium bromide or of a copper salt; it is very suitable for the detection of bromine in organic materials.

S. I. L.

**Detection of Minute Quantities of Bromine [in Blood].** H. BERNHARDT and H. UCKO.—(See i, 454.)

**Colorimetric Determination of Oxygen.** W. W. EFIMOFF.—(See i, 481.)

**Determination of Dissolved Oxygen.** J. N. FRIEND (*Chem. News*, 1925, **130**, 163—164).—When using Winkler's method for determining dissolved oxygen, introduction of air may be avoided by using a 250-c.c. flask closed by the stem of a tap funnel, which is a capillary glass tube accurately fitting the neck of the flask, so that when the stopper is inserted a space of about 2 c.c. is left above the 250-c.c. mark. The addition of the manganese chloride

solution after introduction of the sodium hydroxide and potassium iodide solution fills the capillary tube on insertion of the stopper, and at the end of the reaction the hydrochloric acid is put in the funnel, the tap opened, and the stopper gradually withdrawn. [Cf. *B.*, 1925, May 1.]

D. G. H.

**Determination of Oxygen in Pure Iron.** T. E. ROONEY (*J. Iron and Steel Inst.*, 1924, 110, 122—128).—For the determination of oxygen in iron by heating the metal in hydrogen and weighing the water formed, it is essential to use extremely fine millings of the metal as the depth of penetration of the hydrogen is only about 0.5 mm. even after prolonged heating at 1200°. This temperature is necessary in order to effect complete removal of the oxygen, and is best obtained by using an alundum tube electric furnace wound with platinum strip and capable of giving a temperature of 1300°. A calcium chloride bulb for the absorption of the water is preferable to a sulphuric acid tube. Care should be taken not to allow the temperature to rise much above 1200° as high results will be obtained owing to reduction of the silica boat by hydrogen in the presence of iron to form iron silicide. Consistent results, usually a little lower than those obtained by the above method, may be obtained by heating a mixture of the iron millings with three times their weight of an alloy of 60% Sn and 40% Sb at 950—1000° in a stream of hydrogen. In all cases a blank test should be carried out and the appropriate deduction made.

A. R. P.

**Determination of Sulphide, Polysulphide, and Thiosulphate Sulphur in Solutions of Alkali and Alkaline-earth Sulphides.**

E. SCHULEK (*Z. anal. Chem.*, 1925, 65, 352—358).—The solution to be analysed is allowed to fall into a boiling solution of boric acid and potassium cyanide free from air and the evolved hydrogen sulphide is collected in potassium hydroxide and hydrogen peroxide, the sulphate formed being determined as usual. The residual liquid in the distilling flask contains thiocyanate from the polysulphide sulphur, and undecomposed thiosulphate; it is divided into two parts in one of which the thiosulphate is determined iodometrically, and in the other the thiocyanate by treatment with bromine, removal of excess of the latter with phenol, and titration of the bromocyanogen with thiosulphate, after addition of potassium iodide. [Cf. *B.*, 1925, 241.]

A. R. P.

**Preparation of Nessler's Solution.** H. D. RICHMOND (*Analyst*, 1925, 50, 67).—The precipitate obtained on mixing aqueous solutions of potassium iodide (17.5 g. in 100 c.c.) and mercuric chloride (15 g. in 300 c.c.) is washed by decantation and dissolved in potassium iodide solution (17.5 g. in 100 c.c.), a few drops of mercuric chloride added until a permanent red precipitate appears, and then water to 500 c.c. Aqueous sodium hydroxide (105 g. in 300 c.c.) is added at 0°, and the mixture diluted to 1 litre. The clear portion is sensitive immediately after preparation.

D. G. H.

**Tromsdorff Reagent for Nitrites.** A. COQUILLAT (*Anal. Fis. Quím.*, 1924, 22, 523—544).—Directions are given for the preparation of a more sensitive and stable modification of the Tromsdorff reagent for nitrites. The delicacy of the reaction is increased by the presence of dissolved oxygen. [See B., 1925, 261.]

G. W. R.

**Separation of Phosphoric Acid in Qualitative Analysis by means of Basic Bismuth Nitrate.** A. KESCHAN (*Z. anal. Chem.*, 1925, 65, 346—351).—The solubility of bismuth phosphate in dilute nitric acid is proportional to the concentration of acid up to 0.4*N*, but is considerably increased in the presence of halogen acids. For the separation of phosphoric acid from a solution to be tested for metals of groups III, IV, and V the slightly acid solution is treated with hydrazine hydrochloride to reduce ferric salts to ferrous, then with solid bismuth oxynitrate which removes the halogen ions first, then phosphoric acid. The precipitate filters readily and the filtrate will contain less than 1 mg. of phosphoric anhydride per litre.

A. R. P.

**Determination of Lipoid Phosphorus in Cereal Products.** O. S. RASK and I. K. PHELPS (*Ind. Eng. Chem.*, 1925, 17, 189—190).—Since the ammoniacal method extracts all the lipoids, the phospholipins will be included and may be computed by a determination of total phosphorus in the extract. The result is higher than by direct determination. [Cf. B., 1925, 224.]

D. G. H.

**Salts of Cupferron.** V. AUGER, L. LAFONTAINE, and C. CASPAR (*Compt. rend.*, 1925, 180, 376—378).—The preparation, appearance, and solubilities of the following cupferron salts are described: (a) salts precipitated by hydrogen sulphide (generally in acid solution): silver, decomp. 130°, lead, m. p. 147°, mercurous, decomp. 215°, mercuric, decomp. 160°, bismuth, m. p. 170° (decomp.), cadmium, m. p. 245° (decomp.), stannous, m. p. 138°, stannic, m. p. 180° (decomp.), antimony, decomp. 112°, also  $[\text{Ph}\cdot\text{N}(\text{NO})\text{O}]\text{MoO}_3$ , decomp. 165°, and  $[\text{Ph}\cdot\text{N}(\text{NO})\text{O}]_2\text{MoO}_3$ , m. p. 139° (decomp.); (b) ammonium sulphide group: cerous, ceric, chromic, indium, m. p. 90°, cobaltic, m. p. 116° (decomp.), cobaltous, m. p. 162° (decomp.), nickel, decomp. 200°, zinc, m. p. 138°; (c) alkaline-earth group: barium (+3H<sub>2</sub>O), decomp. 245°, strontium (+2H<sub>2</sub>O), decomp. 290°, calcium (+2H<sub>2</sub>O), decomp. 275°.

F. M. H.

**Electrolytic Separation of Copper, Antimony, Lead, and Tin.** A. LASSIEUR (*Compt. rend.*, 1924, 179, 827—829; cf. this vol., ii, 159).—Lead and tin are deposited together from hydrochloric acid solution and cannot be separated by variation of the cathode potential. On adding hydrofluoric acid, stannic salts form a complex which does not yield tin on electrolysis; after deposition of lead, tin may then be determined in the resulting solution. In depositing copper and antimony in presence of lead by the method already described, tin is reduced to the stannous

form. This should be oxidised by means of hydrogen peroxide before separating the lead.

H. J. E.

**Complex-chemical Methods for the Volumetric Determination of Acidity, Basicity, and Aluminium Content of Aluminium Solutions.** F. FEIGL and G. KRAUSS (*Ber.*, 1925, 58, [B], 398—400).—The solution is treated with a suitable excess of alkali oxalate with which the aluminium salt reacts:  $\text{AlCl}_3 + 3\text{K}_2\text{C}_2\text{O}_4 = \text{K}_3[\text{Al}(\text{C}_2\text{O}_4)_3] + 3\text{KCl}$ , whereby the acid formed by hydrolysis of the aluminium salt is converted into neutral products. "Residual acidity" is determined by addition of potassium iodide-potassium iodate and titration of the liberated iodine. Aluminium is determined from the difference between "residual" and "total" acidity determined iodometrically. For the determination of basicity (*e.g.*, in basic aluminium acetate), the total acid is determined, after which a measured excess of 0.1N-hydrochloric acid is added and the experiment finished as in the determination of "residual" acid. The difference between the found and added acid indicates the amount of base which is liberated by formation of the complex.

H. W.

**Separation of Iron and Aluminium from Manganese and Magnesium and from Phosphoric Acid by Means of Sulphosalicylic Acid.** L. MOSER and A. BRUKL [and, in part, I. VÉN] (*Ber.*, 1925, 58, [B], 380—385; cf. A., 1923, ii, 438).—Manganese is separated from ferric iron by precipitation with disodium hydrogen phosphate in a solution containing ammonium chloride and sufficient sulphosalicylic acid, ammonia being finally added in slight excess. The precipitated manganese ammonium phosphate is weighed as the pyrophosphate, whilst iron is precipitated in the filtrate by hydrogen sulphide and finally weighed as ferric oxide.

Iron and manganese are separated from aluminium by precipitation with hydrogen sulphide in ammoniacal solution in the presence of sulphosalicylic acid (cf. Moser, *loc. cit.*); the precipitated sulphides are dissolved and iron and manganese are separated as described above.

Magnesium may be determined in the presence of iron and aluminium by rapidly adding a solution of diammonium hydrogen phosphate to a boiling solution of the salts (chloride, sulphate, or nitrate) in the presence of ammonium chloride, sulphosalicylic acid, and an excess of ammonia; the solution is boiled for a few minutes, treated with one-third of its volume of concentrated ammonia, and kept at the atmospheric temperature for a few hours, after which the magnesium ammonium phosphate is treated in the usual manner. Precipitates formed in neutral solution contain aluminium. The method is applicable to the determination of magnesium in the presence of a large excess of aluminium.

Phosphate is determined in the presence of iron and aluminium by precipitation with magnesia mixture in boiling ammoniacal solution containing ammonium chloride and sulphosalicylic acid. Iron is precipitated from the filtrate by ammonium sulphide.

Aluminium is determined from the difference in weight of the oxides. [Cf. *B.*, 1925, 269.] H. W.

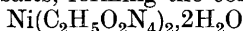
**Separation of Aluminium from Calcium by Means of Hexamethylenetetramine.** (MRS.) C. KOLLO and N. GEORGIAN (*Bul. Soc. Chim. România*, 1924, 6, 111—112).—Owing to the absorption of carbon dioxide by ammonia solution and the consequent formation of ammonium carbonate, calcium is sometimes precipitated to some extent with aluminium. Replacement of the ammonia by hexamethylenetetramine, which decomposes with formation of ammonia when boiled with the salt solution, yields results of far greater accuracy. [Cf. *B.*, 1925, 192.]

T. H. P.

**Volumetric Determination of Manganese.** B. N. ANGELESCU (*Bul. Soc. Chim. România*, 1924, 6, 109—110).—In presence of alcohol, potassium chromate precipitates manganous salts quantitatively as manganous chromate,  $\text{MnCrO}_4 \cdot 2\text{H}_2\text{O}$ , the excess of the known amount of potassium chromate taken being then determinable by titration with sodium thiosulphate. The method gives accurate results. [Cf. *B.*, 1925, 192.]

T. H. P.

**Use of Oxalenediuramidoxime in the Detection and Determination of Nickel.** F. FEIGL and A. CHRISTIANI-KRONWALD (*Z. anal. Chem.*, 1925, 65, 341—345).—Oxalenediamidoxime (Zinkeisen, A., 1890, 122) functions as an oxime and as an ammonia derivative with nickel salts, forming the compounds,



and  $\text{Ni}(\text{C}_2\text{H}_6\text{O}_2\text{N}_4)_3\text{Cl}_2$ ; cobalt salts yield a sparingly soluble derivative of the first type, so that this reagent is useless for separating these elements. If, however, two  $\text{NH}_2 \cdot \text{CO} \cdot$  groups are introduced into the molecule, the acidic properties of the compound so formed, oxalenediuramidoxime (Zinkeisen, *loc. cit.*), become more pronounced and the basic properties entirely suppressed, so that compounds of the first type only are formed with nickel salts. Oxalenediuramidoxime in ammoniacal solution produces a visible precipitate in ammoniacal nickel solutions containing more than 1 part of the metal in 150,000 parts. The precipitate is orange-yellow, crystalline, slightly soluble in hot water, but insoluble in cold water or ammonia, and contains 19.92% Ni when dried at 110—130°; it may be used for the gravimetric determination of nickel and for the separation of nickel from cobalt. [Cf. *B.*, 1925, 269.]

A. R. P.

**Colorimetric Determination of Molybdenum.** H. TER MEULEN (*Chem. Weekblad*, 1925, 22, 80—81).—The dark red colour of ammonium thiomolybdate,  $(\text{NH}_4)_2\text{MoS}_4$ , allows of colorimetric titration. The comparison solution is one of ammonium molybdate, to which an equal volume of ammonia is added, and hydrogen sulphide passed in. The method is rapid and fairly accurate, and not affected by alkalis. Vanadium and tungsten interfere.

S. I. L.

**Oxidimetric Titration of Uranium.** O. KOBILIC (*Chem. Listy*, 1925, 19, 1—3).—When salts of sexavalent uranium are reduced with the usual metallic reducing agents the greater part of the uranium is converted into the quadrivalent form, but there is always a certain amount of a derivative of a lower oxide produced. Lead, in the presence of hydrochloric acid, quantitatively reduces uranyl chloride to uranium tetrachloride, which, after addition of manganese sulphate and sulphuric acid, may be titrated with permanganate with good results. [Cf. *B.*, 1925, 270.]

A. R. P.

**Volumetric Determination of Sugar by Schoorl's Process.** C. VAN DER HOEVEN (*Chem. Weekblad*, 1925, 22, 79—80; cf. this vol., ii, 74).—The statement of van den Hout, Neeteson, and van Scherpenberg that the concentration of the Fehling's solution influences the result is confirmed; the effect can be compensated by altering the time of boiling.

S. I. L.

**Sugar Analysis by Fehling's Method.** P. KLASON (*Svensk Kem. Tidskr.*, 36, 195—202; from *Chem. Zentr.*, 1924, ii, 2798).—A critical study of Fehling's method for the determination of sugars. The conversion of the cuprous into cupric oxide is best effected in a silica crucible.

R. B.

**Micro-determination of Blood-sugar.** C. J. DIAZ and B. S. CUENCA.—(See i, 453.)

**Comparison of certain Chemical Methods for the Determination of Dextrose.** A. IONESCU and (MLLE.) E. SPIRESCU (*Bul. Soc. Chim. România*, 1924, 6, 101—108).—The methods of Fehling, Bertrand, and Lehmann give good results in the determination of dextrose in liquids containing 0.1—1% of the sugar, but they are more difficult to operate than the ferricyanide method (cf. Ionescu and Vargolici, A., 1921, ii, 283), which furnishes equally exact results. This last method yields accurate results also with solutions such as cerebro-spinal fluid, containing between 0.05% and 0.1% of the sugar, and is easier to apply than the Folin and Wu (A., 1920, ii, 337) and the Fontès and Thivolle methods (A., 1921, ii, 563), although these are capable of affording satisfactory results.

T. H. P.

**Determination of Dextrose in presence of Sucrose in Organic Liquids.** M. BUFANO.—(See i, 453.)

**Influence of Hydrogen-ion Concentration on the Colorimetric Determination of Pyrogallol and Pyrocatechol Derivatives.** S. GLASSTONE (*Analyst*, 1925, 50, 49—53).—The violet colorations produced by certain phenolic compounds with Mitchell's ferrous tartrate reagent are seen only between certain definite  $p_H$  limits which even vary between different substances of the same group. The addition of 5—10 c.c. of 10% ammonium acetate solution to the usual reaction quantities, together with a little ammonia solution in the case of pyrocatechol derivatives, usually ensures the development of maximum colours. [Cf. *B.*, 1925, 226.]

D. G. H.



**Gravimetric Micro-determination of Cholesterol.** T. TOMINAGA.—(See i, 453.)

**Determination of Cyanates in Blood.** E. G. MONTGOMERY.—(See i, 455.)

**Application of Sodium Hyposulphite in Qualitative Organic Analysis.** E. CLARK (*Chem. News*, 1925, 130, 132—133).—The reduction of aromatic nitro compounds in qualitative analysis is effected in the presence of alkali by solid sodium hyposulphite, the excess of which is removed by boiling with excess of concentrated hydrochloric acid. S. K. T.

**Colour Standards for Use in the Determination of Glyoxalines.** G. HUNTER (*Biochem. J.*, 1925, 19, 42—46).—Commercial Congo-red and methyl-orange must be purified before use as artificial standards in colorimetric work. Details are given for the preparation of a colour standard made from pure Congo-red and methyl-orange suitable for the determination of histidine or carnosine. S. S. Z.

**Determination of Lipoids in Blood Serum.** S. MINOVICI and (MISS) M. ILIESCO.—(See i, 452.)

**Determination of Lecithin in Blood.** A. GRIGAUT.—(See i, 453.)

**Detection of Urobilin and Urobilinogen in Urine.** C. BENGUEREL.—(See i, 460.)

**Determination of Methæmoglobin in the Presence of its Cleavage Products.** J. B. CONANT and L. F. FIESER.—(See i, 456.)

**Detection of Chlorophyll Degradation Products in Urine.** M. HOFSTETTER.—(See i, 460.)

**Enzymic Hydrolysis of Proteins. III. Determination of Peptic and Tryptic Digestion of Caseinogen.** P. RONA and H. KLEINMANN.—(See i, 473.)

**Source of Error in the Use of Lintner's Starch Solution for determining Diastatic Power.** W. SYNIEWSKI.—(See i, 470.)

**Determination of Diastase in Fæces.** W. FRANK and F. DOLESCHALL.—(See i, 461.)

**Determination of Lipase in Body Fluids and in Tissues.** P. RONA and A. LASNITZKI.—(See i, 471.)

**Standards for the Colorimetric Determination of Trypsin.** J. A. SMORODINZEV and A. N. ADOVA.—(See i, 473.)

**Chemical Analysis of Soil.** K. K. GEDROIZ.—(See i, 489.)

## General, Physical, and Inorganic Chemistry.

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**Continuous Hydrogen Spectrum.** A. CARST (*Ann. Physik*, 1924, [iv], 75, 665—672).—The continuous ultra-violet hydrogen spectrum found by Stark (A., 1917, ii, 281; 1918, ii, 141) in the canal rays, and ascribed by him to an atomic quantum pair, has been examined. The spectrum is found when the hydrogen or nitrogen canal rays pass into hydrogen, but not when hydrogen canal rays pass into nitrogen, and it coincides with the Geissler tube spectrum. The starting point is in the visible spectrum and changes with the pressure. The spectrum appears to be due to the hydrogen molecule and has nothing to do with the Bohr continuous spectrum, which is probably only obtained if the higher members of the Balmer series are excited at the same time. M. S. B.

**Excitation of the Secondary Spectrum of Hydrogen by Electron Impacts.** O. S. DUFFENDACK (*Astrophys. J.*, 1924, 60, 122—132).—Practically the entire secondary spectrum of hydrogen was developed below the ionisation potential of 16 volts. The spectrum is apparently due to the neutral molecule, and its excitation is not intimately connected with the dissociation of the molecule. Support is afforded for the existence of a characteristic ultra-violet spectrum due to the molecule the initial state of which is identical with the final state of the molecule after the emission of the secondary lines. A. A. E.

**Spectrum of Nitrogen.** T. R. MERTON and J. G. PILLEY (*Proc. Roy. Soc.*, 1925, A, 107, 411—422).—The nitrogen arc spectrum can be obtained free from the band or spark spectrum by passing a weak condensed discharge through helium at a pressure of about 30 mm. of mercury and adding a little nitrogen to the gas by heating alumina which has been soaked in sodium azide solution. Argon will not serve the same purpose. The explanation offered is that the resonance potential of helium is 20·4 volts and that of argon 11·5 volts; the value for the arc spectrum of nitrogen may lie between these. The spark spectrum requiring more than 20·4 volts will not be produced, because the helium will act as a "safety valve" for the energy. The small partial pressure of the nitrogen will favour the existence of atoms. A table of wave-lengths of the lines in the arc spectrum is given.

From a study of the spectrum of the light excited by electronic impact it was deduced that as the energy of impact increased there was direct transition from the negative band spectrum to the spark spectrum, indicating that the nitrogen molecule did not break up into neutral atoms but into ions. E. B. L.

**Spontaneous Reversal of Rays in the Neon Spectrum.** H. BUISSON and C. JAUSSEAN (*Compt. rend.*, 1924, 180, 505—507).—Many of the fine lines in the spectrum of neon which were pro-

posed as standards of wave-length measurements have previously been shown (Pérard, *ibid.*, 1923, 176, 375) to consist of doublets; and this is now shown, by means of interference effects with silvered slides, to be due to the spontaneous reversal of several of the rays. The phenomenon is shown to the greatest extent by the line 6402, where a separation of 0.060 Å. occurs with a current of 3 milliamps. These observations render the use of the neon lines as a wave-length standard inadvisable.

J. W. B.

**Spark Spectrum of Neon.** L. BLOCH, E. BLOCH, and G. DÉJARDIN (*Compt. rend.*, 1925, 180, 731—733).—The method previously described (A., 1924, ii, 286) has been applied to the examination of the first order spark spectrum of neon. About 250 lines are recorded in the region 4900—2700 Å. The values given are accurate to within 0.05 Å.

J. S. C.

**First Spark Spectra of Zinc and Cadmium.** G. VON SALIS (*Ann. Physik*, 1925, [iv], 76, 145—162).—The first spark spectra, Zn II and Cd II, of zinc and cadmium, respectively, have been examined photographically, the discharge taking place in a tube in which the vapour of the metal itself formed the carrier, the metal being vaporized from a hollow cathode. The Ritz formula has been applied. For every term value the effective quantum number,  $n^*$ , and the nuclear charge number,  $p^*$ , have been determined. The relation of the chief quantum numbers,  $n$ , to the term values is in agreement with the standard given by Bohr (A., 1923, ii, 679), who foretold a penetration of the  $p$ -orbit. The  $d$ -orbit is also penetrated. The tables given are so arranged that the term values of zinc and cadmium, and the quantities  $n^*$ ,  $p^*$ , and  $(n - n^*)$  may be easily compared.

M. S. B.

**Spark Spectrum of Mercury in the Extreme Red.** J. LAFFAY (*Compt. rend.*, 1925, 180, 823—825).—The spark spectrum of mercury was not hitherto known on the red side of 600  $\mu\mu$ . About 70 new lines extending to 800  $\mu\mu$  have been found by using pan-chromatic plates and a grating spectrograph of high dispersion. The mercury arc lines in the same region are given for comparison.

R. A. M.

**Spectrum of Potassium Excited during its Spontaneous Combination with Chlorine.** L. A. RAMDAS (*Nature*, 1925, 115, 533—534).—Spectrum photographs of potassium spontaneously burning in chlorine at the ordinary pressure show a strong emission band extending from 7200 to 6150 Å., many arc lines, and the enhanced lines 4466, 4388, 4307, 4220, and 4115 Å. The excitation of the enhanced lines in the absence of any external electrical forces is accounted for by the electron affinity of the chlorine atom, together with the temperature attained by the potassium vapour.

A. A. E.

**Regularities in the Arc Spectrum of Cobalt.** F. M. WALTERS, jun. (*J. Washington Acad. Sci.*, 1924, 17, 407).—An extension of

previous work (A., 1923, ii, 519) on the arc spectra of elements of group VIII. Eighty-eight lines of the arc spectrum of cobalt have been classified into twelve multiplets in the quartet system resulting from the combination of two *P*-levels, two *D*-levels, three *F*-levels and one *G*-level. Whilst the terms found previously for the arc spectrum of iron belong to systems of odd permanent multiplicity, those found for cobalt belong to even systems. In addition to the quartet terms, there is evidence for the existence of a doublet or sextet system. The separations of the sub-levels of the quartet system of cobalt are on the average four to five times larger than the corresponding separations of the sub-levels of the quintet system terms in iron.

A. E. M.

**Regularities in the Arc Spectrum of Nickel.** F. M. WALTERS (*J. Washington Acad. Sci.*, 1925, **15**, 88—100).—A preliminary analysis of the arc spectrum in which 345 lines are classified. The distribution of the inner quantum numbers indicates that the spectrum consists of singlets and triplets. The spectroscopic alternation law holds in the triad Fe, Co, Ni.

F. G. T.

**Vacuum-arc Spectrum of Titanium.** H. CREW (*Astrophys. J.*, 1924, **60**, 108—121).—Measurements of the vacuum-arc spectrum of titanium between 6366–382 Å. and 3653–499 Å. revealed 78 new lines. Practically no impurity was found in cast titanium. Temperature regulation by the toluene control was made more frequent by wrapping a portion of the heating coil directly on the bulb.

A. A. E.

**Spectrometric Methods of Investigation of the Infra-red.** H. WITT (*Z. Physik*, 1924, **28**, 236—248).—The construction of sensitive bolometers and thermopiles for infra-red spectrometry is given in detail. In the course of testing the apparatus, measurements of the infra-red absorption of water-vapour were obtained.

S. B.

**Spectroscopy in the Infra-red Region of the Spectrum.** A. TROWBRIDGE (*J. Franklin Inst.*, 1925, **199**, 343—352).—A review of advances in the technique and of the treatment of series and band spectra in the infra-red region.

F. G. T.

**Intensity Measurements in the Ultra-violet.** H. B. DORGELO (*Z. Physik*, 1925, **31**, 827—835).—An extension of a method already published (*ibid.*, 1923, **13**, 206; A., 1924, ii, 282) for determining the relative intensities of the components of multiplets. The relative intensities are found by comparing the densities of photographs taken through screens of graduated transparency. Screens transparent to 2200 Å. were prepared by coating quartz plates with films of platinum. The relative intensities of the spark doublets of the first and second subsidiary series of calcium were measured; the ratio depends on the current, but it is concluded that it would be 2 : 1 if self-reversal were prevented; for the multiplet 3181, 3179, 3158, the ratio is 11 : 100 : 54.

E. B. L.

**Exact Measurements of Spectral Frequencies in the Region between Light and X-Rays ( $L_{III}$ -Discontinuities of Cl, S, P, Si, Al).** F. HOLWECK (*Compt. rend.*, 1925, **180**, 658—661; cf. *ibid.*, 1925, **180**, 266).—By the absorption method previously described, the critical potentials for the levels  $L_{III}$   $L_{II}$  have been found for the elements of atomic number 13—18, as follow: argon, 246·5, chlorine 203, sulphur 163, phosphorus 128, silicon 98, and aluminium 68 volts, with a probable error of  $\pm 1$  to  $\pm 2$ . These results, which fit excellently on a Moseley diagram, are compared with other determinations in the same region. G. M. B.

**Relative Intensities of Fluorescent and Scattered X-Rays.** G. L. CLARK and W. DUANE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 173—175; cf. A., 1924, ii, 368, 369).—The scattered and tertiary radiation due to tungsten X-rays falling upon chemical elements of atomic weights near that of molybdenum are extremely weak as compared with the fluorescent radiation. The scattered radiation from these heavy elements is much weaker than that from light elements.

F. G. T.

**Total Intensity of Scattered X-Radiation.** O. K. DE FOE and W. W. NIPPER (*Nature*, 1925, **115**, 607).

**Spectroscopic Evidence of  $J$ -Transformation of X-Rays.** S. R. KHASTGIR and W. H. WATSON (*Nature*, 1925, **115**, 604—605).—Deviations from the simple relation between the atomic number of a radiator and the wave-lengths of its X-ray emission spectrum of  $K$ -series, occurring at  $n = 52$  and  $n = 56$ , are ascribed to the  $J$ -transformation of X-radiation taking place in the crystal used for its analysis or in the anti-cathode or walls of the X-ray tube.

A. A. E.

**Soft X-Rays from Iron.** C. H. THOMAS (*Physical Rev.*, 1925, [ii], **25**, 322—332).—When the ratio of the photo-electric current produced from a protected platinum semi-cylinder by soft X-radiation from a bombarded iron target to the thermionic bombarding current is plotted as a function of the exciting voltage, breaks appear corresponding with the radiation potentials, 7·3, 14·1, 16·5, 24·3, 28·8, 34·3, 48·0, 51·3, 62·0, 75·3, 82·7, 94·8, 112·2, 131·8, 158·5, 181·6, 192·0, 221·3, 277·4, 288·6, 303·7, 331·0, and 639·0 (?) volts, and the ionisation potentials, 11·1, 19·4, 41·2, 54·6, 103·5, 169·4, 228·1, 704·3, and 818·5 volts. The ionisation potentials at 818·5, 704·3, and 54·6 volts are identified with the lines  $L_I$ ,  $L_{III}$ , and  $M_{III}$ .

A. A. E.

**Absorption Spectrum of Oxygen in the Extreme Ultra-violet.** E. SCHMIDT (*Z. Physik*, 1925, **31**, 475—487).—The band spectrum visible in photographs of the extreme ultra-violet taken with long exposures using a quartz mercury vapour lamp as the source of light has been previously regarded as a fluorescence spectrum from the atmosphere. The author shows that it is an absorption spectrum of the oxygen molecule, not of ozone. The absorption is quite different from what would be expected according

to Beer's law; it is much more intense for pure oxygen than for a column of air five times as long. Carbon dioxide is quite transparent in this region, 2000 to 1840 Å.

E. B. L.

**Absorption in Excited Neon.** K. W. MEISSNER (*Ann. Physik*, 1925, [iv], 76, 124—144).—The secondary light absorption, shown by gases when under the influence of an electric discharge, depends on metastable states of the atom caused by the electrical disturbance. The relation between the intensity of the absorption lines and the strength of the current required to produce them gives indications as to the average life of these different states. The absorption spectrum of neon has been studied from this point of view, the intensity of the lines being examined photographically. Absorption in neon begins at a very low current density. The combinations with an  $s_2$ - or an  $s_4$ -term show feeble or zero absorption, but with the  $s_3$ -term, and especially with the  $s_5$ -term, the absorption is much stronger, the strongest absorption line being 6402 in the  $p_3s_5$  combination. This probably means that the  $s_2$ - and  $s_4$ -terms correspond with short-lived, and the other two with long-lived states. The dependence of absorption on the strength of the current in the absorption tube has been studied. It has also been found to depend on the strength of the current in the emission tube. The presence of impurities in the gas reduces the absorption. The intensity distribution in the lines is not the same in the emission as in the absorption tubes, the greater current density and higher temperature in the former giving a greater breadth of line. Further information on the period of duration of the excited states has been sought by sending one half-wave of the rectified alternating current through the emission tube, and the opposite one through the absorption tube. The light from the emission tube thus passes through the absorption tube during its dark period. No indication of even the strongly-absorbing  $s_5$ -term was obtained in 0.01 sec., but with suitable variation of frequency of the alternating current it may be possible to make the absorption lines persistent and thus determine the life-period of the state of excitation which produces them.

M. S. B.

**Absorption of Excited Neon.** P. JORDAN (*Z. Physik*, 1925, 31, 877—881; cf. preceding abstract).—Of the lines  $1s_i-2p_j$  absorbed by neon excited by the passage of a weak direct current, the members  $1s_2$  and  $1s_4$  are only slightly absorbed, if at all, whilst  $1s_3$  and  $1s_5$  are strongly absorbed. The positive neon ion exists in two conditions the neutralisation of which should lead to a triplet-quintet and a singlet-triplet system, respectively. A consideration of the term-multiplicities in the light of Stoner's theory of the distribution of electrons among the different energy levels leads to the conclusion that the ground term is a  $p$  term of inner quantum number  $\frac{1}{2}$ , and that  $1s_3$  and  $1s_5$  must be metastable.

E. B. L.

**Absorption of Magnesium Vapour.** A. L. NARAYAN, D. GUNNAIYA, and K. R. RAO (*Astrophys. J.*, 1924, 60, 204—205).—The magnesium line 4571 Å. ( $1s-2p_2$ ) has been obtained as an

absorption line. The line  $2852 \text{ \AA.}$ , but not  $4571 \text{ \AA.}$ , increased in width with rise of temperature. A. A. E.

**Absorption Spectrum of Aluminium.** K. MAJUMDER and N. K. SWE (*Nature*, 1925, **115**, 459).—No aluminium lines were obtained below  $1500^\circ$ . At  $1520^\circ$ , the pair, 3961, 3944, appear reversed; at  $1650^\circ$ , the leading members of  $2p_1$ — $md$  appear reversed, but the higher members require a somewhat higher temperature. Gallium is present in ordinary aluminium. A. A. E.

**Absorption Spectrum of the Neutral and Ionised Cadmium Atom in the Spark Discharge under Water.** H. STÜCKLEN (*Z. Physik*, 1924, **30**, 24—39).—By sparking between cadmium electrodes under water, both absorption and emission spectra against a background of a continuous spectrum can be obtained, the proportion of lines in the two varying with the frequency, voltage, and electrode diameter. The absorption lines are divisible into six groups. From the sequence in which these groups appear conclusions may be reached with regard to the states of excitation through which a neutral or ionised atom may pass. The group most easily obtained corresponds with the passage of the electron in the neutral atom from the normal  $1s$ -orbit to the next higher one,  $2P$ . The corresponding line for the ionised atom is less easily obtained. M. S. B.

**Absorption Line of the Iodine Atom.** C. FÜCHTBAUER, F. WAIBEL, and E. HOLM (*Z. Physik*, 1925, **31**, 523; cf. A., 1924, ii, 220).—Addendum to the paper (*ibid.*, 1924, **29**, 367) giving the exact value of the wave-length  $2062.25 \text{ \AA.}$  in a vacuum. Other absorption lines are noted still further in the ultra-violet and a preliminary suggestion is made as to series terms. E. B. L.

**Resonance Radiation from Thallium Vapour.** A. L. NARAYAN and K. R. RAO (*Nature*, 1925, **115**, 534).—Further experimental confirmation of the view that  $1\pi_2$  is the ground orbit of the valency electron of the thallium atom is afforded. A. A. E.

**Broadening of Spectral Lines. III.** J. HOLTSMARK and B. TRUMPY (*Z. Physik*, 1925, **31**, 803—812; cf. A., 1924, ii, 363).—Photographs of the arc spectra of lithium, silver, copper, and nickel were taken and the widening of the lines was measured by comparing the width of those which were broad with those which were not. The results agree with the values calculated from the Stark effect. The apparent reversal of the silver line, 4055, is explained as a splitting of the line by a peculiar type of Stark effect. For a current of five amperes the molecular electrical field is 12,600 volts per cm.

E. B. L.

**Excitation of Spectral Lines by Electron Impact. II.** G. HERTZ and J. C. S. DE VISSER (*Z. Physik*, 1925, **31**, 470—474).—Neon was subjected to the bombardment of accelerated electrons in an apparatus previously described (A., 1924, ii, 283), and the intensity of the lines in the spectrum of the emitted radiation was

measured in a spectrometer by comparison with the light from a tungsten filament lamp which had been calibrated for different voltages in a Nutting spectrophotometer. Using the results to calculate the ionisation potential for neon, the value 21.6 volts was obtained, in good agreement with the result 21.5 volts obtained by the electrical method. E. B. L.

**Relation between the Distribution of Electrons in the Atom into Sub-groups and the Complex Structure of Spectra.** W. PAULI, jun. (*Z. Physik*, 1925, **31**, 765—783).—Development of a scheme of distribution of electrons in the atom to overcome the difficulties arising from the usual grouping referred to in a previous paper (this vol., ii, 251). A general classification of all the electrons in the atom is obtained through the principal quantum number  $n$  and two subsidiary quantum numbers  $k_1$  and  $k_2$ , to which must be added another,  $m_1$ , in the presence of an external magnetic field. In conjunction with the work of Stoner (this vol., ii, 85) this leads to a grouping of electrons which satisfies the quantum conditions.

E. B. L.

**Metastable States in Low-voltage Mercury Arcs.** M. MARSHALL (*Astrophys. J.*, 1924, **60**, 243—255).—Experiments with alternating and intermittent arcs indicate that the life of the two metastable forms of the mercury atom,  $2p_1$  and  $2p_3$ , is about 1/22 and 1/170 second, respectively. The life of the latter, but not of the former, is reduced by the presence of carbon monoxide, carbon dioxide, nitrogen, water vapour, or hydrogen. A. A. E.

**Fine Structures in the First Lithium Spark Spectrum.** H. SCHÜLER (*Ann. Physik*, 1925, [iv], **76**, 292—298).—By means of the arrangement described by Lorensen (*Diss.*, Tübingen, 1913), the existence of fine structures in the three  $\text{Li}^+$  lines, 5485, 2934, and 3714 Å., has been demonstrated. The intensities and wave-lengths of eleven components of the first, three of the second, and three of the third line are given. The theoretical significance of these results is discussed. M. S. B.

**Auroral Green Line.** J. C. McLENNAN (*Nature*, 1925, **115**, 607).—The line at 5577 Å. can be obtained with a mixture of oxygen and excess of helium at the ordinary temperature; it probably originates from the oxygen. A. A. E.

**Structure of the Mercury Line, 2536 Å.** R. W. WOOD (*Nature*, 1925, **115**, 461).—The structure of the mercury line 2536 Å. observed by Nagaoka was that caused by the self-reversal of the true components. In the true structure now observed, there are five components of uniform intensity, four at sensibly equal intervals, the fifth having a slightly greater separation. The error was associated with the type of lamp employed. A. A. E.

**Peculiarity of some Red Neon Lines.** W. H. J. CHILDS (*Nature*, 1925, **115**, 572).—The value  $6402.251 \pm 0.001$  Å. is found for the wave-length of the reversal of the neon line 6402 Å.

A. A. E.



**Spectroscopic Shift Law.** I. E. FUES (*Ann. Physik*, 1925, [iv], 76, 299—316).—Theoretical. The relationship between the spectra due to similarly constructed atoms or ions, for example, neutral Li, Be<sup>+</sup>, B<sup>++</sup>, and C<sup>+++</sup>, or neutral Na, Mg<sup>+</sup>, Al<sup>++</sup>, and Si<sup>+++</sup>, is discussed.

M. S. B.

**Duration of the Quantic State  $2p_2$  of the Mercury Atom.** F. RASETTI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 223—225).—In view of the discordant values published for the mean duration of the mercury atom in the  $2p_2$  state, the monochromatised light from a mercury lamp, immersed in cold water, was passed through the slit of a revolving disc on to mercury vapour contained in a quartz flask. Photographic examination revealed no trace of resonance in the mercury vapour even when the interval between excitation and observation was reduced to  $5 \times 10^{-5}$  sec. It is hence concluded that the  $2p_2$  condition is not metastable at the ordinary temperature. At 200°, the resonance radiation begins to exhibit sensible duration, but the phenomenon is then complicated by the appearance of a green fluorescence, attributable to a molecule Hg<sub>2</sub>, formed by the shock between an excited and a normal atom and possessed of a long life. The spectrum of the green luminescence observed when mercury is shaken in an evacuated vessel at about 200° shows, besides a continuous band reaching from the yellow to the violet, also the more intense of the mercury lines, such as 5790, 5769, 5460, 4358 Å., and, less strongly, 2536 Å. This excitation is evidently analogous to electrification by friction.

T. H. P.

**Intensity of Multiple Lines.** E. FERMI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 120—124).—A theoretical interpretation is suggested for the empirical rules governing the intensities of the components of multiple lines.

T. H. P.

**Intensities of Components in the Zeeman Effect.** L. S. ORNSTEIN and H. C. BURGER (*Z. Physik*, 1924, 28, 135—141).—A theoretical paper, giving a generalisation of the rules already described (cf. A., 1924, ii, 433) for the calculation of the intensities of multiplets, which make it possible to predict the intensities of the components in the Zeeman effect. A preliminary announcement is made of experimental verifications of the theory.

S. B.

**Zeeman Effect in Multiplets of Higher Grade.** A. LANDÉ (*Ann. Physik*, 1925, [iv], 76, 273—283).—The regularities of the splitting factor  $g$  in the Zeeman effect are discussed. Not all the  $g$ -values of the higher grades are rational and constant with increasing sequence number, but the  $g$ -values of the terms with common  $K$  and  $J$  values, the impulse quantum number, and inner quantum number, respectively, add up to rational and constant  $g$ -totals which all obey a general law. Two methods for the calculation of  $g$  are given. The first depends on the branching principle (Landé and Heisenberg, A., 1924, ii, 710) and the permanence of the  $g$ -sum in the passage from a weak to a strong field (Pauli, *Z. Physik*, 1923, 16, 155). The second method rests on a conjecture not yet verified that limiting values of  $g$  for higher sequence numbers are the "ideal"

$g$ -values in a weak field, the latter being determined by the first method. As a result, it appears evident that a simple and uniform scheme governs the structure and Zeeman effect of the multiplets. The details of the scheme give clear evidence of the inadequacy of the theoretical principles based on quanta, for coupled systems.

M. S. B.

**Zeeman Effect of Neon.** E. BACK (*Ann. Physik*, 1925, [iv], 76, 317—332).—Very exact determinations have been made of the splitting up by a magnetic field of the neon lines  $1s_i-2p_i$  and also of the term separation factor  $g$  and the inner quantum number  $j$  deduced from them. The  $g$ -values are found to be rational numbers which can all be reduced to Runge fractions with a denominator of 30. They are thus in agreement with Landé's theory (see preceding abstract).

M. S. B.

**Paschen-Back Effect.** C. RUNGE (*Ann. Physik*, 1925, [iv], 76, 266—272).—A theoretical paper in which it is shown that Sommerfeld's interpretation (*Z. Physik*, 1922, 8, 269) of Voigt's theory of the Paschen-Back effect for the pairs of lines  $s-p_1$  and  $s-p_2$  is not in agreement with the facts, as is shown by Kent's work (*Astrophys. J.*, 1914, 40, 337) on the splitting up of the lithium line 6708 by a magnetic field. Kent's observation of the behaviour of component 7, however, cannot be reconciled with the author's views on the term resolution of spectral lines.

M. S. B.

**New Spectrum Apparatus, Monochromator, and Quartz Spectrograph with Crossed Prisms to Secure Highest Spectral Purity in the Region  $200\mu\mu$  to  $2\mu$ .** C. LEISS (*Z. Physik*, 1925, 31, 488—495).—The instrument is designed to give great range and adaptability with purity of spectral lines and without clumsiness.

E. B. L.

**New Type of Electric Discharge. Streamer Discharge.** I. LANGMUIR, C. G. FOUND, and A. F. DITTMER (*Science*, 1924, 60, 392—394).

**Cathode Fall, Current Density, and Dark Space in Mixtures of Gases which do not React Chemically.** A. GÜNTHER-SCHULZE (*Z. Physik*, 1924, 28, 129—134).—The cathode fall, current density, and dark space in the discharge through binary mixtures of the inert gases with each other and with hydrogen have been measured. From inflexions in the curves connecting cathode fall with gas composition it is inferred that in the electric discharge the inert gases probably have the power of forming temporary compounds.

S. B.

**Processes in the Vacuum Mercury Arc.** A. GÜNTHER-SCHULZE (*Z. Physik*, 1925, 31, 509—513).—The fall of potential round the anode and cathode is discussed and the energy changes are calculated. The cathode fall of potential is not very different from the ionisation potential and about half the current is carried by electrons. Previous results obtained by using probe electrodes gave values much

too low. At the anode, previous results obtained by calculation from the intensity of the radiation caused by the heating were much too high, as the energy of neutralisation of the electrons had not been considered.

E. B. L.

**Pseudo-high Vacuum.** A. GÜNTHER-SCHULZE (*Z. Physik*, 1925, **31**, 606—616).—After prolonged use, a Wehnelt high-voltage rectifier behaves as though the vacuum had become too high for the discharge to pass, although there is plenty of argon present. The explanation is that the electrostatic charge on the walls of the bulb deflects the electric field between the electrodes and prevents the discharge. At first a film of moisture on the surface provides a leak, but this is removed in time by a deposit from the disintegrating cathode.

E. B. L.

**Simple Kinetic Derivation of the Ionisation and Vapour Pressure Equations.** R. BECKER (*Z. Physik*, 1924, **28**, 256—260).—The theory of equilibrium in a thermally ionised gas and of the process of evaporation are considered, and are shown to submit to analogous mathematical treatment.

S. B.

**Excitation and Ionisation Potentials of the Noble Gases.** G. HERTZ and R. K. KLOPPERS (*Z. Physik*, 1925, **31**, 463—469).—The method employed was that of the impact of electrons accelerated by a known potential; the gases examined were argon, krypton, and xenon. As impurities could not be removed from the two last-named by cooling in liquid air, solid carbon dioxide in alcohol was used and traces of impurities may have been present. The electrons were emitted from a nickel cathode coated with barium oxide and heated by a fine tungsten wire, the advantage of the arrangement being that there was no fall of potential along the cathode itself. The ionisation potentials found were: argon 15.4, krypton 13.3, xenon 11.5 volts; the values found for the excitation potentials do not indicate the passage of the atom from its normal state into a definite stationary state of higher energy but an average value, corresponding with terms of the spectral series which lie close together. The lowest values found were: argon 11.5, krypton 9.9, xenon 8.3 volts.

E. B. L.

**Work of Escape of Positive Ions.** A. GÜNTHER-SCHULZE (*Z. Physik*, 1925, **31**, 507—508).—The values are obtained by taking the algebraic sum of the energies necessary to eject both positive ions and negative electrons from the surface of a metal, the ionisation potential of the gaseous atom of the metal and its latent heat of vaporisation, and equating this sum to zero. The result of this cyclic process is to show that the energy necessary to remove a positive ion is two or three times as great as is required to eject an electron and about the same as the ionisation energy for the gaseous metal.

E. B. L.

**Series Spectra of the Stripped Atoms of Phosphorus (P V), Sulphur (S VI), and Chlorine (Cl VII).** I. S. BOWEN and R. A. MILLIKAN (*Physical Rev.*, 1925, [ii], **25**, 295—305).—More accurate values have been obtained for the ( $3p_2-3p_1$ ),

( $3s-3p_2$ ), and ( $3p_1-3d$ ) terms of Al III, Si IV, P V, and S VI, leading to the determination of 18 series lines of P V, 11 series lines of S VI, and the first doublet of the principal series of Cl VII, as already predicted (cf. A., 1924, ii, 710). Both the regular and the irregular doublet laws of X-ray spectra appear to hold also throughout the field of optics. When values of  $\sqrt{v}/R$  for the stripped atom levels are plotted as a function of atomic number, approximately straight lines are obtained (Moseley's law). The general similarity of the stripped atoms of sodium, magnesium, aluminium, silicon, phosphorus, sulphur, and chlorine is demonstrated, but the  $D$  doublets deviate from their calculated position, that of sodium to the greatest extent. Ionisation potentials of P V and S VI are computed to be 64.7 and 87.6 volts, respectively. A. A. E.

**Influence of Radiation on Ionisation Equilibrium.** J. WOLTJER, jun. (*Nature*, 1925, 115, 534).—An alternative method of arriving at the results of Saha and Swe (this vol., ii, 254) is based on a formulation of the conditions required for a stationary state by means of probability laws governing the elementary processes involved. A. A. E.

**Total Ionisation produced in Air by Electrons of Various Energies.** G. A. ANSLOW (*Science*, 1924, 60, 432—433).—An experimental verification of Bohr's theory of ionisation as corrected by Fowler. A. A. E.

**Thermionic Work-functions and Photo-electric Thresholds of the Alkali Metals.** O. W. RICHARDSON and A. F. A. YOUNG (*Proc. Roy. Soc.*, 1925, A, 107, 377—410).—Both sodium and potassium show more than one value for the thermionic work function and for the photo-electric threshold. Photo-electric currents soon reach the saturation value, but thermionic currents do not. The authors suggest that the surface of the metal is not uniform, but that there are small patches associated with the lower value of the work function. A photo-electric threshold has been found for potassium at about  $\lambda=10,000$  Å. by exposing the metal to a luminous discharge in hydrogen or a trace of water vapour, the suggestion being that this encourages the growth of the patches. E. B. L.

**Photo-electric Primary Current in Sodium Chloride Crystals.** B. GUDDEN and R. POHL (*Z. Physik*, 1925, 31, 651—665; cf. A., 1921, ii, 145).—Rock-salt crystals coloured yellow by X-rays were exposed alternately to mercury radiation 405 and 436  $\mu\mu$ , and to infra-red radiation from an arc lamp, and the photo-electric current measured by a string galvanometer. Current-time curves are given for great and for small light intensity for temperatures between 30° and 130°. The primary current is caused by the electrons detached by the high-frequency light moving towards the anode; the reverse, positive current is due to the return of the electrons under the influence of the infra-red radiation or thermal agitation. Below 40°, heat does not produce the positive current; above 100°, it reaches its full value. Differences in the

behaviour of rock-salt and diamond are due to the electrons in the former penetrating only a small distance. In agreement with Lenard's theory of phosphorescence, there is a correspondence between the intensity of phosphorescence and the positive portion of the primary current.

E. B. L.

**Photo-electric Properties of Thin Films of Alkali Metals.** H. E. IVES (*Astrophys. J.*, 1924, 60, 209—230).—Thin films of sodium, potassium, rubidium, and caesium, spontaneously deposited on clean metal surfaces in a vacuum, exhibit a selective photo-electric effect. The selective characteristic depends on the thickness of the film. The effect is ascribed to a particular orientation of the atoms completely covering the surface.

A. A. E.

**Normal and Selective Photo-electric Effects in the Alkali Metals and their Alloys.** H. E. IVES and A. L. JOHNSRUD (*Astrophys. J.*, 1924, 60, 231—242; cf. preceding abstract).—The selective photo-electric effect observed in the case of an alloy of sodium and potassium is not exhibited by the pure bulk metals, nor by other alloys of alkali metals.

A. A. E.

**Selective Photo-electric Effect on Metallic Films Prepared in Various Ways.** F. GROSS (*Z. Physik*, 1925, 31, 637—646).—The photo-electric behaviour of various kinds of copper, bismuth, and silver films towards the mercury radiation, 254  $\mu\mu$ , was studied. A selective effect was found for a copper film evaporated in a vacuum from an alloy of copper and molybdenum but smaller than that obtained from a film spluttered from a copper cathode in hydrogen. A film prepared in a high vacuum by evaporation of copper in a magnesium crucible showed only the normal effect. The selective effect is attributed to the dissolved gases in the metal. Bismuth films exhibited no selective effect. A definite conclusion was not reached for silver. Copper films retain their photo-electric sensitivity; those of silver and bismuth lose it in time.

E. B. L.

**Mechanism of the Photo-electric Primary Current in Crystals.** B. GUDDEN and R. POHL (*Z. Physik*, 1924, 30, 14—23; cf. *ibid.*, 1921, 6, 248).—The absorption of light by diamond has been examined in different portions of the spectrum by the amount of positive and negative electricity liberated. For the same amount of light energy, the negative primary current constantly decreases with the increase in wave-length. If the diamond be previously illuminated with light of wave-length 436  $\mu\mu$ , the absorption of light of wave-length greater than 540  $\mu\mu$  is increased, as shown by the increased current, and this increase becomes relatively greater as the infra-red end of the spectrum is approached. This excess current is ascribed to the positive charges stored up during the preliminary illumination with light of short wave-length. Previous disturbance of the crystal lattice by the presence of positive charges, therefore, appears to extend the absorption of light by the diamond towards the long-wave region. It is probable that the mechanism of the primary positive current consists in the

passage of electrons between positive ions and neutral atoms made possible by increased temperature vibrations of the molecules due to absorption of infra-red radiations. By continued illumination with blue light, a gradually increasing fraction of the positive charges takes part in the primary current, so that less than the equivalent quantity is obtained by subsequent treatment with infra-red rays. When equilibrium is reached between the positive charges formed and those displaced to the cathode, the current reaches a stationary state when its value may be greater or less than at first. The latter happens when the lowering of field-strength through the presence of the positive charges outweighs the increase due to the spontaneously flowing positive constituent of the primary current.

M. S. B.

**"Phenomenology" of the Richardson Effect.** D. REICHSTEIN (*Z. Elektrochem.*, 1925, **31**, 124—135).—A discussion of current theories of electron emission in vacuum tubes of the thermionic valve type. Richardson's equation connecting saturation current with temperature requires the immediate establishment of the equilibrium between the filament and the electron vapour, but this is contrary to experience. A "phenomenological" description of the electron emission is therefore necessary. The probable results of such an interpretation are indicated and lines of research suggested. In particular, it would be of interest to study the behaviour of the grid electrode at the temperature of liquid air.

N. H. H.

**Study under Reduced Pressure of the Radiations Emitted by Bodies of High Resistance traversed by an Electric Current.** G. REBOUL (*Compt. rend.*, 1925, **180**, 916—919; cf. A., 1924, ii, 578).—The coefficients of absorption of the radiations emitted by conductors of high resistance traversed by an electric current, by air, carbon dioxide, and hydrogen have been investigated at various reduced pressures. The radiations traverse a layer of gas to enter an ionisation chamber, their intensity being estimated from the magnitude of the ionisation current. The nature of the results obtained indicates that these radiations form a continuous spectrum, successive wave-lengths differing only by a very small fraction of an Å.

J. S. C.

**Electron Emission from Tungsten, Molybdenum, and Tantalum.** S. DUSHMAN, H. N. ROWE, J. EWALD, and C. A. KIDNER (*Physical Rev.*, 1925, [ii], **25**, 338—360).—The equation  $I = AT^2 e^{-b_0/T}$  holds in the case of tungsten; the accuracy of results with tantalum and molybdenum is not so great. In the former, but not the latter case, the value of  $A$  is approximately the same as that for tungsten.

A. A. E.

**Various Magnetic States of an Ion.** G. FOEX (*Compt. rend.*, 1925, **180**, 919—921).—Specimens of the same salt often possess varying magnetic properties which appear to be connected with distinct structural differences in the paramagnetic ion which they contain. This diversity, which has already been examined for

salts in aqueous solution (*Ann. Physique*, 1921, **16**, 174) is now extended to crystalline salts. A specimen of ferrous ammonium sulphate has been prepared, corresponding with 26 magnetons and possessing a strong positive molecular field, there being in addition a sudden change in the direction of the temperature-coefficient of magnetisation curve at 100°. A specimen of the same salt examined by Jackson (*Phil. Trans.*, 1923, **A**, 224, 1) corresponded with 27.5 magnetons, the molecular field being very weak and the influence of temperature quite normal.

Anhydrous cobalt sulphate has been shown to exist in two forms, the varieties having 25 and 24 magnetons, respectively, the respective magnetic fields being negative and feebly positive. J. S. C.

**Isotope Effect in Band Spectra. II. Spectrum of Boron Monoxide.** R. S. MULLIKEN (*Physical Rev.*, 1925, [ii], **25**, 259—294).—An extension of measurements of bands ascribed by Jevons (A., 1924, ii, 366, 438, 640) to boron nitride, but by the author (A., 1924, ii, 3, 294, 446, 640) to boron monoxide. The predicted vibrational isotope effect has been verified for both  $\alpha$  and  $\beta$  systems; no indications were obtained of isotopes other than B<sup>10</sup> and B<sup>11</sup>. Equations are given representing the measured positions of all the heads of the bands. In view of the complete agreement between the experimental measurements and theoretical considerations, it is considered to be practically certain that the bands in question are due to boron monoxide. An indicated electronic isotope effect of unprecedented magnitude vanishes if the minimum values of the initial and final vibrational quantum numbers are assumed to be 0.5 instead of zero. Thus the existence of half-integral vibrational quantum numbers and a null-point vibrational energy of one half-quantum is probable. The rotational isotope effect is approximately confirmed. A new system of boron monoxide bands has been investigated, and the arc and active nitrogen spectra of boron monoxide have been compared. The possible analogy between BO and CN molecules and sodium atoms is discussed.

A. A. E.

**Fundamental Atomic Weights.** E. MOLES (*Anal. Fis. Quim.*, 1925, **23**, 39—75; *Z. physikal. Chem.*, 1925, **115**, 61—90).—The author discusses modern physico-chemical and chemical values for the atomic weights of hydrogen, chlorine, bromine, and silver, respectively. It is considered that there is no discordance between the values obtained for hydrogen, chlorine, and bromine by physico-chemical methods and those obtained by purely chemical methods, and the mean values are given as hydrogen, 1.00777; chlorine, 35.458; bromine, 79.918. The atomic weight of silver, according to the author, cannot be less than 107.880, but is somewhat greater than 107.882.

G. W. R.

**Redetermination of the Atomic Weight of Boron.** H. V. A. BRISCOE and P. L. ROBINSON (*J. Chem. Soc.*, 1925, **127**, 696—720).—The atomic weight of boron has been determined using samples of boron from widely-separated known sources in order to determine

whether the isotope ratio is always and everywhere the same. The value of the ratio  $\text{BCl}_3 : 3\text{Ag}$  was determined, the actual method used consisting in breaking sealed bulbs containing boron trichloride under water and titrating the resulting solution with pure silver nitrate, the end-point being ascertained nephelometrically. The various refinements introduced and also the method for the isolation of boron trichloride in a state of purity are described in detail. Some evidence was obtained indicating a partial isotopic separation during the distillation of boron trichloride. The mean value of the atomic weight of boron from California was found to be 10.840 and that from boron from Tuscany and Asia Minor 10.820. These values indicate that a partial separation of the isotopes 10 and 11 has occurred in nature, the American boron containing 84% and the Eurasian boron 82% of the heavier isotope. Atomic weight determinations based on the analysis of fused borax are open to criticism.

J. S. C.

#### Atomic Weight of Hafnium. Analysis of Hafnium Bromide.

O. HÖNIGSCHMID and E. ZINTL (*Ber.*, 1925, **58**, [B], 453—459).—Analysis of hafnium bromide, prepared by heating more highly-purified hafnium oxide with sugar charcoal in an atmosphere of nitrogen laden with bromine vapour (cf. this vol., ii, 174) gives the value 178.6 ( $\pm 0.08$ ) for the atomic weight of hafnium. The specimens of hafnium bromide are reconverted into the dioxide, which is found to contain 0.57 ( $\pm 0.06$ )% and 0.16 ( $\pm 0.02$ )% of zirconium dioxide, for which the necessary correction is applied. H. W.

**Quantum Theory of Radioactive Process. II.** A. SMEKAL (*Z. Physik*, 1924, **28**, 142—145; cf. A., 1924, ii, 717).—Meitner's views on the mechanism of the transformation of a disintegrating nucleus are in agreement with the author's quantum theory of the process.

S. B.

#### Measurements of $\beta$ -Rays associated with Scattered X-Rays.

A. H. COMPTON and A. W. SIMON (*Physical Rev.*, 1925, [ii], **25**, 306—313).—Stereoscopic photographs of  $\beta$ -ray tracks excited by strongly filtered X-rays in moist air confirm Wilson and Bothe's observations of *P* (longer) and *R* (shorter) tracks, and yield strong evidence that there is about one *R* track or recoil electron associated with each quantum of scattered radiation, and possessing, both in direction and magnitude, the vector difference of momentum between the incident and the scattered X-ray quantum. A. A. E.

**$\beta$ -Ray Spectrum of Thorium-B+C.** W. POHLMAYER (*Z. Physik*, 1924, **28**, 216—230).—The  $\beta$ -ray spectrum of a mixture of thorium-B+C was obtained by magnetic resolution, and registered by the ionisation method. The results indicate that the continuous background present in  $\beta$ -ray spectra is due to secondary effects, the true  $\beta$ -ray spectrum being a simple "line" spectrum. S. B.

**High-energy  $\gamma$ -Rays and their Photo-electric Effect.** M. DE BROGLIE (*Nature*, 1925, **115**, 461).—A correlation of the results of Black (this vol., ii, 177) with those of Thibaud (A., 1924, ii, 515, 717; this vol., ii 10, 85).

A. A. E.



**Homogeneity of Initial Velocities of  $\alpha$ -Particles from Polonium.** (MLLE.) I. CURIE (*Compt. rend.*, 1925, **180**, 831—833; cf. A., 1923, ii, 207).—Geiger (A., 1910, ii, 473) claimed an accuracy of 0.5% in verifying for radium-C the view that all  $\alpha$ -particles are emitted at the same velocity by a radioelement (A., 1923, ii, 207).

The author criticises adversely Geiger's reasoning, but confirms his conclusion. She finds there is no evidence of initial differences in velocity for  $\alpha$ -particles emitted by polonium. On the assumption of a uniform distribution of velocities between two extremes, the maximum difference is not greater than 0.3%. The alternative assumption of distribution about a velocity  $V$  according to the probability law  $v = \gamma V$  results in a value for  $\gamma < 0.15\%$  so that three-quarters of the  $\alpha$ -particles have velocities differing by  $< 0.3\%$ .

R. A. M.

**Number of Ions Produced by the  $\alpha$ -Particle from Polonium.** M. V. BIANU (*Bull. Acad. Sci. Roumaine*, 1924, **9**, [5—6], 37—39).—The method employed was to determine total ionisation due to the  $\alpha$ -particles and the charge of an  $\alpha$ -particle in the same apparatus, current being measured by the quartz-piezo electrometer. The number of ions per  $\alpha$ -particle was found to be  $1.58 \cdot 10^5$ , in agreement with  $1.62 \cdot 10^5$  (Geiger) and  $1.64 \cdot 10^5$  (Taylor).

A. S. R.

**Effect of the Sun on Radioactivity.** (MLLE.) S. MARACINEANU (*Bull. Acad. Sci. Roumaine*, 1924, **9**, [3—4], 1—11).—Preliminary experiments. Peculiar changes in the radioactive properties of actinium-B, polonium, and of lead, detected principally by the effects produced on a photographic plate, are ascribed to the sun's rays. The magnetic field, cold, pressure, and friction are found to excite lead. Ionised water is necessary for the effects to be produced.

A. S. R.

**Disintegration of Atomic Nuclei.** (SIR) E. RUTHERFORD (*Nature*, 1925, **115**, 493—494).—A discussion of the results of Blackett (this vol., ii, 256), Harkins and Ryan (A., 1923, ii, 601, 720), Akiyama (A., 1924, ii, 814), and Pettersson and Kirsch (*Physikal. Z.*, 1924, **25**, 588) on the branched tracks observed on collision between  $\alpha$ -particles and nuclei.

A. A. E.

**Electrical Explosion of Tungsten Wires.** H. V. A. BRISCOE, P. L. ROBINSON, and G. E. STEPHENSON (*J. Chem. Soc.*, 1925, **127**, 240—247).—Anderson (*Astrophys. J.*, 1920, **51**, 37) has shown that, by the passage of heavy high-tension discharges through thin metallic wires temperatures are momentarily attained which are much higher than can be reached by any other known means. Experiments by Wendt and Irion (A., 1922, ii, 773) appear to indicate that, when a fine tungsten wire is exploded by this method, helium is produced. These conclusions have been tested by passing the high-tension discharge between molybdenum electrodes, connected by a fine tungsten wire, in an evacuated bulb, and then examining the residual gas spectroscopically on passing an induction coil discharge between a supplementary electrode and one of

the main electrodes. Some mercury and hydrogen lines were observed, but no trace of the yellow helium line. These results confirm the recent work of other investigators (cf. Smith, *Proc. Nat. Acad. Science*, 1924, 10, 4; Harkins and Allison, A., 1924, ii, 407).  
M. S. B.

**Theory of the Electron.** H. REISSNER (*Z. Physik*, 1925, 31, 844—865).—A theory of point charges exhibiting the properties of the electron and of the proton is developed mathematically on the basis of Einstein's field equations of the point charge. The solution with unchanged Maxwellian energy tensor gives incorrect values for the mass of the positive and negative charges, making them equal and much too great. The introduction of an additional member of the energy tensor contributing only at the charge-point, with the help of three universal constants, leads to the correct value of the positive and negative charges and of the difference in mass of the two kinds of charge.  
E. B. L.

**Statistical Investigations on the Sub-electron.** H. DAECKE (*Z. Physik*, 1925, 31, 552—575).—Mathematical treatment of independent series of results in which the values of  $e$  were less than  $4.77 \times 10^{-10}$ . If the sub-electron is defined as  $(m/n) \cdot e$ , in which  $m < n$  and  $n$  is not large, then the assumption of a sub-electron is more probable than any other deduction.  
E. B. L.

**Static Model for Helium.** H. S. ALLEN (*Proc. Roy. Soc. Edin.*, 1924, 44, 116—128).—By assuming the existence of a quantum force as postulated by Langmuir (*Physical Rev.*, 1921, [ii], 18, 104) acting along the line joining two charged particles, static models have been deduced for the ionised helium atom, the neutral helium atom, and the helium molecule. The introduction of three quantum numbers renders the models adjustable by the choice of these numbers. The results obtained for the atom are in agreement with the original model of Bohr, but are not in agreement with the experimentally determined ionisation potential. For the molecule, the moment of inertia obtained is of the same order of magnitude as that determined by Curtis from the band spectrum.  
A. E. M.

**Relative Sizes of the Kernels of Ten Electrons of Sodium, Magnesium, Aluminium, and Silicon.** L. A. TURNER (*Astrophys. J.*, 1924, 60, 81—86).—From optical data, the relative sizes of the ten-electron-kernels of neutral sodium, singly ionised magnesium, doubly ionised aluminium, and trebly ionised silicon have been computed as 1 : 0.740 : 0.575 : 0.472. Thus the effective nuclear charge for the outer orbits of the kernel is equal to the true nuclear charge less an unvarying screening constant which is approximately that predicted from the  $L$  X-ray term values.  
A. A. E.

**Emission Spectrum of Water Vapour.** W. W. WATSON (*Astrophys. J.*, 1924, 60, 145—158).—Accurate wave-lengths have been determined for all the lines of the band 2811 Å., and every

line has been assigned to a parabolic series. Fifteen new lines of a band at  $3021 \text{ \AA}$ ., which form a single parabolic series, have also been measured. Analysis of the series for the bands  $2811 \text{ \AA}$ . and  $3064 \text{ \AA}$ . indicates that they are due to hydroxyl ions. A. A. E.

**Ultra-violet Emission Spectra of the Halogens.** E. B. LUDLAM and W. WEST (*Proc. Roy. Soc. Edin.*, 1924, **44**, 185—196).—Examination of the emission spectra of chlorine, bromine, and iodine excited in silica tubes by means of the Tesla discharge shows that their most prominent features are two continuous bands rising sharply on the long wave side with a displacement of corresponding features to the less refrangible side with increase of atomic weight. The long wave limits of the first continuous band are  $3200 \text{ \AA}$ . for chlorine,  $3700 \text{ \AA}$ . for bromine, and  $4800 \text{ \AA}$ . for iodine. The corresponding energies calculated from the frequencies of the long wave limits are 89.1, 77.0, and 96.6 cal., respectively. These values do not hold for any conceivable chemical reactions, and it is suggested that the first continuous band is of molecular origin. The long wave limits of the second continuous bands are 2650, 2950, and  $3450 \text{ \AA}$ ., respectively, and the corresponding calculated energies are 107.3, 96.6, and 82.3 cal. These values are in agreement with the electron affinities calculated on the lattice theory, and it is suggested that the second continuous band is the electron affinity spectrum. In addition, iodine shows a sharp line spectrum the first member of which is at  $2061 \text{ \AA}$ . This is suggested as the principal line series of iodine. The corresponding hydrides showed the same features together with the hydrogen spectrum. A. E. M.

**Visible Radiation from Niobium Oxide.** E. L. NICHOLS (*Physical Rev.*, 1925, [ii], **25**, 376—385).—When niobium oxide,  $\text{Nb}_2\text{O}_5$ , is gradually introduced into a hydrogen flame, it glows with a pale greenish-blue colour when in the oxidising portion, but in the reducing region the colour changes abruptly to deep red. The former phase is selective with luminescence bands superposed on the radiation due to temperature, whilst the latter resembles that of a black body and is due to the formation of the oxide  $\text{Nb}_2\text{O}_4$ , which is black at the temperature of incandescence. The formation of similar black suboxides was observed in the cases of titanium and tantalum. A. A. E.

**Negative Nitrogen Band Spectrum.** M. FASSBENDER (*Z. Physik*, 1924, **20**, 73—92).—An extensive examination of the negative nitrogen band spectrum has been made, precautions being taken to reduce to a minimum intensity the bands of the second positive nitrogen group, which overlaps it in the violet and ultra-violet. Seven of the twenty bands observed have been measured and arranged in series. *P* and *R* branches, zero lines, and intensity distribution have been determined. M. S. B.

**Vibration-Rotation Spectrum of Gaseous Ammonia at  $3 \mu$ .** B. J. SPENCE (*J. Opt. Soc. Amer.*, 1925, **10**, 127—132).—The ammonia band at  $3 \mu$  is double, with serrated branches unequally distributed about a central branch. This is in disagreement with

the theory of Lenz for the points of maximum absorption for diatomic molecules, but agrees with the views of Kratzer that for larger periods of oscillation the vibrations are non-harmonic, and that the moment of inertia of the molecule is not constant. The prominence of the central branch indicates that many ammonia molecules exist in the rotationless state. A doubly branched, faint, harmonic band at approximately  $1.5\ \mu$  was observed. F. G. T.

**Structure of a Class of Band Spectra.** R. MECKE (*Z. Physik*, 1925, **31**, 709—712).—The band spectra of molecules having identical constituent atoms exhibit anomalies in the intensities of the individual lines. According to an earlier paper (this vol., ii, 259), the total impulse of a molecule is made up of two components, the nuclear impulse and the electron impulse. The observed anomalies can now be accounted for by assuming the electron impulse of the diatomic molecule of an element to be subdivided unsymmetrically into two components, one to each atom. It is concluded that the series of strong lines in the band is emitted only by an electron of one atom, the remaining portion by an electron of the other atom. These spectra are analogous to a series of infra-red bands exhibited by all compounds containing a carbon-hydrogen linkage. E. B. L.

**Fulcher Hydrogen Bands.** W. E. CURTIS (*Proc. Roy. Soc.*, 1925, **A**, **107**, 570—587).—A theoretical discussion of existing data indicating that the bands are due to simultaneous rotation and vibration changes in the "excited" molecule. The unique structure of the system is accounted for by the nuclear vibrations within the hydrogen molecule being very nearly simple harmonic. E. B. L.

**Infra-red Absorption Spectra of Alcohols.** J. LECOMTE (*Compt. rend.*, 1925, **180**, 825—827).—Monohydric alcohols absorb strongly in the regions  $3\text{--}3.5\ \mu$  and  $6.85\text{--}8\ \mu$ . They transmit freely in the intermediate region. Sharp maxima are found at  $2.98\text{--}3.08$ ,  $3.42\text{--}3.50$ ,  $3.42\text{--}3.50$ ,  $6.85\text{--}6.93$  for all alcohols. The secondary alcohols show an additional band at  $7.70$  which is shifted to  $7.90$  for the tertiary alcohols. There is little difference between straight chain and branched chain members of the series. Between  $3.5$  and  $6.85$  there are feeble bands irregularly distributed. The higher homologues are exceptional, since they absorb strongly between  $5.8$  and  $6.15$ . Polyhydric alcohols, glycerol, and glycols absorb similarly, but two of the feeble secondary bands disappear. The maxima for 26 alcohols are given correct to  $\pm 0.02\ \mu$ . R. A. M.

**Photographic Method for Absorption Spectra in the Ultra-violet.** W. CROSS (*Z. Elektrochem.*, 1924, **30**, 18—20).—To overcome the difficulties in the determination of absorption spectra due to changes in the intensity of the arc light, a method of comparing the spectra of two solutions simultaneously by means of a "dual" spectrograph is described. Some measurements of the absorption spectra of copper solutions at concentrations  $0.01$ ,

0.001, and 0.0001  $N$  are given, and the deviations of the observed data from Beer's law discussed.

H. T.

**Absorption of Light by Ammonia.** G. LANDSBERG and A. PREDWODITELEFF (*Z. Physik*, 1925, 31, 544—551).—Light from the spark between metallic electrodes was passed through mixtures of air and ammonia, then through a quartz spectrograph and the intensity in the region 1858 to 2195 Å. determined by means of a photo-electric cell. Absorption coefficients are given and also a photograph; the maximum absorption is at 1935 Å. There is no apparent deviation from Beer's law.

E. B. L.

**Series in Absorption Spectrum of Water Vapour.** H. WITT (*Z. Physik*, 1924, 28, 249—255).—In the region between 20 and 170  $\mu$ , the absorption spectrum of water vapour can be represented by two series of the form  $V=a(n+\frac{1}{2})$ , where  $a$  has the values 16.83 and 24.55. In the region 6500—9000 Å., the lines fall into three series, which may be correlated with the three principal moments of inertia of the triatomic molecule. From the spacing of the water bands in the ultra-violet, in comparison with the above, it is inferred that they probably originate from an OH molecule, or ion.

S. B.

**Mutability of the Absorption Spectra of Non-polar Compounds and Halochromism of Unsaturated Ketones. II.** G. SCHEIBE [with G. RÖSSLER and F. BACKENKÖHLER] (*Ber.*, 1925, 58, [B], 586—601; cf. A., 1924, ii, 712).—The absorption curves of acetone in hexane, ethyl alcohol, water, calcium chloride solution, and aqueous ammonia have been determined together with the position of maximal absorption in mixtures of hexane with chloroform or ethyl alcohol, ethyl alcohol with carbon tetrachloride or water, and in calcium chloride solution. An attempt is made to correlate the results thus obtained with the dipolar character of the solvents, for which the dielectric constant is used as a rough index. Measurements are also recorded for ethyl iodide in hexane, carbon tetrachloride, alcohol, and water, iodoform in hexane, carbon tetrachloride, and alcohol, mesityl oxide in hexane, methyl alcohol, and calcium chloride solution, and phorone in hexane, carbon tetrachloride, ether, chloroform, ethyl and methyl alcohol, glacial acetic acid, water, and concentrated sulphuric acid. If the position of the absorption bands in almost indifferent media such as hexane and carbon tetrachloride be regarded as normal it is found that two classes of bands may be distinguished. One class is invariably displaced towards the ultra-violet by strongly dipolar solvents such as alcohol and water (carbonyl, CI chromophore), whereas the other class is displaced by the same solvents towards the red (ethylene chromophore). A new possibility is thus opened of disentangling complex absorption spectra and of assigning bands to definite groups of atoms.

H. W.

**Ultra-violet Absorption of Aqueous Potassium Permanganate Solutions.** E. VITERBI (*Gazzetta*, 1925, 55, 127—135).—The ultra-violet absorption spectrum of aqueous potassium

permanganate solutions exhibits two wide principal bands, one between two minima at 4188.5 Å. and at about 2707 Å., respectively, and the other starting from 2707 Å. and extending towards the extreme ultra-violet. The first of these bands possesses seven or more striæ analogous to the eight present in the visible band; the order in which these are arranged according to their molecular absorption coefficients is the same in the two cases, the maximum coefficients being thus sensibly equal. Each of these two bands, as well as that in the extreme ultra-violet, shows in its less refractive part a band of less absorption not belonging to the system of striæ. The differences between the frequencies at the centres of two contiguous ultra-violet striæ are sensibly equal, not only to one another, but also to that shown by the visible striæ. These results, in conjunction with those obtained by Henri ("Études de Photochimie," 112 *et seq.*, 162 *et seq.*) for aromatic compounds, render it probable that the absorption spectrum of potassium permanganate contains an infra-red band of the frequency  $\nu$  = about 22.1.

T. H. P.

#### Ultra-violet Absorption Spectra of Organic Compounds.

VI. L. MARCHLEWSKI and A. MOROZ (*Bull. Soc. chim.*, 1925, [iv], 37, 404—412).—The ultra-violet absorption spectra of isatin (in alcoholic, aqueous, and in sodium hydroxide solution) and of acetylising (in alcoholic solution) and their extinction coefficients are given in tabular and in graphical form. Isatin in aqueous and alcoholic solution has bands at, approximately, 4170, 2940, and 2420 Å. (cf. Hartley and Dobbie, T., 1899, 75, 640), whilst acetylising has a completely different absorption spectrum (similar to that of isatin in sodium hydroxide solution) with bands at 3340 and 2660 Å. This is further evidence (cf. A., 1900, i, 100; 1901, i, 347; 1902, i, 646) that acetylising has the structure of *o*-acetamidobenzoylformic acid.

L. F. H.

#### Theory of Polarised Fluorescence. Influence of Viscosity.

F. PERRIN (*Compt. rend.*, 1925, 180, 581—583).—The degree of polarisation of the light emitted by fluorescent solutions is small unless the solvent has a large viscosity. This is attributed to the influence of the viscous solvent in retarding any rotation of the molecules oriented in a certain position, during the interval of time between absorption and emission of light. This conception is developed mathematically on the assumption that the active agents in the fluorescent molecules are electronic orbits, and the degree of polarisation is shown to be of the form  $0.25 \eta / \eta + s$ , where  $s$  is a constant. The values calculated according to this theory are in good agreement with values which have been observed with solutions of erythrosin and rose-bengal in various alcohols.

G. M. B.

#### Fluorescence Spectra. III. Aromatic Amine Vapours.

T. H. NUNAN and J. K. MARSH (*J. Chem. Soc.*, 1924, 125, 2123—2128).—Whilst previous study of the fluorescence spectra of the vapours of substances normally fluorescent in solution (A., 1924,

ii, 219) has shown that in many cases the vapour spectrum shows a number of fine lines not given in solution, the phenomena are only exhibited to a limited degree in the aromatic amine class. Of the toluidines, *p*-toluidine gives the most banded spectrum. The band interval is 42 Å. and extends from 3327 to 2966 Å. This band interval is practically the same as that previously recorded for *p*-cresol (A., 1924, ii, 219) and *p*-xylene (this vol., ii, 12).

A. E. M.

**Glow of Phosphorus.** H. J. EMELÉUS (*Nature*, 1925, 115, 460—461).—The light from glowing phosphorus trioxide and from phosphine spontaneously burning in oxygen gives the same spectrum as that previously observed (Emeléus and Downey, this vol., ii, 89); the glow of phosphorus and of phosphorus trioxide are analogous, but not necessarily identical, processes.

A. A. E.

**Phosphorescence Properties of Rare Earths in Alkaline-earth Phosphors. II.** R. TOMASCHEK (*Ann. Physik*, 1924, [iv], 75, 561—597; cf. this vol., ii, 12).—Phosphors of the sulphides and oxides of the alkaline-earth metals with the rare earths, in particular samarium, have been studied with reference to the relative effects of the different alkaline-earth metals on the duration and intensity of the after-glow, the intensity, wave-lengths, and distances apart of the doublet lines of the emission spectra. The relation of these to the type atom (sulphur or oxygen) has also been studied. From the results conclusions are reached as to the structure of the centres of phosphorescence and the mechanism of phosphorescence phenomena. A large complex, held together in loose chemical combination, appears to be necessary, the centre of the complex being capable of taking up molecules of metallic compounds. Hence compounds showing subsidiary valencies, for example, the alkaline-earth sulphides and oxides, are necessary. The type atom acts as the bridging atom between the heavy metal or rare earth atom of the phosphorogen and the alkaline-earth atom. The differences in behaviour of the various alkaline-earths are intimately associated with the differences between the heats of formation of the different sulphides and oxides. The phosphorescence process probably takes place as follows: absorption of a light quantum by the centre; transference of energy to the bridging atom, resulting in the removal of an electron which then attaches itself to the complex in a new position of equilibrium; simultaneous change of the electron orbits of the heavy metal atom through change of the valency field of the type atom; thermal or optical disturbance of the new position of equilibrium of the photo-electric electron and return of the latter to its original position in the type atom, accompanied by a simultaneous reversal of the changes in the electron orbits of the heavy metal atom with the emission of light. The change in wave-length of the characteristic groups, in passing from one metal to another, can apparently be expressed as a function of the heats of formation and the dielectric constants of the compounds between the two alkaline-earth metals and the type atom, the heat of formation of the

phosphorogen, and certain factors depending on the electron orbits and on the structure of the complex. M. S. B.

**Photo-electric and Phosphorogenic Effect.** M. CURIE (*J. Chim. physique*, 1925, 22, 45—47).—From measurements of the fluorescence, phosphorescence, and photo-electric effect of calcium sulphide preparations containing various amounts of bismuth, it is found that whilst the photo-electric effect is dependent on the presence, although scarcely at all on the concentration, of the bismuth, fluorescence and phosphorescence are dependent on the bismuth concentration. It is suggested that a layer rich in bismuth on the surface of the calcium sulphide grains is responsible for the photo-electric effect, and that the luminescence effects are derived from the whole of the grains. F. G. T.

**Electrical Conductivity and Hall Effect for Nickel Films.** A. RIEDE (*Z. Physik*, 1924, 28, 177—215).—Nickel films have been prepared by cathodic sputtering in hydrogen. Their conductivity was found to be proportional to their cross-section even for the thinnest films. The Hall effect in such films is proportional to the field strength in weak magnetic fields, but approaches a limiting value in intense fields. The sign of the effect is negative. S. B.

**Dielectric Constants and Absorption-coefficients of Glycerol.** R. BOCK (*Z. Physik*, 1925, 31, 534—543).—The dielectric constants were determined at temperatures from  $-140^{\circ}$  to  $225^{\circ}$ ; the method was that of Drude using Lecher wires, but producing the short wave-length oscillations by means of a thermionic valve and measuring the intensity by means of a crystal detector in circuit with a string galvanometer. Waves of about 1 metre length were employed. There is a sudden rise in the dielectric constant, beginning at  $-15^{\circ}$  and ending at  $60^{\circ}$ , the value rising from about 3 to 36; in this same temperature region, there is also a strong increase in absorption for these waves with a maximum at  $22^{\circ}$ . Theories based on earlier experimental results are shown to be valueless. E. B. L.

**Dielectric Constant of Liquid Phosgene [Carbonyl Chloride].** H. SCHLUNDT and A. F. O. GERMANN (*J. Physical Chem.*, 1925, 29, 353—355).—The dielectric constant of liquid carbonyl chloride, measured by the method of Drude (A., 1897, ii, 438), is  $4.34 \pm 0.04$  at  $22^{\circ}$  and  $4.72$  at  $0^{\circ}$ . This value is based on the constants given by Drude for benzene and solutions of acetone in benzene. M. B. D.

**Alternation in Molecular Volume of the Normal Monobasic Fatty Acids.** W. E. GARNER and E. A. RYDER (*J. Chem. Soc.*, 1925, 127, 720—729).—The molecular volumes of octoic,  $\alpha$ -nonoic, decoic,  $\alpha$ - and  $\beta$ -undecoic, and lauric acids have been determined. Whilst the values for the liquid state at  $50^{\circ}$  increase linearly by  $16.8$  c.c./g.-mol. for each  $\text{CH}_2$  group added, those for the solid state alternate as the series is ascended. Calculations of the area of the cross-section of one molecule in the crystal show that this



value is independent of the acid, acids so far apart in the series as acetic and lauric having the same cross-sectional area. The alternation in molecular volume is due entirely to changes in the length of the chain as the number of carbon atoms is increased. The magnitude of the alternation is in agreement with views previously advanced (A., 1924, ii, 385) regarding the structures of these acids in the solid state. The area of cross-section of the unit cell, 23.8 sq. Å., is very large and indicates that the structure of the crystal must be very open. J. S. C.

**Volume of the Water in the Hydrates of Calcium Sulphate.** W. BILTZ (*Z. anorg. Chem.*, 1925, 143, 231—232).—From the determinations by Linck and Jung (A., 1924, ii, 758) of the densities of calcium sulphate and its hydrates, it is shown that the gradual (zeolitic) dehydration of the hemihydrate occurs without alteration of the molecular volume. The difference between the molecular volumes of the dihydrate and the  $\alpha$ -anhydrite is 27.3, twice the molecular volume of water at 0° Abs. Hydration in stages is accompanied by increasing increments of molecular volume, as in the ammoniates. S. I. L.

**Molecular Volume and Molecular Refraction.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1925, 142, 80—82).—The expression  $V_o = 3M \cdot R$  (where  $V_o$  is the zero point molecular volume and  $M \cdot R$  the molecular refractivity) is deduced for non-associated substances. Application of the formula shows that it is approximately true, even with associated substances such as water, ammonia, and methyl alcohol. N. H. H.

**Variations in the Rotatory Power of Tartaric Acid as a Function of  $p_H$ .** F. VLÈS and E. VELLINGER (*Compt. rend.*, 1925, 180, 742—745).—The rotatory power of tartaric acid has been examined in its relation to the  $p_H$  value of the aqueous medium. The curve representing rotatory power as a function of  $p_H$  rises rapidly between  $p_H$  2 and 5. Above  $p_H$  5, the rotatory power is practically independent of the acidity of the solution until the medium becomes quite alkaline ( $p_H$  13), when there is a falling off in value. It is found that the experimental numbers are in agreement with the assumption that, for each  $p_H$  value, the rotatory power is the sum of the effects due to the two tartrate ions and the undissociated acid molecule. The question as to the change in the space arrangements consequent on the removal of a hydrogen ion from a molecule of tartaric acid is considered. J. S. C.

**Rotatory Dispersive Power of Organic Compounds. XV. Borneol, Camphor, and Camphorquinone. Origin of Complex and Anomalous Rotatory Dispersion.** T. M. LOWRY and J. O. CUTTER (*J. Chem. Soc.*, 1925, 127, 604—615).—The following equations represent satisfactorily the rotatory power of concentrated solutions of camphor in benzene (41 lines,  $\lambda$  6708—3599), acetone (27 lines,  $\lambda$  6708—3941), and cyclohexane (18 lines,  $\lambda$  6708—4358) at 20°, respectively;  $[\alpha] = 29.384/(\lambda^2 - 0.0872) - 20.138/(\lambda^2 - 0.05428)$ ,  $[\alpha] = 18.022/(\lambda^2 - 0.09363) - 7.1324/\lambda^2$ , and

$[\alpha] = 20.007/(\lambda^2 - 0.09114) - 9.2255/\lambda^2$ . The rotatory power of borneol in benzene at  $20^\circ$  (18 lines,  $\lambda$  6708—4358) can be expressed by the equation  $[\alpha] = 9.7866/(\lambda^2 - 0.07442) - 3.2862/\lambda^2$ , and the rotatory power of camphorquinone in the same solvent, also at  $20^\circ$  (9 lines,  $\lambda$  6708—5461), by  $[\alpha] = -13.170/(\lambda^2 - 0.022352)$ . Although these equations are in the first instance empirical, they appear to have a real theoretical significance.

The general theory of the origin of anomalous rotatory dispersion is discussed and a summary is made of the methods of superposing opposite partial rotations. Evidence is put forward in favour of the view that optical activity is not to be regarded as a property of the total molecule, but rather that the optical effects are localised in certain of the groups present. J. S. C.

**Action of Boric Acid on the Rotatory Power of Malic Acid and Malates.** E. DARMOIS (*Compt. rend.*, 1925, 180, 921—924).—The optical activities of solutions containing definite amounts of malic and boric acids and variable amounts of ammonia or sodium hydroxide have been determined. The results are interpreted in favour of the assumption of the existence of *l*- and *d*-complexes, the former being stable in solutions which are distinctly acid and are to be regarded as combinations of the acid salts of malic acid with boric acid. The *d*-complexes are considered to be complexes of neutral malates with boric acid, the magnitude of the rotatory dispersion pointing to the fact that they are considerably hydrolysed in aqueous solution. J. S. C.

**Rotatory Powers of Fluoro Derivatives of Benzene and its Homologues as a Function of the Wave-length.** F. RIZZI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 124—126).—The curves representing the dependence of the optical rotation of fluorobenzene, fluorotoluene, fluoro-*m*-s-, and fluoro-*m*-*as*-xylenes on the wave-length exhibit a change in direction at approximately zero rotation, the rotation being dextro for red and lævo for violet light. T. H. P.

**Effect of Reading Errors on the Rotatory Dispersion Constants.** R. RINDERKNECHT (*Helv. Chim. Acta*, 1925, 8, 179—184).—The constants  $[\alpha]_F/[\alpha]_C$ ,  $\lambda_a$ ,  $\lambda^2_0$  were determined from readings of the rotations for the *C*-, *D*-, *E*-, and *F*-lines of a Schmidt and Haensch polarimeter. The quotient  $[\alpha]_F/[\alpha]_C$  was found untrustworthy in the first decimal place for rotations under  $3$ – $6^\circ$  (*C*–*F*) on account of reading errors of  $\pm 0.02$  for a 0.5 dm. tube. In the citronellal group, the characteristic wave-length  $\lambda_a$  is untrustworthy for rotations less than  $5$ – $10^\circ$  (*C*–*F*) and quite untrustworthy for rotations less than  $3$ – $6^\circ$ . The values of the constant  $\lambda^2_0$  are strongly affected by the assumed reading errors and become untrustworthy for rotations of about  $10^\circ$  in the citronellal group. For maximum readings the second decimals, for minimum readings the third decimals, are untrustworthy. A. C.

**Transparence of Varieties of Glass in the Infra-red.** F. LIANA (*Compt. rend.*, 1925, 180, 578—579).—A sheet of flint glass

15.6 mm. thick showing complete absorption at  $3.19 \mu$  was found to transmit 74% of light of wave-length  $2.75 \mu$ . G. M. B.

**Electrostatic and Electrodynamic Significance of Electrons in the Crystallisation of the Elements of the Fourth Periodic Group.** J. BECKENKAMP (*Z. anorg. Chem.*, 1925, **143**, 394—404).—A continuation of previous work (A., 1924, ii, 754), with special reference to carbon. It is considered that the two inner electrons in the atom of this element may be replaced by four half electrons rotating in planes parallel to the faces of a tetrahedron. Since the positive charge on the nucleus is greater than the total negative charge of the inner electrons, there will be outside these a surface of zero potential, and the points of intersection of the normals to the paths of the valency electrons with this surface are described as epicentres. Carbon has four epicentres arranged at the corners of a tetrahedron, and since the four inner electrons are also arranged tetrahedrally, the neutral surface is nearly spherical. Such atoms may combine in two ways, (1) the epicentres of one half of the atoms (*b*) lie on points opposite the epicentres of the other half of the atoms (*a*); all the atoms are then similarly oriented and the neutral surfaces of atoms (*a*) contain 8 electrons whilst those of atoms (*b*) contain 4; (2) the epicentres of atoms (*b*) are at three corners of an eicositetrahedron; with respect to their epicentres, the two sets of atoms are indirect mirror images and the neutral spheres of atoms (*a*) contain 7 electrons whilst those of atoms (*b*) contain 4. The first form corresponds with diamond (type  $\alpha_2$ ) and leads to four groups of six-membered rings the axes of which are parallel to the normals of a tetrahedron. The second form (somewhat distorted) corresponds with graphite ( $\beta_2$ ) and the axial ratios thus calculated agree with those found by W. L. Bragg. The form  $\alpha_2$  is electrostatically stable, but  $\beta_2$  is labile, whereas the second possible electrostatically stable arrangement of the epicentres, the rhombic dodecahedron, is unknown among elements. There must therefore be some other controlling force, and this is believed to be magnetic. The two forms of carbon are the arrangements which are most perfectly astatic; the eight valency electrons of the noble gases and of sodium chloride are also arranged astatically, and the thirty electrons in benzene are arranged in several astatic groups. In the elements of the iron-platinum group, the arrangement is not perfectly astatic. The rupture of an astatic group absorbs energy and its formation releases it; the tendency to form astatic groups is therefore a consequence of the second law of thermodynamics.

A benzene formula is proposed which contains the same six-membered ring, which, according to Bragg, is present in both diamond and graphite; this has the maximum possible symmetry and the carbon atoms are equivalent. A. G.

**Rare Earths and the Magnetron.** B. CABRERA (*Compt. rend.*, 1925, **180**, 668—671).—Measurements of the magnetic properties of oxides or sulphates of the rare-earth metals are described and from the values of Curie's constant the following numbers *n* of Weiss magnetons are calculated for each element: La 0, Ce 11.89,

Pr 17.89, Nd 18.00, Sm 7.64 (?), Eu 17.92, Gd 40.07, Tb 47.92, Dy 52.25, Ho 52.00, Er 46.98, Tu 35.85, Yb 21.64, Lu 0. The diamagnetism of the atom itself of samarium is probably appreciable, whilst in the atom of gadolinium there are two magnetic states with 38 and 40 magnetons, respectively. The number  $n$  of magnetons when considered as a function of the atomic numbers of the elements falls on two curves, the first from  $n=0$  for La to  $n=0$  for Eu, and the second from  $n=0$  for Sm to  $n=0$  for Lu, but their superposition between Sm and Eu is hypothetical. The difficulties of finding a physical interpretation of these results are discussed. G. M. B.

**Nature of Hydrogen Halides.** A. HANTZSCH (*Ber.*, 1925, 58, [B], 612—641).—On account of the great optical similarity of HI with  $C_nH_{2n+1}I$  and of HBr with  $C_nH_{2n+1}Br$  and optical difference from the much more feebly absorbent salt solutions, the hydrogen halides are to be regarded as homopolar compounds and therefore as the inorganic, initial members of the series of alkyl derivatives for which  $n=0$ . This is established also for the transparent chlorides by a simple rule of boiling points. The quotient obtained by dividing the absolute boiling point of HCl, HBr, HI by 6 and of the boiling points of the corresponding methyl, ethyl, propyl, etc. derivatives by 8, 9, 10, etc., is almost constant. The gap between the hydrogen and methyl derivatives, "the carbon increment," is due to the tetrahedral configuration of the molecule which occurs here for the first time in the series. Accordingly, HCl, HBr, and HI are not appreciably associated; this is confirmed indirectly by the exceptional relationship of dimolar hydrogen fluoride to the alkyl fluorides which follow the rule.

In aqueous, alcoholic, and ethereal solution, HBr is optically identical with solutions of potassium and ammonium bromide in contrast to nitric acid, which in alcohol and ether is optically similar to its esters, and hence has the *pseudo* form,  $O_2N\cdot OH$ ; the halogen acid is therefore present as the hydroxonium bromides,  $Br[H_3O]$ ,  $Br[H_2OEt]$ ,  $Br[HOEt_2]$ , in these solvents, which function as basic anhydrides. On account of its instability, this could be established for hydrogen iodide only in aqueous solution, and not at all for hydrogen chloride by reason of its transparency. The strength of HCl, HBr, and HI has been determined (1) from the rate of inversion of sucrose under the influence of the three acids in highly concentrated aqueous solution, (2) by indicators in non-aqueous solution, and (3) by the decomposition of ethyl diazoacetate in the presence of these acids in as many media as possible. According to the inversion method, the acidity, which is approximately equal in dilute solution, increases with increasing concentration of each acid and for all three acids in the sequence,  $HCl < HBr < HI$ . In non-aqueous solution, hydrogen bromide is much stronger than hydrogen chloride; in addition, the acidity is very greatly influenced by the nature of the solvent. This is also established by the indicator method by determining the limit of inactivation, *i.e.*, the dilution at which the intensely coloured indicator salt is transformed by solvolysis into acid and the less intensely coloured, free indicator.

Thus hydrogen chloride is inactive towards *p*-dimethylaminazobenzene in water at  $n=0.0005$ , in ether at  $n=0.02$ . A more accurate modification of the indicator method which depends on comparison of colour shows that hydrogen chloride becomes much more rapidly inactive with increasing dilution in ether than in water. The diazoacetate method gives corresponding but more important results. According to the nature of acid and solvent, the decomposition takes place in a different manner chemically and as a change of the first or second order, but invariably depends primarily on the addition of acid and ester to yield a diazonium salt,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{N}(\text{:N})\cdot\text{X}$ ; this, and not the subsequent decomposition of the diazonium salt, is the change which is measured. The "diazo constants,"  $R_{\text{N}_2}$ , and the corresponding activities,  $R_{\text{N}_2}:N$  (normality) are entirely concordant with the values obtained by the other two methods. With increasing concentration, hydrogen bromide decomposes the diazo ester invariably much more rapidly than hydrogen chloride. The activities of the two acids in non-ionising solvents are greater and more distinct from one another when the solvent is most completely saturated in character, and thus are at a maximum and almost independent of dilution in chloroform and tetrachloroethane. In unsaturated hydrocarbons such as toluene, the activities are less and decrease with increasing dilution owing to formation of compounds of the type  $\text{HCl}(\text{C}_7\text{H}_8)_n$ , which are in part already known and become more stable with increasing dilution. Accordingly, the homogeneous hydrogen halides are most active, hydrogen bromide being more active than the chloride. These great differences are practically obliterated by the levelling action of water in consequence of the optically established additive formation of hydroxonium compounds,  $\text{X}[\text{H}_3\text{O}]$  or  $\text{X}[\text{H}\dots(\text{OH}_2)_n]$ . All reactions of these strong acids in dilute aqueous solution do not depend primarily on simple additive salt formation but on distribution of the acid between two basic anhydrides, one of which is water.

Hydrogen chloride and bromide differ in their behaviour in ethereal solution. The latter, which is shown by optical analysis to be present as the salt,  $\text{Br}[\text{HOEt}_2]$ , retains almost the same high activity as in chloroform or tetrachloroethane, and this is nearly independent of the dilution. The salt, therefore, decomposes very readily into its components and appears almost as strongly acidic as hydrogen bromide, in contrast with nitric acid, which optically resembles the esters in ethereal solution and is readily inactivated chemically by ether. The other great difference, that hydrogen bromide is present in water as hydroxonium salt but is much less active in this solution and moderately rapidly attains a minimum of acidity with increasing dilution, is due to the attachment, not only of its hydrogen atom to the oxygen of the water, but also of the hydrogen of the latter to its bromine atom, and, further, to the formation of aquo salts,  $[\text{Br}(\text{H}_2\text{O})]$ ,  $[(\text{H}_2\text{O})_n\text{H}]$ , which, in consequence of the great heat of solution of hydrogen bromide in water, are much more stable than the salt,  $\text{Br}[\text{HOEt}_2]$ , and with increasing dilution become richer in water and hence additionally stable.

Hydrogen chloride, on the other hand, at moderate dilution rapidly becomes inactive towards indicators and ethyl diazoacetate in ethereal solution; it appears, therefore, to exist solely as the etherate of the *pseudo*-acid,  $\text{ClH} \dots \text{OEt}_2$ , thus resembling nitric acid. In contrast with the levelling action of water, ether increases the difference in acidity between hydrogen chloride and bromide, which in chloroform are approximately in the ratio 1 : 2, whereas in ether the ratio becomes almost unmeasurable at great dilution.

Hydrogen iodide is the strongest halogen acid as judged by its ability to invert sucrose in aqueous solution. Its character could not be observed directly in non-aqueous solutions on account of their instability. Indirect evidence is afforded by the observations that, in alcohol and ether, certain reactions which depend on the primary formation of oxonium salts as intermediate products occur most rapidly in the presence of hydrogen iodide (corresponding with its greatest tendency towards salt formation) and most slowly in the presence of hydrogen chloride. The chief reactions are the esterification of the halogen acids,  $\text{EtOH} + \text{HX} \rightleftharpoons [\text{EtOH}_2]\text{X} \rightleftharpoons \text{EtX} + \text{H}_2\text{O}$ , and the production of ether from alcohol in consequence of the "catalytic" (actually salt-forming) action:  $2[\text{Et}\cdot\text{OH}_2]\text{X} \rightleftharpoons [\text{Et}_2\text{OH}]\text{X} + [\text{HOEt}_2]\text{X}$ . The apparently catalytic ability of the halogen acids to loosen the bond between alkyl group and hydroxylic oxygen in alcohols depends on the production of oxonium cations or *pseudo*-oxonium halides, in which the central oxygen atom is combined directly with 3 or 4 other atoms with consequent weakening of the linking between alkyl and oxygen.

The strengths of the homopolar hydrogen halides increases in the order  $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$ , which is also the order of activity of their alkyl derivatives,  $\text{MeF} < \text{MeCl} < \text{MeBr} < \text{MeI}$ . This is due to the same cause in each case. In consequence of its great heat of formation, hydrogen fluoride is the most stable *pseudo*-acid and has the smallest tendency to permit salt formation, either by the replacement of hydrogen by metal or by additive production of onium halides; in methyl fluoride, the halogen atom is most firmly attached to the carbon. Precisely the reverse is true for hydrogen iodide (with a negative heat of formation) and its alkyl derivatives. The apparent gap between hydrogen fluoride and the other halogen acids is bridged to some extent by the observation that whereas hydrogen fluoride, as the weakest acid, has a much smaller tendency than hydrogen chloride to form hydroxonium halides with water, so also hydrogen chloride only partly yields diethylhydroxonium chloride with the weakest basic anhydride, ether, whereas the corresponding compound with hydrogen bromide is completely stable.

H. W.

**Possible Structure of the Hydrogen Halides.** F. J. von WISNIEWSKI (*Z. Physik*, 1925, **31**, 869—876).—A model consisting of a positive hydrogen ion and a negative halogen ion rotating round their common centre of gravity leads to impossible values of the ionisation potential. If it is assumed that the hydrides consist of a positive halogen ion and a positive hydrogen ion at rest in the

axis of the molecule, whilst two electrons rotate at the ends of a diameter in an orbit with plane perpendicular to the axis (as in the Bohr-Debye hydrogen molecule), the calculated ionisation potentials are near the observed values, and the calculated moments of inertia agree with those indicated by the rotation-vibration spectra.

E. B. L.

**Internal Pressures produced by Chemical Affinity.** T. W. RICHARDS (*J. Amer. Chem. Soc.*, 1925, 47, 731—742; cf. A., 1924, ii, 723).—Problems involved in attempts to calculate the enormous internal pressures determining the existence of chemical compounds are considered, a more exhaustive treatment being promised later. Some tentative results are recorded, which, although not very trustworthy, show that the chemical pressures are much greater than the cohesive pressures. The heat energy necessary for evaporation and thermal dissociation is probably of the same order as the work needed to overcome the cohesive and chemical pressures, respectively.

J. S. C.

**Geometry of the Co-ordination Number.** I. R. STRAUBEL (*Z. anorg. Chem.*, 1925, 142, 133—134).—A theoretical paper directed towards the quantitative treatment of the maximum co-ordination number, sought by Hüttig. Values are given for the radius of  $n$  equal spheres (where  $n = 3$  to 12), representing co-ordinated atoms or groups, packed round a central sphere, representing the central atom, and touching it. The percentage of the surface of the central sphere "covered" by the planetary spheres is also calculated.

N. H. H.

**Geometry of the Co-ordination Number.** II. G. F. HÜTTIG (*Z. anorg. Chem.*, 1925, 142, 135—142).—From the results of Straubel (cf. preceding abstract), the theoretical relation between maximum co-ordination number and atomic volume has been worked out. By application of the figures to the ordinary atomic volume curve, the elements fall into areas each of which corresponds with a particular maximum co-ordination number. Although many exceptions may be cited, the results on the whole are in striking agreement with the facts.

N. H. H.

**Solid State from the Electrical Point of View.** Dispersion in the Hertzian Region. J. ERRERA (*Bull. Soc. chim. Belg.*, 1925, 34, 35—38).—The variation of the specific inductive capacity with frequency at temperatures both in the vicinity of, and far removed from, their melting points has been determined for ice and other solids. At all temperatures, the specific inductive capacity increases with the wave-length, especially at the melting point, although at lower temperatures the increase becomes very small, and practically no variation in the specific inductive capacity of ice is found between  $-47^{\circ}$  and  $-200^{\circ}$ . A sudden change in the value occurs on solidification, a diminution occurring with high frequencies, but an increase with low frequencies. The author suggests that two phenomena are concerned in electrical polarisation, (1) the movement, linear or angular, of the atoms, molecules, or ions, (2) the

movement of the electrons in the interior of each particle, and shows how the relative importance of these effects varies with the frequency and the temperature. At low temperatures, the former is negligible compared with the latter, and the specific inductive capacity is, therefore, almost independent of frequency, but the importance of the latter increases as the temperature rises. At high frequencies, the first effect is practically eliminated and the specific inductive capacity approaches a limit which is independent of temperature and thus from the electrical point of view the solid state begins at a different temperature according to the frequency, illustrating the continuity of state.

J. W. B.

**Valency Problems.** E. MÜLLER (*Z. Elektrochem.*, 1925, **31**, 143—157).—The author develops a scheme for the graphic representation of chemical compounds by an extension of the theory that atoms have a tendency to form an outer shell having the "inert gas number" of electrons, namely, eight. The number of electrons in the outer shell is denoted by strokes attached to the atomic symbol in a manner similar to the representation of ordinary valency. To simplify the formulæ, a thick stroke may be used to denote two electrons and a thin stroke one electron. Compounds may be either "heteropolar," in which electrons are given up by one component to "satisfy" the outer shell of the other, resulting in two oppositely charged ions, or may be "homopolar," in which the electrons are shared by the components. Application of the scheme serves to throw light on problems presented by the following: aliphatic and aromatic double bonds; the benzene ring and other single ring systems; naphthalene and other condensed ring systems; conjugated double bonds; bivalent carbon; quadrivalent oxygen; vinyl alcohol; nitro and *pseudo*-nitro compounds; chlorine dioxide; the oxides of nitrogen; ammonium salts; triphenylmethyl; the change from propyl to isopropyl alcohol; the formation of alcohol and carbon dioxide from sucrose; the hydration of ions; polymerisation. Reference is made to the views of Knorr (*A.*, 1924, ii, 34).

N. H. H.

**Periodic Sphere and Position of the Rare-earth Metals.** J. N. FRIEND (*Chem. News*, 1925, **130**, 196—197).—The elements are arranged in the form of a spiral coiled round the surface of a sphere. The rare-earth elements lie in the equatorial belt and show marked resemblances to adjacent elements. Many regularities not hitherto attainable are revealed. According to this scheme, the missing element 61 belongs to group V, and the metals of group VIII appear as a sub-group of group 0.

F. G. T.

**Physical Structure of the Elements.** C. G. BEDREAG (*Compt. rend.*, 1925, **180**, 653—655; cf. *ibid.*, 1924, **179**, 768).—The probable distributions of electrons in the atom are described for elements of variable valency such as manganese, chromium, iron, sulphur, chlorine, and phosphorus. The reduction of valency corresponds with the transfer of various numbers up to eight of the mobile outer



electrons to a more permanent inner shell. The configurations proposed are supported by a consideration of the magnetic properties for the metals chromium, manganese, iron, and cobalt, and of discontinuity in absorption for sulphur, phosphorus, and chlorine, the frequency of such discontinuity being found to be largest for the element in the state of maximum valency, as is required by theory.

G. M. B.

**New Determination of the Constant  $N$  of Avogadro.** L. M. ALEXANDER (*Phil. Mag.*, 1925, [vi], 49, 663—664).—Du Noüy's paper (this vol., ii, 109) contains errors. The probable error is  $\pm 0.009$  instead of  $\pm 0.08$ . The value  $N = (6.003 \pm 0.009) \times 10^{23}$  is different from that of Millikan  $N = 6.062 \times 10^{23}$  by 1% and not 0.1% as claimed. Du Noüy's three experiments are dependent on one another; his "control" calculations are fallacious.

R. A. M.

**Molecular Diameters.** H. SIRK (*Phil. Mag.*, 1925, [vi], 49, 708—711).—A re-statement (cf. this vol., ii, 184) showing that conclusions similar to Mokroushin's (A., 1924, ii, 820) had been reached independently.

R. A. M.

**Heats of Combustion of Three Oxides [ $\alpha$ -Propylene Oxide,  $\alpha$ -Trimethylethylene Oxide, and  $\gamma\delta$ -Hexylene Oxide].** P. W. ZUBOW and W. SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1925, [iv], 37, 271—274).—The molecular heats of combustion at constant pressure of the above three (liquid) oxides, in the order named, are 450.5, 748.8, and 912.6 kg.-cal., respectively. Assuming Trouton's rule and taking the specific heat of each oxide as 0.55, the molecular heat of fusion over the range  $18^\circ$  to the boiling point,  $t^\circ$ , is given by the expression:  $0.55\bar{M}(t-18) + 20.7(273+t)$ . The heats of combustion of the three oxides in the gaseous state are then calculated to be 467.4, 758.7, and 925.6 kg.-cal., respectively.

S. K. T.

**Thermochemistry of the  $\alpha$ -Oxides.** W. SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1925, [iv], 37, 274—276).—From results previously recorded (see preceding abstract) the heats of formation of the carbon-carbon and carbon-oxygen linkings in the ethylene oxide ring are shown to differ from the values obtained in saturated hydrocarbons and carbon dioxide; the values also vary with the number of carbon atoms in the ring. They increase when the hydrogen atoms in ethylene oxide are replaced by methyl or ethyl groups.

S. K. T.

**Molecular Heat of Combustion of Successive Terms of Homologous Series.** P. E. VERKADE, H. HARTMAN, and J. COOPS, jun. (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, 27, 859—866).—The heats of combustion of the first twelve members of the oxalic acid series have been determined. At least two preparations of each acid were burned, the heats of combustion being based on that of benzoic acid, 6324 cal. per g. The results obtained agree well with those of Stohmann and his collaborators (A., 1889, 1097; 1893, ii, 59). Oxalic and malonic acids give

abnormally high values, whilst the other acids fall into two thermal homologous series, the odd and the even series, one series being shifted about 1.5 cal. with respect to the other. There are indications of a similar alternation of heat of combustion increments in the series of monoalkyl-substituted malonic acids, and that the alternation is of about the same order of magnitude. According to Garner and Randall (A., 1924, ii, 385), the heats of crystallisation of the normal fatty acids also show an alternation in the successive terms of the homologous series. The question is discussed as to whether the oscillation of the combustion heat increments in the crystalline normal saturated dibasic acids is due, partly or entirely, to a different crystal structure of the even and odd terms. To decide this, the molecular heats of combustion for the crystalline acids should be compared with those of the supercooled, liquid acids at the same temperature (19.5° in this case). A scheme of research to investigate a number of problems in connexion with this is outlined.

L. L. B.

**Dissipation of Heat of Reaction.** M. BORN and J. FRANCK (*Ann. Physik*, 1925, [iv], 76, 225—230).—A theoretical paper in which the removal of the excess energy from a recently formed molecule by collision (Póányi, *Z. Physik*, 1920, 1, 337; Herzfeld, *ibid.*, 1922, 8, 132), or by the emission of light rays (Lewis, A., 1920, ii, 100), is discussed. It is possible for a molecule to contain, without decomposition, a greater amount of energy than that required for dissociation. In the formation of non-polar molecules from neutral atoms or molecules no radiation is possible, but when polar molecules are obtained the removal of energy may take place by either method depending on the pressure.

M. S. B.

**Dissolution of Mixed Crystals of (Na,Ag)Cl and Tammann's n/8 Mol. Law.** M. LE BLANC and A. RÖSSLER (*Z. anorg. Chem.*, 1925, 143, 1—59).—Rapid cooling of a fused mass of silver chloride and sodium chloride leads to a more coarsely dispersed solid than freezing brought about slowly and with constant stirring. By long tempering just below the m. p., further homogeneity is obtained. A study of the rate of solution of the mixed crystals by means of conductivity measurements showed that tempering essentially altered the attackability by saturated silver chloride solution. In the quenched untempered mixture, the relative quantity of sodium chloride going into solution rose continuously with increasing original sodium chloride content. The tempered solid, up to about  $\frac{5}{8}$  mol. silver chloride content, gave up its sodium chloride more rapidly and more completely than the corresponding untempered mixture. A strong retardation of the rate of solution was observed, however, with a silver chloride content of 0.68 mol. In the quenched solids, spontaneous decomposition of larger particles occurred at a sodium chloride content of 0.9 mol., whilst with tempered particles it was observed at 0.6 mol. With more resistant mixtures, the sodium chloride was given up slowly even after 800 hours' action of the solvent. For crystals of the same composition, the relative mass of sodium chloride given up increased with decreasing size of the

particles. Therefore only large particles of tempered mass with more than 0.68 mol. of silver chloride can be regarded as practically resistant. A comparative study was made for tempered and untempered particles of the colouring effect on the mixed crystal of hydrogen sulphide and of sunlight. An endeavour was made to explain the various results in terms of dispersoid chemistry, and it was concluded that the  $n/8$  mol. law of Tammann is only approximately true, and that sharp resistance limits do not exist.

L. L. B.

**X-Ray Investigation of some Mixed Crystals of the Systems (Na,Ag)Cl and K(Cl,Br).** B. H. BROOMÉ (*Z. anorg. Chem.*, 1925, **143**, 60—75).—The possibility of distinguishing disperse from homogeneous structures by means of X-ray analysis is discussed, and an attempt is made to confirm Tammann's hypothesis of regular atomic distribution. In the quenched masses of the system (Na,Ag)Cl, two kinds of lattice are found, of which the dimensions differ very little from those of the pure components. The "tempered" masses behave differently. For a mixed crystal of the composition  $\frac{2}{3}$  mol. of sodium chloride and  $\frac{1}{3}$  mol. of silver chloride, the sodium chloride lattice disappears after tempering. Such a crystal is relatively stable, whereas that containing  $\frac{4}{5}$  mol. of sodium chloride and  $\frac{1}{5}$  mol. of silver chloride decomposes at the ordinary temperature into two lattices which have the same dimensions as those of the quenched preparation. The observations confirm the conception of Le Blanc and Rössler (cf. preceding abstract) that a quenched mass is a dispersion of sodium chloride aggregates containing a little silver chloride in a molecular dispersed mass of (Na,Ag)Cl rich in silver chloride. The view that a finer structure is produced by tempering also receives confirmation. From a study of the X-ray spectra of the systems (Na,Ag)Cl and K(Cl,Br), it is concluded that the normal distribution postulated by Tammann does not exist.

L. L. B.

**Extraction Limit of the NaCl-AgCl Mixed Crystal.** G. TAMMANN (*Z. anorg. Chem.*, 1925, **143**, 76—79).—The work of Le Blanc and Rössler and of Broomé (cf. preceding abstracts) is criticised, and it is pointed out that, according to Schmidt (*Diss.*, Göttingen, 1917), the NaCl-AgCl mixed crystal cannot be obtained in a state of sufficient homogeneity to render it suitable for use in testing the  $n/8$  law. It is probable that, if a completely homogeneous mixed crystal were obtained, an influence-boundary would be found at  $\frac{6}{8}$  mol. of silver chloride.

L. L. B.

**X-Ray Investigation of Saturated Aliphatic Ketones.** W. B. SAVILLE and G. SHEARER (*J. Chem. Soc.*, 1925, **127**, 591—598).—A continuation of the work of Müller and Shearer (*ibid.*, 1923, **123**, 2043, 3152, 3156) on X-ray measurements of the higher members of the fatty acid series and their esters, in which it was shown that the spacings obtained represent within narrow limits the length of a single molecule or, in certain circumstances, of two molecules end to end. Sixteen ketones have been investigated, the

number of carbon atoms varying from 13 to 35. The substances fall into two sets, in each of which the spacing is a linear function of the number of carbon atoms, the increase per carbon atom being greater for the methyl ketones than for the others. Confirmation of the view that the presence of the active group,  $-\text{CO}\cdot\text{CH}_3$ , produces a tendency for the molecules to arrange themselves end to end in pairs is obtained from the fact that if the spacings of the methyl ketones be halved, the resulting values fall on the same straight line as for the remainder, in which the increase per  $\text{CH}_2$  group is  $1.30 \text{ \AA}$ . Although the position of the CO group has no effect on the length of the molecule, which appears to be a function of the total number of carbon atoms alone, it has a marked influence on the intensity distribution. This peculiar property may be used to locate within reasonably narrow limits the position of carbonyl groups in ketones from considerations of intensity distribution. The suggestion that these substances are not truly crystalline, but rather in an intermediate condition between the liquid and solid states, is considered to be untenable. J. S. C.

**Further X-Ray Measurements on Long-chain Compounds (*n*-Hydrocarbons).** A. MÜLLER and W. B. SAVILLE (*J. Chem. Soc.*, 1925, 127, 599—603; cf. preceding abstract).—Ten normal hydrocarbons, the number of carbon atoms ranging from 17 to 35, have been investigated by the X-ray method. Two characteristic spacings are common to all the substances, one relatively large spacing which is a linear function of the number of carbon atoms and another set which is almost independent of this. The increase per carbon atom of the long spacing,  $1.3 \text{ \AA}$ ., is considerably larger than the value predicted from considerations of the theory of Müller and Shearer (T., 1923, 123, 3158). Octadecane and eicosane have been shown to exist in two crystalline modifications. J. S. C.

**X-Ray Researches on the Dehydration Products of Gypsum.** H. JUNG (*Z. anorg. Chem.*, 1925, 142, 73—79).—Hydrated and anhydrous forms of calcium sulphate, both natural and artificial, have been examined by the X-ray method of Debye and Scherrer. All give results corresponding with  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ ,  $\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$ , or  $\text{CaSO}_4$ . The gradual loss of water by the hemihydrate when heated up to  $200^\circ$ , does not alter the lattice structure; only at higher temperatures is the anhydrite structure formed. N. H. H.

**Variation with Temperature of the Intensity of Reflexion of X-Rays from Quartz and its Bearing on the Crystal Structure.** R. E. GIBBS (*Proc. Roy. Soc.*, 1925, A, 107, 561—570).—Intensity of reflexion was measured at various temperatures up to  $800^\circ$ , also on cooling both rapidly and slowly. The results are in agreement with a transition point at about  $575^\circ$ . The oxygen atoms cannot lie in the same basal planes as the silicon, but in a plane between at a distance from them,  $d=0.63 \text{ \AA}$ . E. B. L.

**Effect of a Surrounding Box on the Spectrum of Scattered X-Rays.** A. H. COMPTON and J. A. BEARDEN (*Proc. Nat. Acad. Sci.*, 1925, 11, 117—119).—In a recent paper by Allison, Clark, and

Duane (*ibid.*, 1924, 10, 379), it appeared that the spectrum of the scattered X-rays altered considerably when the tube and the radiator were surrounded by a wooden box. It was suggested that the modified lines were due to tertiary radiation from the carbon of the wood. The present authors find no measurable "box effect." Woo, collaborating, examined the K-rays from a molybdenum target after scattering from magnesium, aluminium, silicon, and sulphur; the normal and modified lines appeared whether the wooden box was lead-lined or not.

A second experiment was made using sulphur as radiator, with no box, and a modified Seeman spectrograph. The photograph shows the  $K\alpha$ - and  $K\beta$ -lines distinctly, with a more diffuse modified  $\alpha$ -line and indications of a modified  $\beta$ -line. Compton's formula requires a wave-length change for the  $\alpha$ -line of  $0.036 \pm 0.001 \text{ \AA.}$ ; measurement gives the value  $0.037 \text{ \AA.}$  There is thus no evidence in this work for the Duane effect.

R. A. M.

**Compton Effect and Tertiary X-Radiation.** Y. H. Woo (*Proc. Nat. Acad. Sci.*, 1925, 11, 123—125; cf. preceding abstract).—Clark, Duane, and Stifler (*A.*, 1924, ii, 368) have measured the wave-lengths of molybdenum  $K\alpha$ -rays scattered from ice, rock-salt, aluminium, and sulphur and find tertiary radiation (Duane effect) to be present. The author has now used rock-salt, magnesium, aluminium, silicon, and sulphur as secondary radiators. In all five cases the  $K\alpha$ -line appears unmodified together with a modified line the peak of which occurs at the position predicted by Compton's formula. The "tertiary" peak was not observed in any experiment, nor was any box effect recognised.

R. A. M.

**Compton and Duane Effects.** G. E. M. JAUNCEY (*Nature*, 1925, 115, 456—457).

**Quantum Theory of the Unmodified Spectrum Line in the Compton Effect.** G. E. M. JAUNCEY (*Physical Rev.*, 1925, [ii], 25, 314—321).—If certain assumptions are accepted, there must be certain positions of the electron in its orbit from which the electron cannot be ejected by the primary quantum. The mass of the whole atom is then added to that of the electron, and the change in wave-length given by Compton's equation,  $\lambda_\phi - \lambda_0 = h(1 - \cos\phi)/mc$ , where  $\phi$  is the angle of scattering, is negligible. Application of the theory to molybdenum  $K\alpha$ -rays scattered by the K electrons of carbon yields results in accord with known experimental data.

A. A. E.

**Crystal Structures of Haematite and Corundum.** L. PAULING and S. B. HENDRICKS (*J. Amer. Chem. Soc.*, 1925, 47, 781—790).—A thorough X-ray study of crystals of haematite and corundum has been made, utilising the results of the theory of space groups in the interpretation of data from Laue and spectral photographs. The arrangement of atoms in the units of structure is such that each metal atom is surrounded by six atoms of oxygen which are not at the corners of a regular octahedron, three of these atoms being a few per cent. nearer the metal than the others. This indicates

that the location of electrons in the outer shells of an ion causes it to have different effective radii in different directions. The differences between the two oxygen-metal distances for hæmatite and corundum are in agreement with the conception that an iron ion with 23 electrons, with a volume only slightly larger than the 10-electron aluminium ion, would approximate much more closely to a sphere than would the aluminium ion. Each oxygen atom is surrounded by four metal atoms, two of which are nearer than the other two. The structures determined show that crystals of hæmatite and corundum consist of a compact arrangement of approximately spherical ions of oxygen and of iron or aluminium held together by inter-ionic forces of an electrostatic nature. The inter-ionic distances for hæmatite are: smallest oxygen-oxygen distance  $2.545 \pm 0.060$ , metal-oxygen distances  $2.060 \pm 0.035$  and  $1.985 \pm 0.025$  Å.; the corresponding numbers for corundum are  $2.495 \pm 0.025$ ,  $1.990 \pm 0.020$ , and  $1.845 \pm 0.015$  Å.

J. S. C.

**Crystal Structure of Tellurium and Selenium and of Strontium and Barium Selenides.** M. K. SLATTERY (*Physical Rev.*, 1925, [ii], 25, 333—337).—In addition to results already abstracted (A., 1924, ii, 849, 859), the following calculated densities are given: selenium, 4.84; tellurium, 6.25; strontium selenide, 4.53.

A. A. E.

**Electrolysis of Crystals.** P. LUKIRSKY, S. SČUKAREV, and O. TRAPESNIKOV (*Z. Physik*, 1925, 31, 524—533).—Crystals of rock-salt were clamped between metal electrodes at temperatures from  $300^\circ$  to  $600^\circ$  and submitted to potential differences from 300 to 3000 volts, whereby currents approaching 1 ma. become possible. The passage of current is permitted by motion of the crystal lattice, but essentially by the sodium, not the chlorine ion. Sodium is liberated at the cathode and chlorine at the anode and in conformity with Faraday's law. Fern-like structures are produced in the crystal at the electrodes, in some cases coloration, and the crystal structure breaks down in numerous centres inside the crystal.

E. B. L.

**Magnetic Properties of Iron Crystals.** W. L. WEBSTER (*Proc. Roy. Soc.*, 1925, A, 107, 496—509).—Thin discs were cut from crystals of iron and the component of the magnetisation was measured parallel and perpendicular to the applied field. The results may be explained by the theory of Weiss, the deviation in the direction of magnetisation being ascribed to a "molecular field" due to the mutual action of the molecules of the crystal. The magnitude of this field was found to be 620 and 479 gauss, respectively, for two crystals; impurities affect the value considerably. The molecular field is considered not to be due to magnetic forces.

E. B. L.

**Relationship between Atomic Numbers and the Properties of Ions in the Crystal Lattice.** A. F. SCOTT (*J. Physical Chem.*, 1925, 29, 304—318).—The relation  $d_0 = a \log (Z_c - Z_a) + b$ , where  $d_0$  is the shortest distance between ions,  $Z_c - Z_a$  represents the absolute

value of the difference of the atomic numbers of the cation and anion, and  $a$  and  $b$  are constants, gives in a number of cases a linear relationship between lattice distance and a function of the atomic numbers. For elements, the equation becomes  $d_0 = a \log (Z + e) + b$ , where  $d_0$  is equal to one-half of the distance of nearest approach of ions,  $Z$  is the atomic number of the element, and  $e$  represents the number of valency electrons or the maximum valency of the element.

M. B. D.

**Crystal Deformation and Hardening.** M. PÓLÁNYI (*Z. Metallk.*, 1925, 17, 94—95).—It is shown that the assumption that a thin layer of crystal dust is formed along the slip boundaries of metals as the result of cold work, whilst the remaining crystal grains are distorted but not broken, will account for the phenomena of hardening by cold work and recrystallisation on annealing, as well as for those exhibited by X-ray examination of the worked metal. [Cf. *B.*, 1925, 322.]

A. R. P.

**Hardening of Metals.** G. SACHS (*Z. Metallk.*, 1925, 17, 85—93).—From an extensive review of the results of previous investigators together with his own results the author concludes that the hardening of metals by cold work is due to distortion of the lattices, bending of the slip planes, or the development of internal stress varying in intensity from place to place; on annealing, the internal stress is relieved by the re-forming of the lattices. Hardening by alloying to form a solid solution is due to bending of the slip planes by the entrance of the solute atoms into the space lattices of the solvent and consequent distortion of the lattices; the hardening effect increases with an increase in the difference in size between the atoms of the solute and the solvent and with the number of the solute atoms. Hardening by heat treatment depends on the setting up of internal stress or internal deformation of the crystallites caused by volume changes due to the decomposition of solid solutions. The hardness of heterogeneous mixtures may be explained by considerations based on the size, shape, and distribution of the particles of the constituents, whilst that produced in eutectic mixtures by quenching from the liquid state is due to cold deformation of the crystallites or to a state of internal stress set up by the sudden cooling. The influence of decreasing grain size on the hardness of metals may be explained by the production of a very uneven state of internal stress due to deformation. [Cf. *B.*, 1925, 322.]

A. R. P.

**Tensile Strength of Zinc and Cold Working.** G. MASING and M. PÓLÁNYI (*Z. Physik*, 1924, 28, 169—176).—The tensile strength of freshly-rolled zinc at 85° Abs. is 45 kg./mm.<sup>2</sup>, and is much increased by cold rolling. The tensile strength is greater for samples composed of fine grains than for those of coarse grains, and is smaller for single crystals.

S. B.

**Strength and Elastic Limits of Rock-salt.** A. JOFFÉ and M. LEWITSKY (*Z. Physik*, 1925, 31, 576—583).—The breaking strain of rock-salt crystals of different area of cross-section was

found to be independent of the area; the presence of moisture may account for the different results of other workers. One piece of crystal which, when dry, broke under a load of 450 g./mm.<sup>2</sup> remained unbroken under a stress of 4000 g./mm.<sup>2</sup> when in water. The elastic limit for compression and extension is not affected by water and is about 920 g./mm.<sup>2</sup> at the ordinary temperature. For bending, the transition temperature from brittle to plastic is about the ordinary temperature. E. B. L.

**Strength and Elastic Limits of Natural Rock-salt.** W. EWALD and M. PÓLÁNYI (*Z. Physik*, 1925, 31, 746—749; cf. preceding abstract).—The authors claim that the increased strength of rock-salt crystals in water is due to the action of the water while the crystal is under stress and not merely to any change in the surface caused by solution; there is an internal change in the crystal, and the resistance to plastic change of shape is diminished. E. B. L.

**Magnetochemistry of Polymerides.** P. PASCAL (*Compt. rend.*, 1925, 180, 664—666; cf. A., 1924, ii, 39, 171, 605, 856).—Values for the molecular susceptibility are recorded for ten distinct phosphates of various degrees of complexity, and from these figures, assuming a constant atomic susceptibility for the metal, the value contributed by the radical  $\text{PO}_3$  is calculated for each compound, as follows: sodium monometaphosphate, 333; Maddrell's sodium salt, 325; sodium trimetaphosphate, 315; sodium tetrametaphosphate, 298; Graham's hexametaphosphate, 289; ethyl hexametaphosphate, 277; the three colloidal salts of Kurrol, 266, 268, and 268, and the non-colloidal salt,  $254 \times 10^{-7}$  C.G.S. units. From the known complexity of the mono-, tri-, tetra-, and hexa-metaphosphates and the regularity of the above figures, the conclusion is reached that Maddrell's salt is a dimetaphosphate, that Kurrol's colloidal salts are three forms of an octometaphosphate, and that the non-colloidal salt is probably a decametaphosphate. The change in diamagnetism with increased complexity is in the same direction and of the same order of magnitude as that caused by double bonds in organic compounds. G. M. B.

**Magnetic Quality of Pure Nickel.** A. M. MALCOLM (*Proc. Roy. Soc. Edin.*, 1924, 44, 206—208).—Pure nickel has no retentivity and the susceptibility and permeability are constant. In a field of 9.18 gauss the susceptibility is 4.17 and the permeability 53.53 with a horizontal rod. In the same field and with the rod vertical, the values are 4.20 and 53.77, respectively. In these weak fields, the magnetic qualities are independent of stresses in the metal.

A. E. M.

**Photomagnetic Properties of the Silver Halides.** A. GARRISON (*J. Amer. Chem. Soc.*, 1925, 47, 622—625).—The magnetic permeabilities of the silver halides are increased by the visible radiation, the chloride becoming less diamagnetic and the bromide and iodide more paramagnetic on illumination. Rise in temperature brings about a similar increase in permeability, the change being, however, comparatively slow. It is pointed out that an increase



in magnetic permeability will be accompanied by a parallel increase in electrical polarity. This view is supported by the fact that illumination increases the solubility and electrical conductivity of these halides.

J. S. C.

**Magnetic Properties of the 50% Iron-Nickel Alloy.** T. D. YENSEN (*J. Franklin Inst.*, 1925, **199**, 333—342).—The magnetic and electrical properties of the 50% alloy determined by the author (*Trans. Amer. Inst. Elec. Eng.*, 1920, **39**, 791) are compared with those of the 78% Ni-Fe alloy (Arnold and Elmen, *J. Franklin Inst.*, 1923, **195**, 621), of pure iron, and of a 4% Si-Fe alloy. The 50% alloy has a much lower hysteresis loss and a higher permeability and resistance than pure iron, but, to preserve these properties, must be annealed in a reducing atmosphere. [Cf. *B.*, 1925, 320.]

F. G. T.

**Transformation of Nickel in the Neighbourhood of the Curie Point.** W. DEL REGNO (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 179—181).—The transformation of ferromagnetic  $\alpha$ -nickel into the paramagnetic  $\beta$ -variety, with its accompanying changes in other physical properties, seems not to take place at any one definite temperature, but to occupy a range of temperature extending over about 100°, namely, 300—400°. Certain properties of the metal show a variation as soon as the smallest portion of the metal has undergone the change, whereas others require an appreciable proportion of the whole mass to undergo the transformation before they exhibit any peculiarity.

T. H. P.

**Effect of some Inorganic Salts on the Polarisation of Raw Sugar Solutions.** R. J. BROWN (*Ind. Eng. Chem.*, 1925, **17**, 39—40).—The following values for  $K$  in the formula of Jackson and Gillis (cf. *A.*, 1921, ii, 67) for the calculation of the effect of a salt on the polarisation of a solution of sucrose are given: sodium chloride, 0.00246; potassium sulphate, 0.00199; sodium sulphate, 0.00205, and disodium phosphate, 0.00305. For solutions of raw sugar, containing 10—15% of sucrose and about 5% of ash, the decrease in the polarisation caused by sodium chloride, for example, would be less than 0.01%, and is therefore negligible. J. P. O.

**Significance of Cold Working in the Light of Electrical Measurements.** II. W. GEISS and J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1925, **143**, 259—267).—The specific resistance of tungsten is increased to 160% and the temperature coefficient reduced to 60% of the original value by drawing to fine filaments at the ordinary temperature. The law of Matthiesen, that for mixed crystals the product of the specific resistance and the temperature coefficient remains constant, is found to apply to a pure metal after working in the cold. The change in conductivity is not due to lattice modification, nor to change in orientation of atomic axes; it is connected, as is also the change in mechanical properties, with the inter-crystalline relations. By cold working, as also by taking up a mixed-crystal component, the energy content of a metal is increased; calculation from the electrical measurements

indicates an increase of 775 cal. per g.-atom of tungsten after cold-working.  
S. I. L.

**Measurement of the Ratio of the Specific Heats, using Small Volumes of Gas. Ratios of the Specific Heats of Air and of Hydrogen at Atmospheric Pressure and at Temperatures between 20° and -183°.** J. H. BRINKWORTH (*Proc. Roy. Soc.*, 1925, **A**, 107, 510—543).—The general method was the same as that of Clément and Désormes, except that the temperatures before and after expansion of the gas were measured by means of a compensated thermometer of platinum wire. For air, the values of  $\gamma$  at 17° and -118° were 1.4032 and 1.4154; for hydrogen at 17°, -118°, and -183°, the values were 1.4070, 1.4800, 1.6054. The variations of molecular heat with temperature were discussed; for hydrogen the experimental values are in better agreement with Callendar's formula than with the formulæ of Planck and Einstein.

E. B. L.

**Velocity of Sound and Ratio of Specific Heats of Organic Liquids.** W. BUSSE (*Ann. Physik*, 1924, [iv], 75, 657—664).—By modifying Doersing's method (A., 1908, ii, 153) of determining the velocity of sound in liquid in a Kundt's tube, measurements of the ratio of specific heats at constant pressure and constant volume have been made in a number of organic liquids, using aluminium or magnesium powder. The values obtained are in good agreement with those calculated thermodynamically. For compounds of the same homologous series, the ratio diminishes with increasing molecular weight if the phase remains the same, but increases in passing from a gaseous to a liquid member. Substitution of hydrogen in the alkyl or aryl group, especially by -NO<sub>2</sub>, -NH<sub>2</sub>, or -OH, appears to cause a decrease in the ratio.

M. S. B.

**Specific Heats of Carbon Monoxide and Hydrocyanic Acid Vapour.** J. R. PARTINGTON and M. F. CARROLL (*Phil. Mag.*, 1925, [vi], 49, 665—680).—Values of  $C_p/C_v$  ranging from 1.385 to 1.425 for carbon monoxide are recorded in the literature. Usherwood's results (T., 1922, 121, 1604) for the specific heat of hydrogen cyanide are approximate only. The experimental methods used by the authors have been described earlier (A., 1923, ii, 214). Pure hydrogen cyanide was prepared by the action of hydrogen sulphide on mercuric cyanide, pure carbon monoxide by the action of cold concentrated sulphuric acid on sodium formate. The following results were obtained:—

Gas.	<i>t</i> .	<i>P</i> (mm. Hg).	$\gamma =$ $C_p/C_v$ .	$C_p$ .	$C_v$ .
Carbon monoxide .....	10.3°	760	1.404	6.94 cal.	4.94 cal.
Hydrogen cyanide .....	20.8	422	1.282	9.69 „	7.56 „
„ „ .....	17.35	505	1.268	10.22 „	8.08 „

The values for carbon monoxide confirm those obtained by recalculating the more trustworthy earlier data.  $C_p - C_v$  is given as 1.998 cal. The values of  $C_p$  and  $C_v$  and hence  $C_p/C_v$  for nitrogen and carbon monoxide agree closely. This might seem important, since the two gases have the same molecular weight and the same

number of electrons in the outer shell of the molecule according to the Lewis-Langmuir theory. Unpublished work on carbon dioxide and nitrous oxide shows that this agreement is fortuitous.

As the critical constants for hydrogen cyanide are not known, approximate values have been calculated by Walden's methods. The value of  $C_p/C_v$  given must therefore be regarded as provisional. Complicated factors make alternative interpretations possible, and it is concluded that since association almost certainly occurs in the gaseous state, specific heat data do not necessarily afford evidence of tautomerism in hydrocyanic acid. The applicability of Berthelot's equation of state to associated vapours is discussed, and thence it seems probable that association accounts for the results of Usherwood as well as for those of the authors.

R. A. M.

**Metastability of Elements and Compounds as a Result of Enantiotropy and Monotropy.** E. COHEN and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1925, **115**, 151—159; cf. Cohen and others, A., 1924, ii, 382, 449, 603; this vol., ii, 23).—Examination of the methods by which the specific heats of the tin allotropes have been determined shows that the values obtained may be those of metastable mixtures of unknown composition.

L. F. G.

**Ratio Melting Point : Critical Temperature.** J. J. VAN LAAR and R. LORENZ (*Z. anorg. Chem.*, 1925, **142**, 189—192).—The equation  $T_K/T_E = 2/\gamma \cdot a_K/a_E + \gamma/(1+\gamma)$  is deduced.  $T_K$  and  $T_E$  are the critical and melting points,  $a_K$  and  $a_E$  the values for van der Waals' constant at the critical and melting points, whilst  $\gamma$  is the "reduced direction coefficient of the straight line joining  $d_K$  and  $\frac{1}{2}d_0$ ," these symbols referring apparently to the density at the critical and zero points.

N. H. H.

**Melting Point and Vaporisation of Graphite.** E. RYSCHKEWITSCH (*Z. Elektrochem.*, 1925, **31**, 160).—A correction to a previous paper (see this vol., ii, 276).

N. H. H.

**Determination of the Melting and Transition Points of Potassium Dichromate.** P. L. ROBINSON, G. E. STEPHENSON, and H. V. A. BRISCOE (*J. Chem. Soc.*, 1925, **127**, 547—549).—A description of the phenomena accompanying the solidification and cooling of potassium dichromate is recorded. The salt separates from the fused state in a compact mass of dark brownish-red, tabular crystals with marked reduction in volume. On further cooling, the crystals change to a loose, orange-red powder. The m. p. of potassium dichromate was found to be  $398.4 \pm 0.5^\circ$  and the transition temperature of the two solid modifications, as determined by the thermometric method,  $236.8 \pm 0.5^\circ$ . No evidence was obtained for the existence of two forms of the sodium salt.

J. S. C.

**Properties of Simple Compounds and Types of the Solid State.** E. FRIEDERICH (*Z. Physik*, 1925, **31**, 813—826).—The nitrides of zirconium, m. p.  $3200^\circ$  Abs., scandium, m. p.  $2920^\circ$  Abs., niobium, m. p.  $2320^\circ$  Abs., and erbium were prepared for the first

time by heating a mixture of the oxide with carbon in nitrogen at  $1200^{\circ}$ . The known nitrides of titanium, vanadium, boron, silicon, and lanthanum were similarly prepared. With the exception of tantalum, these nitrides have the same lattice form as sodium chloride. Carbides were prepared: titanium, m. p.  $3400-3500^{\circ}$  Abs.; zirconium, m. p.  $3400-3500^{\circ}$  Abs.; vanadium, m. p.  $3100^{\circ}$  Abs.; niobium, m. p.  $4000-4100^{\circ}$  Abs.; tantalum, m. p.  $4000-4100^{\circ}$  Abs.; molybdenum,  $\text{Mo}_2\text{C}$ , m. p.  $2500-2600^{\circ}$  Abs.; and  $\text{MoC}$ , m. p.  $2840^{\circ}$  Abs.; tungsten, m. p.  $3150^{\circ}$  Abs.; silicon, dissociates at  $2220^{\circ}$  Abs. The space lattices of the carbides of titanium, zirconium, vanadium, niobium, and tantalum were the same as that of sodium chloride. A list is given of compounds which exhibit metallic conductivity; the condition is that the metal should possess unsatisfied valencies. The classification of solids is based on the external fields of the valency electrons. The ionic lattice, as of sodium chloride, always shows electrolytic conductivity; the metallic conductivity of metals and their unsaturated compounds is due to the free valency electrons, and in some cases to the kernel electrons, and in these cases the metals show superconductivity at low temperatures (cf. ii, 419).

E. B. L.

**Thermal Expansion of Alkali-metal Halides at Low Temperatures.** A. HENGLEIN (*Z. physikal. Chem.*, 1925, **115**, 91—120; cf. Baxter and Wallace, A., 1916, ii, 220).—The densities of the chlorides, bromides, and iodides of sodium and potassium have been determined at  $0^{\circ}$  and  $-79^{\circ}$  by a pycnometric method. A gas-volumeter by which the densities of solid salts can be obtained at all temperatures is described. This was used at the ordinary temperature,  $0^{\circ}$ ,  $-79^{\circ}$ , and  $-184^{\circ}$ , the results at  $0^{\circ}$  and  $-79^{\circ}$  agreeing with those previously obtained. Fused salts have slightly higher densities than those crystallised from aqueous solution; this is ascribed to the enclosure of air, and perhaps mother-liquor, in the latter case. The coefficient of expansion decreases with decreasing temperature, and the ratio atomic heat/coefficient of expansion is shown to be constant. The molecular volume at absolute zero can thus be calculated. The percentage change of molecular volume between  $-273^{\circ}$  and  $0^{\circ}$  is approximately the same for each salt. For the same cation the coefficient of expansion increases with the atomic weight of the anion; for the same anion it decreases with increasing atomic weight of the cation.

L. F. G.

**Thermal Expansion of Aluminium and Various Important Aluminium Alloys.** P. HIDNERT (*U.S. Bur. Standards, Sci. Paper* 497).—The linear thermal expansion was determined for 4 samples of aluminium and 51 aluminium alloys. The formula  $L_t = L_0[1 + (22.58t + 0.00989t^2)10^{-6}]$  represents the change in length between  $20^{\circ}$  and  $600^{\circ}$  for the purest cast aluminium (99.95%). Commercially pure rolled aluminium sheet (91.15%) showed a larger coefficient of expansion for nearly all temperature ranges. A series of cast aluminium-copper alloys containing 4—12% Cu showed a maximum between 6 and 8% Cu. The coefficients of expansion

of aluminium-silicon alloys decrease with increase in silicon up to 12%. The normal alloys showed irregularities at 250° which were not found when the alloys were modified with 0.1% of sodium. The expansion curves of zinc-aluminium alloys (Zn 77 and 95%) showed anomalous expansion at about 270°, due to the formation of  $\beta$  constituent. The coefficients of expansion were determined for duralumin in various conditions, and for the ternary alloys of aluminium with copper and silicon, and with copper and manganese. The permanent change in length of the specimens as a result of the heat treatment during test was recorded in each case. The expansion curves are discussed in connexion with the equilibrium diagrams for the alloys. [Cf., *B.*, 1925, 321.] C. S.

**Van der Waals' Equation and the Liquid State of Aggregation.** II. J. BERGER (*Z. physikal. Chem.*, 1925, **115**, 1—28).—A continuation of previous work (cf. *A.*, 1924, ii, 654). Apart from the disturbance due to association, satisfactory results are obtained when Kopp's law is tested with the author's value for  $b$ . It is probable that the coefficient  $a$  is also additive. Deviations caused by association run parallel to deviations of thermal expansion and heat of vaporisation. The new values of  $a$  and  $b$  have been used in the calculation of compressibilities, critical volumes, saturation pressures, and boiling points. L. F. G.

**Molecular Association and the Gas Equation of State.** A. LEDUC (*Compt. rend.*, 1925, **180**, 502—505).—The gas equation obtained by Duclaux on theoretical grounds (*J. Phys. Radium*, 1924, [vi], **5**, 331) for a gas in which partial bimolecular association occurs is practically identical in conditions with that obtained previously by the author (*Compt. rend.*, 1923, **176**, 1132), viz.,  $p = RT[V/(V-A)^2 - 3 \cdot 160A(4\chi - 1)/(V+A)^2]$ , where  $A$  = molecular co-volume,  $V$  = g.-molar volume,  $R$  = gas constant, and  $\chi$  = reciprocal of the reduced temperature. On the basis of these equations, the value of the heat of formation ( $Q$ ), and the fraction of association ( $f$ ) for carbon dioxide at various temperatures are calculated. It is found that in the saturated vapour  $f$  is about 0.4, and that the variation of  $Q$  is almost linear between 0° and 500°. The product  $fQ$  approaches zero as  $T$  is increased. J. W. B.

**Viscosities of the Liquid Halogens.** E. W. R. STEACIE and F. M. G. JOHNSON (*J. Amer. Chem. Soc.*, 1925, **47**, 754—762).—The viscosities of the liquid halogens have been investigated over the temperature ranges chlorine  $-76^\circ$  to  $-34^\circ$ , bromine  $-4^\circ$  to  $+32^\circ$ , iodine  $116^\circ$  to  $179^\circ$ , and the three viscosity-temperature equations obtained. The viscosity at the boiling point shows an increase with increasing atomic weight as expected from the periodic law. Evidence is put forward in support of the view that whilst chlorine and bromine have association factors in the liquid state of about 2, iodine possesses a higher degree of molecular complexity. J. S. C.

**Thermal Diffusion Measurements.** T. L. IBBS (*Proc. Roy. Soc.*, 1925, **A**, **107**, 470—486).—A glass cylinder was drawn out to a tube

at its lower end to which was attached a catharometer. When the cylinder was heated and the tube kept cold, the mixed gases tended to separate, the lighter gas going to the hot end, the catharometer measuring the change in composition in the cold end. Hydrogen and carbon dioxide, hydrogen and nitrogen, nitrogen and carbon dioxide, hydrogen and argon, and helium and argon were tried. The best separation was obtained in the last case; with 65% of helium in the mixture, the separation was 4.5%. E. B. L.

**Vapour Pressure of Binary Mixtures.** J. BROWN (*J. Soc. Chem. Ind.*, 1925, **44**, 162r).—The divergence of the total vapour pressure of a binary mixture from the simple additive law is given by the expression  $\Delta p_m = p_a(1 - e^{-\Delta\lambda_a/RT}) + p_b(1 - e^{-\Delta\lambda_b/RT})$ , where  $\Delta p_m$  = divergence of the total vapour pressure from that calculated from the simple mixture rule;  $p_a, p_b$  = vapour pressure of pure substances A and B;  $\lambda_a, \lambda_b$  the latent heats of vaporisation of the pure substances;  $\lambda'_a, \lambda'_b$  the latent heats of vaporisation of A and B in the mixture;  $\Delta\lambda_a = \lambda_a - \lambda'_a$ ;  $\Delta\lambda_b = \lambda_b - \lambda'_b$ . The total vapour pressure of the mixture at temperature  $T$  may be expressed as a function of the concentration of one of the components, say B, thus:  $p'_m = p_a + (p_b - p_a)\{(c_b - k^n) + k^n\} / \{(1 - k)^n + k^n\}$ , where  $n$  is a constant depending on the nature of the two substances A and B,  $c_b$  concentration of component B,  $k$  a constant. If the concentration of B is small when the divergence first becomes manifest  $k=0$ , and the equation becomes  $p'_m = p_a + (p_b - p_a)c_b^n$ . For mixtures of ether and 95% alcohol,  $k \rightarrow 0$ , and  $n=0.69$ . F. B.

**Viscosity of Liquids containing Dissolved Gases.** J. E. LEWIS (*J. Amer. Chem. Soc.*, 1925, **47**, 626—640).—The viscosities and densities of the following solutions have been determined in concentrations ranging from zero to saturation at 25° and at atmospheric pressure: sulphur dioxide in carbon tetrachloride, acetone, benzene, toluene, xylene, ether, heptane, carbon disulphide, and acetone-water mixtures, chlorine in carbon tetrachloride, and hydrogen sulphide in chloroform. The complete series of mixtures of sulphur dioxide with ether, toluene, benzene, methyl alcohol, and carbon tetrachloride have also been examined. The viscosity and fluidity curves for these latter systems are discussed from the point of view of the mixture rule. J. S. C.

**Copper and Silver Amalgams.** G. TAMMANN and T. STASSFURTH (*Z. anorg. Chem.*, 1925, **143**, 357—376).—The heating curves and microscopic structure of copper and silver amalgams have been studied. After prolonged heating at 100° amalgams with 5—76% of copper contain a crystalline compound X which on cooling forms CuHg by reaction with the surrounding liquid. The substance CuHg melts partly at 96.2°, and such amalgams when heated show halts at this temperature and at 149.9° corresponding with the crystals X. When the copper content is 40—76% mixed crystals containing 76% of copper are also present, and amalgams still richer in copper are homogeneous. Amalgams which have been allowed to harden at the ordinary temperature do not contain the crystals X,

and those with more than 25% of copper do not contain  $\text{CuHg}$ . Such amalgams show partial melting at  $108\text{--}110^\circ$ , but the heat of fusion of the crystals  $Y$  which are present is so small that no halt is seen on the heating curve; these crystals are intermediate in composition between  $X$  and  $\text{CuHg}$ , and are formed very slowly, thus accounting for the slow hardening of the amalgams.

Silver amalgams produced by heating turnings with mercury at  $360^\circ$  were found not to be homogeneous even after prolonged heating, and finely-divided silver prepared by the reduction of the chloride was therefore used. Amalgams containing 0.08—28.7% Ag consist of  $\text{Ag}_3\text{Hg}_4$  and a saturated liquid amalgam containing 0.08% Ag. From 28.7% to 100% the composition is uncertain, but it is suggested that up to 83% it consists of  $\text{Ag}_3\text{Hg}_4$  and mixed crystals containing 83% Ag, whilst richer amalgams are homogeneous. It is considered that the existence of other compounds is not proved. The slow hardening of the amalgams is due to the diffusion of liquid mercury into the solid mixed crystals, the mercury content of which increases with falling temperature.

A. G.

**Definitions of Steel and Cast Iron.** K. HONDA (*Sci. Rep. Tôhoku Imp. Univ.*, 1924, **13**, 187—191).—Neither the properties, which are variable, nor the method of production, which is not always known, are suitable criteria, but steel is completely defined as “an iron-carbon alloy with a content of carbon lying between 0.035 and 1.7%.” The lower limit is given by the solubility of carbon in iron at the ordinary temperature, the upper limit being the maximum solubility of carbon in iron at high temperatures. On the same grounds, cast iron is defined as “an iron-carbon alloy with a content of carbon lying between 1.7 and 6.7%,” the upper limit in this case representing pure cementite.

C. S.

**Reaction Limits of some Platinum Alloys.** G. TAMMANN (*Z. anorg. Chem.*, 1925, **142**, 61—72).—The homogeneity of the mixed crystal alloys of platinum with nickel, copper, and silver has been investigated by means of determinations of the reaction limit with various reagents. The alloys were prepared by heating the intimately mixed powders of both components or of their compounds in an atmosphere of hydrogen. With the platinum-nickel alloys the normal reaction limit, viz., 25 mol.-% Pt, was found, but with platinum-copper it was 32%, and with platinum-silver greater than 35%. These abnormal results are explained by the assumption that after the removal of the atoms of the base metal from the surface of the alloy the protecting platinum atoms do not remain bound in the crystal lattice.

N. H. H.

**Electrical Conductivity of Metallic Solid Solutions.** E. J. CUY (*Phil. Mag.*, 1925, [vi], **49**, 753—760; cf. Højendahl, A., 1924, ii, 647).—No satisfactory explanation of the catenary form of the electrical conductivity-composition curve of solid solutions has yet been given. Rayleigh regarded solid solutions as made up of sub-microscopic particles of the pure components at the junctions of

which a Peltier counter-*E.M.F.* would decrease the conductivity. Another view was that the atoms of the second metal would lower the mean free path of the electrons and so increase the resistance. X-Ray analysis has rendered both views untenable. The curve for the system gold-silver, in which both kinds of atoms are equal in radius, is similar to the curves obtained for systems in which the atomic radii of the components are unequal. The view that the low conductivity is determined by differences in atomic size cannot therefore be valid.

It is assumed that the valency electrons, to which conduction is due, move in quantum orbits and that in a pure metal they are all in phase, *i.e.*, at the same instant they are all furthest from one atom, and nearest the adjacent one. Since rise of temperature increases the interatomic distance, the electron jump will be hindered and resistance increased. This source of resistance applies to both pure metals and solid solutions. Since, however, the vibration frequencies of the different atoms in the alloy are not the same, they cannot be in phase. The resistance of pure metals is entirely determined by the temperature, whereas only a part of that of solid solutions is affected; thus the temperature coefficient of the resistance of solid solutions should be, and in fact is, less than that of the pure metals. Similarly, the increased conductivity due to pressure can be ascribed to lessening "gap" resistance, and the pressure-coefficient of solid solutions should be less than that of their components. The supra-conducting state of pure metals is due to diminished "gap" resistance, but cannot occur in true solid solutions. In certain alloys where solution is incomplete, a few threads of atoms in phase may, however, render the alloy supra-conducting.

The assumptions account for the similarity of the conductivity-composition curves for various mixtures and for the absence of specific effects due to the properties of the second metal.

It also follows that the addition of a third or fourth metal will have little influence on the conductivity.

R. A. M.

**Fusibility and Viscosity of Glass.** A. LACRENIER and P. GILARD (*Bull. Soc. chim. Belg.*, 1925, **34**, 55—65).—The variation of the viscosity and fusibility of glass with its composition is investigated. The fusibility is measured by determining the time necessary, at a given temperature, for the first drop of molten glass to fall when a known weight of the glass is fused in a platinum vessel fitted with a dropping tube. This period, expressed in seconds, gives the "fusibility number" for the glass, and the ratio of this to the corresponding value for a typical glass yields the "fusibility coefficient." The values of these coefficients for a number of glasses are given, and it is shown that the fusibility is diminished by a partial or total replacement of sodium by potassium, of lime by magnesia, and especially by a partial replacement of lime by alumina. A summary of the methods available for the determination of the viscosity of glass is given, and the authors apply their drop method used in the determination of the surface tension (*ibid.*, 1924, **33**, 119) to



determine the relative viscosities of glasses of different compositions. The period between the fall of two consecutive drops of molten glass from an orifice of circular section and known diameter is observed, and the time necessary for the fall of 1 g. of glass calculated. The results obtained for glasses of various compositions at temperatures of 1050° and 1150° are recorded, and it is shown that the viscosity is increased by the substitution of sodium by potassium and by the partial substitution of calcium by aluminium. The viscosity is decreased when the calcium is partly replaced by magnesium, especially in potash glasses, or by the addition of barium oxide. In soda-lime glasses the progressive diminution of calcium accompanied by a corresponding increase of sodium causes a regular variation in the viscosity. J. W. B.

**Physico-chemical Composition of Glasses.** P. BARY (*Rev. gén. Colloid.*, 1925, 3, 1—8, 43—52).—The properties of glass can be explained by ascribing to it a colloidal structure, in which a crystalloidal alkali silicate (as  $\text{Na}_2\text{SiO}_3$  or  $\text{K}_2\text{SiO}_3$ ) is dissolved in a condensed and polymerised silicate of a bivalent metal, *i.e.*,  $[\text{CaO}=(\text{SiO}_2)_n=\text{CaO}]_m$ . Rigidity, which is due to the large size of the polymerised molecule, is gradually reduced on heating owing to depolymerisation and decondensation. [Cf. B., 1925, 242.]

A. COUSEN.

**Solid Solutions.** G. BRUNI (*Chem. Reviews*, 1925, 1, 345—375).

**Solubility of some Inorganic Salts in Organic Solvents.** R. MÜLLER (*Z. anorg. Chem.*, 1925, 142, 130—132).—The solubilities of silver nitrate in methyl, ethyl, *iso*amyl, and *isopropyl* alcohols, ethyl acetoacetate, acetone, pyridine, quinoline, aniline, acetonitrile, and benzonitrile, and of lead nitrate, aluminium bromide and iodide, manganous chloride, ferrous bromide, cuprous iodide, beryllium bromide, cadmium iodide, cerous chloride, lithium nitrate, sodium nitrite, ammonium nitrate, calcium nitrate, barium iodide, strontium nitrate, calcium chloride, magnesium bromide, zinc bromide and iodide in pyridine, lithium nitrate in acetonitrile and *iso*amyl alcohol, calcium nitrate in the latter and magnesium bromide in the former, are tabulated. All the salts of which the solubilities have been determined at more than one temperature show a positive temperature coefficient, with the exception of magnesium chloride in pyridine. Solvents belonging to the same class of organic substances show an increase of solvent power with increasing dielectric constant. The order of solubility of inorganic radicals of the same family is compared with the order in aqueous solutions.

N. H. H.

**Aqueous and Acetone Solutions of Potassium Bromo- and Iodo-mercurates.** M. TOURNEUX and [MLLE.] PERNOT (*Compt. rend.*, 1925, 180, 740—742).—The fact that the solubility of mercuric halides in water is increased on addition of small amounts of the corresponding sodium or potassium salts demonstrates the existence of soluble complexes of the type,  $m\text{Hg}_2\text{X}$ ,  $n\text{KX}$ . Solubility determinations in aqueous and acetone solutions show that

the value of the ratio  $m : n$  is at least 2 for the bromides and 2.5 for the iodides (cf. A., 1919, ii, 344). J. S. C.

**Co-precipitation of Radium and Barium Sulphates.** H. A. DOERNER and W. M. HOSKINS (*J. Amer. Chem. Soc.*, 1925, **47**, 662—675).—Investigations have been carried out to obtain a satisfactory explanation of the fact that in presence of a large excess of barium over radium, sulphate ions precipitate radium sulphate although the solubility product is not exceeded (Lind, Underwood, and Whittemore, A., 1918, ii, 144) and that barium sulphate will remove radium from radium-barium chloride solutions (Germann, A., 1922, ii, 16). The experimental method consists of a quantitative study of the reactions of a radium-barium chloride solution with (i) sulphuric acid and (ii) barium sulphate. The result of the addition of sulphuric acid is considered as a co-precipitation, and the action of barium sulphate a replacement, the essential difference between the two being that for the latter only the surface of the added barium sulphate comes into equilibrium with the radium-barium chloride solution, whilst in the former case each crystal layer as it forms is in partition equilibrium with the particular concentration of solution momentarily existing. Since the solution has a decreasing radium-barium ratio as the precipitation proceeds, the crystals are not of uniform composition throughout their mass. Equations representing in a fairly satisfactory manner the replacement and co-precipitation data are put forward. The conditions under which crystal growth occurs have a great influence on the equilibrium. The possibility of applying the equations deduced to the phenomena of adsorption and fractional crystallisation is discussed. J. S. C.

**Influence of a Third Substance on the Critical Solution Temperature of Phenol and Water.** J. DUCKETT and W. H. PATTERSON (*J. Physical Chem.*, 1925, **29**, 295—303).—On cooling a mixture of 36.1% phenol in water turbidity sets in at 66.0°. The opalescence, which occurs just above this temperature, polarises light, and there is a critical change in the angle just before turbidity sets in. For substances which are soluble only in water, the molecular rise of the critical solution temperature shows the following order:  $\text{Na} > \text{K} > \text{NH}_4$  and  $\text{SO}_4 > \text{hydrogen tartrate} > \text{Cl} > \text{Br} > \text{I} = \text{NO}_3$ , which is the same as the Hofmeister series except that the iodide ion is equal to, instead of greater than, the  $\text{NO}_3$  ion. Substances soluble in phenol only do not give the same change of critical solution temperature for equimolecular concentrations. An optically active tartrate and the racemate have an identical effect. Curves are given showing the changes in viscosity and electrical conductivity in the region of the critical solution temperature.

M. B. D.

**Adsorption of Vapours by Metallic Oxides: Its Bearing on the Catalysis of Ester Formation.** J. N. PEARCE and A. M. ALVARADO (*J. Physical Chem.*, 1925, **29**, 256—270).—Observations on the adsorption of the vapours of water, ethyl alcohol, acetic acid, and ethyl acetate by aluminium and thorium oxides at

99.4° show that the only vapour which follows the adsorption isotherm is that of water. The adsorption of acetic acid vapour by aluminium oxide and of all four vapours by thorium oxide decreases with successive adsorptions and evacuations, and there seems to be a relation between the hydration of the oxide and its adsorbing power in these cases. The amount of adsorption is greatest for water and least for ethyl acetate. In the production of ethyl acetate by passing alcohol and acetic acid over a catalyst at 300° to 400°, the alcohol molecule is probably strongly adsorbed through the residual valencies of the hydroxyl group. The less highly attracted ethylidene group splits off and combines with the acid to form the ester.

M. B. D.

**Adsorption of Butane by Silica Gel.** W. A. PATRICK and J. S. LONG (*J. Physical Chem.*, 1925, **29**, 336—343).—The adsorption of butane by silica gel has been measured at 0°, 30°, 40°, and 100°. The water content of the gel was varied from 0.03 to 3.77%; maximum activity and capacity were shown by a gel with 1.96% of water. The adsorption data lend support to the capillary theory of adsorption (cf. A., 1920, ii, 417; 1922, ii, 262).

M. B. D.

**Influence of Temperature on the Evolution of Gases from an "Adsorber."** R. LORENZ and E. WIEDBRAUCK (*Z. anorg. Chem.*, 1924, **139**, 324—332).—The composition of the gases evolved at different temperatures from active charcoal saturated at 0° in an atmosphere of carbon dioxide and hydrogen was determined. At lower temperatures, the less readily adsorbed hydrogen is evolved, being almost completely given off at a temperature below 125°, whereas the greater part of the carbon dioxide comes off between the latter temperature and 425°. The use of charcoal in separating or enriching such gaseous mixtures is discussed.

H. T.

**Adsorption Equilibria in Presence of Two Gases.** R. LORENZ and E. WIEDBRAUCK (*Z. anorg. Chem.*, 1925, **143**, 268—276).—Mixtures of carbon dioxide with hydrogen and with carbon monoxide behave similarly towards adsorbent charcoal, the proportion of carbon dioxide in the solid being much greater than in the gaseous phase; thus at 0° charcoal containing carbon dioxide and hydrogen in the proportion of 3 : 1 is in equilibrium with a mixture of the gases containing only 5% of the former. With carbon dioxide and ethylene, the reverse is the case, the ratio of the former to the latter being lower in the adsorbent than in the gas mixture at equilibrium. Measurements of the adsorption of pure gases at varying pressures show that the adsorption of one gas is diminished in presence of another to an extent dependent on the degree to which the second is adsorbed.

S. I. L.

**Adsorption from Solution by Silica in Varying Degrees of Dispersivity.** D. C. JONES (*J. Physical Chem.*, 1925, **29**, 326—335).—The adsorption of acetic acid from its solution in gasoline [petrol] at 27° by silica has been studied, using powdered quartz, precipitated silica, and silica gel containing 6.2%, 3.4%, and 1% of water, respectively. Maximum adsorption was found to

occur with a silica gel containing 1% of water which had been heated at 680° in a stream of dry air for 18 hours. M. B. D.

**Adsorption of Acids by Purified Silica.** J. N. MUKHERJEE (*Nature*, 1925, **115**, 497).—Pure hydrated silica prepared from silicon tetrachloride, when partly dehydrated in air at the ordinary temperature, exhibits a marked increase in its capacity to adsorb acids (cf. this vol., i, 488), but the adsorptive power greatly diminishes if the silica is ignited. A. A. E.

**Action of Silica on Electrolytes.** A. F. JOSEPH (*Nature*, 1925, **115**, 460; cf. Mukherjee, this vol., i, 488).—Polemical and explanatory (cf. T., 1923, **123**, 2027). A. A. E.

**Cryoscopic Method for Adsorption.** H. L. RICHARDSON and P. W. ROBERTSON (*J. Chem. Soc.*, 1925, **127**, 553—556).—The adsorption by activated animal charcoal of a number of organic substances from aqueous solution has been determined by freezing-point measurements. For the compounds examined, the value of  $n$  in Freundlich's equation  $C_2 = KC_1^{1/n}$  lies between 1.45 and 4.8, thus varying round the mean value of 3 obtained by Freundlich. There is no apparent connexion between  $n$  and the relative adsorbability  $C_2/C_1$ . With solutions of methyl alcohol, stearic acid, methyl succinate, water, benzene, and more complex substances in phenol, no adsorption takes place. This is in agreement with the generally recognised fact that compounds such as phenol which are readily adsorbed prevent adsorption when employed as solvents. A. E. M.

**Adsorption of Electrolytes on Charcoal.** I. M. KOLTHOFF (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 742—749).—The view is expressed that molecular adsorption of electrolytes takes place on charcoal. To test this, very pure charcoal, containing 0.08% of ash, was used, in order to exclude adsorption effects due to chemical reaction. Hydrochloric acid was almost entirely adsorbed as such, and there was no chemical adsorption. The molecularly adsorbed acid could not be completely removed by washing with water. Bases, e.g., sodium and barium hydroxides, were also strongly adsorbed, but salts less readily. A marked "hydrolytic" adsorption was not observed. In the adsorption of the strongly hydrolysed sodium salt of veronal, the hydroxyl-ion concentration of the solution was much reduced after the adsorption, owing to the simultaneous adsorption of the salt itself and of the sodium hydroxide liberated by hydrolysis. Neutral salts were found to increase considerably the adsorbability of strong acids and sodium hydroxide, but to have no influence on non-electrolytes. Strong electrolytes are almost completely removed from charcoal by the capillary-active substances phenol and, to a smaller extent, amyl alcohol. In the case of impure charcoal, molecular and ionic adsorption occur simultaneously, and in order to study the adsorption of ions alone, the addition of some capillary-active substance is necessary to prevent molecular adsorption. L. L. B.

**Absorption of Catalytically Poisonous Metals by Platinum.**

**I. Absorption of Lead and Mercury.** E. B. MAXTED (*J. Chem. Soc.*, 1925, **127**, 73—77).—Lead and mercury ions have been previously shown to exert a poisoning effect on the catalysis of hydrogen peroxide decomposition by platinum-black (T., 1921, **119**, 225; 1922, **121**, 1760). A suspension of platinum was added to a solution of a lead or mercury salt of known concentration, and the mixture agitated and left over-night at 20°. A portion of the clear solution was then analysed by determining its inhibiting effect on the activity of a standard catalyst for the decomposition of hydrogen peroxide. By this means small fractions of 1 mg. of lead or mercury can be determined with considerable accuracy. When either the initial or final concentration of metallic ion in solution is plotted against the amount adsorbed, a straight line is obtained, but when the saturation point is nearly reached there is a rather abrupt change and the graph then runs parallel to the axis of concentration of solution. Similar curves are obtained when the poisoning action is plotted against the concentration of the solution, but it has not yet been determined whether the change in direction in this case occurs at the point of incipient saturation or not. The behaviour observed seems to support the view that the poisoning is caused by the saturation of the free valency forces on the surface lattice of the platinum by lead or mercury, so that they are no longer available for the adsorption of, or association with, a potentially reactive system.

M. S. B.

**Mechanism of the Adsorption of Ions.** R. AUDUBERT and [MLLE.] M. QUINTIN (*Compt. rend.*, 1925, **180**, 513—515).—The adsorption of ions by the walls of a vessel depends essentially on the osmotic pressure of the solution and on the electrostatic forces between the ions and the vessel, and not on any chemical interaction between the latter. The cations of the electrolyte diffuse into the electric field of the double layer surrounding the walls of the vessel and become adsorbed on the surface when their electrical pressure in the adsorbed portion is equal to their osmotic pressure in the solution and the electrostatic attraction. Assuming van der Waals' equation to apply to the solution, a quantitative expression for the density of the fixed ionic charge is deduced and broadly verified by measurements of the variation of charge in suspensions of mastic, gum arabic, and gelatin.

J. W. B.

**Comparative Adsorption of some Organic Acids and their Sodium Salts.** C. FROMAGEOT and R. WURMSER (*Compt. rend.*, 1924, **179**, 972—974).—The adsorption of formic, acetic, propionic, oxalic, succinic, citric, and pyruvic acids by carbon when compared with the adsorption of the corresponding sodium salts shows that there is no simple relation between the adsorption and the ionisation constants of the acids. In the case of the acids, adsorption increases with the number of carboxyl groups and the salts are always less adsorbed than the corresponding acids. There are, however, great differences between the amounts of acid and salt which are adsorbed.

H. J. E.

**Electro-osmotic Experiments on Intensity of Adsorption of a Constituent Ion by an Insoluble Salt.** I. J. N. MUKHERJEE and H. L. RAY (*J. Indian Chem. Soc.*, 1924, **1**, 173—188).—The adsorption of ions by carefully washed, precipitated lead chromate is studied by an electro-osmotic method with a view to a decision between the hypotheses, (1) that the adsorbed ions replace those of the same sign in the crystal lattice, thus leaving the crystal and its surface electrically neutral (Paneth, A., 1915, ii, 205), and (2) that they are adsorbed on the surface with or without exchange of ions, the surface thus becoming electrically charged (Mukherjee, A., 1922, ii, 198, 689). A well-digested precipitate of pure lead chromate is shown to be negatively charged in contact with water, this being due, probably, to the adsorption of chromate ions or, alternatively, to the adsorption of hydroxyl ions from the water. The velocity of electrical-osmosis is measured, under exactly similar experimental conditions, when the lead chromate is in contact with solutions of potassium chromate, iodate, nitrate, iodide, sulphate, and chloride, lead nitrate, barium chloride, and calcium chloride of concentrations varying between  $N/15,000$  and  $N/250$ . The order of adsorbability of the cations is  $Pb^{++} > Ba^{++} > Ca^{++} > K^{+}$ , whilst with a constant cation,  $K^{+}$ , the order of adsorption of the anions is that given above. The constituent ions of a precipitate are very strongly adsorbed by it, those of lead being so largely adsorbed as to reverse the charge at a concentration of  $N/2000$ . These observations cannot be explained on the type of adsorption assumed by Paneth (*loc. cit.*). The suggestion that there is a parallelism between the intensity of adsorption of the anion and the solubility of the salt of the adsorbed ion with opposite sign in the precipitate (Fajans and Beckerath, A., 1921, ii, 386) is not tenable, since the nitrate is more strongly adsorbed than the iodide or sulphate, whereas the order of increasing solubility of the lead salts is  $CrO_4^{--} < IO_3^{-} < I^{-}$ ,  $SO_4^{--} < Cl^{-} < NO_3^{-}$ . J. W. B.

**Occlusion of Magnesium [Oxalate] by Calcium Oxalate.** M. LEMARCHAND (*Compt. rend.*, 1925, **180**, 745—748; cf. Richards, McCaffrey, and Bisbee, A., 1901, ii, 624; Korte, T., 1905, **87**, 1508; Murmann, *Monatsh.*, 1911, **32**, 105; Kallanauer and Preller, *Chem.-Ztg.*, 1914, **38**, 249; Canals, A., 1921, ii, 349).—The results of previous workers are shown to be affected by the tendency of magnesium oxalate to form supersaturated solutions, from which it is slowly deposited. Analysis of the precipitates obtained when calcium oxalate is precipitated from solutions, unsaturated, saturated, and supersaturated with regard to magnesium oxalate, shows that the apparent occlusion is the sum of two effects, the real occlusion, which is slight, and the slow deposition of magnesium oxalate from the supersaturated solution, which is mainly responsible for the presence of magnesium in the precipitate. J. S. C.

**Adsorption.** S. LIEPATOFF (*Kolloid-Z.*, 1925, **36**, 148—157).—A cellulose preparation with a low ash content was found to adsorb potassium, sodium, and barium hydroxides in the approximate ratio 1 : 1 : 2. The adsorption of potassium hydroxide was revers-

ible and could be represented equally well by the Freundlich equation or by a distribution formula. In the more concentrated solutions, irregularities were introduced by the swelling and structural changes of the cellulose. Addition of salts to the hydroxides reduced both the adsorption and the swelling, which are supposed to be closely connected. Adsorption is regarded as a chemical change involving hydrolysis. E. M. C.

**Adsorption. IX. Influence of Various Substances and Importance of the Adsorption of Anions in the Coagulation of Arsenious and Antimonious Sulphide Sols.** S. GOSH and N. R. DHAR (*Kolloid-Z.*, 1925, 36, 129—137).—Dilution of arsenious and antimonious sulphide sols reduces the amounts of bi- and ter-valent cations required for flocculation, but increases the amounts of univalent cations. The presence of arsenious acid increases the flocculating power of univalent cations. Hydrogen sulphide reduces the flocculating powers of univalent cations, but increases those of cations of higher valency. The anomalous behaviour of the sols towards univalent cations on dilution is ascribed to hydrolysis, and to the peptising effect of the hydrogen sulphide being greater than the flocculating effect of the arsenious acid. Heating increases the stability of arsenious sulphide sol and decreases that of antimonious sulphide sol towards uni- and bi-valent cations. Both sols become less stable on ageing. The salt concentration for flocculation increases with the valency of the anion. E. M. C.

**Distribution of Hydrogen Ions between Gelatin and Water.** I. I. SHUKOFF and S. A. STSCHOUKAREFF (*J. Physical Chem.*, 1925, 29, 285—294).—When hydrochloric acid is titrated with sodium hydroxide in the presence of commercial gelatin, a hydrogen electrode showed that the titration curves meet at a point corresponding with  $p_H$  5.6. It is suggested that gelatin is a mixture of two substances with different isoelectric points. The decreased amount of sodium hydroxide required to produce a given  $p_H$  value between 3.5 and 5.6 is proportional to the amount of gelatin in solution. Similarly, the increased amount of sodium hydroxide required to produce a given  $p_H$  value between 5.6 and 10.5 is proportional to the amount of gelatin present. Hence, for a definite  $p_H$  value, the number of hydrogen or hydroxyl ions bound by 1 g. of gelatin is constant and independent of the concentration of the gelatin.

M. B. D.

**Surface Tension, Surface Energy, and the Surface Layer.** I. A. M. WILLIAMS (*Mem. Manchester Phil. Soc.*, 1924, 68, 1—11).—The change in volume which occurs in the transference of a substance from the liquid phase to the surface layer makes it necessary to amplify the usual expression for the surface energy of a liquid. The alteration is, however, only of importance at temperatures near to the critical point. It is shown that the surface layer of a liquid, if normally unimolecular at the ordinary temperature, does not become 2 mols. thick until quite close to the critical point, where it increases rapidly. A. E. M.

**Surface Tensions of Aqueous Solutions of Various Organic Compounds.** P. R. EDWARDS (*J. Chem. Soc.*, 1925, 127, 744—747).—The surface tensions of aqueous solutions of amyl alcohol, menthol, camphor, thymol, and *p*-toluidine have been measured by a capillary rise method at 15—18°. In all cases, the surface tension tends to approach a constant value with increasing concentration. The lowering of the surface tension is comparable with that produced by most active colloids, although the substances are crystalloids. Data for aqueous solutions of other organic substances are given; in all cases, the relative lowering produced is in accordance with the Harkins–Langmuir theory of “polar” molecules and surface tension. A. E. M.

**Force of Adhesion between Metal Surfaces. IV. Synthetic Metal Structures.** F. SAUERWALD and E. JAENICHEN (*Z. Elektrochem.*, 1925, 31, 18—24; cf. A., 1922, ii, 746).—Investigations on the effect of pressure, temperature, and duration of heating on the strength and density of test pieces made of iron, copper, and nickel powders show that the force of adhesion increases with temperature, but that at high temperatures a decrease occurs owing to a crystallisation process. The tensile strength depends on the degree of compression and on the size of the original powder grains. Powders composed of two metals gave strengths of the same order of magnitude as those for pure metal powders. The force of adhesion of test pieces of Acheson graphite and carbides was very small. M. B. D.

**Measurement of the Surface Tension of Molten Glass.** A. LACRENIER and P. GILARD (*Bull. Soc. chim. Belg.*, 1925, 34, 27—34).—The effects of various constituents on the surface tension of molten glass is determined by the authors’ “drop” method (cf. *ibid.*, 1924, 33, 119). The surface tension is increased in soda-silica glasses when the proportion of calcium is increased, when calcium is replaced by aluminium, or partly by barium or magnesium; it is decreased when the proportion of silica is reduced, when the proportion of sodium is increased, when the sodium is replaced either wholly or partly by potassium, and by the addition of sodium sulphate or boric acid. The increase of sodium relative to calcium causes a linear reduction in the surface tension. The results do not agree with those of Quincke, and the relative accuracy of the two methods is criticised. By means of comparative experiments, it is shown that the diameter of the tube used to produce the drops has practically no effect on the results. J. W. B.

**Surface Tension of Dilute Electrolytes.** C. WAGNER (*Physikal. Z.*, 1924, 25, 474).—From a consideration of the potential at the interface of two dielectrics and the consequent change in concentration at the surface of an electrolyte a general expression is deduced for the change in the surface tension of an electrolyte in its dependence on the concentration. Good agreement is found between the values predicted by theory and those observed by Heydweiller (*Ann. Physik*, 1910, [iv], 33, 145) for aqueous solutions



of sodium, potassium, and ammonium chlorides, sodium and potassium nitrates.

R. W. L.

**Surface Concentration of Gelatin at a Liquid-Gas Interface as Indicated by the Change in Surface Tension.** J. M. JOHLIN (*J. Physical Chem.*, 1925, 29, 271—284).—The surface tension of gelatin rendered ash-free by the method of Knaggs, Manning, and Schryver (A., 1923, i, 1144) has been determined by the capillary rise and the drop-weight method at 40°. The solutions show a gradual decrease in surface tension with time. For a given interval after the formation of the surface, the surface tension of a 1% solution shows a minimum at the isoelectric point  $p_H$  4.7.

M. B. D.

**Hollow Channels Opening on to the Surface of Metals.** G. TAMMANN and H. BREDEMEIER (*Z. anorg. Chem.*, 1925, 142, 54—60).—A method is described for determining the volume of channels which open on to the surface of metals. The metal is immersed in a 20% solution of potassium eosin and is subjected to a pressure such that the air in the channels is completely dissolved, its place being taken by solution. The absorbed solution is subsequently expelled and its volume and hence the volume of the channels determined colorimetrically. A variation of the method consists of using water instead of dye solution, expelling it by heating, and absorbing in a weighed calcium chloride tube, but this involves complications in cases where the metal decomposes water on heating. The application of the method to zinc, copper, brass, iron, and bismuth, and the influence of annealing, cold working, polishing, and, in the case of brass and iron, composition are described. As was expected, by far the lowest result is given by bismuth, which expands on solidifying.

N. H. H.

**Behaviour of Crystals and Lenses of Fats on the Surface of Water.** A. P. CARY and E. K. RIDEAL (*Nature*, 1925, 115, 457—458).—Solid fatty acids and esters spread on water surfaces until the surface tension of the water falls to a definite equilibrium value, but the rate of spreading is slower than for liquids. A diagram is given for stearic acid in which the two-dimensional pressure of the equilibrium between crystals and liquid lenses and the condensed and expanded types of surface films is plotted as a function of the temperature. The latent heat of fusion of stearic acid is computed to be 12700 cal.

A. A. E.

**Deviations from van't Hoff's Law.** W. SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1925, [iv], 37, 263—271).—The osmotic pressure,  $P$ , of a solution may be approximately expressed by the equation:  $P = xznRT$  (cf. A., 1923, ii, 546), where  $x$  represents the deviation from Raoult's law. The deviation from van't Hoff's law is positive when the molecular volume of the dissolved substance is greater than that of the solvent. When these volumes are practically equal, the solutions obey the law, provided  $n/(n+N) < 0.02$ . For most electrolytes,  $z$  is approximately unity, so that the deviations from van't Hoff's law are not large.

S. K. T.

**So-called "Metal Ammoniums." Vapour Pressure of Solutions of Lithium in Liquid Ammonia.** C. A. KRAUS and W. C. JOHNSON (*J. Amer. Chem. Soc.*, 1925, **47**, 725—731).—The vapour pressures of solutions of lithium in liquid ammonia at  $-39.4^{\circ}$  have been investigated from the saturation point (3.61 mols. of ammonia per atom of lithium) to a concentration of 60 mols. of ammonia per atom of lithium. The pressure rises rapidly with increasing dilution and then more slowly until the region of two liquid phases is reached, when the pressure remains constant at 540 mm. (v. p. of pure ammonia 555 mm.). The curve is continuous and no indication is found of the abnormalities recorded by Benoit (A., 1923, ii, 635). There is no evidence of the formation of compounds of the alkali metals with ammonia of the ammonium type.  
J. S. C.

**Spectrographic Study of the Formation of Complexes in Aqueous Solution.** P. JOB (*Compt. rend.*, 1925, **180**, 928—930).—The existence of complexes in aqueous solution is indicated by the absorption spectra. The method may be used to determine the formula and stability of the complexes.  
J. S. C.

**Method of Determining the Presence or Absence of Complex Salts or Ions in Dilute Aqueous Solution.** H. W. PATTERSON and J. DUCKETT (*J. Chem. Soc.*, 1925, **127**, 624—628).—Determinations have been made of the elevations of the critical solution temperature for water and phenol, on the addition of single salts and pairs of salts. An additive elevation of critical solution temperature with increasing concentration of the salt pair is regarded as indicating no complex formation. Deviations from additivity are attributed to complex formation, the magnitude of the deviation affording a measure of the amount of complex formation. Potash alum and iron alum show indication of the existence of alum molecules only at concentrations greater than 7—8 molar. Definite complex formation is indicated in the case of mixtures of potassium iodide with mercuric iodide and cadmium iodide.  
A. E. M.

**Viscosity of Rubidium Hydroxide Solutions.** R. FRICKE (*Z. anorg. Chem.*, 1924, **139**, 419—420).—Measurements of the viscosity of solutions of rubidium hydroxide through the concentration range 0.09—1.0*N* show that this is smaller than that of potassium hydroxide solutions. This is attributed to the smaller degree of hydration of the rubidium ion.  
H. T.

**Theory of Brownian Movement.** F. ZEILINGER (*Ann. Physik*, 1924, [iv], **75**, 403—425).—The theory of the Brownian movement has been applied to the discussion of the reflexion, or condensation and subsequent evaporation, of particles at a boundary surface.  
S. B.

**Nephelometry.** H. KLEINMANN (*Kolloid-Z.*, 1925, **36**, 168—174; cf. A., 1920, ii, 634; 1921, ii, 56).—The failures of other workers to obtain a simple linear relationship between turbidity and concentration are ascribed to defects in the optical arrangements

employed. An accuracy of 0.3–0.5% can be obtained with the author's nephelometer, provided that the solutions are uniform and within suitable limits, that the turbidities compared are within the range 1 : 4, and that the solutions have equal degrees of dispersion. A systematic exploration of the turbidity-concentration relationships is a necessary preliminary to nephelometric analysis. A new micronephelometer and a standard of turbidity are described (cf. A., 1923, ii, 429).  
E. M. C.

**Jelly State of Matter. I.** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, 36, 175–176).—Disperse systems of salts of fatty acids in dry toluene change gradually from typical elastic transparent jellies into flocculent precipitates. The formation of a jelly is regarded as an extreme case of crystallisation.  
E. M. C.

**Colloidal Sugar. II.** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, 36, 176–177; cf. this vol., ii, 290).—A dispersoid solution of sugar prepared by pouring an acetone solution into an aromatic hydrocarbon was stable for a month with dextrose, a week with sucrose, and 10 minutes with lactose. The solutions exhibit polychromatic phenomena (cf. following abstract).  
E. M. C.

**Disperse Systems, giving all the Spectrum Colours in Order on Temperature Changes.** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, 36, 177–178).—The disperse system prepared by heating glycerol with a solution of caoutchouc in xylene exhibits a continuous colour change covering the whole of the spectrum when the temperature is raised or lowered.  
E. M. C.

**General Colloid Chemistry. XIII. Analysis and Constitution of Silver Sols. III.** E. FRIED and W. PAULI (*Kolloid-Z.*, 1925, 36, 138–148; cf. A., 1923, ii, 636).—The silver sol prepared by the reduction of ammoniacal silver chloride by hydrazine hydrate is shown to contain the ammonium ion. On prolonged dialysis the electrical conductivity passes through a minimum value. The subsequent increase in conductivity is ascribed to the replacement of ammonium by hydrogen ion with the formation of an "acidoid." Direct measurements of the mobility agree with those calculated from the equivalent ionic mobility. The critical value for flocculation by aluminium sulphate corresponds with a concentration  $6.4 \times 10^{-5} N$  of ammonium ions in the sol. On the addition of increasing quantities of aluminium sulphate, the mobility decreases regularly, and only a single flocculation zone is given. Sols treated with sodium carbonate show with aluminium sulphate a reversal of the electrical charge and a series of flocculation zones. The sol is represented as of the type  $(AgCl_2)'NH_4^+$ , with a little  $Ag(NH_3)_2Cl_2'NH_4^+$ .  
E. M. C.

**Preparation and Properties of Silicic Acid Gel.** H. A. FELS and J. B. FIRTH (*J. Physical Chem.*, 1925, 29, 241–248).—The time of setting of silicic acid gel, prepared from sodium silicate and hydrochloric acid, has been determined. In acid solutions, the quickest set is obtained with concentrated acid, and the

time increases as the acid concentration is decreased until, in the vicinity of the neutralisation point, it becomes very indefinite. In alkaline solutions a slight alkalinity produces an immediate set and the time of setting increases with the hydroxyl-ion concentration. Under certain conditions, two gels are obtained, the first of which is cloudy, whilst the second is a very clear gel. The concentration of sodium chloride and the degree of hydration are much greater in the last-formed gel. The removal of sodium chloride from the gel after heating does not materially alter its sorptive capacity for water.

M. B. D.

### **Preparation and Properties of some Protected Silver Sols.**

I. D. GARARD and G. E. DUCKERS (*J. Amer. Chem. Soc.*, 1925, 47, 692—696).—Reversible silver sols have been prepared by reduction with dextrose or formaldehyde, agar-agar, dextrin, or gum arabic being used as protecting agent. The sols protected with gum arabic are stable within wide concentration limits and in the presence of relatively large concentrations of electrolytes. They react with the chlorides of antimony, bismuth, gold, mercury, and copper to give other sols, the rate of the reaction with copper chloride furnishing a measure of the extent of the protection. The bactericidal activity of a sol protected with agar-agar or gum arabic is of the same order as the commercial preparations protected with protein.

J. S. C.

**Isoelectric Points of Gliadin and Glutenin.** E. L. TAGUE (*J. Amer. Chem. Soc.*, 1925, 47, 418—422).—The isoelectric points of gliadin and glutenin, obtained from gluten by successive extraction with 70% alcohol and ether, respectively, were determined by finding a mixture of 0.01*M*-solutions of primary and secondary sodium phosphates, the  $p_H$  of which is not changed by the addition of the protein. The values are  $p_H=6.5$  and  $p_H=7.0$ , respectively. [Cf. *B.*, 1925; 295.]

F. G. W.

**Lyophilic Colloids and Poiseuille's Law.** H. R. KRUYT and C. ROBINSON (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 886—891).—The question as to whether lyophilic sols possess a real viscosity or whether they behave like elastic bodies is discussed. Freundlich and Schalek (this vol., ii, 112) have stated that sols investigated by them deviate from Poiseuille's law. To test this, the Hess viscosimeter, specially modified for the purpose, has been used to investigate gelatin sols at temperatures above and below that at which gelation begins, with the result that Poiseuille's law is found to hold exactly at 40° and 30°, whilst at 23° the expected deviations occur. The contention of Freundlich and others, that viscosity measurements on colloids should not be made with the Ostwald viscosimeter, but with the Couette or Hess apparatus, is criticised. From a review of previous work the authors conclude that sols consisting only of primary particles always follow Poiseuille's law, but that deviations occur when the primary particles have united to form aggregates either by temperature gelation or electrolytic coagulation. The theoretical bearing of this is briefly discussed.

L. L. B.

**Velocity Function of the Viscosity of Disperse Systems. II.**

W. OSTWALD (*Kolloid-Z.*, 1925, **36**, 157—167; cf. this vol., ii, 291).—The equation  $\eta = kp^n \cdot t$ , where  $\eta$  is the viscosity,  $p$  the pressure,  $t$  the time, and  $k$  and  $n$  are constants, is applied to measurements of the viscosity of disperse systems by the Hess and Couette methods. Results with the Hess apparatus may be fitted with an accuracy of 1—2%, whilst those obtained with the Couette apparatus agree within the limits of the rather large errors involved. Attention is directed to certain sources of error in the Hess apparatus, especially for very small pressures. Ostwald's capillary viscosimeter, with lengthened arms or in conjunction with a manometer, is the most suitable for measuring the velocity function, or the structural viscosity, of colloidal systems. E. M. C.

**Gel Replacement. A New Aspect of Metasomatism. W.**

LINDGREN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 5—11).—A paper of geological interest in which consideration is given to gel replacement as a factor in the transformation of minerals. These are decomposed and partly dissolved by aqueous sol solutions which move in subterranean interstices of capillary dimensions, coagulation resulting when the conditions are favourable. J. S. C.

**Action of Bile Salts on Gelatin. G. V. STUCKERT**

(*Anal. Asoc. Quím. Argentina*, 1924, **11**, 352—364).—The effects produced by different bile salts on gelatin gels include liquefaction, periodic formations analogous to the Liesegang phenomenon, and the formation of gaseous spaces. G. W. R.

**Effect of Neutral Salts on Gelatin. I. Swelling Action of Neutral Salts and the Value of the Hofmeister Series.**

E. STIASNY and S. R. D. GUPTA (*Collegium*, 1925, 13—23).—Commercial gelatin containing 2% of ash and having  $p_H$  5.9 was rendered ash-free by washing in a buffer solution of  $p_H$  4.7 until the  $p_H$  had been reduced to 4.7 and then in cold distilled water until free from the salts in the buffer. The product contained 0.015—0.027% of ash and had  $p_H$  4.7—5.08. The specific rotation was 1.85 for a 1% solution. Small quantities of this ash-free gelatin were treated with solutions of sodium chloride, thiocyanate, chlorate, and nitrate of different strengths ( $N/50$ — $2N$ ) for 2 hours, 24 hours, and 6 days, and the swelling was measured by the increase in volume of the gelatin. The volume of the swollen gelatin, the  $p_H$  of the salt solution before and after use, and the  $p_H$  of the gelatin were determined in each case. The swelling was in accordance with the Hofmeister series, decreasing in the following order  $CNS > NO_3 > ClO_3 > Cl > SO_4$ , and was not proportional to the  $p_H$  value. The neutral salt effect outweighs the ordinary acid swelling effect, but the swelling is influenced by the  $p_H$ . The Hofmeister anion effect cannot be denied, but Loeb's view that swelling is due to potential differences only is erroneous, since the amount of swelling is not proportional to the differences in  $p_H$  in the jelly and its surrounding solution. D. W.

**Effect of Neutral Salts on Gelatin. II. Their Dispersive Effect.** E. STIASNY, S. R. D. GUPTA, and P. TRESSER (*Collegium*, 1925, 23—36).—Observations on ultra-filtration, specific rotation, viscosity, dialysis, turbidity, protective colloid action, and the delicacy of the tannin precipitation test are recorded which show that neutral salts increase the dispersivity of the gelatin. Thiocyanates have the greatest effect and for other salts a series is obtained which agrees with the Hofmeister series. Sodium sulphate appears to decrease the dispersion of the gelatin particles. It is uncertain whether the gelatin aggregates are actually dispersed or whether the gelatin is decomposed into simpler protein complexes.  
D. W.

**Protective Action of Soaps on Zsigmondy's Gold Sols.** B. PAPACONSTANTINOU (*J. Physical Chem.*, 1925, 29, 319—322).—At the ordinary temperature the greatest protective action is shown by sodium and potassium linoleates. In decreasing order follow the oleates, palmitates, stearates, myristates, and laurates. With the exception of the linoleates, all the soaps exert a greater protective action at higher temperatures. There is no appreciable difference between the protective action of the sodium and potassium salts.  
M. B. D.

**Protective Action of Soaps on Arsenious Sulphide Sols.** B. PAPACONSTANTINOU (*J. Physical Chem.*, 1925, 29, 323—325; cf. preceding abstract).—With arsenious sulphide sols, the protective effect of the different soaps varies within narrower limits than is the case with gold sols. The protective action is increased by a rise in temperature except in the case of linoleates, which have a greater protective action at the ordinary temperature on both arsenious sulphide and gold sols.  
M. B. D.

**Flocculation of Colloidal Solutions.** A. BOUTARIC (*Bull. Acad. Roy. Belge*, 1924, [v], 10, 560—570).—The change produced by the introduction of an electrolyte into a colloidal solution may be followed by measuring the coefficient of absorption of the solution for a definite ray by means of the Féry spectrophotometer. For an arsenic trisulphide sol containing potassium chloride, a guttapercha suspension containing sulphuric acid, a ferric hydroxide sol containing potassium hydroxide, etc., the absorption coefficient increases at first rapidly but with continually diminishing speed until a limiting value is approached. The liquid in its final state is comparable with an unstable jelly which, if kept still, persists for some time, but gives rise to a flocculent deposit when subjected to very slight disturbances. The speed of flocculation may also be followed by the spectrophotometric method, and observations show that, in all the cases studied, flocks appear before the solution attains its limiting opacity and before the granules assume their maximum size. The above results are in agreement with Spring's hypothesis that the evolution of a sol treated with an electrolyte leads to the formation of an unstable system consisting of a kind of jelly which is ruptured by agitation,

with separation of particles, these remaining suspended in the intermicellar liquid.

T. H. P.

**Coagulation of Hydrosols by Mixtures of Electrolytes and Ionic Antagonism.** J. N. MUKHERJEE and B. N. GHOSH (*J. Indian Chem. Soc.*, 1925, 1, 213—224; cf. Weiser, A., 1922, ii, 262).—The influence of various anions on the coagulation of hydrosols of arsenious sulphide by mixed electrolytes has been studied. The coagulation concentrations of the following electrolytes, both alone and in pairs, are recorded: sodium benzoate, barium chloride, calcium bromide, calcium benzoate, magnesium chloride, barium benzoate, potassium chloride, lithium chloride, sodium chloride, sodium acetate, barium acetate, potassium trichloroacetate, barium trichloroacetate, trichloroacetic acid, and potassium ferrocyanide. The effect of sodium benzoate and sodium acetate on the coagulation concentration of sodium chloride is to increase the concentration of cation required in the mixture, and since sodium acetate or benzoate has practically the same effect on sodium chloride as on barium chloride, this effect is equally pronounced both in cases where displacement of adsorption of one cation by another is or is not possible. It is suggested that the antagonistic effect observed (cf. Weiser, A., 1924, ii, 309) is due to the protecting effect of an initial rise in charge due either to a strong adsorption of an anion (*e.g.*, with sodium benzoate) or a weak adsorption of a cation (*e.g.*, lithium chloride), cations with low coagulating power exhibiting the greatest antagonistic effect on the coagulating concentrations of other ions. Thus the influence of sodium benzoate on the metals of the alkalis and alkaline-earths is in the order,  $Mg > Ca > Ba$  and  $Li > Na > K$ , *i.e.*, in the reverse order of their precipitating powers. The nature of these effects cannot be clearly understood until a simultaneous determination of the electric charge on the precipitate is made.

J. W. B.

**Influence of Radiations on the Flocculation of Colloidal Solutions.** A. BOUTARIC and Y. MANIÈRE (*Bull. Acad. Roy. Belge*, 1924, [v], 10, 571—577).—Neither red nor violet rays appear to exert any appreciable influence on the course or velocity of flocculation of colloidal solutions or suspensions by means of electrolytes.

T. H. P.

**Electrical Conductivity and Coagulating Power of Acids and Bases.** G. ROSSI and M. ANDREANELLI (*Gazzetta*, 1925, 55, 99—103).—The results of experiments on colloidal arsenic trisulphide, Congo-red, ferric oxide, and methyl-violet show the inaccuracy of the statement that solutions of acids (bases) of equal electrical conductivities exert the same coagulating action on a negative (positive) colloid (cf. Picton and Linder, T., 1895, 67, 63; Hardy, A., 1900, ii, 396), the coagulating power depending on a number of different factors. Perrin's modification of the above rule, according to which the coagulating power is similar for solutions containing equal numbers of hydrogen (or hydroxyl) ions (*J. Chim. Physique*, 1905, 3, 50) is valid only if the

coagulation is regarded solely as an electrical phenomenon (cf. Rossi, A., 1924, ii, 459). T. H. P.

**Connexion between the Dispersion Process and the Production of Chemical Compounds.** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, 36, 175).—The possible existence of dynamic forms of hydrogen chloride and silica is discussed. E. M. C.

**Practical Results of the Theoretical Development of Chemistry.** F. HABER (*J. Franklin Inst.*, 1925, 199, 437—456).

**Influence of J. Willard Gibbs on the Science of Physical Chemistry.** F. G. DONNAN (*J. Franklin Inst.*, 1925, 199, 457—483).

**Atomic Dissociation of Chlorine and Hydrogen. I. Dissociation of Chlorine.** K. WOHL (*Z. Elektrochem.*, 1924, 30, 36—46). The mean molecular heat of chlorine determined by the explosion method between 291° and 1335° Abs. was found to be 6.83 cal.  $\pm$  1.3%. At any temperature up to 2000° Abs. the molecular heat is given approximately by the equation  $C = 4.963 + (E_T - E_{291})/(T - 291)$ ,  $E$  being the Einstein function calculated for 2.2 degrees of freedom = 90.2. The heat of dissociation of 1 mol. of chlorine at the absolute zero amounts to  $57000 \pm 2000$  cal. and at constant pressure can be calculated for any temperature by the expression  $Q = 57000 + 2.978T - E$ .

The influence of temperature on the dissociation of chlorine is given by  $\log Kp = -57000/4.571T + 1.5 \log T - F/4.571T + 1.366$ ,  $p$  being expressed in atmospheres and  $F$  being the energy of atomic vibration. H. T.

**Influence of Valency Direction on the Dissociation Constants of Dibasic Acids.** C. H. SPIERS and J. F. THORPE (*J. Chem. Soc.*, 1925, 127, 538—544).—The ionisation constants of various  $\beta$ -substituted glutaric acids indicate that the introduction of *gem*-groupings causes a large increase in the dissociation constant. For glutaric acid  $K = 4.69 \times 10^{-5}$ , whilst for  $\beta\beta$ -dipropylglutaric acid  $K = 33.9 \times 10^{-5}$ . Introduction of alkyl groups into various fatty acids has little influence on the ionisation constants. Similar results are produced by substitution in malonic and succinic acids—the larger the substituting groups up to a certain limit the greater the effect on the value of the dissociation constant, whilst *gem*-groups have a very marked effect. A. E. M.

**Water-gas Equilibrium.** J. R. PARTINGTON and W. G. SHILLING (*J. Soc. Chem. Ind.*, 1925, 44, 149—150T, 242T).—The equilibrium constant  $K = [\text{CO}_2] \cdot [\text{H}_2]/[\text{CO}] \cdot [\text{H}_2\text{O}]$  has been calculated from the formula  $\log K = -2125/T + 1.077 \log T - 0.03898T + 0.06133T^2 + C$  derived by the application of Kirchhoff's equation to the following values for the molecular heat at constant volume,  $C_v$  in cal./g.-mol., carbon dioxide  $6.700 + 0.0045t - 0.05102t^2$ , hydrogen  $4.850 + 0.037t$ , carbon monoxide  $4.970 + 0.0317t + 0.0631t^2$ , water vapour  $6.750 - 0.00119t + 0.05234t^2$ . The value used for  $C$



is  $-0.5425$ , which is the mean of the values obtained by Hahn, Allner, and Haber and Richardt between  $959^\circ$  and  $1645^\circ$  Abs. The calculated values for  $K$  are  $0.630$  ( $1000^\circ$  Abs.),  $0.943$  ( $1100^\circ$ ),  $1.31$  ( $1200^\circ$ ),  $1.71$  ( $1300^\circ$ ),  $2.14$  ( $1400^\circ$ ),  $2.59$  ( $1500^\circ$ ),  $3.05$  ( $1600^\circ$ ),  $3.50$  ( $1700^\circ$ ),  $3.96$  ( $1800^\circ$  Abs.). F. B.

**Equilibrium in Systems of the Type  $\text{Al}_2(\text{SO}_4)_3\text{-M''SO}_4\text{-H}_2\text{O}$ .** I. **Aluminium Sulphate-Copper Sulphate-Water and Aluminium Sulphate-Manganous Sulphate-Water at  $30^\circ$ .** R. M. CAVEN and T. C. MITCHELL (*J. Chem. Soc.*, 1925, 127, 527—531).—The former system shows no double salt formation. In the latter, the double salt  $\text{Al}_2(\text{SO}_4)_3\cdot\text{MnSO}_4\cdot 22\text{H}_2\text{O}$ , identical with the mineral apjohnite, is formed. This bears no resemblance to the alums and should not be termed a "pseudo-alum." A. E. M.

**Buffer Mixtures Prepared without Standard Acid as Base.** I. M. KOLTHOFF (*J. Biol. Chem.*, 1925, 63, 135—141).—The composition is recorded of mixtures of succinic acid and borax giving buffer solutions of  $p_{\text{H}}$   $3.0\text{--}5.8$  and of succinic acid and potassium dihydrogen phosphate covering the range  $p_{\text{H}}$   $5.8\text{--}9.2$ . C. R. H.

**Influence of Solvent on the Equilibrium of Isomerides.** H. VIXSEBOXSE (*Annalen*, 1925, 442, 306—308; cf. Smits, A., 1915, ii, 750; 1917, ii, 232; Vixseboxse, A., 1921, ii, 179).—A reply to Dimroth (this vol., ii, 36). H. W.

**Aqueous Solutions of Carbamates and Carbonates.** C. FAURHOLT (*J. Chim. physique*, 1925, 22, 1—44).—Previous work (A., 1922, ii, 272) on the equilibrium ammonium carbamate  $\rightleftharpoons$  ammonium carbonate is extended to the corresponding salts derived from methylamine, dimethylamine, and glycine. By methods similar to those used previously, the equilibrium constants and velocity coefficients of the reaction carbamate + water  $\rightleftharpoons$  carbonate in buffer solutions of the free base and its chloride have been evaluated. The amounts of carbamate in the equilibrium mixtures at  $18^\circ$  are very much higher for glycine and methylamine than for ammonia and dimethylamine. In strongly alkaline solution, the decomposition of the carbamate is practically complete. Measurements of the velocity of this decomposition were made for the above substances for various concentrations of carbamate and alkali. It is shown on theoretical grounds that in the above equilibria the state of the system is fixed by the concentration of the amine and the amine salt. These concentrations, together with the equilibrium constants, also determine the velocity with which equilibrium is attained in a given mixture. Values for the velocity coefficients calculated for various concentrations of amine and salt are in most cases in agreement with experimental values. F. G. T.

**Anomalous Behaviour of Strong Electrolytes.** A. FRIVOLD (*Physikal. Z.*, 1924, 25, 465).—On the basis of the theory of Debye and Hückel (A., 1923, ii, 459, 724; 1924, ii, 386) an expression is derived which connects the osmotic coefficient, *i.e.*, the variation of the diminution in vapour pressure from the classical value, with

the concentration of a solution whether strong or weak and with the dielectric constant of the solute. The form of this expression is such that as the concentration approaches zero a linear relation obtains between this coefficient and the square root of the molar concentration of the solute. Previous data for aqueous solutions of sodium and potassium chlorides are shown to be in accordance with the predictions of the theory. New observations on b. p. elevation for dilute solutions of lithium chloride in methyl, ethyl, and propyl alcohols lead to values for the osmotic coefficient which vary with the molar concentration of lithium chloride in the manner predicted by the theory. The divergence at higher concentrations is attributed to the solvation of the ions, of which the theory takes no account. A description is given of the technique employed in the work on lithium chloride.

R. W. L.

**Activities of Strong Electrolytes. I. The Activity of Hydrochloric Acid derived from the Electromotive Force of Hydrogen-Silver Chloride Cells.** G. SCATCHARD (*J. Amer. Chem. Soc.*, 1925, **47**, 641—648).—The *E.M.F.* of the cell  $\text{Pt}, \text{H}_2 | \text{HCl}, \text{AgCl} | \text{Ag}$  at  $25^\circ$  has been measured over a range of hydrochloric acid concentration 0.01—1.5*M*. The activity coefficients of the ions have been calculated from these and from the earlier measurements of Linhart (A., 1919, ii, 444) and of Noyes and Ellis (A., 1918, ii, 27). They are in good agreement with those calculated from the freezing-point measurements of Randall and Vanselow (this vol., ii, 33), and at low concentrations are in accordance with the limiting equation of Debye and Hückel.

J. S. C.

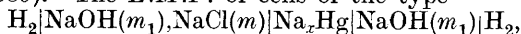
**Activities of Strong Electrolytes. II. A Revision of the Activity Coefficients of Potassium, Sodium, and Lithium Chlorides, and Potassium Hydroxide.** G. SCATCHARD (*J. Amer. Chem. Soc.*, 1925, **47**, 648—661).—The activity coefficients of the above electrolytes have been calculated from all the available measurements of electromotive force, freezing point, and vapour pressure, using the methods of Lewis and Randall ("Thermodynamics," 1923, Chaps. 26—28), modified in accordance with the theory of Debye and Hückel (A., 1923, ii, 459, 724).

J. S. C.

**Activity Coefficient of Sodium Hydroxide in Aqueous Solution.** H. S. HARNED (*J. Amer. Chem. Soc.*, 1925, **47**, 676—684).—The *E.M.F.* of cells of the type  $\text{H}_2 | \text{NaOH}(m_2) | \text{Na}_x\text{Hg} | \text{NaOH}(m_1) | \text{H}_2$ , where  $m_2$  was varied from 0.005 to 3.0*M*,  $m_1$  remaining constant at 0.01*M*, have been determined at  $25^\circ$ . From these, the activity coefficients of sodium hydroxide and the vapour pressures of the solutions have been calculated and compared with the corresponding values for potassium hydroxide, computed from the *E.M.F.* data of Knobel (A., 1923, ii, 116), employing the corresponding potassium hydroxide cells. The activity coefficient of potassium hydroxide is greater than that of sodium hydroxide at concentrations above 0.05*M*. Both coefficients pass through a pronounced minimum value with increasing concentration.

J. S. C.

**Activity Coefficient of Sodium Hydroxide in Sodium Chloride Solutions.** H. S. HARNED (*J. Amer. Chem. Soc.*, 1925, 47, 684—689).—The *E.M.F.* of cells of the type



in which  $m_1$  is 0.1 or 0.01*M*, and  $m$  varies over a considerable range, have been measured at 25°. The values are corrected for the activity of water in the solution and the activity coefficients of sodium hydroxide in the salt solutions calculated. The activity coefficients pass through minimum values with increasing concentration of the chloride.

J. S. C.

**Activity Coefficient of Potassium Hydroxide in Potassium Chloride Solutions.** H. S. HARNED (*J. Amer. Chem. Soc.*, 1925, 47, 689—692; cf. preceding abstract).—The activity coefficient of potassium hydroxide in 0.01 and 0.1*M* concentrations in potassium chloride solutions has been calculated from *E.M.F.* data for the corresponding potassium hydroxide–potassium chloride cells. As in the case of sodium hydroxide, the activity coefficient passes through a minimum value with increasing chloride concentration, the actual values being, however, greater. This behaviour is the reverse of that observed when the influence of the two chlorides on the activity coefficient of hydrochloric acid is investigated, the activity coefficient being greater in the sodium chloride solutions.

J. S. C.

**Activities of Strong Electrolytes. III. The Use of the Flowing Junction to Study the Liquid Junction Potential between Dilute Hydrochloric Acid and Saturated Potassium Chloride Solutions; and the Revision of some Single Electrode Potentials.** G. SCATCHARD (*J. Amer. Chem. Soc.*, 1925, 47, 696—709).—Measurements have been made of the *E.M.F.*'s of the cells of the type  $\text{Hg}|\text{HgCl}, \text{KCl}(\text{sat.})||\text{HCl}(c)\text{AgCl}|\text{Ag}$  at 25° ( $c$ , 0.01—1.5*M*) using a flowing junction. On stopping the flow, the liquid junction potential changes by about 3.5 millivolts. For acid solutions more dilute than 0.1*M*, the results obtained confirm the conclusion that the saturated potassium chloride bridge gives a liquid junction potential independent of the acid concentration, the absolute magnitude of which, using a flowing junction, is 4.7 millivolts. The results accord with the postulates of MacInnes (A., 1919, ii, 385) regarding individual ion activities. The following are the most probable values for some single electrode potentials at 25°, the potential difference between hydrogen at atmospheric pressure and hydrogen ion with an activity of one being considered as zero:  $\text{Ag}|\text{AgCl}(\text{sat.})\text{Cl}^-$ , −0.2222 volt;  $\text{Hg}|\text{HgCl}(\text{sat.})\text{Cl}^-$ , −0.2692 volt; saturated calomel electrode, flowing junction −0.2454 volt; decinormal calomel electrode,  $|\text{KCl}(\text{sat.})$ , flowing junction −0.3373 volt; without liquid junction −0.3353 volt.

J. S. C.

**Vapour-pressure Lowering of Aqueous Sulphuric Acid Solutions at 25°.** A. GROLLMAN and J. C. W. FRAZER (*J. Amer. Chem. Soc.*, 1925, 47, 712—717).—The vapour pressures of aqueous sulphuric acid solutions at 25° have been measured to a concentration 2.9*M*. The activity coefficients derived from these

are in agreement with the activity coefficients calculated by Lewis and Randall ("Thermodynamics," 1923, 354) from freezing points and *E.M.F.* measurements. The accuracy of Bronsted's vapour-pressure measurements (A., 1910, ii, 112) is questioned. J. S. C.

**Activity Coefficients and Transference Numbers of the Alkaline-earth Chlorides.** W. W. LUCASSE (*J. Amer. Chem. Soc.*, 1925, 47, 743—754).—The activity coefficients and transference numbers of the alkaline-earth chlorides have been derived from measurements of the *E.M.F.* of cells with and without liquid junctions. The cells investigated were  $\text{Ag}|\text{AgCl}|\text{MCl}_2(c)|\text{MHg}|\text{MCl}_2(0.01)|\text{AgCl}|\text{Ag}$ , and  $\text{Ag}|\text{AgCl}|\text{MCl}_2(c)|\text{MCl}_2(0.01)|\text{AgCl}|\text{Ag}$ , where M represents barium, strontium, and calcium. All measurements were made at 25°. The concentrations of strontium and calcium chlorides were varied from 0.01 to 3*M*, and that of the barium salt from 0.01 to 1.65. The values obtained for the cation transference numbers agree with previously recorded data. J. S. C.

**Dissociation of Polyatomic Salts.** N. SASAKI (*Z. anorg. Chem.*, 1924, 139, 387—393).—A mathematical discussion in the case of ferric chloride of the dependence of the concentration of the molecule and all its possible dissociation products on the total and on the anion and cation concentrations. H. T.

**The Method of Willard Gibbs in Chemical Thermodynamics.** W. L. MILLER (*Chem. Reviews*, 1925, 1, 293—344).

**Equilibria in Systems in which the Phases are separated by a Semipermeable Membrane. I and II.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 701—720).—The author considers systems in which the liquids (i) remain homogeneous and (ii) separate into conjugate pairs. The equilibria of isotonic liquids in binary and ternary systems are also discussed. L. L. B.

**Moving Boundaries and the Phase Rule.** E. R. SMITH (*J. Amer. Chem. Soc.*, 1925, 47, 795—797).—Beattie's (A., 1924, ii, 838) derivation of the phase rule in its application to the equilibrium state of a system containing *N* components, *P* phases, and *S* surfaces at which electric potentials exist,  $F = N - P + S + 2$ , *F* being the number of degrees of freedom, applies equally well to the equilibrium conditions attained in the determination of ionic mobilities by the moving boundary method. As an illustration, the determination of the mobility of the potassium ion in potassium chloride, by means of a moving boundary between solutions of lithium chloride and of potassium chloride, is considered. The restriction imposed on such a system is expressed by the relation  $C_{\text{Li}}/C_{\text{K}} = T_{\text{Li}}/T_{\text{K}}$ , where *C* denotes concentrations and *T* transference numbers. The number of independent variables is thus reduced from four to three. The mobility is constant with respect to variations in potential gradient only when the above relation is satisfied (Smith and MacInnes, A., 1923, ii, 828; 1924, ii, 727). J. S. C.

**Dehydrating Power of Salts.** N. SCHOORL (*Pharm. Weekblad*, 1925, 62, 276—280; cf. Scheringa, this vol., ii, 296).—Since salts may form solid hydrates, as well as saturated solutions, account should be taken of the “wet” and “dry” hygroscopicity. Scheringa’s conclusion that salts are more deliquescent at higher temperature is not always true—sodium nitrate may be left exposed in summer, but must be protected in winter, the relative vapour pressure being 0.78 at 0° and 0.70 at 38°. The humidity of the air must be considered in each case. S. I. L.

**Dissociation of Lead Carbonate.** M. CENTNERSZWER, G. FALK, and A. AWERBUCH (*Z. physikal. Chem.*, 1925, 115, 29—53; cf. Colson, A., 1905, ii, 304; 1909, ii, 400; Brill, A., 1907, ii, 233).—The dissociation pressures of normal lead carbonate and of its decomposition products have been measured by dynamic and static methods previously described (Centnerszwer and Andrusov, A., 1924, ii, 655). Under a pressure of 760 mm. the following compounds are formed at the temperatures stated:  $3\text{PbO}, 5\text{PbCO}_3$ , 274°;  $\text{PbO}, \text{PbCO}_3$ , 286°;  $2\text{PbO}, \text{PbCO}_3$ , 360°. The several stages of the dissociation are reversible. L. F. G.

**Partial Formaldehyde Vapour Pressures of Aqueous Solutions of Formaldehyde.** I. E. W. BLAIR and W. LEDBURY (*J. Chem. Soc.*, 1925, 127, 26—40).—The partial vapour pressures of aqueous formaldehyde solutions have been determined by the dynamic method at 20° and 0°, after the solutions had previously remained for some time at 15°. As increasing volumes of air were passed through, the vapour pressure gradually rose at 20° until it reached a constant maximum value; at 0°, on the contrary, it fell to a constant minimum value. The addition of methyl alcohol decreased the divergence between the initial and final values, and, at 20°, increased the constant maximum value attained, but did not greatly affect the final value at 0°. The formaldehyde vapour pressure at 20° is more than doubled by 15% alcohol. In the presence of methyl alcohol, also, the relationship between the formaldehyde partial vapour pressure and concentration in solution becomes more nearly linear. The results may be interpreted by assuming an equilibrium between complex or hydrated formaldehyde molecules and simple molecules. On raising the temperature from 15° to 20°, the new equilibrium conditions, involving an increase in the number of simple molecules, and therefore in the value of the vapour pressure governed by these, are only attained gradually. Delay is also caused by the removal of formaldehyde vapour on the passage of an air current. Ultimately, however, a maximum constant vapour pressure will be reached at which the rate of formation of simple molecules is equal to the rate of removal. Similarly, when the temperature is lowered a constant minimum value should be reached. This theory has been tested by keeping solutions at 20° and also at 0° for several days before determining the vapour pressures. They were then found to remain practically constant. The effect of the presence of methyl alcohol explains the relatively high values

generally found for the formaldehyde vapour pressure of commercial formalin solutions, which contain methyl alcohol as an impurity.

M. S. B.

**Partial Vapour Pressures of Aqueous Hydrogen Chloride Solutions.** F. C. ZEISBERG (*Chem. and Met. Eng.*, 1925, **32**, 326—327).—Hurter's formula (*J. Soc. Chem. Ind.*, 1889, **8**, 861) is shown to be untrustworthy and the following substitute is proposed :  $\log p = 10.9528 - 0.009725w - 0.000868w^2 - (4.557 - 65.3w)/T$ , where  $p$  is the pressure in mm. of the hydrogen chloride over a solution containing a weight percentage  $w$ , and  $T$  is the absolute temperature. Over the range 0—100° and  $w = 18$ —32, the error with this formula is less than 5%.

S. K. T.

**Total Vapour Pressure of Cuprous or Lithium Chloride Solutions in Hydrochloric Acid.** N. C. YANNAKIS (*Bull. Soc. chim.*, 1925, [iv], **37**, 253—262).—The vapour pressure of solutions of cuprous chloride in hydrochloric acid solutions is a linear function of the salt concentration; the gradient decreases with decreasing acid concentration and becomes zero when this concentration corresponds with the acid of minimum vapour pressure. In the case of lithium chloride, the pressure increases at first slowly and then very rapidly as the salt concentration increases; these curves, obtained with a salt which can only react with the water, differ entirely from those obtained with cuprous chloride, which only reacts with the acid. With solutions containing less than 22% of acid, the lithium chloride curves show a slight minimum; the lithium salt behaves as though it increases the acid concentration.

S. K. T.

**Affinity of the Metals for Sulphur.** K. JELLINEK and J. ZAKOWSKI (*Z. anorg. Chem.*, 1925, **142**, 1—53).—The equilibrium  $MS + H_2 \rightleftharpoons M + H_2S$  has been determined at several temperatures over a range of 500° to 1100° for the compounds  $Ag_2S$ ,  $Cu_2S$ ,  $SnS$ ,  $PbS$ ,  $Sb_2S_3$ ,  $Bi_2S_3$ ,  $MnS$ ,  $FeS$ , and sulphides of the approximate composition  $NiS$  and  $CoS$ . From this the values of the sulphur tension of the sulphides have been calculated by a simultaneous consideration of the dissociation constant of hydrogen sulphide and the heats of dissociation of the sulphides. At a sufficiently low temperature (about 0°) the values increase in general with decreasing normal potential; thus the affinity of the metals for sulphur decreases with decreasing "nobility." Application of the Nernst and van't Hoff reaction isochores is made and the results are compared with the heats of formation calculated by indirect thermodynamical processes. In this section the figures for the reduction of mercuric sulphide and  $As_2S_3$  obtained by Pélabon (*Z. anorg. Chem.*, 1908, **59**, 278; 1909, **62**, 89) are included. The discrepancies are in most cases considerable, a fact which is attributed to lack of accurate knowledge of the effect of temperature on the molecular heats of the reactants.

N. H. H.

**Iron-Carbon Diagram and the Most Important Constituents of Plain Carbon Steels.** K. DAEVES (*Stahl u. Eisen*, 1925, **45**, 427—434).—The liquidus in the system iron-iron carbide

(cementite) consists of two slightly curved lines starting from the m. p. of iron at  $1528^{\circ}$  and the m. p. of cementite at  $1550^{\circ}$  and meeting at the eutectic point at  $1146^{\circ}$  and 64.2%  $\text{Fe}_3\text{C}$  (4.29% C). The solidus in alloys containing more than 2.9%  $\text{Fe}_3\text{C}$  is a straight line terminating in a curve and meeting the eutectic line at  $1146^{\circ}$  at 26.2%  $\text{Fe}_3\text{C}$  (1.75% C). There is a peritectic line at  $1486^{\circ}$  in alloys containing 1.1 to 4.9%  $\text{Fe}_3\text{C}$  (0.07 to 0.36% C) corresponding with the reaction between  $\delta$  mixed crystals and liquid to form  $\gamma$  mixed crystals (austenite). The area of the  $\delta$  phase is bounded by lines joining  $1401^{\circ}$  and  $1528^{\circ}$  on the iron axis with the end of the peritectic, whilst the  $\gamma$  mixed-crystal region is bounded by the lower of these two lines, by the solidus to the eutectic line, and by two lines, one joining the end of the eutectic and the other the Ac3 point of pure iron ( $906^{\circ}$ ) with the eutectoid point at  $720^{\circ}$  and 13.3%  $\text{Fe}_3\text{C}$  (0.89% C). The eutectoid line, above which pearlite cannot exist, extends right across the diagram at  $720^{\circ}$ , whilst the Ac2 line, caused by a magnetic transformation, extends from pure iron to the boundary of the  $\gamma$  phase at  $769^{\circ}$ . In the iron-graphite system the eutectoid line occurs at  $1152^{\circ}$  and is extended slightly further towards the iron end, thus reducing the area of the  $\gamma$  phase. [Cf. B., 1925, 356.] A. R. P.

**In-, Uni-, and Multi-variant Equilibria. XXVIII.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 800—808; cf. A., 1924, ii, 389, 601).—A continuation of previous work. L. L. B.

**Electrical, Adiabatic Calorimeter, and its Use in the Determination of Heats of Solution.** E. COHEN, A. L. T. MOESVELD, and W. D. HELDERMAN (*Proc. K. Akad. Wetensch. Amst.*, 1924, 27, 657—664).—The adiabatic, electrical calorimeter, described in an earlier paper (A., 1920, ii, 584), has been adapted for the determination of heats of solution. The modified apparatus, the method of its use, and an experiment are described. L. L. B.

**"Electrolytes" and "Ionogens."** W. BLUM (*Trans. Amer. Electrochem. Soc.*, 1925, 47, 99—102).—The dual use of the word "electrolyte" for solutions which conduct electricity and for the dissolved substances which give rise to this conduction sometimes leads to confusion. It is suggested that the word "ionogen," originally proposed by A. Smith, should be adopted for a chemical compound which undergoes ionisation when placed in a suitable environment. The word "electrolyte" would then be retained for any medium or system which may be decomposed by the passage of an electric current, and would include both solutions and fused salts. C. S.

**Volta Effect between Metals and Electrolytes.** J. GUYOT (*Ann. Physique*, 1924, [x], 2, 506—521).—The potential difference between a metal and a dilute electrolyte has been measured by a potentiometer and quadrant electrometer using a null method. The standard ionisation method is adopted in which a metal

electrode is placed parallel to the surface of the electrolyte, the intervening layer of air being maintained slightly ionised.

It has been shown that (1) the Volta effect is independent of the nature of the electrolyte for equimolecular solutions containing the same reversible electrodes; (2) the effect increases or decreases with the concentration according to whether the electrode provides the solution with positive or negative ions, the increment being proportional to the logarithm of the concentration; (3) the apparent potential difference between two solutions  $L$  and  $L'$ , in which are immersed electrodes  $M$  and  $M'$ , respectively, differs but little from that of the pile  $M|L|X|L'|M'$ , formed of the same elements, in which  $X$  is a saturated solution of potassium chloride or of ammonium nitrate; (4) the potential difference between a metal and a solution of one of its salts is given by the expression  $-a \log C + K + \phi(L)$ , where  $K$  is a characteristic constant of the electrode and  $\phi(L)$  a function of the properties of the solution.

Thin films of organic substances on the surface of an electrolyte diminish the Volta effect between a metal and an electrolyte. This diminution increases with the number of molecules on the surface but approaches a limiting value independent of the nature and concentration of the electrolyte. From this limiting value, the quotient  $m/\alpha$  is calculated for trilaurein, trimyristin, myristic and palmitic acids, where  $m$  is the electric moment of the molecule and  $\alpha$  is its degree of polymerisation. The values obtained range from  $10^{-19}$  to  $10^{-18}$  E.S.U., and do not vary appreciably between  $18^\circ$  and  $33^\circ$ . The effect is attributed to a regular orientation of the molecules of the organic substance on the surface of the electrolyte.

R. W. L.

**Influence of Acid Concentration on the Oxidation-Reduction Potential of Cuprous and Cupric Chlorides.** S. R. CARTER and F. M. LEA (*J. Chem. Soc.*, 1925, 127, 499—510).—For solutions which contain equivalent quantities of cuprous and cupric chloride (0.1*N* or 0.025*N*) and varying amounts of hydrochloric acid the cuprous-cupric potential increases with the concentration of the acid and reaches a maximum of 0.88 volt at 7*N*-hydrochloric acid. Above this concentration the potential falls slightly. The initial increase of potential is attributed to a reduction of cuprous-ion concentration by formation of the complex compound  $H_2CuCl_3$ . The maximum at 7*N* corresponds with the concentration at which the ion concentration has a maximum value. The decrease in potential after the maximum is attributed to complex formation between cupric chloride and hydrogen chloride, yielding possibly  $CuCl_2 \cdot HCl \cdot 3H_2O$ . On varying the cuprous-cupric ratio the potential changes approximately in accordance with the usual logarithmic law. These results, combined with those of Carter and James (this vol., ii, 134) for the sulphur dioxide oxidation potential, afford an explanation of the oxidation of cuprous chloride by sulphur dioxide. A. E. M.

**Electrode Potentials.** R. H. GERKE (*Chem. Reviews*, 1925, 1, 377—395).



**Electrode, Contact, and Electro-kinetic Potentials of Galvanic Cells.** J. HEYROVSKY (*J. Physical Chem.*, 1925, **29**, 344—352).—A thermodynamic formula has been derived for the electrode potential of metals and metalloids (cf. A., 1923, ii, 114).

M. B. D.

**Method of Measuring Reduction Potentials of Quinhydrones.** E. BILMANN, A. L. JENSEN, and K. O. PEDERSEN (*J. Chem. Soc.*, 1925, **127**, 199—208).—The reduction potential of a quinhydrone can be determined by measuring the potential of an electrode immersed in a solution which contains the quinol of the quinhydrone under consideration together with the quinone of some other quinhydrone of known reduction potential. It has been shown that the reduction potential of the quinhydrone (A,  $AH_2$ ) is given by  $\pi_0' = 2\pi - \pi_0 = 2\phi + \pi_0$ , where  $\pi$  is the potential of a mixture of the quinol  $AH_2$  with an equimolecular quantity of the quinone B (or conversely), against a hydrogen electrode,  $\phi$  the potential of this mixture against the quinhydrone electrode (B,  $BH_2$ ), and  $\pi_0$  the reduction potential of the quinhydrone electrode (B,  $BH_2$ ).  $\phi$  has been determined experimentally for a number of mixtures against a benzoquinhydrone electrode of potential  $\pi_0$ , and the value of  $\pi_0'$  thus found compared with that determined by other methods. Satisfactory agreement has been obtained. From the value of  $\phi$ , the amounts of the quinhydrone formed in the mixture may also be calculated.

M. S. B.

**Current-Potential Curves for Nickel and Aluminium.** E. LIEBREICH and W. WIEDERHOLT (*Z. Elektrochem.*, 1925, **31**, 6—15).—The complete current-potential curves for nickel and aluminium in 0.02*N*-sulphuric acid, 0.1*N*-hydrochloric acid, and in 0.1*N*-sodium hydroxide solution have been determined and their characteristics compared with those of similar curves previously obtained by the authors for other metals (this vol., ii, 44). On the anodic side, passivity phenomena are observed and are ascribed to the intervention of insoluble films of metallic hydroxide or oxide. It is concluded that anodic passivity, in general, is due to chemical conditions in the immediate neighbourhood of the electrode rather than to some abnormal condition of the metal itself. On the cathodic side, with increasing current density, the formation of metallic salts or hydroxides precedes the evolution of hydrogen, as previously observed with other metal cathodes, but with nickel and aluminium the hydroxides are very insoluble and difficult to reduce and persist even when vigorous hydrogen evolution has set in.

With nickel in 0.02*N*-sulphuric acid, very high anodic current densities cause reversion to an active condition which persists on reducing the current density again, so that, after strong anodic polarisation, the potential in the currentless condition is notably baser than after weak anodic polarisation. Cathodic polarisation of nickel in 2*N*-nickel sulphate solution does not cause deposition of nickel on the electrode until evolution of hydrogen has also set in. On anodic treatment of aluminium in 0.1*N*-hydrochloric acid,

evolution of hydrogen continues up to considerable current densities and eventually may even accompany evolution of oxygen to some extent. The film produced on aluminium by anodic polarisation in 0.1*N*-sodium hydroxide can be observed directly in that it peels off when the current is suddenly reversed so as to cause evolution of hydrogen. M. B. D.

**Mixed Electrodes of the Second Type.** P. GROSS and O. HALPERN (*Z. physikal. Chem.*, 1925, **115**, 54—60).—A theoretical discussion of the differences of potential at the surface of contact of solid-liquid phases of the glass-water type. The conclusions are applied to the results obtained with glass electrodes by Haber and Klemensiewicz (A., 1909, ii, 785), by Horovitz (*Z. Physik*, 1923, **15**, 369), and by Schiller (A., 1924, ii, 459). L. F. G.

**Overvoltage and Transfer Resistance.** E. NEWBERRY (*Proc. Roy. Soc.*, 1925, **A**, **107**, 486—495).—The overvoltage for ten metals was measured, using a rotating commutator and a cathode-ray oscillograph, the deflexions of which were produced by the difference of potential between the metal under examination and the solution in which it was immersed. This potential was magnified by means of a thermionic valve. Photographs are reproduced showing the effect of breaking the main current. There is an instantaneous drop of potential indicating an irreversible resistance effect between the metal and the electrolyte (transfer resistance). The total opposition to the passage of a current is, therefore, made up of two distinct parts, true overvoltage and transfer resistance. All the phenomena observed are explicable on the hydride theory of overvoltage. E. B. L.

**Influence of Acidity on the Polarisation of Nickel.** S. TRIANDAFIL (*Compt. rend.*, 1925, **180**, 737—739).—The polarisation of nickel has been investigated in its relation to the acidity of the aqueous medium, the nickel-ion concentration remaining constant (*N*-nickel chloride solution), whilst the  $p_H$  value was varied from 0 to 7. For a given  $p_H$  value, the polarisation diminishes with increasing temperature. At constant temperature, the polarisation decreases with increasing acidity. The curves representing the polarisation as a function of  $p_H$  at 0°, 25°, and 50° exhibit points of inflexion corresponding approximately with a constant value of  $[H^+]/[Ni^{++}] = 0.29$ . At higher temperatures, 75° and 100°, the influence of acidity is very slight. J. S. C.

**Passivity of Metals.** E. BECKER and H. HILBERG (*Z. Elektrochem.*, 1925, **31**, 31—41).—The "contact distance," i.e., the distance which a metal point can be withdrawn from a metal surface and still give a measurable current, gives no indication as to whether the metals are active or passive. With one and the same metal, the contact distance is greater in the passive than in the active state. The photo-electric effect and passivity undergo similar changes, but there is no precise relation between the two effects. The most certain method for differentiating between the active and the passive states consists in determining whether the metal dis-

solves according to Faraday's law or not. Contrary to the results of Muthmann and Frauenberger (*Sitzungsber. Bayr. Akad. Wiss.*, 1904, **34**, 201), molybdenum could not be obtained in the passive condition. Chromium cathodically deposited on iron by the electrolysis of chromic acid remained active for many hours, whereas on copper it became quickly passive. M. B. D.

**Passivity of Iron and Other Metals.** A. S. RUSSELL (*Nature*, 1925, **115**, 455—456).—It is considered that chromium, manganese, iron, cobalt, and nickel, when in the active state, each have two electrons in the fourth quantum orbit, and that they become passive when one of these electrons is removed to a third quantum orbit. The order of the potentials of certain metals in mercury, proceeding from electropositive to noble metals, is : zinc, cadmium, thallium, tin, lead, copper, manganese and iron, bismuth, cobalt, mercury, nickel, platinum. Only the metals known to show passivity fall out of the normal order for the free metals. The view that the passive state is a definite condition which is produced and maintained when the metal is amalgamated is consistent with Lambert's observation that pure iron is a noble metal when its surface is electrically neutral. The ions of the passive metals do not behave as if they were the ions of noble metals, and it is argued that passive iron, for instance, may have one of the electronic configurations, 2, 8, 15, 1, or 2, 8, 13, 3, probably the former, and nickel, possibly, 2, 8, 17, 1.

Metals, when dissolved in mercury, are much more efficient reducing agents in the presence of sulphuric acid than when in the free state. A. A. E.

**Theories of Passivity.** H. GERDING and A. KARSEN (*Z. Elektrochem.*, 1925, **31**, 135—143).—A critical survey of the theories of the passivity of metals. The theories are classified under the headings : purely physical, purely chemical, and physico-chemical. The theory of Smits is favoured since it explains in addition the phenomena of polarisation and overvoltage. N. H. H.

**Deficit of the Condensed Substances obtained by the Action of the Electric Discharge.** M. Z. YOVITCHITCH (*Bull. Acad. Roy. Belge*, 1924, [v], **10**, 465—477).—The sum of the percentages of carbon and hydrogen in the condensed or polymerised compounds obtained by subjecting hydrocarbons to the influence of the silent electric discharge is often considerably below 100 (cf. A., 1908, i, 118; Löb, A., 1908, i, 117). The author's experiments show that this deficit persists even when precautions are taken to render contact of the condensed compounds with the air as short as possible. The conclusion is reached that the deficit is due partly to absorption of oxygen, water, or other substance, and partly to some action of the electric discharge. T. H. P.

**Calculation of Reaction Velocity Coefficients.** C. WAGNER (*Z. physikal. Chem.*, 1925, **115**, 130—136).—Theoretical, with special reference to the effect of errors (cf. Moesveld, A., 1923, ii, 141). L. F. G.

**Influence of Temperature on Reaction Velocity in Solution.**

C. WAGNER (*Z. physikal. Chem.*, 1925, **115**, 121—129).—No simple relation is found between the values of the integration constant  $B$  in the equation  $\log k = -q/2.3RT + B$ , where  $k$  is the velocity coefficient, and those quantities which for reacting substances in solution correspond with the chemical constants of gases.

L. F. G.

**Mechanism of the Reduction of Permanganate and its Physico-chemical Basis.** X. J. HOLLUTA (*Z. physikal. Chem.*, 1925, **115**, 137—142; cf. Schiloff, A., 1903, ii, 720; Holluta, A., 1922, ii, 448; Holluta and Weiser, A., 1922, ii, 628).—The reduction of potassium permanganate by dilute formic acid is accelerated by the addition of the fluorine ion as sodium fluoride. The general conclusion is reached that all complex-building anions accelerate the reduction.

L. F. G.

**Landolt's Reaction.** III. J. EGGERT and L. PFEFFERMANN (*Z. anorg. Chem.*, 1924, **139**, 310—316).—The course of the Landolt reaction from the commencement to the separation of iodine is more satisfactorily explained as a bimolecular than as a unimolecular reaction (cf. Skrabal, A., 1924, ii, 543).

H. T.

**Pernitric Acid.** F. POLLAK (*Z. anorg. Chem.*, 1925, **143**, 143—163).—The highly-oxidised compound observed by Raschig on mixing nitrous acid and hydrogen peroxide has been more closely investigated with regard to the conditions for its formation and decomposition. For its determination, the bromine liberated from potassium bromide is titrated with phenol solution in presence of carbon disulphide. The fact that simple stoichiometric relations are not found between the reactants indicates that its structure can best be investigated kinetically. The formation of pernitric acid from nitrous acid and hydrogen peroxide, as well as its decomposition into the latter and nitric acid, are difficult to investigate on account of the extreme rapidity of the reaction, and because in the latter case the reverse reaction has a disturbing effect. The formation of pernitric acid from nitric acid and hydrogen peroxide in presence of potassium bromide has been definitely established. At 15°, the initial velocity of bromine separation is proportional to the first power of the nitric acid concentration and the potassium bromide concentration. The exponent for the hydrogen peroxide, however, is approximately 0.80. Different reactions are found to predominate if the same relative quantities of reactants are present, but the total concentration is different. The influence of light is also a disturbing factor.

L. L. B.

**Nitric Oxide Reaction.** A. KLEMENC (*Ber.*, 1925, **58**, [B], 492—494; cf. Stechow, A., 1924, i, 1157).—It does not appear possible to consider the oxidation of arsenious acid, sulphite, sodium sulphide, and ferrous hydroxide by nitric oxide in alkaline solution from a general, kinetic point of view. The oxidation of arsenious oxide (cf. Gutmann, A., 1922, ii, 845) is probably a termolecular change,  $\text{H}_3\text{AsO}_3 + 2\text{NO} = \text{H}_3\text{AsO}_4 + \text{N}_2\text{O}$ , the rate of which increases

with increasing concentration of alkali hydroxide. Oxidation of sulphite and sulphide, on the contrary, is retarded by increasing alkalinity of the solution. H. W.

**Velocity of Addition of Hydrogen Chloride to Quinone in Methyl Alcohol.** L. EBERT (*Z. Elektrochem.*, 1925, **31**, 113—123).—The velocity of the reaction between hydrogen chloride and quinone in methyl alcohol solution has been determined by measurements of the conductivity (giving the hydrogen chloride concentration), the optical extinction (giving the sum of the concentrations of the coloured substances present) and the *E.M.F.* of the quinhydrone electrode (giving the ratio of the concentrations of quinone and quinol). The results correspond with a slow initial reaction  $C_6H_4O_2 + H^+ + Cl^- = C_6H_3(OH)_2Cl$  followed by the extremely rapid reaction  $C_6H_4O_2 + C_6H_3(OH)_2Cl = C_6H_3O_2Cl + C_6H_4(OH)_2$ . The velocity of chlorination is proportional to the product of the activities of the hydrogen and chlorine ions. In dilute solutions of hydrogen chloride, the velocity coefficient for the first reaction is given by  $\log k = 14.45 + \log [H^+] + \log [Cl^-] - 1.61 ([H^+] + [Cl^-])^{1/3}$  when the concentrations of quinone and quinol are small compared with that of the hydrogen chloride. With concentrations of the latter greater than  $0.2N$ , deviations occur which are probably due to undissociated acid. The addition of water slows down the reaction, which is in agreement with the assumption that the ion  $CH_3OH_2^+$  reacts more rapidly than the ion  $OH_3^+$ . The equilibrium lies strongly on the side of chlorination. For the constant for the first reaction the preliminary value  $\log k = 5$  is given. N. H. H.

**Limits for the Propagation of Flame in Inflammable Gas-Air Mixtures. II. Mixtures of more than One Gas and Air.** A. G. WHITE (*J. Chem. Soc.*, 1925, **127**, 48—61).—Le Chatelier's formula connecting the limiting composition for the propagation of flame in a mixture containing two inflammable gases and air, with the limits for these gases mixed separately with air, has been tested for the following pairs of gases mixed with air:  $H_2 + CH_4$ ,  $H_2 + NH_3$ ,  $C_2H_4 + H_2$ ,  $C_2H_2 + H_2$ ,  $C_2H_4 + CH_4$ ,  $CH_4 + H_2S$ ,  $H_2S + H_2$ ,  $H_2S + C_2H_2$ ,  $C_2H_2 + CH_4$ , and  $CH_4 + C_5H_{12}$ . The experimental values approximate more closely to those calculated for downward than for upward propagation, and for lower than for upper limits. Deviations are not always, however, in the same direction, so that mass action is evidently not the most important factor responsible for the divergences (cf. Payman, T., 1923, **123**, 412). In some cases it was possible to get two ranges of inflammability, so that the mixtures showed four limits instead of two. In mixtures containing hydrogen it was frequently found that propagation in a given mixture occurred or did not occur according as the type of flame started was the hydrogen type or the ordinary lower limit type. M. S. B.

**Ignition of Gases. V. Ignition by Induction Sparks. Mixtures of the Paraffins with Air.** R. V. WHEELER (*J. Chem. Soc.*, 1925, **127**, 14—26).—The variable conditions in the

production of inductance sparks may be electrical, namely, the self-inductance of the circuit, the impressed voltage, and the current flowing in the circuit before rupture; or mechanical, that is, the nature of the metal at the spark gap, the rate of break of the circuit, and the area of contact at the moment of break. The influence of each of these factors on the ignition of mixtures of the paraffins with air has been determined. The relationship between the inductance of the circuit and the igniting current is not constant. The amount of current in the circuit is of more importance than the impressed voltage, especially when the voltage is low. When the latter is high, however, the igniting current diminishes as the voltage increases. Contrary to the observations of Thornton (A., 1914, ii, 524), the alternating current necessary for ignition has about the same value as the direct current, but ignition is more "difficult" with the former because the production of a spark at the crest value of the current is a matter of chance. With a more volatile metal a lower igniting current is required, because the break flash has a longer duration. The igniting current diminishes as the speed at which the metallic contacts are separated is increased, and also as the area of the contacts is diminished. Optimum conditions are: low battery voltage and high induction, metal contacts which are not readily oxidised, rapid break of circuit, and small area of contact at moment of break. Experiments made with different hydrocarbons indicate that inductance sparks behave similarly to capacity sparks (or secondary discharges) as a means of ignition (A., 1924, ii, 747), but the longer duration and larger volume of the inductance sparks appear to mask small differences of ignitibility in the mixtures most readily ignited. Three different types of apparatus have been described. M. S. B.

**Rôle of Water in Reactions in the Solid State. IV. D. BALAREW** (*Z. anorg. Chem.*, 1925, **143**, 89—96; cf. A., 1924, ii, 483, 611, 858).—The heating and gas evolution curves for the system barium dioxide-silica are given, and it is maintained that an insight into the mechanism of the system can best be obtained by a study of the two curves. For the system barium monoxide-calcium carbonate, the temperature at which reaction begins depends on the velocity of heating. The reaction between the solid components from 335° to 350° either proceeds to completion or remains unfinished, according to the duration of heating and the velocity with which the temperature rises. The reaction only takes place between the barium hydroxide, which is present in the barium monoxide, and the calcium carbonate, and the velocity of the reaction is determined by the velocity of diffusion of water from the place at which the reaction is already complete, to the free barium monoxide. A comparison of the heating curves of the system barium monoxide-calcium carbonate with those of the system barium monoxide-molybdenum trioxide shows that in the latter case the points at which the reaction takes place are at a much higher temperature than in the first case—possibly above 1500°. The rôle of water in the catalytic decomposition of potass-

ium chlorate by manganese dioxide is further investigated, by a study of the heating curves and gas evolution curves. The mechanism of the reaction is similar to that of the systems barium or strontium oxide and other solid substances, except that, in this case, the potassium chlorate or the system potassium chlorate-potassium chloride melts or softens, and is as such catalysed by the solid manganese dioxide. There is no definite temperature at which the catalytic influence of manganese dioxide on the decomposition of potassium chlorate begins.

L. L. B.

**Reaction Kinetics in a System consisting of Two Liquid Phases.** K. JABŁCZYŃSKI, W. WIECKOWSKI, and (FRL.) A. KLEIN (*Z. anorg. Chem.*, 1925, **143**, 343—356).—The velocities of the reactions between iodine in chloroform and aqueous sodium thio-sulphate and between benzoic acid in carbon tetrachloride and aqueous sodium hydroxide have been measured. As for other heterogeneous reactions, the velocity is controlled by the rate of diffusion through surface layers at the boundary of the phases, and the general equation is deduced:  $K = v/0.4343t \times \log c_0/c$ , in which  $v$  is the volume of chloroform or carbon tetrachloride,  $c_0$  the initial concentration of iodine or benzoic acid, and  $c$  the concentration after time  $t$ . This equation was verified by experiment and it was found, in accordance with expectation, that the velocity constant depended on the rate of stirring of the aqueous layer (the lower layer not being stirred) and that the temperature coefficient was much lower than for chemical processes.

A. G.

**Decomposition of Sulphur Chloride by Water.** B. NEUMANN and E. FUCHS (*Z. angew. Chem.*, 1925, **38**, 277—280).—The extent of the decomposition was measured by the hydrogen chloride formed; it proceeds to the extent of 84.4% in 15 minutes, 85.6% in 8 hours when the chloride is shaken with six times its weight of water, 63.3% in 15 minutes with an equal weight and 37.3% in 30 minutes with half its weight of water. Even with 625 parts of water, the decomposition only proceeds to the extent of 93.68%. The decomposition is restrained by the presence of the hydrochloric acid formed; the separated sulphur encloses undecomposed chloride, and also dissolves in it, both these factors influencing the extent of the action. Hydrogen sulphide is always evolved, and the mechanism suggested by Curtius,  $S_2Cl_2 + 2H_2O = H_2S + 2HCl + SO_2$ , with subsequent reaction between hydrogen sulphide and sulphur dioxide, and between the latter and the sulphur formed, is considered to represent the real course of the decomposition. After complete decomposition by boiling for several hours, the sulphur was found to be present as follows:—as separated sulphur, 29.80; colloidal, 35.14; as trithionic acid, 4.84; as tetrathionic acid, 9.09; as pentathionic acid, 18.26; as sulphuric acid, 1.00; as sulphurous acid, 0.31; as hydrogen sulphide, 0.57; total 99.01% of the sulphur present.

S. I. L.

**Effect of the Addition of some Alkaloids on the Rate of Dissolution of Iron in Dilute Hydrochloric Acid.** M. B. RANE and M. PRASAD (*J. Physical Chem.*, 1925, **29**, 249—255).—The rate

of dissolution of iron wire in hydrochloric acid rises to a maximum after a given period, which is not due to a change in concentration of the acid, but to the increase of porosity of the wire. The evolution of hydrogen is inhibited by alkaloids, the influence of which decreases in the order: brucine, strychnine, cinchonine, nicotine, codeine, cocaine, and coniine. This action is similar to that found by Conroy (A., 1901, ii, 388) for the effect of arsenious oxide on the rate of dissolution of iron by acid. M. B. D.

**Conditions of Maximum Stability for some Organic Substances.** I. BOLIN (*Z. anorg. Chem.*, 1925, **143**, 201—230).—The stability of organic substances has been determined by measurement of the initial velocity of hydrolysis in solutions of known hydrogen-ion concentration. For ethyl formate, chloroacetate, and aminoacetate at 20°, the values of  $p_H$  for maximum stability are 4.65, 4.8, and 3.8 respectively. Benzamide was hydrolysed in 0.02N solution in silica vessels at 80°, the reaction velocity at 20° being too small for accurate measurement, using sodium hydroxide and sulphuric acid; by extrapolation the value of  $p_H$  for maximum stability was found to be 5.80, with a temperature coefficient of 3 for 10° ( $k_{80}/k_{50}=30$ ). With  $\alpha$ -methylglucoside hydrolysis was also effected at 80° in silica vessels, the rate being determined in solutions of  $p_H$  value from 0.8 to 1.5 both polarimetrically and by titration with Fehling's solution; hydrolysis occurs only in acid solution, the velocity sinking with increase in  $p_H$ , the curve becoming asymptotic to the  $p_H$  axis. The temperature coefficient is very high. For acetanilide at 40°, the value for maximum stability was determined by extrapolation as  $p_H$  6.2.

Those substances which are hydrolysed both by acids and bases may be divided into two classes, the first having maximum stability in solutions of  $p_H$  5 and above, the second in more nearly neutral solutions. The acidity of solutions in which the stability of esters of the fatty acid series is a maximum is lower for esters of weaker acids, increasing with the strength of the acid. S. I. L.

**Kinetics of Hydrogenation. II. Stationary Films.** E. J. LUSH (*J. Soc. Chem. Ind.*, 1925, **44**, 129—134T).—Hydrogenation of stationary thin films of cotton-seed oil and trilinolin on nickel was found to be a unimolecular reaction and constant values for  $K$  were obtained when the catalyst was maintained at a constant temperature. Hydrogenation consists of three successive reactions: when unsaturated oil is in excess and hydrogen can reach the catalyst in limited amount only, the rate of hydrogenation is linear and is proportional to the hydrogen pressure; when unsaturated oil is in excess and the amount of hydrogen reacting is increased the rate is linear and proportional to the square root of the hydrogen pressure; when the oil approaches saturation the reaction is unimolecular and the rate is proportional to the hydrogen pressure.

F. B.

**Rôle of Oxygen in Catalytic Hydrogenation by means of Platinum.** E. WALDSCHMIDT-LEITZ and F. SEITZ (*Ber.*, 1925, **58**, [B], 563—566).—A reply to Bodenstein (this vol., ii, 216), in



which justification is deduced from the literature for the conception, denied by Bodenstein, of the co-existence of oxygen and hydrogen in the presence of platinum. H. W.

**Catalytic Hydrogenation of Inorganic Substances.** H. GALL and W. MANCHOT (*Ber.*, 1925, 58, [B], 482—485).—Catalytic reduction of nitric acid in aqueous solution in the presence of spongy platinum yields ammonia and nitrous acid. Hydrogenation of complex metallic salts occurs with initial reduction of the complex metallic atom; thus potassium ferricyanide yields potassium hydrogen ferrocyanide and sodium nitroprusside gives a compound of bivalent iron, whereas the expected conversion of the NO into the  $\text{NH}_3$  group could not be established definitely. Simpler relationships are observed with the normal salts of metals which exhibit varying valency. Thus, ferric and cupric chlorides are smoothly converted into ferrous and cuprous chlorides; copper sulphate, however, could not be reduced. Quadrivalent titanium is converted into an equilibrium mixture of the quadrivalent and tervalent forms. Quinque- or quadri-valent vanadium is transformed quantitatively into the tervalent condition and sexavalent uranium is reduced to the quadrivalent stage. It is not possible, however, to limit the action to a definite, reproducible phase in all cases. Thus, chromic acid and chromates give variable and indefinite results. Potassium chlorate and iodate yield the corresponding chloride and iodide smoothly in neutral solution; potassium perchlorate could not be reduced, whereas potassium periodate gives potassium iodide in quantitative yield. Chlorine is converted into hydrogen chloride and bromine in dilute aqueous solution into hydrogen bromide. The quantitative conversion of iodine into hydrogen iodide appears to be in contradiction to Willstätter's view that the presence of oxygen in platinum is essential to its catalytic activity. H. W.

**Reducing Action of Hydrogen Adsorbed in Silica Gel.** M. LATSHAW and L. H. REYERSON (*J. Amer. Chem. Soc.*, 1925, 47, 610—612).—Negatively charged silica gel does not reduce silver nitrate to metallic silver. Hydrogen adsorbed in silica gel reduces the ions of copper, silver, gold, platinum, and palladium, but not of nickel. Microscopical examination shows the entire gel surface to be covered with the reduced metal and that the deposit is distributed throughout the gel granules. The bonds between the atoms of hydrogen molecules are weakened by adsorption and the atoms may act independently, *e.g.*,  $\text{H} + \text{Ag}^+ = \text{Ag} + \text{H}^+$ . The metalised silica gels are active catalysts. J. S. C.

**Decomposition of Hydrogen Peroxide in Presence of Nickel Hydroxide.** (MLLE.) S. VEIL (*Compt. rend.*, 1925, 180, 932—934).—When nickel hydroxide is suspended in aqueous solutions of hydrogen peroxide, it becomes less and less magnetic. The corresponding values for the oxide obtained by calcination of the hydroxide are found to pass through a maximum value. The magnetic properties of nickel hydroxide are unchanged after con-

tinued suspension in pure water. These facts are believed to have an important bearing on the catalytic decomposition of hydrogen peroxide in presence of nickel hydroxide. J. S. C.

**Explosive Limits of Mixtures of Gas or Vapour with Air.** E. BERL and H. FISCHER (*Z. Elektrochem.*, 1920, **30**, 29—35).—The limits of explosion for mixtures of air and other gases and vapours are dependent on the size and material of the container as well as on the temperature, pressure, and method of sparking. The phenomenon of pre-ignition noted previously with mixtures of carbon monoxide and air was also observed with mixtures of acetylene, ethylene, alcohol, and carbon disulphide with air. In the upper limits, products of incomplete combustion were observed, e.g., formaldehyde, acetaldehyde, and acetic acid from air and ether, acetaldehyde and acetic acid from ethyl alcohol, and acetaldehyde from mixtures of air with acetone and ethylene.

H. T.

**So-called Poisoning of Oxidising Catalysts.** C. MOUREU and C. DUFRAISSE (*J. Chem. Soc.*, 1925, **127**, 1—4).—The fact that certain combustible gases prevent the combination of hydrogen and oxygen by the electric spark or by contact with platinum-black is closely related to recent observations of the action of gases such as acetylene, hydrogen sulphide, and hydrogen phosphide in hindering the catalytic oxidation of gaseous ammonia in the presence of platinum (Decarrière, A., 1921, ii, 503, 546; 1922, ii, 284). This action evidently cannot be due in all cases to the poisoning of the catalyst, and it has been ascribed to the "antioxygenic" action of the inhibiting compound (cf. A., 1922, i, 250). The antioxygens decompose catalytically the peroxide  $A[O_2]$  produced by the union of the autoxidisable substance A with a molecule of free oxygen. This peroxide oxidises the antioxygen B, giving two peroxides  $A[O]$  and  $B[O]$ , which are antagonistic and destroy each other, giving A, B, and  $O_2$ . An antioxygen must necessarily be an oxidisable substance, and every oxidisable substance should show some antioxygenic properties under suitable conditions. Further, a given catalyst, B, should be able to function either as a positive or negative catalyst, according as the peroxide  $B[O]$  attacks more readily the substance A or the peroxide  $A[O_2]$ . The theory accounts for the facts already known and has enabled the authors to foretell catalytic properties in substances in which they were hitherto unsuspected, for example, iodine, sulphur, etc. (A., 1923, ii, 308; 1924, i, 635; ii, 602). The "poisoning" of a platinum-black catalyst may be due to the simultaneous oxidation of A and B, by the catalyst, to form antagonistic peroxides which destroy each other, or, assuming that the catalytic effect of platinum is the result of the intermediate formation of an unstable  $Pt[O_2]$ , the latter may be unable to exist in the presence of the antioxygen B. M. S. B.

**Material Basis of the "Nitroxan" Process for the Catalytic Oxidation of Ammonia to Nitric Acid.** G. KASSNER (*Arch. Pharm.*, 1925, **263**, 112—120; cf. A. 1924, ii, 604).—A digest of

an earlier paper. Barium orthoplumbate, required in the preparation of nitroxan, may be prepared in a very reactive condition by heating a mixture, in the required proportions, of lead monoxide and barium hydroxide (or peroxide), in a stream of air free from carbon dioxide at 500–600°.

B. F.

**Dissociation of Sodium Hydrogen Carbonate.** A. RANC (*Bull. Soc. chim.*, 1925, [iv], 37, 276–277).—The rate of thermal dissociation of sodium hydrogen carbonate is greatly retarded by the presence of small quantities (3%) of “saccharin.”

S. K. T.

**Catalytic Decomposition of Formaldehyde. III.** E. MÜLLER and F. MÜLLER (*Z. Elektrochem.*, 1925, 31, 41–45; cf. A., 1922, i, 110; 1924, i, 833).—A 13% aqueous solution of formaldehyde is decomposed at its b. p. by highly-dispersed metals of the platinum group or their compounds. In neutral or slightly acid solutions, the chief decomposition products with ruthenium, palladium, and osmium are carbon dioxide, hydrogen, carbon monoxide, and a small quantity of methane. With osmium, only a small amount of carbon monoxide is evolved. Iridium and platinum and their compounds have very little action, but rhodium produces slight decomposition. The compounds are reduced during the reaction to colloidal metal. Excepting the reaction obtained with osmium, the decomposition is similar to that observed with formic acid (cf. A., 1924, ii, 844).

M. B. D.

**Catalytic Decomposition of Pyruvic Acid.** E. MÜLLER and F. MÜLLER (*Z. Elektrochem.*, 1925, 31, 45–46; cf. preceding abstract).—A 20% aqueous solution of pyruvic acid is catalytically decomposed by highly-dispersed osmium, palladium, and ruthenium at 100° into acetaldehyde and carbon dioxide. No carbon dioxide is evolved on boiling the solution for 4 hrs. when a catalyst is not added.

M. B. D.

**Course of Organic Reactions.** E. MÜLLER (*Z. Elektrochem.*, 1925, 31, 46–50; cf. preceding abstracts).—The author explains the decomposition of formic, malonic, and pyruvic acids on Knorr's theory (cf. A., 1924, ii, 34) by assuming a rearrangement of the electron orbits in the interacting molecules.

M. B. D.

**Formation of Perborates by Electrolysis using Unsymmetrical Alternating Current.** S. BODFORSS and A. ARSTAL (*Z. Elektrochem.*, 1925, 31, 1–5).—The optimum conditions for the anodic production of perborates by electrolysis are: a temperature of 0° or lower, an electrolyte containing sodium hydroxide and boric acid in the molecular ratio of 5 : 1, a ratio of direct to alternating current of 1 : 2.8, and a total current density of 0.06 amp./cm<sup>2</sup>. The zinc anode is enclosed in a porous pot, and it is essential to have good temperature control. The alternating current used had a period of 48 cycles and was very nearly a pure sine wave. The quantity of perborate formed is a maximum after 15 mins. and then sinks to a steady value. There appears to be no connexion

between the amount of zinc dissolved and the perborate formed. The probable explanation is that, whilst the electrode is acting as a cathode under the influence of the alternating current, the oxygen is reduced to hydrogen peroxide by the hydrogen evolved (cf. Fischer and Priess, A., 1913, ii, 285). M. B. D.

**Production of Antimony Hydride at an Antimony Cathode in Alkaline Solution.** II. E. J. WEEKS (*Rec. trav. chim.*, 1925, 44, 201—205; cf. Sand and Weeks, A., 1924, ii, 152).—The percentage yield  $x$  of stibine at an antimony cathode in alkaline solution varies with the temperature according to  $x=c/T-20$ , and with varying hydrogen concentration  $[H]$  in the electrode according to  $x=c_1-c_2 \log [H]$ , where  $c$ ,  $c_1$ , and  $c_2$  are constants. G. M. B.

**Sensitiveness of Actinometers with Mercury Electrodes.** G. ATHANASIU (*Compt. rend.*, 1925, 180, 587—589).—Actinometers having electrodes of mercurous chloride, bromide, and iodide or of mercuric sulphide in contact with 10% sulphuric acid (cf. *ibid.*, 1922, 175, 214), have now been examined as regards sensitiveness to light of various wave-lengths. The wave-length corresponding with maximum sensitiveness increases with the atomic weight of the halogen involved, and has the values 2536 Å., 2967 Å., and 4046 Å. for the chloride, bromide, and iodide, respectively. The chloride and bromide are only sensitive to ultra-violet light; under its influence they show fluorescence, emitting a strong visible orange-rose light. The actinometer with mercuric sulphide electrode gives a much smaller E.M.F. of opposite sign and has a maximum sensitiveness at 4046 Å. G. M. B.

**Variation of Temperature Coefficients of Photochemical Reactions with the Frequency.** M. PADOA (*Gazzetta*, 1925, 55, 87—92; cf. A., 1915, ii, 678, 719; 1916, ii, 508, 592; 1918, ii, 345; also Trautz, A., 1918, ii, 151; Pratolongo, A., 1918, ii, 70).—The results previously obtained are discussed in the light of modern views on chemical kinetics. In all the photochemical reactions as yet studied the temperature coefficient increases as the frequency of the light diminishes. This is regarded as the result of a variation of the affinity between atoms and electrons, separation of these requiring increasing expenditure of energy as the light absorbed by the atoms or molecules diminishes in frequency.

[With N. VITA.]—The temperature coefficient of the photochemical oxidation of hydriodic acid shows, however, a diminution as the light frequency falls. This may be due either to the affinity between atoms and electrons or the energy of activation being greater with the greater frequencies in this instance or, more probably, to transformation of the frequency by the absorbent substance. T. H. P.

**Oxalic Acid-Uranyl Sulphate Ultra-violet Radiometer.** W. T. ANDERSON, jun., and F. W. ROBINSON (*J. Amer. Chem. Soc.*, 1925, 47, 718—725).—The photochemical decomposition of

oxalic acid in oxalic acid-uranyl sulphate solutions is found to be a reaction of zero order, not greatly influenced by temperature, and possessing the characteristics desired in an efficient chemical radiometer for use in the ultra-violet region. The results obtained using this method are in excellent agreement with those obtained by the employment of the usual copper-constantan thermopile and filters.

J. S. C.

**Action of Light on the Ferrous Ferric Iodine Iodide Equilibrium.** E. K. RIDEAL and E. G. WILLIAMS (*J. Chem. Soc.*, 1925, 127, 258—269).—The reaction  $2\text{Fe}^{++} + \text{I}_2 \rightleftharpoons 2\text{Fe}^{+++} + 2\text{I}^-$  is photo-sensitive to both ultra-violet and visible light, the latter within the range 5500—6500 Å., with an apparent maximum at 5800 Å. The tri-iodide ion is the photosensitive constituent and the energy of excitation is equivalent to 2.14 volts, almost identical with the resonance potential of the iodine molecule. One quantum of absorbed radiant energy causes 1 mol. of iodine to react. The dark equilibrium constant,  $(\text{Fe}^{++})(\text{I}_2)^{1/2}/(\text{Fe}^{+++})(\text{I}^-)$  is 23.6 at 25°. The ratio of the velocity constant of the liberation of iodine at 35° to that at 25° is 2.713, whilst for the photochemical reaction this ratio is 1.17. The addition of potassium chloride increases the thermodynamic concentrations of all the reactants, increasing the velocity of reaction thereby, but not affecting the final equilibrium.

L. J. H.

**Action of Bromine on Sodium and Silver Azides.** D. A. SPENCER (*J. Chem. Soc.*, 1925, 127, 216—224).—Dry bromine vapour reacts with sodium or silver azide, giving bromoazoimide,  $\text{N}_3\text{Br}$ . This substance is extremely unstable, decomposing explosively on shock in all states of aggregation, and even at  $-200^\circ$ ; it has m. p. about  $-45^\circ$ . It is instantly hydrolysed by water, consequently bromine water reacts with sodium azide to form sodium bromide, azoimide, and hypobromous acid, and these further react, yielding nitrogen. Hypobromous acid reacts even more rapidly with sodium azide so that two equivalents of bromine are able to decompose two equivalents of sodium azide.

No polymeride of nitrogen was formed in the experiments with bromine vapour, but some compound rich in bromine, perhaps nitrogen tribromide, appeared to be present.

L. J. H.

**Behaviour of Gold and Platinum towards Silicate and Salt Fusions.** W. JANDER (*Z. anorg. Chem.*, 1925, 143, 377—382).—It is probable for geological reasons that gold and platinum are dissolved by molten silicates as metals and not as ions. This conclusion is confirmed by the investigation of the partition of gold between metals (lead, tin, silver, and iron) and fused chlorides and glass, the proportion of gold found in the metallic layer being very much less than that calculated from the differences of potential of gold and the other metal used in their aqueous solutions. Natural platinum always contains iron and it is shown that at its m. p. platinum takes up iron from fused silicates in the presence of reducing gases.

A. G.

**Action of Acids and Water on Magnesium Boride.** R. C. RAY (*J. Indian Chem. Soc.*, 1925, 1, 125—132).—When magnesium boride is treated with water the quantity of hydrogen liberated, containing only traces of boron hydrides, is only one-half that obtained by the action of dilute hydrochloric acid, the main action being  $\text{Mg}_3\text{B}_2 + 6\text{H}_2\text{O} = \text{Mg}_3\text{B}_2(\text{OH})_6 + 3\text{H}_2$ . The product of the reaction is completely insoluble in and inactive towards hot and cold water, and is regarded as a magnesium salt of the borohydrate,  $[\text{B}_2(\text{H}_2\text{O})_6]_n$ . The mechanism of the reaction may be similar to that suggested for the action of water on magnesium silicide (Schwarz and Konrad, A., 1922, ii, 846), viz.,  $\text{Mg}_3\text{B}_2 + 3\text{H}_2\text{O} = \text{H}_3\text{B}_2(\text{MgOH})_3$ ;  $n[\text{H}_3\text{B}_2(\text{MgOH})_3] + 3n\text{H}_2\text{O} = n[\text{Mg}_3\text{B}_2(\text{OH})_6] + 3n\text{H}_2$ , the latter equation representing the decomposition of 90% of the initial product. The secondary reactions, by means of which borohydrates and boron hydrides are produced, may be represented,  $\text{H}_3\text{B}_2(\text{MgOH})_3 + 5\text{H}_2\text{O} = 3\text{Mg}(\text{OH})_2 + \text{H}_6\text{B}_2\text{O}_2 + 2\text{H}_2$  and  $\text{H}_3\text{B}_2(\text{MgOH})_3 + 6\text{HCl} = 3\text{MgCl}_2 + 3\text{H}_2\text{O} + \text{B}_2\text{H}_6$ . No boric acid or magnesium borate is formed by the action of water on magnesium boride as is the case when dilute hydrochloric acid is employed:  $\text{Mg}_3\text{B}_2(\text{OH})_6 + 6\text{HCl} = 3\text{MgCl}_2 + 2\text{B}(\text{OH})_3 + 3\text{H}_2$ . J. W. B.

**Behaviour of Calcium Fluoride in Strong Acids.** T. SABALITSCHKA and W. MOSES (*Pharm. Zentr.*, 1925, 66, 177—178).—Calcium fluoride is readily soluble in boiling 25% hydrochloric acid, and does not separate from the solution on cooling. S. I. L.

**Thermal Analysis of the Binary Systems: Aluminium Bromide and various Halides.** W. ISBEKOV (*Z. anorg. Chem.*, 1925, 143, 80—88).—Electrolytes in aluminium bromide solution exist in the associated condition, and form molecular compounds with the solvent. Only solvated molecules undergo electrolytic dissociation. Non-electrolytes, on the other hand, form no molecular compounds. M. p. curves are given for the systems aluminium bromide with aluminium chloride, arsenic tribromide, carbon tetrabromide, mercuric bromide, antimony tribromide, and bismuth tribromide, respectively. The first three of these and zinc bromide do not form compounds with aluminium bromide. For the fourth, the curve shows a maximum at 33%  $\text{HgBr}_2$ , corresponding with a compound  $2\text{Al}_2\text{Br}_6 \cdot \text{Hg}_2\text{Br}_4$ . Antimony and bismuth tribromides form the compounds  $\text{Sb}_2\text{Br}_6 \cdot \text{Al}_2\text{Br}_6$  and  $\text{Bi}_2\text{Br}_6 \cdot \text{Al}_2\text{Br}_6$ , respectively. The thermal analysis, in conjunction with cryoscopic measurements (A., 1914, ii, 26), proves that polymeric complexes occur in the systems investigated. L. L. B.

**Gallium.** R. FRICKE and W. BLÉNCKE (*Z. anorg. Chem.*, 1925, 143, 183—200).—Gallium sulphate,  $\text{Ga}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , obtained from gallium ammonium alum, is stable in air. Gallium oxide is slightly volatile in sulphuric acid vapour. The acidic nature of the hydroxide is more strongly marked than that of aluminium hydroxide, the alkaline properties less so. By measuring respectively the conductivity, the velocity of hydrolysis of

ethyl acetate, and the depression of f. p. for dilute sodium gallate solution, it was found that at the ordinary temperature the second hydrogen atom is largely replaced by sodium. The solubility curve of gallium hydroxide in sodium hydroxide showed a maximum at about 10.3*N*-sodium hydroxide. This represents the boundary of the region of existence of trisodium gallate (solid phase soluble in water), and of di- or mono-sodium gallate (solid phase insoluble in water). The hydroxide shows ageing phenomena, closely connected with which is the fact that the solubility of the hydroxide in sodium hydroxide solution of low and medium concentration increases with the quantity of solid phase in excess. The hydroxide is readily soluble in aqueous ammonia. L. L. B.

**Mechanism of Silane Formation. II.** R. SCHWARZ and T. HOEFER (*Z. anorg. Chem.*, 1925, **143**, 321—335).—The residue of the approximate composition  $\text{Si}_2\text{H}_2\text{O}_3$  previously obtained (A., 1922, ii, 846) by the interaction of hydrochloric acid and magnesium silicide has been investigated. The composition depends on the conditions of its formation, and the action of aqueous hydrochloric acid at 0° is preferred. The reaction takes place in three stages, during the first and last of which hydrogen is evolved, whilst the silane is obtained in the middle stage. The solid residue reacts with sodium hydroxide with evolution of hydrogen, and the ratio of the hydrogen thus obtained to that found by combustion slowly decreases to 2 : 1 if the material is kept in air; the silicon content simultaneously decreases and the change is thus due to absorption of oxygen. If the temperature is raised, all the hydrogen is evolved as water and elementary silicon is liberated; this does not occur at the ordinary temperature. Apparently the oxidisable substance is a hydride, and when the temperature is raised its combustion causes thermal decomposition of the oxyhydride with deposition of silicon. The only known oxyhydrides which would yield twice as much hydrogen when treated with sodium hydroxide as is found by combustion have the compositions  $\text{Si}_2\text{H}_2\text{O}_3$  and  $\text{SiH}_2\text{O}$ . When the substance is treated with ammonium hydroxide, which decomposes the oxyhydride with evolution of hydrogen and formation of ammonium silicate whilst the other constituents of the mixture are only slowly attacked, the ratio obtained of hydrogen to silica dissolved agrees best with the formula  $\text{SiH}_2\text{O}$  and the solid residue thus contains a hydride, "prosiloxan" ( $\text{SiH}_2\text{O}$ ) and silica. The mechanism of the reaction is therefore formulated as follows:  $\text{Mg}_2\text{Si} + 2\text{H}_2\text{O} = (\text{MgOH})_2\text{SiH}_2$ ;  $(\text{MgOH})_2\text{SiH}_2 + 4\text{HCl} = 2\text{MgCl}_2 + 2\text{H}_2\text{O} + \text{SiH}_2 + \text{H}_2$ . The radical  $\text{SiH}_2$  polymerises to polysilenes,  $(\text{SiH}_2)_x$ , which remain in the solid residue, but before this is complete the hydrides formed as intermediate products are partly decomposed, yielding "prosiloxan" and silanes, e.g.,  $\text{Si}_2\text{H}_4 + \text{H}_2\text{O} = \text{SiH}_2\text{O} + \text{SiH}_4$ ;  $\text{Si}_3\text{H}_6 + \text{H}_2\text{O} = \text{SiH}_2\text{O} + \text{Si}_2\text{H}_6$ . This explains how various silanes can be produced from a single silicide. Finally, silica may be formed either from "prosiloxan" or from slightly polymerised silene:  $\text{SiH}_2\text{O} + \text{H}_2\text{O} = \text{SiO}_2 + 2\text{H}_2$ ;  $\text{SiH}_2 + 2\text{H}_2\text{O} = \text{SiO}_2 + 3\text{H}_2$ .

A. G.

**Chemical Equilibria between Lead Sulphide and its Roasting Products.** II. R. SCHENCK and W. BORKENSTEIN (*Z. anorg. Chem.*, 1925, **142**, 143—179).—In answer to the criticisms by Reinders of the previous work of Schenck and Albers on the chemical equilibria between lead sulphide and its roasting products (A., 1919, ii, 222), the system has been reinvestigated without any appreciable divergences from the earlier results being obtained. The fundamental reactions are shown to be  $10(\text{PbSO}_4, \text{PbO}) + \text{PbS} \rightleftharpoons 7(\text{PbSO}_4, 2\text{PbO}) + 4\text{SO}_2$ ;  $13(\text{PbSO}_4, 2\text{PbO}) + \text{PbS} \rightleftharpoons 10(\text{PbSO}_4, 3\text{PbO}) + 4\text{SO}_2$ ;  $3(\text{PbSO}_4, 3\text{PbO}) + \text{PbS} \rightleftharpoons 13\text{PbO} + 4\text{SO}_2$ ;  $2\text{PbO} + \text{PbS} \rightleftharpoons 3\text{Pb} + \text{SO}_2$ . Vapour-pressure curves for these reactions have been obtained and a chemical and microscopical examination of the solid phases has been made. The isothermal decomposition of the compound  $\text{PbSO}_4, \text{PbO}$  in the presence of lead sulphide gives results in accordance with the equations. The investigation includes a thermodynamical treatment and the representation of the equilibria by means of a solid figure. N. H. H.

**Lead Nitrite.** A. THIEL and L. STOLL (*Z. anorg. Chem.*, 1924, **139**, 317—323).—By the action of lead on lead nitrate solutions at 25° about 40 mol.-% of the nitrate undergoes reduction to nitrite, part of which separates together with nitrate as basic salts. This reduction is more complete at 100° or in the presence of acetic acid. Conversely, lead nitrite solutions, alone or in the presence of lead, are partly converted, with the simultaneous formation of basic salts, into nitrate. Thus, only by treating solid lead bromide with solid silver nitrite in the presence of a little water can pure lead nitrite be obtained. Some measurements were made on the conductivity and on the electrode potential of lead in nitrite solutions (cf. Chilesotti, A., 1908, ii, 845, 948; 1909, ii, 43). H. T.

**Reduction of Metallic Oxides by Alkali Cyanides.** L. HACKSPILL and R. GRANDADAM (*Compt. rend.*, 1925, **180**, 930—931).—Although under ordinary atmospheric conditions metallic oxides are reduced by fusion with alkali cyanides to form the metal and the alkali carbimide, lead, tin, copper, iron, nickel, barium, and strontium oxides, when heated at 570—750° with sodium cyanide in a vacuum yield heavy metal and sodium in approximately equivalent proportions, nitrogen, carbon monoxide and dioxide, and finely-divided carbon. Alumina, chalk, and manganese dioxide undergo only partial reduction under these conditions. Sodium carbimide is probably first formed, since under the same temperature conditions this salt rapidly decomposes under considerably reduced pressure to form sodium, nitrogen, carbon oxides, and carbon. J. S. C.

**Preparation and Properties of Nitrides.** E. FRIEDERICH and L. SITTIG (*Z. anorg. Chem.*, 1925, **143**, 293—320).—Nitrides of the compositions  $\text{TiN}$ ,  $\text{VN}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{BN}$ , and  $\text{LaN}$  have been prepared in the pure state by heating the corresponding oxides with the calculated weight of carbon at 1250° in nitrogen. By the same method, the previously unknown nitrides  $\text{ZrN}$ ,  $\text{ScN}$ ,



NbN, and ErN have been obtained, but only traces of nitrides of yttrium, ytterbium, cerium, didymium, thorium, and uranium were formed. The previously unknown or doubtful sesquioxides,  $\text{Ce}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_3$ , have been prepared by reducing the higher oxides with hydrogen. The m. p. of the nitrides were determined by passing a current of electricity through a rod of the material and comparing the energy consumption at the m. p. with that at the known m. p. of molybdenum and tungsten. (Cf. ii, 374.)

Titanium nitride, TiN, is a light brown powder, m. p.  $2930^\circ$ , specific resistance ( $10^4\sigma$ ) 1.3 ohms at the ordinary temperature,  $d$  5.29. Zirconium nitride, ZrN, is a yellowish-brown powder or golden-yellow crystals, m. p.  $2930^\circ$ ,  $d$  6.93, specific resistance 1.6 ohm at the ordinary temperature. Vanadium nitride, VN, is a greyish-brown powder, m. p.  $2050^\circ$  (decomp.),  $d$  5.91. The statement of Roscoe that vanadium nitride is formed when the oxide is heated in a current of ammonia (or  $\text{N}_2 + 3\text{H}_2$ ) is confirmed, but the nitride so obtained is not pure. Niobium sesquioxide,  $\text{Nb}_2\text{O}_3$ , a grey powder, was prepared by the reduction of the higher oxide with hydrogen. The nitride, NbN, a light grey powder, has m. p.  $2050^\circ$ ,  $d$  8.4, specific resistance 2 ohms at the ordinary temperature. Tantalum nitride, TaN, was obtained by heating metallic tantalum in hydrogen, powdering, and then heating in nitrogen; it has m. p.  $2800^\circ$  (decomp.). Only traces of scandium nitride, ScN, were obtained by the usual procedure, but the nearly pure nitride was formed if a mixture of sodium carbonate and carbon was added to the mixed sesquioxide and carbon, or if the temperature was raised to  $1700$ — $1800^\circ$ . It is dark blue, m. p.  $2650^\circ$ ,  $d$  4.2, specific resistance 3.08 ohms at the ordinary temperature. Boron nitride, BN, has m. p. above  $2530^\circ$ . Silicon nitride,  $\text{Si}_3\text{N}_4$ , is formed quantitatively at  $1250^\circ$  if 10% of ferric oxide is added to the mixture of silica and carbon; otherwise a temperature of  $1500^\circ$  is required. It is a nearly white powder insoluble in acids but decomposed by molten alkalis; it volatilises at  $1900^\circ$ . Erbium nitride, ErN, was prepared by the normal procedure with the addition of sodium carbonate and carbon to the mixture of oxide with carbon. It decomposes in air. Cerium sesquioxide,  $\text{Ce}_2\text{O}_3$ , was prepared by reducing the dioxide with hydrogen at  $1250^\circ$ . It is a yellow powder slowly oxidised by the air. The formation of the dark blue, unstable oxides previously described is due to the use of impure hydrogen.

Nitrides of cerium, didymium, thorium, and uranium were not obtained pure. Titanium, zirconium, vanadium, niobium, and scandium nitrides are decomposed by aqueous alkali hydroxides.

A. G.

**Definition and Preparation of Hexametaphosphates.** P. PASCAL (*Compt. rend.*, 1924, 179, 966—968; cf. A., 1924, ii, 856 and previous abstracts).—"Graham's soluble salt" behaves as  $\text{Na}_2[\text{Na}_4(\text{PO}_2)_6]$ , a complex hexametaphosphate with a portion of the sodium masked by reason of its position in the complex. It is unstable when in solution and in presence of excess of a lead salt

is precipitated as a hexametaphosphate from which the corresponding alkaline salts,  $M_6(PO_3)_6$ , may be obtained. H. J. E.

**Action of Arsenious Anhydride on Alkali Carbonates.** B. L. VANZETTI (*Gazzetta*, 1925, 55, 110—118).—Quantitative measurement of the interaction of sodium or potassium carbonate and arsenious anhydride in aqueous solution at the temperature of boiling water shows that the reaction proceeds only slowly, but may be brought virtually to completion if the carbon dioxide gradually liberated is eliminated by means of a current of hydrogen. T. H. P.

**Existence of Alkali Ortho-arsenites.** B. L. VANZETTI (*Gazzetta*, 1925, 55, 106—110).—In order to ascertain if alkali arsenites are obtainable in absence of water in accordance with the reaction,  $As_2O_3 + 6NaOR = 2Na_3AsO_3 + 3R_2O$ , arsenious anhydride was dissolved in a methyl-alcoholic solution of the theoretical amount of sodium methoxide and the excess of the alcohol evaporated to give a syrup, which was left to crystallise in a vacuum exsiccator over calcium chloride. The crystals formed were all highly hygroscopic and varied in composition, the arsenic content, determined either iodometrically or as sulphide, diminishing from about 80% to about 20% of that required by the formula  $Na_3AsO_3$ . Very little ether is apparently liberated during the reaction. T. H. P.

**So-called Molybdenum Dibromide and some of its Derivatives.** K. LINDNER and H. HELWIG (*Z. anorg. Chem.*, 1925, 142, 180—188).—Pure molybdenum “dibromide,”  $Mo_3Br_6$ , was prepared by passing nitrogen and bromine vapour over pure molybdenum powder heated at 600—700°. With pyridine, the bromide forms the compound  $Mo_3Br_6 \cdot C_5H_5N$  and with ammonia in alcoholic solution the *ammine*,  $Mo_3Br_6(NH_3)_2 \cdot 2EtOH$ . The action of alcoholic halogen acids gives acids which were isolated in the form of their pyridine salts. Thus the compounds  $C_5H_5N \cdot HMo_3Br_7$ ,  $(C_5H_5N)_5 \cdot H_5Mo_6Br_{17} \cdot 2EtOH$ , and  $C_5H_5N \cdot HMo_3Br_4Cl_3$ ;  $C_5H_5N \cdot HMo_3Br_4Cl_3 \cdot EtOH$ ;  $(C_5H_5N)_3 \cdot H_3Mo_6Br_8Cl_7 \cdot 3EtOH$ ; and  $C_5H_5N \cdot HMo_3Br_4Cl_3$  were prepared. The compounds are of the same type as those obtained previously with bivalent molybdenum, tungsten, and tantalum. N. H. H.

**Binary Systems Sodium and Lithium Tungstates, Potassium and Lithium Tungstates, Lithium Tungstate–Tungsten Trioxide, Sodium Tungstate–Tungsten Trioxide and Potassium Tungstate–Tungsten Trioxide.** J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1925, 143, 285—292).—Lithium tungstate melts at 742°, and has no transition points. With sodium tungstate (m. p. 705°), it forms a simple eutectic at 45% of the latter (crystallisation begins at 501°, eutectic crystallises at 491°). Potassium tungstate (m. p. 933°; transition point 352°) forms with lithium tungstate a compound,  $K_2WO_4 \cdot Li_2WO_4$ , crystallising at 632°, which gives eutectics with both simple salts (70%  $Li_2WO_4$ , 579°; 40%  $Li_2WO_4$ , 607°). With tungsten trioxide, sodium tungstate forms a compound,  $Na_2W_2O_7$  (m. p. 738°), which gives a eutectic

with the normal tungstate (m. p.  $628^{\circ}$ ); addition of the trioxide also lowers the second transition point ( $577^{\circ}$ ) of the latter. Lithium tungstate behaves similarly ( $\text{Li}_3\text{W}_2\text{O}_7$  has m. p.  $745^{\circ}$ , transition point  $687^{\circ}$ ); the eutectic has m. p.  $696^{\circ}$ . The system potassium tungstate-tungsten trioxide has a eutectic at 50%  $\text{WO}_3$  (crystallisation begins at  $637^{\circ}$ , eutectic crystallises at  $584^{\circ}$ ), no stable compound being formed. S. I. L.

**Decomposition of Permanganate.** J. HOLLUTA (*Z. physikal. Chem.*, 1925, **115**, 143—150; cf. this vol., ii, 49).—Carefully prepared 0.004*N*-solutions of potassium permanganate are not decomposed on long boiling, even on addition of small quantities of manganese sulphate. More dilute solutions (0.002*N*) are slowly decomposed by boiling. It is probable that the compound  $\text{KMnO}_3$  (cf. Moles and Crespi, A., 1922, ii, 565; 1923, ii, 374) is the primary decomposition product and that this decomposes further with the formation of  $\text{K}_2\text{MnO}_4$  and  $\text{MnO}_2$ . L. F. G.

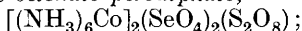
**Reaction between Ferric Chloride and Potassium Thiocyanate.** K. C. BAILEY (*Proc. Roy. Irish Acad.*, 1924, **37**, [B], 6—15).—The apparently anomalous behaviour on extraction with ether of solutions of potassium thiocyanate and ferric chloride containing predominating proportions of each constituent is discussed, and evidence is put forward that in the case where the thiocyanate predominates, and where the colour is paler, the ether extracts practically pure thiocyanate, whilst when the ferric chloride is in excess and the solution is sufficiently concentrated to impart some colour to the ether, hydrochloric acid formed by hydrolysis of ferric chloride liberates thiocyanic acid, and the extract contains both ferric chloride and thiocyanic acid. The reason for the variation in the colours of the two types of solution is investigated, and it is shown that Lachs and Friedenthal's method (A., 1911, ii, 542) for determining small quantities of iron must be used with caution since extraction of iron by the ether becomes progressively more difficult with diminution in the proportion of iron present. The behaviour of thiocyanic acid in organic solvents is also discussed. [Cf. B., 1925, 313.] D. G. H.

**Freezing Points of Solutions containing Ferric Chloride and Potassium Thiocyanate.** K. C. BAILEY and J. D. KIDD (*Proc. Roy. Irish Acad.*, 1924, **37**, [B], 16—18).—The freezing-point curve for solutions containing a constant proportion of ferric chloride (0.54%) and varying proportions of potassium thiocyanate (0.1 to 9.7%) showed no breaks indicative of the formation of molecular compounds, although the depression of the freezing-point was slightly smaller than would be expected. D. G. H.

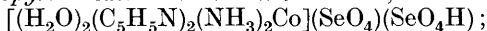
**Complex Cobaltic Selenates.** J. MEYER, G. DIRSKA, and F. CLEMENS (*Z. anorg. Chem.*, 1924, **139**, 333—386).—The substitution of sulphate ion by the selenate ion in mono- and poly-nuclear cobaltic sulphates has little influence on the properties of the salt. The differences are less as the complexity of the cobalt-

ammine increases, and are most marked in the case of the solubility and the degree of hydration, both the latter being greater with the selenates than with the sulphates. The following new compounds are described.

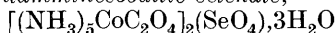
*Hexamminecobaltic selenate persulphate*,



*acid diaquodipyridinediamminecobaltic selenate*,

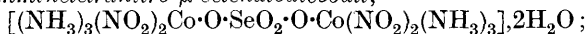


*nitratopentamminecobaltic selenate*,  $[(\text{NO}_3)\text{Co}(\text{NH}_3)_5]\text{SeO}_4$ ; *thiocarbimidopentamminecobaltic selenate*,  $[(\text{NCS})(\text{NH}_3)_5\text{Co}]\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ ; *carbonatopentamminecobaltic selenate*,  $[(\text{CO}_3)(\text{NH}_3)_5]_2\text{SeO}_4$ ; *normal and acid oxalatopentamminecobaltic selenate*,

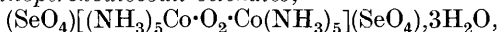


and  $[(\text{NH}_3)_5\text{CoC}_2\text{O}_4]\text{SeO}_4\text{H} \cdot \text{H}_2\text{O}$ ; *hydroxyaquotetramminecobaltic selenate*,  $[(\text{OH})(\text{H}_2\text{O})\text{Co}(\text{NH}_3)_4]\text{SeO}_4$ ; *chloro- and bromo-aquatetramminecobaltic selenate*,  $[\text{X}(\text{H}_2\text{O})\text{Co}(\text{NH}_3)_4]\text{SeO}_4$ ; *chlorodiaquotriamminecobaltic selenate*,  $[\text{Cl}(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_3]\text{SeO}_4$ ; *dibromotetramminecobaltic selenate*; *acid dichlorodiaquodiamminecobaltic selenate*,  $[\text{Cl}_2(\text{H}_2\text{O})_2\text{Co}(\text{NH}_3)_2]\text{SeO}_4\text{H}$ ; *oxalatotetramminecobaltic selenate*,  $[(\text{NH}_3)_4\text{CoC}_2\text{O}_4]_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$ ; *oxalatodiethylenediamminecobaltic selenate*,  $[\text{en}_2\text{CoC}_2\text{O}_4]_2\text{SeO}_4 \cdot 3\text{H}_2\text{O}$ ; *dithiocarbimidodiethylenediamminecobaltic selenate*,  $[\text{en}_2\text{Co}(\text{CNS})_2]_2\text{SeO}_4\text{H}$ ; *diamminebisdimethylglyoximinocobaltic selenate*,  $[(\text{NH}_3)_2\text{Co}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2]_2\text{SeO}_4$ .

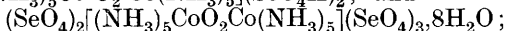
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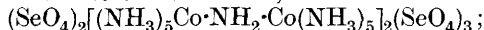
*the decammineperoxodicobalt selenates*,



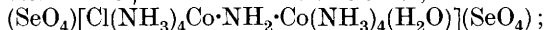
$(\text{HO}_4\text{Se})_2[(\text{NH}_3)_5\text{Co} \cdot \text{O}_2 \cdot \text{Co}(\text{NH}_3)_5](\text{SeO}_4\text{H})_2$ ; and



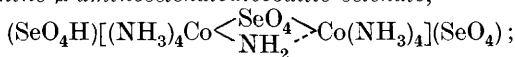
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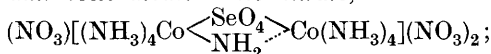
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*acid octammine-μ-aminoselenatodicobaltic selenate*,



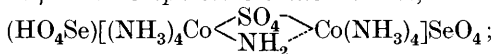
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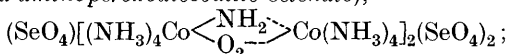
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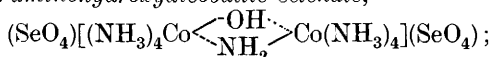
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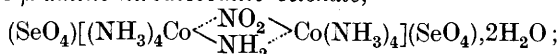
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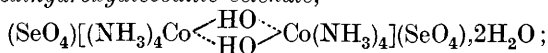
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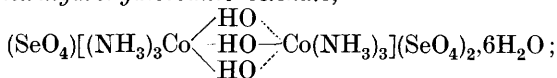
octammine- $\mu$ -aminonitrodicobaltic selenate,



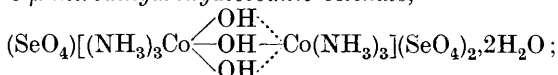
octamminedihydroxydicobaltic selenate,



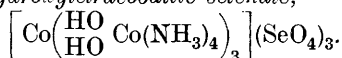
hexamminetrihydroxydicobaltic selenate,



hexammine- $\mu$ -nitrodihydroxydicobaltic selenate,



dodecamminehexahydroxytetracobaltic selenate,



H. T.

**Non-existence of Nickel Suboxide.** G. R. LEVI and G. TACCHINI (*Gazzetta*, 1925, **55**, 28—32).—X-Ray examination (cf. Levi, A., 1924, ii, 681) shows that the products obtained by Glaser (A., 1903, ii, 646) from partial oxidation of nickel and partial reduction of nickeloso-nickelic oxide,  $\text{Ni}_3\text{O}_4$ , are mixtures of nickelous oxide and nickel containing no nickel suboxide,  $\text{Ni}_2\text{O}$ . W. E. E.

**Chlorides of Ruthenium.** L. WÖHLER and P. BALZ (*Z. anorg. Chem.*, 1924, **139**, 411—418).—By treating finely-divided ruthenium with chlorine between  $300^\circ$  and  $840^\circ$ , only the trichloride is formed, which decomposes into its elements at  $845^\circ$ . No evidence was obtained for the formation of mono- or di-chloride by the direct action or by the decomposition of the trichloride. The product formed by the action of a mixture of carbon monoxide and chlorine at  $400^\circ$  has the same vapour pressure as the trichloride, and the formation of a blue colour by treatment of this product with dilute alcohol is probably due to reduction of the formed trichloride to dichloride by the alcohol. The anhydrous tetrachloride could not be obtained from chlororuthenic acid nor by chlorinating the trichloride. The vapour-pressure curve of the trichloride from  $450^\circ$  upwards was determined. Owing to the volatility of the trichloride, the values above  $700^\circ$  are unsatisfactory. H. T.

**Iridium Tetroxide.** F. KRAUSS and H. GERLACH (*Z. anorg. Chem.*, 1925, **143**, 125—128).—The oxide is prepared by heating the pure hydroxide for a short time in nitrogen at  $350^\circ$ . The hydroxide is prepared free from chlorine and alkali by employing the method used by Krauss and Kükenthal for the preparation of pure ruthenium trihydroxide (A., 1924, ii, 770). The compound was analysed by heating in carbon dioxide, absorbing the water by calcium chloride and weighing, and reducing the residual oxide in hydrogen to metal, which is finally weighed. L. L. B.

**Boron and Boron Suboxide.** H. H. KAHLENBERG (*Trans. Amer. Electrochem. Soc.*, 1925, 47, 59—91).—Boron was prepared by all the important methods, but in most cases was impure. Reduction with sodium or potassium gave a product which could not be freed from the alkali metal and oxides. Moissan's method of reduction with magnesium gave a substance of composition  $B_7O$  contaminated with magnesium. Reduction with aluminium and sulphur gave a product containing the former, as also did interaction of aluminium and potassium fluoborate. Boron trichloride formed by passing chlorine over Moissan's "boron" ( $B_7O$ ) was passed mixed with hydrogen over an electric arc between copper electrodes, and gave a deposit of pure amorphous boron, but in low yield. A small quantity of pure amorphous boron was obtained by electrolysing a fused mixture of potassium carbonate, potassium chloride, and boron trioxide, using a copper cathode and a carbon anode. Fused boron was obtained by reduction of Moissan's "boron" with aluminium powder in an arc. The single potential of boron is  $-0.028$  volt with neutral potassium borate as electrolyte. The single potential is lower in acid, and higher in alkaline, electrolytes. Boron replaces gold, platinum, palladium, silver, mercury, copper, and lead from their solutions, the last-named very slowly. In the electrochemical series, boron comes just above lead. Moissan's "boron," which is shown to be a mixture of boron with a new oxide,  $B_3O$ , will not entirely replace gold from its solutions, the residue consisting of displaced gold and the oxide  $B_3O$ , which has a lower potential than boron. Boron has a high electrical resistance when cold, but becomes a good conductor at high temperatures. C. S.

**Separation of Hafnium from Zirconium.** G. VON HEVESY and E. MADSEN (*Z. angew. Chem.*, 1925, 38, 228; cf. A., 1924, ii, 53, 571).—A partial separation of hafnium and zirconium can be effected by means of fractional precipitation of the phosphates (cf. A., 1923, ii, 570), and also by recrystallisation through the double oxalates, double sulphates, and the oxychlorides. The preparation of pure hafnium salts is best effected by fractional crystallisation of the double fluorides. The following solubilities are given:  $K_2HfF_6$ , 0.1008 mol./litre in  $N/8$ -hydrofluoric acid at  $20^\circ$ ;  $K_2ZrF_6$ , 0.0655 mol./litre;  $(NH_4)_2HfF_6$ , 1.425 mol./litre;  $(NH_4)_2ZrF_6$ , 1.050 mol./litre.

The mineral (silicate) is decomposed by fusion with ammonium hydrogen fluoride, by alkaline fusion, or by treatment with hydrofluoric acid. The product is converted into the sulphate and then into the oxychloride. This is either recrystallised or treated with sulphur dioxide, which precipitates hafnium and zirconium from the boiling solution, leaving most of the iron in solution.

The double fluorides are obtained by warming the dioxide with ammonium fluoride and hydrofluoric acid; the compound  $(NH_4)_3ZrF_7$  resulting from the fusion is unsuitable. The hafnium content (2—5%) is raised to 38% by means of the ammonium compounds; subsequent fractionation of the potassium compounds

yields a hafnium salt of more than 99.9% purity. Incidentally a product probably analogous to Marignac's  $\text{KZrF}_5 \cdot \text{H}_2\text{O}$  was obtained.

The separation was controlled by X-ray spectroscopy and by density determinations; the hafnium content  $x$  is given by the expression  $x = (d - 5.73) / 0.0394$ , where  $d$  is the observed density of the mixture of oxides.

R. A. M.

**Separation of Thorium from Zirconium and from the Tervalent Rare-earth Metals.** L. FERNANDES (*Gazzetta*, 1925, 55, 3—6; cf. A., 1924, ii, 861).—A concentrated solution of thorium sulphate cooled with a large excess of thallous sulphate deposits thorium thallous sulphate (I),  $2\text{Th}(\text{SO}_4)_2 \cdot 7\text{Tl}_2\text{SO}_4$ , stable over a wide range of temperature. Evaporation at a low temperature of thorium sulphate solution containing a little thallous sulphate yields  $\text{Th}(\text{SO}_4)_2 \cdot \text{Tl}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , much less stable than I. A hydrate,  $2\text{Th}(\text{SO}_4)_2 \cdot 7\text{Tl}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ , is stable from 70° to 100°. A solution of zirconium and thallous sulphates in concentrated sulphuric acid, when evaporated at a high temperature and then cooled gives two zirconium thallous sulphates:  $\text{Zr}(\text{SO}_4)_2 \cdot 2\text{Tl}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$  (II), and  $2\text{Zr}(\text{SO}_4)_2 \cdot \text{Tl}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ . On the other hand, evaporation at the ordinary temperature at reduced pressure, over concentrated sulphuric acid, of a solution of the mixed salts in dilute sulphuric acid produces the double salt,  $2\text{Zr}(\text{SO}_4)_2 \cdot 7\text{Tl}_2\text{SO}_4$ , and finally the compound II. A study of the solubility curves of  $2\text{Th}(\text{SO}_4)_2 \cdot 7\text{Tl}_2\text{SO}_4$ , and  $\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{Tl}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  in water and of that of zirconium sulphate in the presence of excess of thallous sulphate in 20% sulphuric acid, suggested the following method of separating cerium, thorium, and zirconium. The mixed hydroxides, precipitated by ammonium hydroxide, are washed with boiling water and dissolved in dilute sulphuric acid and treated cold with excess of thallous sulphate; this precipitates nearly all the cerium. After evaporating the filtrate to less than two-thirds of its volume, it is again filtered. On cooling, the first fraction of thorium is deposited in a pure state. Succeeding fractions of thorium are obtained by evaporating the filtrate until the sulphuric acid is nearly concentrated and the last traces are deposited on boiling. The liquid is then filtered through asbestos and the zirconium precipitated by cooling.

W. E. E.

**Preparation of Selenium Monochloride and Monobromide.** V. LENHER and C. H. KAO (*J. Amer. Chem. Soc.*, 1925, 47, 772—774).—Selenium monochloride, b. p. 130°, is prepared in 90% yield by the addition of selenium, followed (dropwise) by sulphuric acid, to a solution of selenium dioxide in concentrated hydrochloric acid; the reddish-brown, oily layer is separated, and washed with sulphuric acid or precipitated by hydrogen chloride from its solution in fuming sulphuric acid. Selenium monobromide is prepared similarly, using the mixture of sulphuric and hydrobromic acids produced by interaction of bromine, sulphur dioxide, and water at 0°.

J. S. C.

**Laboratory Circulating Pump for Corrosive Vapours.** H. C. KREMERS (*Ind. Eng. Chem.*, 1925, 17, 298—299).—The circulation of hydrogen chloride (*e.g.*, for the dehydration of rare-earth chlorides) is effected by a reciprocating pump constructed of glass, the plungers in which are of an elongated bell-shape and work in a liquid seal composed of high b. p. paraffin oil or other suitable liquid. The valves are of glass. W. A. S.

**Micropyrometer of the Spectrometer Type.** F. HENNING and W. HAUSE (*Z. Physik*, 1924, 29, 157—174).—A complete description is given of the instrument together with a detailed account of the method of calibration. The principle adopted is that of comparison of the intensity of radiation of a given wavelength from the source of which the temperature is to be determined with that of the same wave-length emitted by a glowing filament the temperature of which is under very sensitive control. Typical data are given of the behaviour of the instrument in the region 1500—2000°, and it is stated that temperatures up to 3000° can be determined in this way. R. W. L.

**Destruction of Berthelot's Calorimetric Bomb. Its Replacement by a New Type of Bomb.** C. MOUREU (*Compt. rend.*, 1925, 180, 557—560).—In replacing the original calorimetric bomb of Berthelot, which exploded in 1918, the design has been modified in order to reduce the amount of platinum used in its construction. The lining consists of 0.4 mm. thickness of copper, covered with 0.4 mm. of gold and finally 0.2 mm. of platinum. G. M. B.

**Process and Apparatus for Carrying out Chemical Reactions.** E. BUHTZ (*Chem.-Ztg.*, 1925, 49, 267).—An apparatus for carrying out reactions between two or more solid substances so that no part of the mixture is overheated and an efficient mixing of the reagents is effected, thereby avoiding as far as possible any side reactions, consists of a closed reaction vessel containing a large rotating plate slightly conical in shape, above which is a smaller rotating baffle plate which serves to distribute the reacting substances over the larger plate. The apparatus is charged through two concentric tubes, the outer of which leads directly to the baffle plate and the inner to the reaction plate. Provision is made for heating or cooling the latter by passing a stream of hot or cold liquid through pipes in the plate. A. R. P.

**Effect of Chemicals on various kinds of Glass.** C. E. KLAMER (*Chem. Weekblad*, 1925, 22, 140—141).—Tables are given showing the losses of weight of vessels of Pyrex, Jena, Sphinx, and Murano glass after heating acids and alkalis in them. The conductivities of distilled water after being boiled in selected vessels were also determined. S. I. L.

**Dynamic Study of Dehydration by means of a Hydrostatically-compensated Balance.** M. GUICHARD (*Bull. Soc. chim.*, 1925, [iv], 37, 251—253).—The apparatus and method used



in previous experiments are described in detail. The furnace is arranged so that its temperature increases regularly. The substance being dehydrated is balanced against a long cylindrical body partly immersed in oil, the level of which can be raised by addition from a burette. The volume thus added to preserve equilibrium after an experiment is proportional to the loss in weight of the substance.

S. K. T.

**Simple Apparatus for the Distillation of Mercury in a Vacuum.** J. ŠVÉDA (*Chem. Listy*, 1925, **19**, 51—53).—The apparatus consists of a large glass bulb connected, by a long glass tube provided with a stopcock, with a reservoir of mercury, and having at its upper end an upwardly inclined tube bent vertically downwards at its upper end and sealed to a long glass tube terminating in a receiver with side tube for connexion to the vacuum pump. The apparatus will distil 600—700 g. of mercury per hour.

A. R. P.

**Drying Tube for Phosphorus Pentoxide.** L. M. DENNIS (*J. Amer. Chem. Soc.*, 1925, **47**, 797).—A modified form of drying tube is described, in which the gas is passed in and out through side tubes, the phosphorus pentoxide in the tube being stirred and a fresh surface exposed by turning two stoppers fitted at the ends of the tube and carrying heavy bent glass rods.

J. S. C.

**Simple Tangentimeter.** M. LATSHAW (*J. Amer. Chem. Soc.*, 1925, **47**, 793—794).—A simple apparatus whereby the slope of a plotted curve at any point may be determined, consists of a plane mirror mounted on one leg of a steel "square" so that the mirror face extends to the plane at the bottom of the square and is normal to the other leg. When the mirror is standing normally across a given curve, there will appear no break between the curve and its image at the foot of the mirror. The second leg of the square is then parallel to the tangent to the curve at that point.

J. S. C.

**Simple Automatic Mercury Pump.** H. M. McLAUGHLIN and F. E. BROWN (*J. Amer. Chem. Soc.*, 1925, **47**, 613—615).—A modified form of Toepler pump is described, which, with the aid of a small water pump, will operate continuously and automatically, returning the mercury to the reservoir after each stroke. The design of the apparatus permits collection of the exhaust gas and guards against its contamination.

J. S. C.

**Fractionating Column with Moving Parts.** J. E. MYERS and W. J. JONES (*J. Chem. Soc.*, 1925, **127**, 4—8).—The column is divided into sections by downwardly-directed conical trays equally spaced at 3.5 cm., each having at the centre a circular hole 1.25 cm. in diameter. Through these holes passes a vertical shaft which bears horizontal discs, 2.5 cm. in diameter, one just below each tray. The shaft works on a bearing fixed to the bottom of the column and emerges at the top through a stuffing-box. At about 2400 revolutions per minute the column compares very favourably with other patterns.

L. J. H.

## Mineralogical Chemistry.

**New Type of Eruptive, Mesocratic Alkaline Rock.** A. LACROIX (*Compt. rend.*, 1925, **180**, 481—484).—A new type of mesocratic, alkaline rock, intermediate between lujavrite, which is poor in silica, and fasilitikite, rich in silica, has been found amongst the quaternary gravels in the deserts of Santas-ho, China. The name "ordosite" is proposed for this rock. It consists of needles of green ægyrine with porphyritic crystals of felspar showing crossed albite twinning and enclosing laminae of mica. It belongs to the syenite class, but for this class contains an unusually large amount (60%) of pyroxene soda, which is embedded in the felspar and is acicular in form. The analyses of nine ægyrine mesocratic rocks are given, that of ordosite being :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	Na <sub>2</sub> O.
56.90	7.00	17.41	1.25	1.22	1.62	6.86
K <sub>2</sub> O.	TiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O (+).	H <sub>2</sub> O (-).	MnO.	
5.36	1.60	0.10	0.20	0.11	0.27	

The richness in pyroxene soda is shown to be independent of the nature of the felspar of which the rock is composed. J. W. B.

**Native Arsenic in Cornwall.** A. RUSSELL [with H. F. HARWOOD] (*Min. Mag.*, 1925, **20**, 299—304).—Massive material with a curved lamellar structure and columnar jointing was found in some quantity (several cwt.) along a joint in dolerite in a road-metal quarry near Saltash in Cornwall. Analysis gave :

As.	Sb.	Fe.	S.	Insol.	Total.	Sp. gr.
94.80	5.15	0.15	0.11	0.10	100.31	5.636

Native arsenic has also recently been found in small amount in the Tolgus mine at Redruth. These are the first authentic records of the occurrence of this mineral in the British Isles. The occurrence of bismuthinite in granite at Shap in Westmorland, and of smaltite and niccolite in the old copper mine at Coniston in Lancashire, are also recorded. L. J. S.

**Pyrites of Majdan-Pek (Serbia).** J. BARTHOUX (*Compt. rend.*, 1924, **179**, 982—984).—The beds of pyrite and chalcopyrite result from magmatic differentiation. These minerals tend to occur in vertical bands, most freely in contact with the face of an eruptive formation. The method of investigating the deposits consists, therefore, in finding the edge of the eruptive rock and exploring the lateral surface of contact. H. J. E.

**Afwillite, a New Hydrous Calcium Silicate.** J. PARRY and F. E. WRIGHT (*Min. Mag.*, 1925, **20**, 277—286).—A columnar aggregate of clear, colourless crystals was found by A. F. Williams in the Dutoitspan diamond mine at Kimberley, South Africa. The crystals are monoclinic ( $a : b : c = 2.097 : 1 : 2.381$ ,  $\beta = 81^{\circ} 34'$ ) with

prismatic habit in the direction of the axis of symmetry, and perfect (001) cleavage.  $d$  2.630, hardness 4. The optical characters are given in detail and compared with those of the several known hydrous calcium silicates. Analysis I by J. PARRY was made by decomposing the mineral with hydrochloric acid, and II by H. S. WASHINGTON by fusion with sodium carbonate.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> + Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	BaO.	H <sub>2</sub> O (+110°).	H <sub>2</sub> O (-110°).	Total.
I.	33.96	0.60	—	49.28	—	15.89	0.12	99.85
II.	35.10	0.05	0.02	49.00	Nil	15.81	0.01	99.99

The formula is  $3\text{CaO}, 2\text{SiO}_2, 3\text{H}_2\text{O}$ , which may be written  $2\text{H}_2\text{CaSiO}_4, \text{Ca}(\text{OH})_2$ , since two-thirds of the water is lost at about 300° and only one-third of the lime is taken up by water from the ignited material. The rate at which water is lost at different temperatures depends on the pressure of aqueous vapour in the atmosphere. The mineral gives an alkaline reaction; it is slowly decomposed by water and more readily by hydrochloric acid.

L. J. S.

**Hafnium Content of Zirconium Ores. II.** G. HEVESY and V. T. JANTZEN (*Chem. News*, 1925, **130**, 179—180; cf. A., 1924, ii, 492, 571, 620).—A comparison of the proportion of hafnium in 20 zircons of known radioactivity, helium content, and density, showed a rough connexion between the proportion of hafnium present and the radioactivity, but not with the density. The ratio  $\text{HfO}_2/\text{ZrO}_2$  was found to be appreciably lower in zirconium minerals than in minerals of a less silicious magma. [Cf. B., 1925, 314.]

D. G. H.

**Tyuyamunite from the Tyuya-Muyun Radium Mine in Fergana.** P. N. CHIRVINSKY (*Min. Mag.*, 1925, **20**, 287—295).—Tyuyamunite ( $\text{CaO}, 2\text{UO}_3, \text{V}_2\text{O}_5, m\text{H}_2\text{O}$ ) corresponds in composition with carnotite ( $\text{K}_2\text{O}, 2\text{UO}_3, \text{V}_2\text{O}_5, n\text{H}_2\text{O}$ ) and is consequently also known as calciocarnotite. An account is given of its occurrence and mining in Russian Turkestan. It is found with copper ores in limestone. Analyses of the ore show  $\text{CuO}$  3.10—10.88%,  $\text{U}_3\text{O}_8$  0.80—4.61%,  $\text{V}_2\text{O}_5$  1.83—6.39%, together with barytes and calcite. The copper is present as malachite and the vanadate turanite ( $5\text{CuO}, \text{V}_2\text{O}_5, 2\text{H}_2\text{O}$ ). Of wide distribution in the same region is a nickel vanadate, named kolovratite by Vernadsky in 1922. The optical characters of the minute orthorhombic crystals of tyuyamunite are described.

L. J. S.

**X-Ray Examination of Calcium Formate.** K. YARDLEY (*Min. Mag.*, 1925, **20**, 296—298).—It is shown that crystals of calcium formate are orthorhombic bipyramidal, and not bisphenoidal as suggested by Plathan (*Z. anorg. Chem.*, 1898, **18**, 86). The dimensions of the unit cell containing eight molecules are  $a=10.19$ ,  $b=13.41$ ,  $c=6.27$  Å. The half spacing for certain of the planes shows that the lattice is  $\Gamma_o$  and the space-group  $Q_h^5$ .

L. J. S.

## Analytical Chemistry.

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**Laboratory Vacuum Gauge.** M. L. HAMLIN (*J. Amer. Chem. Soc.*, 1925, **47**, 709—712).—Details are given for the construction and calibration of a vacuum gauge having a useful range of 10—0.05 mm., which may be so modified as to cover a second range of pressures one-fifth or one-tenth of this. J. S. C.

**Gas Absorption Pipette.** A. O. JONES (*J. Soc. Chem. Ind.*, 1925, **44**, 115—116r).—A two-bulbed absorption pipette is described in which the bulbs are joined by rubber tubing in place of the usual rigid glass tube, and a funnel and tap are attached to the top of the absorption bulb. By this means, the gas in the pipette may be washed with more than one reagent without transferring it to the burette, one pipette can be used for all the reagents, and fouling of the mercury in the burette by the reagents is lessened. L. F. H.

**Modification of Geissler's Bulbs.** G. ODDO (*Annali Chim. Appl.*, 1925, **15**, 3—4).—When the tightness of the joints of a combustion apparatus is being tested, the potassium hydroxide solution tends to spurt into the calcium chloride tube. This is prevented if the narrow tube passing down into the first small bulb of the Geissler absorption apparatus is continued, at its upper end, into the large bulb and bent over in the form of a crook. T. H. P.

**Apparatus for Quantitative Microanalysis.** J. POLLAK (*Mikrochem.*, 1924, **2**, 189—192).—When mixing solutions in test-tubes immersed in a water-bath for quantitative microanalysis, stirring by means of a slow current of air is the only satisfactory way. The air should be purified from dust and possible halogen compounds by passing it from an aspirator through a wad of cotton wool, then through asbestos soaked in silver nitrate solution, and bubbled into the test solution through a capillary tube. For suspending a number of test-tubes in a water-bath (beaker), a stand consisting of two perforated brass plates some distance apart and fixed to arms bent at right angles at the top to rest on the edge of the bath is useful. A. R. P.

**Use of Glass Filters in Qualitative Analysis.** G. F. HÜTTIG and M. NETTE (*Z. anal. Chem.*, 1925, **65**, 385—399).—Büchner or Nutsche funnels with porous filter-beds of sintered glass have many advantages over filter-papers for qualitative group analysis. The one funnel may be used throughout the analysis; the precipitate is sucked dry on each occasion, thereby keeping the volume of the filtrate low, and the different constituents of a group precipitate may be extracted by passing the appropriate solvents through the filter in succession. None of the ordinary group reagents except alkali hydroxides has any solvent action on the filter, which may, if necessary, be cleaned by the use of the strongest acids at high temperatures. Suitable forms of apparatus for the purpose are

described and a detailed account is given of the procedure for conducting an ordinary group analysis. A. R. P.

**Shimer Filter Tube.** E. C. BINGHAM (*Ind. Eng. Chem.*, 1925, 17, 293—294).—The improved form is described (cf. A., 1905, ii, 349). The "filter-mat" is now made of surgical lint. W. A. S.

**Determination of Combustible Gases by Combustion with Cupric Oxide.** II. J. ŠVĚDA (*Chem. Listy*, 1925, 19, 41—48, 73—79).—A fuller account of work previously published (this vol., ii, 154). The combustion of the gases is carried out in a special gas pipette which may be exhausted of air before introducing the gas mixture, thus eliminating errors due to absorption of air and carbon dioxide by the contact mass of ceric and cupric oxides. The combustion of both hydrogen and carbon monoxide is complete at 280—290°, contrary to the statement of Scherb that the completeness of the oxidation of carbon monoxide depends on the partial pressure of the hydrogen. A. R. P.

**Adsorption of Cresol-red by Serum in Spectrophotometric Determination of  $p_{\text{H}}$ .** E. F. HIRSCH.—(See i, 606.)

**Bromate Determination of Hydrogen Peroxide, Peroxides, and Per-salts.** E. RUPP and G. SIEBLER (*Pharm. Zentr.*, 1925, 66, 193—196).—0.1N-Solutions of potassium bromate and arsenious acid do not alter on keeping. Titration of the latter with the former is carried out in hot, strongly acid solution in presence of methyl-orange; excess of bromate liberates bromine, which decolorises the indicator. Hydrogen peroxide is run into excess of arsenious oxide in alkaline solution, the whole acidified, and the excess titrated with bromate. Other peroxides are treated, in presence of excess of the arsenic solution, with acid, to liberate hydrogen peroxide, and the determination is completed as for the latter. Persulphates are reduced by excess of the arsenic solution in 5 min., at the b. p., perborates even more quickly. S. I. L.

**Preparation of *o*-Tolidine Solution for the Determination of Chlorine [in Chlorinated Water].** C. E. ROAKE (*Ind. Eng. Chem.*, 1925, 17, 257).—The *o*-tolidine is first treated with concentrated hydrochloric acid; dissolution is then easier. [Cf. B., 1925, 333.] W. A. S.

**Detection and Determination of Chloride, Bromide, and Thiocyanate in the Presence of Cyanide.** E. SCHULEK (*Z. anal. Chem.*, 1925, 65, 433—435).—In the presence of free alkali or of sodium hydrogen carbonate, cyanides are converted by formaldehyde into alkali glycollate and hexamethylenetetramine. If the solution is then acidified with nitric acid, the chloride, bromide, or thiocyanate ions may be determined by Volhard's method in the usual way. An alternative procedure for the elimination of the cyanide consists in distilling the liquid with boric acid; the residual solution in the distilling flask is then acidified with nitric acid and the analysis finished as described above. A. R. P.

**Electrometric Titration of Hypochlorous Acid.** A. SCHLEICHER and L. TOUSSAINT (*Z. anal. Chem.*, 1925, 65, 399—405).—In Treadwell's process for the electrometric titration of hypochlorous acid (A., 1921, ii, 410), the comparison electrode may consist of solutions of many neutral salts or weak oxidising agents instead of a previously titrated hypochlorite solution. Such salts are sodium chloride, nitrate, and sulphate, ammonium chloride and acetate, and chromates of the alkali metals. The potential at the end-point may be displaced as much as 0.2 volt without affecting the results if the titration is carried out in the simplified compensation apparatus of A. Fischer ("Elektroanalytische Schnellmethoden," Stuttgart, 1908).  
A. R. P.

**Electrometric Titration of Chlorous Acid and its Determination in Presence of Hypochlorous Acid.** A. SCHLEICHER and W. WESLY (*Z. anal. Chem.*, 1925, 65, 406—411).—Chlorous acid reacts with potassium iodide and sulphuric acid, liberating 2 mols. of iodine, which may be measured by titration of the solution with sodium thiosulphate and electrometric determination of the end-point. This acid does not react with sodium arsenite in the presence of sodium hydrogen carbonate, whilst hypochlorous acid may be determined electrometrically by titration with this reagent. The titrated solution is treated with potassium iodide and sulphuric acid and the chlorous acid determined as above, allowance being made for the excess of arsenite used in the first titration. Chlorites are not decomposed by heating the solution for 15 hrs. on the water-bath, but hydrogen peroxide decomposes them readily without attacking any chlorate present.  
A. R. P.

**Volumetric Determination of Iodides.** N. SASAKI (*Z. anorg. Chem.*, 1924, 139, 394—396).—Iodides in the presence of an equal amount of bromide and forty times as much chloride can be accurately determined by treating a solution with an excess of 0.1*N*-potassium dichromate solution, followed after 10—60 secs. by an excess of ferrous ammonium sulphate solution, and titrating the liberated iodine immediately with thiosulphate solution, the reactions between iodide and ferric salts and free iodine and ferrous salts taking place very slowly. Direct sunlight should be avoided and the iodide solution should contain 1 mg.-equivalent of iodide in 300 c.c. and be acidified with sulphuric acid until the solution has about *N*-acidity. If more bromide or chloride is present, approximate results can be obtained by shortening the time of action of the dichromate solution.  
H. T.

**Determination of Hydrofluoric Acid.** O. WÄELZEL (*Z. Unters. Nahr. Genussm.*, 1925, 49, 31—37).—The method of Greef (A., 1913, ii, 975) by which soluble fluorides are titrated with ferric chloride in the presence of ammonium thiocyanate, is adapted for the analysis of disinfectants etc.  
A. G. P.

**Determination of Sulphur in Polysulphides.** A. KURTENACKER and K. BITTNER (*Z. anorg. Chem.*, 1925, 142, 115—118).—Sodium polysulphide solution is converted into thiosulphate and

sulphide by the action of sodium sulphite solution as in the methods of Chapin and of Wöber. The sulphide is then precipitated with zinc acetate and the excess of sulphite removed with formaldehyde. After addition of acetic acid, the thiosulphate is titrated with iodine. The results show excellent agreement with those obtained indirectly by oxidation of the sulphur with bromate and bromide (Treadwell and Mayr).  
N. H. H.

**Determination of Polythionic Acids in Presence of One Another.** A. KURTENACKER and K. BITTNER (*Z. anorg. Chem.*, 1925, **142**, 119—129).—A volumetric method is described for the determination together of the radicals  $S_3O_6''$ ,  $S_4O_6''$ , and  $S_5O_6''$ . By treatment with excess of mercuric chloride, all the radicals react to give four equivalents of acid for each mol. of polythionate,  $2S_{3+z}O_6'' + 3HgCl_2 + 4H_2O \rightarrow Hg_3S_2Cl_2 + 4Cl + 8H + 2zS$ . Thus titration with sodium hydroxide solution gives the total polythionate. On treatment of another portion with excess of sodium sulphite solution, the reactions  $S_4O_6'' + SO_3'' = S_3O_6'' + S_2O_3''$  and  $S_5O_6'' + 2SO_3'' = S_3O_6'' + 2S_2O_3''$  occur, and after removal of the excess of sulphite with formaldehyde the thiosulphate may be titrated with iodine. A third portion is treated with potassium cyanide solution, giving  $S_4O_6'' + 3CN' + H_2O = SO_4'' + CNS' + 2HCN + S_2O_3''$  and  $S_5O_6'' + 4CN' + H_2O = SO_4'' + 2CNS' + 2HCN + S_2O_3''$ . If the original solution contains  $x$ ,  $y$ , and  $z$  mols. of tri-, tetra-, and penta-thionate, respectively, and the three titrations are  $a$  mols. of sodium hydroxide and  $b$  and  $c$  mols. of iodine, then  $x = a/4 - c$ ,  $y = 2c - b$ , and  $z = b - c$ . The results are in satisfactory agreement with the theoretical when arbitrary mixtures of the pure substances are used and with results obtained by certain other methods.  
N. H. H.

**[Quantitative] Separation of Selenium and Tellurium by Sulphur Dioxide in Hydrochloric Acid Solution.** V. LENHER and C. H. KAO (*J. Amer. Chem. Soc.*, 1925, **47**, 769—772).—Selenium is precipitated by sulphur dioxide from cold solutions of the two oxides in concentrated hydrochloric acid, washed with concentrated hydrochloric acid, water, and finally with alcohol and ether, care being taken to remove the last traces of water. The precipitate is dried for 3 or 4 hrs. at 30—40° and finally for 2 hrs. at 120—130°. Tellurium is precipitated from the concentrated filtrate by the sulphur dioxide-hydrazine hydrochloride method previously described (A., 1908, ii, 426), washed with hot water and alcohol, and finally dried at 105°.  
J. S. C.

**Determination of Nitrogen by Kjeldahl's Method; an Attempt at Generalisation and One Source of Error.** P. FLEURY and H. LEVALTIER (*Bull. Soc. chim.*, 1925, [iv], **37**, 330—335).—In the determination of nitrogen by the Kjeldahl-Gunning method, using potassium sulphate, some nitrogen is always lost as such (70% in the case of phenylhydrazine) and some is lost in another, unknown form (about 28% with piperidine). Carbon monoxide is always produced, so that the mechanism of the reaction

must involve mainly a process of reduction (cf. A., 1924, ii, 273; this vol., ii, 66). S. K. T.

**Preparation of Nessler's Solution.** R. C. FREDERICK (*Analyst*, 1925, 50, 183).—Increasing age does not increase the sensitiveness of Nessler's solution, and the maximum effect following from sensitising the reagent by means of saturated mercuric chloride solution lasts only for 2 hrs. D. G. H.

**Determination of Phosphoric Acid in Metabolic Investigations.** C. SCHMITT-KRAHMER.—(See i, 613.)

**Qualitative Microanalysis. II.** F. FEIGL (*Mikrochem.*, 1924, 2, 186—188).—Addition of ammonium molybdate followed by a strongly acid solution of stannous chloride to a hydrochloric acid solution containing phosphoric acid, but free from arsenic acid, produces a brown to yellow colour, and on shaking the mixture with amyl alcohol the latter is coloured blue if only 1 part of phosphoric acid is present in 1,250,000 parts of solution.

Magnesium salts, when boiled with alcoholic potassium hydroxide and diphenylcarbazide, yield a red precipitate insoluble in hot water; to detect traces of magnesium, the solution must be filtered and the paper washed with hot water to remove the soluble potassium salt.

Bismuth nitrate solutions yield characteristic orange-yellow, crystalline precipitates with pyrogallol and tribromopyrogallol; lead does not interfere in the test.

Barium and strontium salts give red precipitates with sodium rhodizonate in neutral solution; the strontium compound is readily soluble in 1% hydrochloric acid, whilst the barium compound is turned scarlet by the acid. By converting the barium into chromate before testing with the reagent, strontium may be detected in presence of barium. [Cf. B., 1925, 340.] A. R. P.

**Double-reacting Turmeric Paper.** W. BRINSMAID (*Ind. Eng. Chem.*, 1925, 17, 264).—When the paper is prepared as described, the effect of boric acid is, as usual, to change the colour to pink or cherry-red, but a confirmatory reaction is now possible, in that this colour is turned to a clear blue by the action of 0.1N-sodium hydroxide. [Cf. B., 1925, 342.] W. A. S.

**Volumetric Determination of Small Quantities of Carbon in Tungsten.** W. J. KING (*J. Amer. Chem. Soc.*, 1925, 47, 615—621).—The method depends on the combustion of tungsten in pure oxygen, passage of the products of combustion into a special absorption apparatus containing hot 0.01N-barium hydroxide solution, and titration of the cold, filtered solution with 0.01N-hydrochloric acid, using thymolphthalein as indicator. The special absorption apparatus provides for the complete absorption of carbon dioxide, the precipitation and filtration of barium carbonate in the hot solution, and finally a method of titrating the excess of barium hydroxide without transferring to a second vessel. The addition of 15% of ethyl alcohol and 1%



of barium chloride to the standard 0.01N-solutions is recommended. The combustion furnace is maintained at 700—1000°, and 65° is selected as the most suitable temperature for the barium hydroxide solution from considerations of minimum corrosion of the glass, complete absorption of carbon dioxide, and coagulation of the precipitated barium carbonate. J. S. C.

**Determination of Carbon in Organic Substances.** A. DESGREZ and R. VIVARIO (*Compt. rend.*, 1925, 180, 886—890).—By the action of a large excess of potassium dichromate and sulphuric acid, the carbon of organic matter is oxidised to carbon dioxide, which is absorbed by weighed potassium hydroxide; before absorption, the vapours are passed over potassium ferrocyanide and borax to remove the volatile chlorine and nitrogen derivatives, and then over heated cupric oxide to complete the oxidation. The method is recommended for the determination of carbon in blood. [Cf. *B.*, 1925, 342.] F. M. H.

**Conditions for Applying the Argentosulphochromic Method in Determining Carbon.** L. J. SIMON (*Compt. rend.*, 1924, 179, 975—977; cf. *A.*, 1924, ii, 567, and previous abstracts).—The determining factors in the sulphochromic oxidation of organic compounds are the relative quantity of silver dichromate and the time of heating. Experiments with benzaldehyde, salicylaldehyde, and cinnamaldehyde show that if one of these factors is changed, the other varies in the opposite sense. The author recommends the use of 4.0 g. of silver dichromate for each 0.2 g. of the substance to be oxidised and heating for 30 mins. at 100° or 12.0 g. and 4 mins., but recognises that the method is empirical. H. J. E.

**Absorption of Carbon Monoxide. I. Critical Comparison of some Methods Employed in Gas Analysis.** H. R. AMBLER. **II. Advantages of Using Hot Reagent.** T. C. SUTTON and H. R. AMBLER (*Analyst*, 1925, 50, 167—174).—Acid cuprous chloride solution was not satisfactory but ammoniacal cuprous chloride solution effected complete absorption of carbon monoxide, provided that it had not previously absorbed more than 5% of its volume of the gas. Cuprous oxide in sulphuric acid containing  $\beta$ -naphthol also brought about complete absorption, but at a slower rate. The time may, however, be reduced to 3 mins. by using the solution at a temperature of about 60°. [Cf. *B.*, May 29th.] D. G. H.

**Separation and Determination of the Alkali Metals, using Perchloric Acid. I. Solubilities of the Perchlorates of the Alkali Metals in Mixed Organic Solvents.** G. F. SMITH (*J. Amer. Chem. Soc.*, 1925, 47, 762—769).—The solubilities of sodium, potassium, rubidium, caesium, and ammonium perchlorates, sodium perchlorate monohydrate, and lithium perchlorate trihydrate have been determined in various mixtures of methyl, ethyl, and *n*-butyl

alcohol with ethyl acetate. The salts fall into two groups, the readily soluble sodium, lithium, and ammonium salts, and the sparingly soluble potassium, rubidium, and caesium salts. The solubility data are discussed from the point of view of the separation and determination of the alkali metals, and it is shown that the use of mixed solvents has many advantages over that of individual solvents (A., 1923, ii, 239). J. S. C.

**Separation and Determination of the Alkali Metals Using Perchloric Acid. II. Precise Determination of the Insoluble Alkali Metal Perchlorates.** G. F. SMITH and J. F. ROSS (*J. Amer. Chem. Soc.*, 1925, 47, 774—781; cf. preceding abstract).—The alkali chlorides, free from ammonium salts, are evaporated with perchloric acid and then taken twice to dryness on the hot plate. The soluble sodium or lithium salts are removed by extraction with one of the mixed solvents previously studied. The insoluble potassium, rubidium, or caesium perchlorate is dried to constant weight at 350°. The evaporation of the chlorides with excess of perchloric acid results in the concentration of the latter to 72.5%, in which the perchlorates are freely soluble. Photomicrographs show that the perchlorates crystallise from such solutions in long, tubular crystals, in the hollow parts of which mother-liquor is frequently enclosed. The extent of acid occlusion is usually very small. Previous methods for the perchlorate separation are shown to have appeared exact as the result of a fortuitous compensation of errors. J. S. C.

**Determination of Potassium in Potassium Salts as Perchlorate.** A. VÜRTHEIM (*Chem. Weekblad*, 1925, 22, 138—140).—With suitable precautions, the method yields very accurate results. Potassium perchlorate is insoluble in 96% alcohol containing 3 c.c. of 50% perchloric acid per litre; the minimum quantity of neutral 96% alcohol must be used for the final wash-liquid, since if neutral alcohol saturated with the perchlorate be used the results are too high. Barium perchlorate is very soluble in 96% alcohol containing the above quantity of perchloric acid; 40 c.c. dissolve 28 g. Even in presence of other salts, the results are accurate if sulphates be carefully removed. S. I. L.

**Reaction for Magnesium and Calcium and for Rubidium and Caesium.** E. MURMANN (*Oesterr. Chem.-Ztg.*, 1925, 28, 42—44; cf. A., 1924, i, 20).—The caesium magnesium ferrocyanide precipitate is a fine white powder, practically insoluble in water; it is a mixture of composition approximately corresponding with the formula  $\text{Cs}_3\text{Mg}_2\text{Fe}_2(\text{CN})_{12}\cdot 4\text{H}_2\text{O}$ . The sensitiveness for varying proportions of the reagents is given. S. I. L.

**Separation of Small Quantities of Calcium from Large Amounts of Magnesium.** R. HEILINGÖTTER (*Chem.-Ztg.*, 1925, 49, 241).—For the determination of less than 5% of calcium oxide in commercial magnesites, the method of Dede (A., 1912, ii, 491) gives sufficiently accurate results in a shorter time than that of

Rodt and Kindscher (this vol., ii, 158), but no comparative figures of the two methods are given. A. R. P.

**Oxalate Separation of Calcium and Magnesium.** G. LUFF (*Z. anal. Chem.*, 1925, 65, 439—448).—The presence of ammonium chloride and too great an excess of ammonium oxalate tends to cause co-precipitation of magnesium from solutions containing much magnesium in the presence of little calcium. In the absence of ammonium chloride and by using only a very slight excess of ammonium oxalate and digesting the liquid for 1—2 hrs. on the water-bath, good separations of calcium from relatively large amounts of magnesium may be effected in one operation. In the usual course of analysis, the solution from which the calcium is to be precipitated generally contains a quantity of ammonium chloride; in such cases, the boiling, slightly ammoniacal solution is treated drop by drop with a saturated ammonium oxalate solution from a burette until a drop of the clear liquor shows the presence of an excess of the reagent in a spot test with calcium nitrate solution. The precipitate is collected after digestion for 1 hr. on the water-bath. From acetic acid solutions, considerable co-precipitation of magnesium takes place, even under the most carefully controlled conditions. A. R. P.

**Fractional Crystallisation of Radioactive Substances.** W. CHLOPIN (*Z. anorg. Chem.*, 1925, 143, 97—117; cf. A., 1924, ii, 42).—The fractional crystallisation of barium-radium salts by evaporation of the solution can be successfully replaced by fractional precipitation of the given solution by increasing the concentration of the anion. Acids or salts which contain the same anion as the barium-radium salt, and form no double or complex compounds with this, may be used. Precipitants which favour hydrate formation are of special value. It is found that the "coefficient of enrichment" is approximately only dependent on the relative mass of the precipitated barium salt in the case of chlorides, bromides, and nitrates. The fractional precipitation of the chlorides by means of hydrochloric acid has been utilised for the separation of radium from barium on the large scale. The fractional crystallisation or precipitation of the nitrates leads to a concentration of radium in the solid phase, and thus to a gradual separation of radium from barium. The distribution of radium between solid and liquid phases follows approximately the Nernst-Berthelot distribution law. The value of the "coefficient of enrichment" is different according as the fractionation is brought about by partial precipitation or by partial crystallisation of the barium-radium salt. L. L. B.

**Volumetric Determination of Zinc.** E. BEYNE (*Bull. Soc. chim. Belg.*, 1925, 34, 38—41; cf. this vol., ii, 69).—In the Schaffner method (for which the author suggests the unambiguous name "Vieille-Montagne" method), a small error is involved in the incomplete separation of zinc with iron, aluminium, and manganese hydroxides by ammonia in the presence of ammonium salts. [Cf. *B.*, 1925, 246.] J. W. B.

**Separation of Zinc and Nickel by Hydrogen Sulphide.** A. KLING and [MME.] A. LASSIEUR (*Compt. rend.*, 1925, **180**, 517—519).—The  $p_H$  values necessary for the precipitation of zinc and nickel by hydrogen sulphide are determined with a view to obtain a satisfactory separation of these two metals by this reagent. In the case of nickel, when hydrogen sulphide is passed for 45 mins., the minimum  $p_H$  value is 2.80, whilst the corresponding value for the quantitative precipitation of zinc is 2.4, and thus separation is not possible in a short time. If the gas be passed for 1 hr. and the solution left for a further 12 hrs., nickel is precipitated from solutions with  $p_H > 2.0$ , whilst zinc requires  $p_H$  1.35 for complete precipitation; again, the margin is too small to allow the separation to be trustworthy. The presence of ammonium sulphate does not affect the precipitation of nickel, but in the case of zinc the presence of this salt (10 g. per litre) causes precipitation to commence at  $p_H$  1.0, and to be quantitative at  $p_H$  2.4. J. W. B.

**Electroanalytical Determination of Cadmium in Sulphuric Acid Solutions.** E. BÜTTGENBACH (*Z. anal. Chem.*, 1925, **65**, 452—455).—Cadmium may be deposited electrolytically on a stationary cathode from a solution containing 6 g. of potassium hydrogen sulphate in 200 c.c. by the use of a rotating anode and an *E.M.F.* of 3.8 volts. With small amounts of cadmium a cadmium-plated cathode should be used with a stationary anode.  
A. R. P.

**Separation of the Rare-earths by Basic Precipitation.**  
**VIII. Preparation of Pure Yttrium Oxide.** W. PRANDTL (*Z. anorg. Chem.*, 1925, **143**, 277—284).—The solubilities of yttrium oxide in *N*-, 2*N*-, 3*N*-, 4*N*-, and 5*N*-ammonium nitrate solutions, at temperatures up to 100°, alone and in presence of zinc and cadmium nitrates, are recorded. In absence of heavy metals, the solubilities are lower (one-third to one-half) than the solubilities of samaria, the weakest base of the ceria group. The presence of cadmium nitrate raises the solubilities considerably, that of zinc nitrate much more; in this, yttria behaves differently from the ceria earths, the solubilities of which in ammonium nitrate solutions are greater in presence of cadmium nitrate than of zinc nitrate. Yttrium is readily concentrated by taking advantage of these solubility differences; of three crude yttrium fractions obtained by this fractional basic precipitation, the most basic was further treated by bromate fractionation; yttrium from the most soluble fractions contained only a trace of holmium and gave an atomic weight 89.09. The middle and least basic fractions were treated by bromate fractionation, followed again by basic precipitation fractionation; the yttrium so obtained had an atomic weight 88.95, and its *X*-ray spectrum gave no rare-earth lines other than those of that element. The last traces of erbium in this yttrium were removed by the ferrocyanide method; the final product showed no absorption lines in a thickness of 20 cm. of the concentrated nitrate solution. The ferrocyanide precipitation is carried out in presence of ammonia or zinc nitrate to assist

filtration; the precipitate is dried and ignited, the residue extracted with nitric acid, and the earths precipitated as oxalates.

S. I. L.

**Goppelsroeder's Reaction for Aluminium and its Application in Microchemistry.** E. SCHANTL (*Mikrochem.*, 1924, 2, 174—185).—Aluminium salts in neutral solution yield a characteristic green fluorescence with alcoholic solutions of morin (tetrahydroxyflavonol) due to the formation of the neutral salt  $\text{Al}(\text{C}_{15}\text{H}_9\text{O}_7)_3$ . Mineral and organic acids, except acetic, reduce the sensitivity appreciably. If the test is carried out in a dark room and the solution viewed through a Tswett's luminoscope (*Z. physikal. Chem.*, 36, 450), as little as 0.0000001 mg. of aluminium in 10 c.c. of solution is readily detected; the method is therefore as delicate as the spectrographic test. Iron and chromium salts give dark-coloured, colloidal precipitates with the reagent, but these may be separated by filtration through a filter-candle and the filtrate tested for fluorescence in the luminoscope. Manganese, cobalt, nickel, and zinc salts do not interfere. Morinsulphonic acid, which is readily soluble in water, may be used in place of morin itself without appreciably affecting the sensitivity of the test and, in this case, the presence of mineral acids has a much less marked inhibiting power on the development of the fluorescence.

A. R. P.

**Determination of Large Quantities of Manganese by Titration with Permonophosphoric Acid.** T. HECZKO (*Z. anorg. Chem.*, 1925, 143, 129—142).—By the action of permonophosphoric acid, prepared from phosphoric acid, phosphorus pentoxide, and hydrogen peroxide, in acid solution on manganese salts, a stable complex compound of tervalent manganese is obtained in solution. After complete oxidation of the manganese, the excess of the oxidising agent decomposes in a short time. Iodometric titration is employed. [Cf. *B.*, May 29th.]

L. L. B.

**Certain and Exact Establishment of the End-point in the Titration of Manganese.** O. HACKL (*Chem.-Ztg.*, 1925, 49, 257).—In the titration of manganese by Volhard's method, the end-point is often masked, especially if much iron is present, by the presence of finely-divided suspended particles which do not settle well. In these cases, a portion of the solution should be filtered by suction through an asbestos filter and the colour of the filtrate compared with a standard made by tinting with 0.1 c.c. of permanganate a volume of water equal to the volume of the solution being titrated. If the end-point is not yet reached, the filtrate is returned to the main solution and the process repeated. Before use, the asbestos should be ignited, then washed successively with hydrochloric acid, water, dilute permanganate, and water again to ensure the absence of reducing compounds.

A. R. P.

**Reaction between Potassium Permanganate and Hydrogen Peroxide in Presence of Ammonium Sulphate.** N. A. TANANAEV (*Z. anorg. Chem.*, 1925, 143, 118—124).—Potassium

permanganate is reduced by hydrogen peroxide in the presence of ammonium sulphate:  $2\text{KMnO}_4 + 3(\text{NH}_4)_2\text{SO}_4 + 5\text{H}_2\text{O}_2 = \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 8\text{H}_2\text{O} + 5\text{O}_2 + 6\text{NH}_3$ . The ammonia set free can be determined with standard sulphuric acid, and the titre of the permanganate thus calculated. For an exact determination of the end-point of the reaction the use of methyl-red is recommended.

L. L. B.

**General Application of the Alloxantin Reaction for Ferric Iron.** G. DENIGÈS (*Compt. rend.*, 1925, 180, 519—520).—The blue colour produced by the action of ferric salts on alloxantin in alkaline solutions serves as a sensitive test for ferric iron and as a means for its colorimetric determination. The reagent consists of 0.1 g. of alloxantin dissolved in 10 c.c. of *N*-sodium hydroxide solution (if rose-coloured the solution is first boiled to destroy the colour and rapidly cooled). A distinct blue colour is developed on adding 1 c.c. to 2 c.c. of a solution containing 0.001 g. of ferric iron per litre. By using five times these quantities and examining the colour through a long column, a few tenths of 1 mg. per litre can be detected. The presence of tartaric and citric acids, which prevents the use of salicylic, thiocyanic, and even Prussian-blue tests, seems favourable to the alloxantin reaction.

J. W. B.

**Electrometric Titrations. Use of Titanous Chloride for Ore Analysis.** A. McMILLAN and W. C. FERGUSON (*J. Soc. Chem. Ind.*, 1925, 44, 141—142T).—In the analysis of iron ore, ferrous iron is oxidised with bromine; manganese is determined by oxidising the solution of the ore with ammonium persulphate, adding ammonia in excess, dissolving the precipitate containing manganese dioxide in the least possible quantity of acid ferrous ammonium sulphate solution, and determining the amount of iron oxidised by electrometric titration. The results agree with those obtained by more tedious methods.

F. B.

**Separation of Nickel and Iron in Presence of Chromium by Electrolysis.** E. ROUSSEAU (*Chim. et Ind.*, 1925, 13, 199—201).—The electrolytic deposition of nickel from an alkaline solution of its salts is prevented, in presence of chromium, by the simultaneous formation of ammonium chromate. This can be avoided by the addition of ammonium oxalate to the solution before electrolysis together with ammonium citrate to retain iron in solution. With this and other precautions, the electrolytic method is accurate when applied to the analysis of chromium alloys or their solutions. [Cf. *B.*, 1925, 341.]

C. I.

**Determination of Thorium-X.** F. GAZZONI (*Compt. rend.*, 1924, 179, 963—965).—The precipitating reagent used for other substances which may be present is either hydrogen peroxide or ammonia; both leave the thorium-X in solution but accompanied in the former case by its active deposit. The thorium-X is in part carried down by the precipitate and four or five precipitations are necessary to effect a good separation; this is more difficult when using hydrogen peroxide. The vessels containing the original

mixture and the thorium-X, evaporated to dryness, are compared in an ionisation chamber protected by lead. The results obtained for the thorium-X are modified by the factor 0.88, which is calculated from the increase and subsequent decrease of the radiation from the separated product, which attains a maximum after 2.50 days.  
H. J. E.

**Germanium. X. Determination of Germanium.** E. B. JOHNSON and L. M. DENNIS (*J. Amer. Chem. Soc.*, 1925, **47**, 790—793).—The metal is precipitated from acid solutions as the disulphide, the precipitate dissolved in ammonia, oxidised with 3% hydrogen peroxide, and weighed as the dioxide.  
J. S. C.

**Diphenylamine as Indicator in the Reduction of Vanadic Acid.** N. H. FURMAN (*Ind. Eng. Chem.*, 1925, **17**, 314—316).—In titrating vanadic acid with ferrous sulphate, diphenylamine can be used as indicator, as in the analogous determination of chromic acid (cf. Knop, A., 1924, ii, 351). A small correction must be made for the vanadic acid consumed in oxidising the diphenylamine to the blue compound that actually serves as indicator. Vanadium in ores and steels may be determined by Willard and Fenwick's methods (A., 1923, ii, 187) using this indicator.  
W. A. S.

**Use of Pyrogallol in the Gravimetric Determination of Bismuth and its Separation from Lead.** F. FEIGL and H. ORDELT (*Z. anal. Chem.*, 1925, **65**, 448—451).—The solution of the two metals as nitrates is treated with ammonia until a faint turbidity is produced, heated to boiling, and treated with a slight excess of pyrogallol. The heavy, yellow, crystalline precipitate having the composition  $C_6H_3O_3Bi$  is collected on a Gooch crucible, washed with very dilute nitric acid, then with cold water, dried at 110°, and weighed; it contains 62.84% Bi. The lead is recovered from the filtrate by saturation with hydrogen sulphide and is converted into sulphate for weighing.  
A. R. P.

**Electrometric Titration of Bismuth alone and together with Lead.** E. ZINTL and A. RAUCH (*Z. anorg. Chem.*, 1924, **139**, 397—410).—Bismuth solutions can be readily titrated by reduction from the tervalent condition to metal by means of titanous chloride solution, the end-point being determined electrometrically in the usual way. The best results are obtained in 3% hydrochloric acid or in acetic acid solution, the precipitation of basic bismuth chloride being prevented by the addition of sodium chloride, and titanous acid by the addition of tartaric acid. Sulphates are without influence, but nitrates must be absent. The operation can be carried out in the same way in the presence of lead. Owing to the ease of oxidation of the finely-divided bismuth, the titration must be carried out in an inert atmosphere.  
H. T.

**Precipitation of Tantalum and Niobium by "Cupferron" and their Separation from Iron.** H. PIED (*Compt. rend.*, 1924, **179**, 897—899).—The method of Weiss and Landecker (A., 1909, ii, 942) for separation of iron may be used in the case of

tantalum and niobium by dissolving the freshly-precipitated hydroxides in oxalic acid and adding tartaric acid to the solution. It is then boiled and the iron precipitated as sulphide in the manner recommended (*loc. cit.*). The precipitate is filtered off, the filtrate acidified with sulphuric acid, boiled, and again filtered. When quite cold, the filtrate is shaken vigorously with "cupferron," the end of the reaction being indicated by the appearance of a white film at the surface of the liquid. The precipitate, which contains all the tantalum and niobium, also titanium if present, is filtered off, washed with water containing a little sulphuric acid, dried, and calcined. This method as compared with that of Thornton (A., 1914, ii, 583) gives a more complete separation, and does not necessitate prolonged boiling. H. J. E.

**Determination of Palladium.** H. E. ZSCHIEGNER (*Ind. Eng. Chem.*, 1925, 17, 294).—The sample, *e.g.*, of technical platinum, is dissolved in aqua regia and evaporated to dryness; the chlorides obtained are dissolved in water and treated at 80° with sodium nitrite in excess. The cooled solution is made just alkaline with sodium carbonate; gold, silver, and base metals are so precipitated. The palladium in the cold filtrate is now precipitated as the compound with dimethylglyoxime. [Cf. B., 1925, 341.] W. A. S.

**Ruthenium Pentafluoride. Separation of Platinum and Ruthenium.** O. RUFF and E. VIDIC (*Z. anorg. Chem.*, 1925, 143, 163—182).—A solution containing platinum and ruthenium, when made alkaline with sodium hydroxide solution containing glycerol, boiled, then kept 1 hr. after addition of sodium hydroxide and bromine, and finally warmed, deposits the platinum quantitatively; the ruthenium is precipitated from the filtrate as sulphide. By a modification of the method, fluorine may also be determined. In the preparation of pure ruthenium pentafluoride, the powdered metal, prepared from ruthenium tetroxide, is heated with fluorine at about 280° in an apparatus previously used by Ruff and Tschirch (A., 1913, ii, 416). It is a dark green, transparent mass, m. p. 101°, b. p. 270—275°;  $d^{16.5}$  2.963. It is readily decomposed by water, yielding the tetroxide. Concentrated hydrochloric acid yields first the tetrachloride; on boiling, further evolution of chlorine takes place. Vigorous interaction takes place with chloroform and carbon tetrachloride. L. L. B.

**Determination of Ethyl Alcohol.** A. ASTRUC and RADET (*Ann. Falsif.*, 1925, 195, 165—171).—Small proportions of ethyl alcohol (0.15—0.25 c.c.%) may be accurately determined by oxidation with alkaline permanganate solution. The active oxygen content of the hot alkaline permanganate solution is first determined by addition of excess of oxalic acid, followed by sulphuric acid and titration with permanganate; the process is then repeated on another sample after addition of the alcoholic liquid. [Cf. B., May 29th.] D. G. H.

**Cinchonine as a Tannin Precipitant, with Special Reference to the Analysis of Cutch and Gambier.** D. HOOPER (*Analyst*, 1925, 50, 162—166).—The cinchonine method for the determination



of tannin (Chapman, *J. Inst. Brewing*, 1907, **13**, 646—667; 1909, **15**, 360—374; *J. Soc. Chem. Ind.*, 1908, **27**, 135; 1909, **28**, 619) may be used to differentiate the proportion of catechin and tannin in commercial samples of cutch and gambier, since the catechin is not affected by the addition of cinchonine sulphate whereas it is largely absorbed by hide powder. [Cf. *B.*, May 29th.] D. G. H.

**Use of Mitchell's Ferrous Tartrate Reagent in Qualitative Analysis.** A. H. WARE (*Analyst*, 1925, **50**, 127—130).—A practical method of classifying pyrogallol-tannin substances is based on the colorations formed after either adding acetic acid subsequently to the addition of Mitchell's ferrous tartrate reagent (A., 1923, ii, 188), boiling, and cooling, or making the solution or extract in the presence of acetic acid, cooling, and adding the ferrous tartrate reagent. Gallic acid, the bark and leaves of *Hamamelis virginica*, logwood, bearberry leaves, and commercial cloves give no definite blue or violet colours; certain ellagitannin extractives give colloidal black precipitates or green colorations, whilst a bluish-violet colour is given by commercially pure gallotannic acid, certain galls, divi-divi, valonia, true sumach, etc. Ordinary gallotannin may thus be detected in gallic acid. [Cf. *B.*, 1925, 302.] D. G. H.

**Differentiation of the Naphthols, and Condensation Product of  $\alpha$ -Naphthol with Formaldehyde.** A. ZAMPARO (*Boll. Chim. Farm.*, 1925, **64**, 97—100).—The two naphthols may be differentiated by means of their colour reactions with (i) sulphuric acid in alcoholic solution containing hydrogen peroxide, and (ii) formaldehyde in presence of hydrochloric acid.

The di- $\alpha$ -naphthylmethane obtained by the condensation of  $\alpha$ -naphthol in alcoholic solution with formaldehyde in presence of hydrochloric acid readily undergoes oxidation to  $\alpha$ -naphthyl-naphthylidenemethane (?), which is a red compound turned blue by alkali and may be used as an indicator. [Cf. *B.*, 1925, 278.]

T. H. P.

**Detection and Determination of Small Amounts of  $\alpha$ -Naphthol in  $\beta$ -Naphthol.** T. CALLAN (*J. Soc. Chem. Ind.*, 1925, **44**, 125—127T).—An examination of the sensitiveness of the various tests for  $\alpha$ -naphthol shows that it can be detected when present to the following minimal extents in  $\beta$ -naphthol:—Dan's test (*L'Union pharm.*, 1909, **50**, 1), 5%; Driver's test (*J. Soc. Chem. Ind.*, 1924, **43**, 206T), 1%; Leger's test (A., 1897, ii, 526), 0.5%; a modified B.P. test (cf. *Annalen*, **152**, 281), the Volcy-Boucher test (A., 1908, ii, 990) and the Artzberger test (*Pharm. J.*, 1903, **70**, 89), 0.2%; and the Liebmann and Prochazka tests (A., 1899, ii, 65; 1924, ii, 70), 0.1%. The two last-named methods may also be employed for the determination with the same limiting concentration of not less than 0.1% of  $\alpha$ -naphthol present. L. F. H.

**Determination of the Iodine Number of Cholesterol.** H. DAM (*Biochem. Z.*, 1924, **152**, 101—110).—A comparative investigation of various methods of determining the iodine number of cholesterol. The methods of Hanuš, of Winkler, and the pyridine

sulphate-dibromide method are preferred to those of Hübl, Waller, Wijs, and Obermüller. The most trustworthy is the pyridine sulphate method, the least so those of Obermüller and Wijs—the latter giving values which may vary greatly with the excess of iodine used. J. P.

**Preparation of Fehling's Solution for the Volumetric Determination of Reducing Sugars.** J. H. LANE and L. EYNON (*J. Soc. Chem. Ind.*, 1925, 44, 150—152t).—In the determination of reducing sugars, using the method and tables previously published (A., 1923, ii, 193), a control titration with invert-sugar is desirable, since errors up to 0.7% may be incurred owing to the copper sulphate pentahydrate containing excess of moisture. F. B.

**Volumetric Determination of Invert-sugar by Reduction in Presence of Sucrose.** M. A. H. VAN DEN HOUT, P. A. NEETESON, and E. L. VAN SCHERPENBERG (*Chem. Weekblad*, 1925, 22, 126—132; cf. this vol., ii, 74).—The reduction of cupric compounds in alkaline solution by sucrose reaches a maximum at a concentration of 4 g. of sucrose in 100 c.c. of reaction liquid and then rapidly diminishes; if tartrates are present, the maximum is at 8 g. of sucrose per 100 c.c., and with increasing concentration of sucrose the diminution is very gradual. Theoretical explanations are advanced. This behaviour is altered by the presence of invert-sugar; the cuprous oxide precipitated by a given quantity of invert-sugar in presence of tartrate increases continuously with the amount of sucrose present, the increase being very great at high concentrations of invert-sugar, but in absence of tartrate the effect is reversed; the influence of sucrose in absence of tartrate disappears at a definite concentration of invert-sugar. The methods in use are reviewed in the light of these results, and a procedure is laid down by which a control test, a titration with the sample, which must contain sucrose in specified concentration, and a titration with sucrose free from invert-sugar, are carried out, the results being obtained from tables. S. I. L.

**Determination of Invert-sugar in Presence of Sucrose, and Development of Invert-sugar in Sucrose Solutions.** N. SCHOORL (*Chem. Weekblad*, 1925, 22, 132—134; cf. preceding abstract).—Luff's solution of copper sulphate, citric acid, and sodium hydrogen carbonate is much less readily reduced by sucrose than Fehling's solution; the reduction by sucrose is proportional to the time of boiling and a constant correction may therefore be applied. Using this reagent, the inversion of sucrose in distilled water of  $p_H$  5 observed by van den Hout and others (this vol., ii, 74) could not be confirmed. S. I. L.

**Detection of Small Quantities of Formaldehyde in Cases of Poisoning.** C. GHIGLIOTTO (*Ann. Chim. Analyt.*, 1925, [ii], 7, 39).—Tests for formaldehyde may be applied directly to pieces of stomach wall since the combination formed by the protein material and the formaldehyde retains properties of the latter. D. G. H.

**Gravimetric Determination of the Iodine-Bromine Number.**

L. W. WINKLER (*Pharm. Zentr.*, 1925, 66, 241—244).—A rapid gravimetric method of determining the iodine-bromine number of oils and fats is described (cf. Winkler, A., 1922, ii, 534; Becker, A., 1923, ii, 886; Sabalitschka and Dietrich, A., 1924, ii, 707; Oestermann, B., 1924, 719; Köpke, A., 1925, ii, 246). Bromine dissolved in a mixture of acetic acid and carbon tetrachloride is added to a weighed amount of the material in a shallow dish and the mixture is evaporated to dryness. In some cases one or, in others, two repetitions of this process are necessary. The evaporations are conducted in the dark, and, on the average, 1/15th of the bromine is used for substitution in place of addition. The iodine-bromine value is calculated from the increase in weight of the material. The results obtained in the case of forty oils, fats, waxes, and fatty acids are tabulated. L. F. H.

**Determination of the Acetyl Value of Fats.** E. ANDRÉ

(*Bull. Soc. chim.*, 1925, [iv], 37, 335—339).—The author defines the acetyl value of an oil or fat as the number of mg. of acetic acid taken up in acetylation by 1 g. of the oil. The sample is heated with excess of acetic anhydride and xylene, the distillation of the excess being repeated twice at 175° by the addition of xylene. A control sample is similarly heated with xylene alone, and the difference between the saponification values of the acetylated sample and the control, multiplied by 1.071, gives the true acetyl value of the oil. The values obtained agree with those obtained by the method previously described (A., 1921, ii, 419). R. B.

**Micro-determinations of Acetyl Groups.** K. FREUDENBERG and E. WEBER (*Z. angew. Chem.*, 1925, 38, 280—285).—

The compound is decomposed in absolute alcohol with toluenesulphonic acid, and the ethyl acetate distilled off and determined by hydrolysis and titration; 0.05*N*-solutions of sodium hydroxide and sulphuric acid are employed, the former being standardised with succinic acid. About 20 mg. of the acetyl compound, 0.1 g. of toluenesulphonic acid, and 5 c.c. of absolute alcohol are required. The receiving flask is cooled with ice. If halogens are present, 10—30 mg. of silver toluenesulphonate are added. The apparatus and procedure are described minutely. S. I. L.

**Detection of Methylamine in Presence of Excess of Ammonia.** P. A. VALTON (*J. Chem. Soc.*, 1925, 127, 40—41).

—The solution is treated with 30 c.c. of 2*N*-sodium hydroxide, diluted to 80 c.c., and distilled through a Kjeldahl trap into 10 c.c. of a 0.5% alcoholic solution of chloro-2:4-dinitrobenzene. When the distillate has increased this volume to 20 c.c., distillation is stopped. On keeping for 20 hrs., 2:4-dinitromethylaniline separates, is recrystallised from alcohol, and identified by the method of mixed m. p. No dinitroaniline separates in this time. By this method 0.02 g. of methylamine hydrochloride was detected in the presence of 20 g. of ammonium chloride. L. J. H.

**Determination of Aniline in Aqueous Solutions.** C. M. CARSON (*Ind. Eng. Chem.*, 1925, **17**, 62—63).—Aqueous solutions containing from 0.1 to 2.0% of aniline are titrated with 0.1*N*-sulphuric acid, the best indicators being (in the order named) bromophenol-blue, *p*-dimethylaminoazobenzene, and Congo-red. The end-point is found by comparing the colour with that of a standard solution of aniline which has been exactly neutralised with 0.1*N*-sulphuric acid and contains exactly the same quantity of indicator as is used in the titration. For solutions containing less than 0.1% of aniline, the colorimetric methods are preferable. *o*-Toluidine can be thus determined with fair accuracy, but less favourable results are obtained with *p*-toluidine owing to its small solubility in water.

W. T. K. B.

**Colorimetric Determination of Thiocyanates and Cyanates.** K. C. BAILEY and D. F. H. BAILEY (*Proc. Roy. Irish. Acad.*, 1924, **37**, [B], 1—6).—The method of Spacu (A., 1923, ii, 40) for the detection of copper by formation of the compound  $\text{Cu}(\text{SCN})_2 \cdot (\text{C}_5\text{H}_5\text{N})_2$ , and Werner's application thereof (T., 1923, **123**, 2577) to the detection of cyanates are adapted for the colorimetric determination of thiocyanates and cyanates under comparable conditions. Ammonium cyanate may be determined in the presence of carbamide, but the method fails if disodium hydrogen phosphate, sodium hydrogen tartrate, sodium nitrite, sulphate, or cyanide, or thiocarbamide is present. [Cf. B., 1925, 313.]

D. G. H.

**Determination of the Composition of Phenol Nitration Products.** L. DESVERGNES (*Ann. Chim. Analyt.*, 1925, [ii], 7, 35—38).—After removal of any substances insoluble in 10% sodium carbonate solution at 50°, the amount of bromine absorbed by the mono- and di-nitrophenols is determined by the Callan and Henderson method (A., 1922, ii, 524) and trinitrophenol as nitron picrate. The nitrated product is dissolved in a dilute solution of sodium carbonate, sulphuric acid added in slight excess, and the mixture cooled. Any crystals of dinitrophenol are filtered off, 10% nitron acetate solution is added, and the precipitate of nitron picrate left to form at 0°. [Cf. B., 1925, 199.]

D. G. H.

**Gravimetric Determination of Trinitrophenol and a Mixture of Picric Acid and Trinitrocresol.** L. DESVERGNES (*Ann. Chim. Analyt.*, 1925, [ii], 7, 65—66).—The material may be dissolved in a saturated solution of picric acid of known concentration and either kept for 5 days and the crystals of picric acid collected and weighed, or the total weight of trinitrophenol and trinitro-*m*-cresol determined in the filtered liquid. [Cf. B., 1925, 339.]

D. G. H.

**Micro-determination of Carbamide and Ammonium Salts.** J. GOLSE.—(See i, 609.)

**Determination of Uric Acid in Blood.** F. M. R. BULMER, B. A. EAGLES, and G. HUNTER.—(See i, 605.)

**Grant's Test for Sparteine.** J. F. COUCH (*Amer. J. Pharm.*, 1925, 97, 38—39).—Grant's test for sparteine (A., 1921, ii, 71) is very specific, exciting no response from lupinine, spathulatine, *d*-lupanine, *dl*-lupanine, hydroxylupanine, or nicotine. The test is conveniently modified thus: a strip of filter-paper is moistened with the chloroform extract of the ammoniacal solution of the alkaloid, allowed to dry, exposed to bromine fumes, then to ammonia fumes, and finally warmed, when the characteristic bright pink colour appears. B. F.

**Extraction and Determination of Lipoids in Cereal Products.** O. S. RASK and I. K. PHELPS (*Ind. Eng. Chem.*, 1925, 17, 187—189).—Determination of the fat content of cereal materials by direct extraction with ether yields less than one-half of the lipid or ether-soluble material obtained by the ammoniacal extraction method proposed. [Cf. B., 1925, 224.] D. G. H.

**Determination of the Tyrosine Content of Proteins. III.** O. FÜRTH and A. FISCHER (*Biochem. Z.*, 1924, 154, 1—23).—It is confirmed that the methods previously described (A., 1924, ii, 575) are unsatisfactory for tyrosine determination in protein. The Pierre-Thomas modification of the Millon reaction and the mercuric sulphate and nitrate precipitation methods are also unsuitable. By successive treatment of the sulphuric acid hydrolysates with phosphotungstic acid, quinine sulphate, and sodium hydroxide solutions, a filtrate is obtained in which, after neutralisation, the tyrosine is determined by the Millon colorimetric method. Tyrosine can also be determined by addition of bromine, but this must be regarded only as confirmatory. The hydrolysis of casein and fibrin by trypsin and alkali has been followed, and it is shown that the liberation of tyrosine considerably precedes the complete disintegration of the protein molecule, thus differing from tryptophan (A., 1924, i, 64). P. W. C.

**Colorimetric Determination of Tryptophan and Its Separation from Indole and Skatole.** I. KRAUS (*J. Biol. Chem.*, 1925, 63, 157—178).—The blue condensation product with vanillin given by tryptophan in presence of concentrated hydrochloric acid was used for the colorimetric determination of the amino-acid; interference by indole and skatole could be prevented by preliminary extraction of these substances with toluene. It was not, however, found possible to recover tryptophan quantitatively from the products of the hydrolysis of protein by barium hydroxide or trypsin, nor after incubation of mixtures of the amino-acid with trypsin and the mixed diamino-acids of casein or with trypsin and glucosamine. Pure tryptophan heated on a water-bath for 40 hours with 14% barium hydroxide is destroyed to the extent of 20%; the use of the phenol reagent of Folin and Looney (A., 1922, ii, 539) involves a loss of about 7% of tryptophan. The vanillin method gave a positive test for tryptophan with gelatin and with zein. C. R. H.

## General, Physical, and Inorganic Chemistry.

**Sommerfeld's Theory of Fine Structure [of Spectral Lines] from the Point of View of General Relativity.** M. S. VALLARTA (*J. Math. Phys. Mass. Inst. Tech.*, 1925, 4, 65—83).—A mathematical paper in which it is shown that, keeping in mind the relations between the magnitudes of the electronic mass and charge, on the one hand, and the nuclear mass and charge on the other, it is possible to obtain the relativistic Keplerian conditioned-periodic orbits of Sommerfeld's theory (*Ann. Physik*, 1916, [iv], 51, 53) from considerations of general relativity. For the hydrogen atom and hydrogenic ions, of the type  $\text{He}^+$ ,  $\text{Li}^{++}$ ,  $\text{Be}^{+++}$ , etc., the material field of the nucleus is almost Euclidean and almost static.

J. S. C.

**S-Term.** F. J. VON WIŚNIEWSKI (*Physikal. Z.*, 1925, 26, 255).—The energy level  $E_s$  corresponding with the  $s$ -terms in the arc and spark spectra of elements belonging to the 1st, 2nd, 3rd, and 8th periodic groups can be expressed as:  $-E_s = -Nh/[n + \beta + \sigma_p]^2$ , where  $n=1, 2, 3, 4 \dots$ ,  $\sigma_p$  = the correction in  $p$ -spectral terms,  $\beta$  is a constant differing for different groups but the same for elements in the same vertical row,  $N$  and  $h$  are the Rydberg and Planck constants respectively. Thus  $\sqrt{13.53/V_{\text{ion}}} = n + \beta + \sigma_p$ , where  $V_{\text{ion}}$  is the ionisation potential;  $\sigma_p$  is given by the expression  $2 + \sigma_p = (13.53/V_{\text{ion}} - V_{\text{res}})^{1/2}$ , where  $V_{\text{res}}$  is the resonance potential. The values of  $\beta$  are: 1st group, 0.50; 2nd group arc (a) 0.682, (b) 0.608, spark 0.634; 3rd group, 0.679, 8th [He, Ne]—0.324. Hence  $E_s = -Nh/(n + \sigma_s)^2$ , where  $n=1, 2 \dots$ ,  $\sigma_s$  being the  $s$ -spectral term correction, so that  $\sigma_s = \beta + \sigma_p$ . It follows that  $\sigma_s - \sigma_p = \text{constant}$  for the elements of the same vertical column.

R. A. M.

**Simple Demonstration Screen for Ultra-violet Radiations.** W. STEUBING (*Physikal. Z.*, 1925, 26, 329—331).—For the visual perception of spectral lines in the ultra-violet a thinner layer of fluorescent material than the usual uranium glass is desirable. A suitable screen is made as follows: on a desilverised photographic plate, of which the edges have just been allowed to dry out, finely-powdered ammonium uranyl fluoride is uniformly sprinkled from a lawn sieve. The powder is rubbed into the damp gelatin, which on drying assumes a fine-grained matt aspect.

W. A. C.

**Hydrogen Balmer Series.** L. JANICKI (*Ann. Physik*, 1925, [iv], 76, 561—566).—Shrum's measurements of the fine structure of the hydrogen lines (A., 1924, ii, 282) require correction for errors arising from physiological and photographic effects, which lead to too high values for the doublet separations. Values smaller and more probable than Shrum's were obtained by an objective photometric examination of the reproductions of Shrum's photographs

by the Koch-Gooschen recording photometer. The most probable values for the separation of the  $\alpha$ ,  $\beta$ , and  $\gamma$  lines are 0.130, 0.076, and 0.060 Å., respectively.  
F. G. T.

**Spectroheliograms with Different Parts of the  $H_\alpha$  Line.** T. ROYDS (*Month. Not. Roy. Astr. Soc.*, 1925, **85**, 464—466).—Spectroheliograms obtained when a slit of about 0.5 Å. width is set on either the red or violet edge of the  $H_\alpha$  line show a bright spot ring, often complete and unbroken, round nearly all sunspots of medium size. At the same time, dark flocculi are produced outside the bright ring, where the  $H_\alpha$  line is wider than normal. A less striking feature is a bright surround intervening between the dark flocculus and the coarse network of the general body of the sun.  
F. G. T.

**Intensities in the Many-lined Spectrum of Hydrogen.** G. H. DIECKE (*Z. Physik*, 1925, **32**, 180—185).—The intensities of the lines and their grouping are discussed, particularly with regard to the effect of temperature and pressure on the relative intensities.  
E. B. L.

**Variations in the Structure of the Lithium Red Line 6708 Å.** D. S. AINSLIE (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 137—143).—Using both a glass Lummer plate and a 30-plate echelon grating as resolving instruments, the fine structure of the red lithium line, 6708, has been investigated. Several photographs were taken using various lithium compounds and metallic lithium in the vacuum arc. With a current of 4—6 amp., a simple doublet is obtained. With currents of 7 amp., both components appear as double, giving a close quadruplet pattern. This pattern is easily changed into a triplet, the components of which vary considerably in relative intensity. The measured separations between the components are given for various current-strengths and lithium salts. The suggestion that each lithium isotope gives rise to a pair of lines in the quadruplet (A., 1922, ii, 541) must be modified. The absorption spectrum of lithium vapour shows 12 bands between 3966 and 3387.  
J. S. C.

**Ground Term of the Neon Spectrum.** S. GOUDSMIT (*Z. Physik*, 1925, **32**, 111—112).—Reasons are given for concluding that the ground term is simple, with the quantum numbers  $k=2$  and  $J=\frac{1}{2}$ .  
E. B. L.

**Low-voltage Arcs in Sodium and Potassium Vapours.** F. H. NEWMAN (*Phil. Mag.*, 1925, [vi], **49**, 1057—1064).—Details are given of the construction of a tube for producing low-voltage arcs in metallic vapours. The potentials necessary to strike and maintain arcs in sodium and potassium vapours depend primarily on the density of the vapour and temperature of the cathode, the potentials decreasing as these increase. At a very high cathode filament temperature, an arc, struck at 3.8 volts, may be maintained at 2.8 volts in sodium vapour at 450°. Slightly higher voltages are necessary for potassium, and the arcs are less steady. The differ-

ence between the striking and maintenance voltages becomes less as the density of the vapour decreases. With intensely hot cathodes arcs may be struck and maintained with potentials less than the ionising potentials of the vapours. The ionisation in these cases probably arises through the absorption of radiation emitted from atoms already excited, but not ionised. This ionisation by photo-impact (*Physical Rev.*, 1922, [ii], 20, 296) results in complete ionisation of the vapour atoms by electrons, none of which has a velocity greater than that corresponding with the resonance potential.

F. G. T.

**Arc Spectrum of Sodium.** F. J. VON WIŚNIEWSKI (*Physikal. Z.*, 1924, 25, 480—482).—A mathematical theory of the arc spectrum based on an analogy between the structure of a neutral sodium atom and that of a doubly-ionised aluminium atom. The analogy is extended to the structure of the neon atom, and on the basis of theory the difference between the ionisation potential (21.5 volts) and the second excitation potential (18.45 volts) is calculated to be  $-2.98$  volts whilst the observed value is  $-3.05$  volts. R. W. L.

**Extreme Ultra-violet Spectra of the Alkali Metals.** W. W. SHAVER (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 23—34).—The spectra of the electrodeless discharge in the vapours of sodium, potassium, rubidium, and caesium have been investigated using a fluoride spectrograph, the frequencies and wave-lengths of the lines being recorded. The results with sodium were negative in character, but it is thought that at a higher temperature a second spectrum would appear corresponding with the many-lined spectra of the other metals. The spectra of the electrodeless discharge in the vapours of rubidium and caesium were investigated in the region between 1850 and 2300 Å. and a number of lines in addition to those discovered by Dunoyer (*A.*, 1922, ii, 729) were obtained. A number of frequencies in the potassium spectrum agreed with values predicted from energy levels calculated by Nissen (*A.*, 1923, ii, 671) for the singly-ionised potassium atom.

J. S. C.

**Double Excitation Spectra of Magnesium and Related Elements.** J. B. GREEN and M. PETERSEN (*Astrophys. J.*, 1924, 60, 301—312).—The occurrence of the  $pp'$  group of five strong lines at about 2780 Å. in the spectrum of magnesium is not correlated with the strength of the spark spectrum; thus the origin of the  $p'$  terms cannot be related to the ionised state of the atom. The  $p'$  and  $d'$  terms of magnesium and the alkaline earths are proposed as designating doubly excited states of the neutral atoms independent of metastable ionised states.

A. A. E.

**Theory of the Spark Spectra of Aluminium.** F. J. VON WIŚNIEWSKI (*Physikal. Z.*, 1924, 25, 477—480).—The arguments concerning the atomic structure of helium and lithium (*A.*, 1924, ii, 361, 637) are now applied to a deduction of a theory of the core structure of doubly-ionised aluminium atoms.

R. W. L.



**Series, Ultra-violet, and Infra-red Spectra of Silicon.** J. C. McLENNAN and W. W. SHAVER (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 1—22).—The wave-lengths and frequencies of 50 new lines in the extreme ultra-violet spectrum of the silicon vacuum spark in the region between 2000 and 458 Å. are recorded; 21 lines belonging to the Si IV series spectra as worked out by Fowler (A., 1923, ii, 447) were recorded on the vacuum spark spectrogram. The spectrum of the silicon arc and spark in air have been investigated with a quartz spectrograph and a large number of new lines between 2300 and 1842 obtained. The vacuum arc spectrum was studied, using a fluorite spectrograph, in the region between 1850 and 1500. In an examination of the Si I spectrum for series relations a scheme of constant frequency differences has been worked out and energy levels accounting for a number of the lines have been calculated. Thirty-three wave-lengths in the hitherto unstudied infra-red spectrum were observed and measured in the region 6300—11235 Å. J. S. C.

**Spectrum of Silicon at Successive Stages of Ionisation.** A. FOWLER (*Phil. Trans.*, 1925, **A**, **225**, 1—48).—Lines in the spectrum fall into four groups, Si I = neutral atoms, Si II or Si<sup>+</sup> = singly-ionised atoms, Si III or Si<sup>++</sup> = doubly-ionised atoms, Si IV or Si<sup>+++</sup> = trebly-ionised atoms. In these classes, the series constant changes from Rydberg's  $R$  to  $4R$ ,  $9R$ ,  $16R$ , and the series systems consist alternately of triplets and doublets in accordance with the displacement law of Kossel and Sommerfeld. Notation is reviewed and the various series are dealt with in detail, a catalogue of wave-lengths is given, with plates showing photographs of the progressive spectra. E. B. L.

**Low-voltage Arcs in Phosphorus Vapour.** O. S. DUFFEN-DACK and H. HUTHSTEINER (*Physical Rev.*, 1925, [ii], **25**, 501—508).—The minimum arcing potential for phosphorus vapour is 10.3 volts, which is regarded as the ionising potential of the phosphorus atom. The low-voltage arc spectrum contains arc lines and bands. A. A. E.

**Continuous Spectra of the Halogens.** W. STEUBING (*Z. Physik*, 1925, **32**, 159—162).—As considerable doubt has recently been thrown on the interpretation of the continuous spectrum of iodine and the other halogens as due to the acquisition of an electron by a neutral atom (electron affinity spectrum), it is suggested that the peculiarities are due to instability in the outer shell of electrons. E. B. L.

**Intensities in the Argon Spectrum.** P. LOWE and D. C. ROSE (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 313—323).—Fifty-one lines in the argon spectrum were identified and measured. Quantitative measurements of intensities show that the red spectrum may be divided into two groups: (I) lines showing no maximum intensity at any voltage, which after 40 volts are sensibly constant; (II) those which have a maximum intensity at 27 volts and decrease continually. The lines of the blue spectrum are listed in a third

group, the more intense of which appear at 39 volts, others appearing and increasing in intensity as the applied voltage is increased, reaching a maximum at 65 volts.

J. S. C.

**Absorption Spectrum of Potassium Vapour at High Temperatures.** N. K. SUR and R. N. GHOSH (*Phil. Mag.*, 1925, [vi], 49, 60—64).—The absorption spectrum of potassium vapour was investigated at different temperatures. The temperature most suitable for obtaining reversals of lines of the subordinate series is 1300°. Above this, lines were obtained which could not be identified with known potassium lines, or placed in any series relation. Between 500° and 1000° channelled bands were obtained. The line 4641 was obtained and supports the views of Foote, Meggers, and Mohler (A., 1922, ii, 4).

C. W. B.

**Extreme Ultra-violet Spectrum of Germanium and Scandium.** H. J. C. IRETON (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 103—109).—The spark spectrum of germanium has been extended from 2138·7 to 319·7 Å., 64 new lines being recorded. The spark spectrum of scandium has been extended from 2233·7 to 507·0, 45 new lines being observed.

J. S. C.

**Electric Furnace Spectra of Vanadium and Chromium in the Ultra-violet.** A. S. KING (*Astrophys. J.*, 1924, 60, 282—300).—The temperature classification and relative intensities are tabulated for 515 vanadium lines between 2340 and 3185 Å., and for 640 chromium lines between 2362 and 3575 Å., new wave-lengths being ascribed to 133 vanadium lines and 94 chromium lines. Initial temperatures for the appearance of enhanced lines of vanadium and chromium are 2200° and 2600°, respectively.

A. A. E.

**Absorption Spectra of Copper, Silver, and Gold Vapours in the Ultra-violet.** R. V. ZUMSTEIN (*Physical Rev.*, 1925, [ii], 25, 523—526).—The metals were vaporised in a carbon tube by external heating, the absorption spectra being observed without the use of windows. Copper gave lines at 3273·9, 3247, 2225, 2182, 2178·9, 2165, 2024·3, and 2244 Å., silver at 3382, 3280, 2070·0, and 2061·2 Å., and gold at 2675·9 and 2427·9 Å. The component of the doublet having the shorter wave-length is always the stronger, as in the case of the alkali metals. There is also similarity in the increase in the separation of the doublets with increasing atomic weight.

A. A. E.

**Arc Spectra of Silver and Copper.** A. G. SHENSTONE (*Phil. Mag.*, 1925, [vi], 49, 951—962; cf. *Nature*, 1924, 114, 501).—The spectra of un-ionised silver and copper atoms may be obtained by bombarding the vapour of the metals by hot filament electrons, accelerated by the application of low voltages. Measurements of the silver lines confirm the accepted energy levels of that atom. A table is given of the intensities and wave-lengths of copper lines excited by this method. The direct absorption of copper lines by copper vapour was measured, definite absorption occurring in the

case of the lines 2165.06, 2225.665, 2244.24, 2441.625, 2492.142 Å. From these data and from the low-voltage arc lines combinations were calculated for 64 of the lines found.

F. G. T.

**Absorption and Series Spectra of Tin.** J. C. McLENNAN, J. F. T. YOUNG, and A. B. McLAY (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 57—75).—The tin arc spectrum has been re-investigated in the region between 2251 and 1850 Å. and a number of new wave-lengths are recorded. Seventeen new lines have been observed in the absorption spectrum of tin vapour at 1200°. By means of an arc-reversal method in an atmosphere of hydrogen, about 40 new wave-lengths have been added to the tin arc spectrum in the Schumann region. Tables of groups of constant frequency differences are given for the arc spectrum and two possible multiplets of the  $pp'$  type have been found. Six limits in the arc spectrum have been evaluated and the sharp and diffuse subordinate series arising from them built up. The ionisation and resonance potentials are calculated to be 7.3 and 4.3—4.8 volts, respectively.

J. S. C.

**Spectral Series of Lead and Tin.** H. SPONER (*Z. Physik*, 1925, **32**, 19—26).—In the arc spectra of these metals the ground terms are  $p$ -terms with inner quantum numbers 0, 1, 2, 2, and possibly also 0 for lead and 0, 1, 2, 2, 0 for tin. The ground terms in Thorsen's series for lead are  $p_0$ ,  $p_1$ ,  $p_2$ .

E. B. L.

**Determination of the Terms in the Lanthanum Spectrum.** S. GOUDSMIT (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 23—31).—Measurements of the Zeeman effect in certain spectra are insufficient for the application of Landé's rules for the arrangement of the lines (cf. *Z. Physik*, 1923, **15**, 189). Previous measurements by Paulson (*Ann. Physik*, 1914, [iv], **45**, 1203) enabled a number of lines in the lanthanum spectrum to be arranged in a term system, and the inner quantum number,  $J$ , and factor of resolution,  $g$ , could be found for every term. From these data it is usually possible to determine also the quantum numbers  $K$  and  $R$  with the aid of Landé's formulæ, and the term system can also be found. For certain terms in the lanthanum spectrum, however, this has been found to be inapplicable. Tables of spectra are given in illustration of this.

L. L. B.

**Spark Spectrum of Tungsten in a Helium Vacuum Arc.** H. B. LEMON (*Nature*, 1925, **115**, 802).—A hot tungsten cathode used in the operation of an arc at low pressure in helium is capable of developing the spark spectrum of tungsten. The relative intensities of the lines are modified from those given in the standard tables of wave-lengths.

A. A. E.

**Platinum Metals. VII. Arc Spectra of the Platinum Metals (4500—9000 Å.).** W. F. MEGGERS (*U.S. Bur. Standards, Sci. Papers* No. 499, 1925, **20**, 19—45).—Grating measurements were made of the arc spectra of the six platinum metals over the above range. Tables are given of the wave-length and estimated

relative intensity of 1260 lines for ruthenium, 572 for rhodium, 172 for palladium, 942 for osmium, 605 for iridium, and 239 for platinum. These were measured with an accuracy of  $0.01 \text{ \AA.}$ , and include several hundred new lines in the visible and infra-red. Tables are given of lines recorded by earlier observers and here shown to be due to impurities. One or more bands converging to heads toward short waves were found in the spectra of ruthenium, rhodium, osmium, and platinum. In the group VIII metals the general tendency within any triad as well as between triads is for the number of lines to decrease as the atomic number increases.

F. G. T.

**Absorption of the Green Line of Thallium Vapour.** K. R. RAO (*Proc. Roy. Soc.*, 1925, **A**, **107**, 762—765; cf. this vol., ii, 5).—Work on the absorption of 5461 of mercury (cf. Metcalfe and Venkatesachar, A., 1924, ii, 439) suggested a study of the green line 5350 of thallium. The structure of the line was examined, using a glass Lummer-Gehrcke plate of resolving power about 300,000 for 5350, and a Fabry-Perot étalon (thickness of air layer,  $10.016 \text{ mm.}$ ). The source was the radiation from a vacuum tube through which was passed a condenser discharge from an induction coil between thallium electrodes. The main line is a close doublet accompanied by a satellite with separation  $0.116 \text{ \AA.}$ , the existence of the other satellite being shown by the étalon. In the absorption experiments, the column of absorbing vapour was contained at low pressure in a tube 2 ft. long. As the temperature was raised, gradual absorption of the central doublet began at  $600^\circ$  and was complete at  $800^\circ$ ; absorption of the satellite began when that of the main line was complete, and was itself complete at about  $950^\circ$ . This is discussed theoretically. The intensities of the satellites relative to the main line are 0.2 and 0.75 for 0.024 and  $0.116 \text{ \AA.}$ , respectively.

L. L. B.

**Absorption and Series Spectra of Lead.** J. C. McLENNAN, J. F. T. YOUNG, and A. B. McLAY (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, **III**, 77—88).—The Thorsen scheme for the lead arc series (*Naturwiss.*, 1923, 78) and its extension by Grotian (A., 1923, ii, 710) are discussed and converted into vacuum frequencies. The lead arc spectrum has been re-measured in the region 2250—1850  $\text{\AA.}$  and many new lines are recorded. The arc-reversal spectrum of the lead arc in hydrogen has been investigated and 12 new wavelengths were observed. The results are shown to confirm and extend the Thorsen-Grotian arrangement.

J. S. C.

**J-Phenomena and the Quantum Theory of Scattering of X-Radiation.** R. T. DUNBAR (*Phil. Mag.*, 1925, [vi], **49**, 210—236).—Experiments on the relative absorptions of X-rays by copper, aluminium, and paper show that under the stated conditions the J-discontinuities of Barkla and White (*ibid.*, 1917, [vi], **34**, 270) do not appear. Absorption associated with scattering agrees with that calculated on the quantum theory by Compton (*Physical Rev.*, 1923, [ii], **21**, 483). Using the ionisation of sulphur dioxide

and ethyl bromide, evidence was obtained of abnormal corpuscular emission from air. Measured by ionisation of hydrogen, corpuscular emissions from paper, aluminium, copper, and lead show that the lighter elements emit an additional corpuscular radiation for short wave-lengths of incident radiation, the energy required giving no discontinuity in the absorption curve for paper. Compton's theory of the change in quality and intensity of scattered radiation is supported by results with filter-paper, over a considerable range of wave-lengths, for scattering at right angles to the primary. It is deduced that the scattered X-rays carry only a fraction of the energy absorbed in association with scattering. C. W. B.

**J-Transformation of Scattered X-Rays.** C. G. BARKLA and S. R. KHASTGIR (*Phil. Mag.*, 1925, [vi], **49**, 251—256).—Differences between the primary and secondary radiations are described in a previous paper (*Nature*, 1923, **112**, 723). Compared by their power of penetrating thin sheets they appear to be identical, but a big difference is observed with thicker sheets. At a critical thickness, an abrupt absorption of the secondary occurs, and the transmitted radiation is subsequently more readily absorbed than the primary transmitted through the same thickness of absorbing sheet. The experiments show that the transformation in the secondary radiation is not produced by scattering. C. W. B.

**J-Phenomenon in X-Rays.** C. G. BARKLA (*Phil. Mag.*, 1925, [vi], **49**, 1033—1056).—A general account of the *J* absorption discontinuities, supplemented by additional experimental evidence. As the penetrating power of a radiation is increased there occur sudden increases in its absorption by any particular substance. Absorption discontinuities have been observed directly in the cases of carbon, oxygen, aluminium, copper, platinum, and gold, and indirectly in those of nitrogen, sulphur, and lead. They fall into several series,  $J_1$ ,  $J_2$ ,  $J_3$ , and possibly  $J_4$  and  $J_5$ . The increase in absorption is accompanied by the emission of slowly moving electrons from the absorbing substance, producing, when that substance is in a gaseous state, an even more strongly marked discontinuity in ionisation. From experiments quoted, it is concluded that the activity of an X-ray radiation is dependent on factors which have not hitherto been considered, and that alternative absorptions are possible for what are apparently identical radiations. Two levels of activity are definitely, and others probably, indicated. F. G. T.

**Characteristic X-Rays from Light Elements.** (MISS) M. LEVI (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 159—176).—The minimum potential necessary for the excitation of the characteristic radiation was determined experimentally, the wave-length of the radiation being then computed from the quantum relation. The critical *K*- and *L*-absorption limits of lithium, beryllium, boron, and carbon, the critical *L*-absorption limit of fluorine, sodium, silicon, and vanadium, the *L*- and *M*-absorption limits of chlorine, scandium, titanium, and nickel, and the *M*-absorption limits of chromium, manganese, and cobalt have been determined.

J. S. C.

**K-Series of X-Rays.** A. LEIDE (*Compt. rend.*, 1925, **180**, 1203—1204).—Accurate measurements are recorded of  $\alpha_1$  and  $\beta_1$  lines for copper,  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ , and  $\beta_4$  for molybdenum and palladium and, omitting  $\beta_4$ , for silver, cadmium, indium, and tin. The  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_1$ ,  $\beta_2$  lines for all the elements of atomic number 29 (copper) to 53 (iodine) have been measured with the exceptions 36 (krypton) and 43 (unknown). The standard lines chosen were  $\text{CuK}\alpha_1$  1537.29,  $\text{MoK}\alpha_1$  707.80,  $\text{WK}\alpha_1$  208.71. R. A. M.

**K-Series of Heavy Elements.** G. RÉCHOU (*Compt. rend.*, 1925, **180**, 1107—1108).—Wave-lengths of  $\alpha_2$ ,  $\alpha_1$ ,  $\beta$ , and  $\gamma$  lines of *K*-series have been determined with an accuracy of  $0.1 \times 10^{11}$  cm. for the following elements: tantalum, tungsten, osmium, iridium, platinum, gold, thallium, lead, bismuth, and uranium. Experimental difficulties are as yet too great for determinations with mercury and thorium. For tungsten, the values agree with those found by other investigators. Rogers' recent work on platinum is confirmed and de Broglie's values are accurate except for the  $\gamma$  line. R. A. M.

**Dependence of the  $K\alpha$  Doublet with Different Chemical Compounds.** B. B. RAY (*Phil. Mag.*, 1925, [vi], **49**, 168—170).—For chlorine, potassium, vanadium, and iron, the value of  $\Delta\lambda$  for the  $K\alpha$  doublet decreases with increasing valency of the element, in the chemical compounds investigated. Mean values of the distance between the two  $K\alpha$  lines are obtained correct to 1%. C. W. B.

**Absorption Limits of K-Series.** F. J. VON WIŚNIEWSKI (*Z. Physik*, 1924, **28**, 231—235).—The explanation of the *K*-absorption limit which was developed for light atoms in a previous paper (A., 1924, ii, 639) has been extended to heavier elements. The arrangements of the electrons in the *K*-systems of the atoms are deduced on the basis of the theory. S. B.

**L-Absorption Spectra of the Elements from Sn(60) to W(74) and their Relation to Atomic Constitution.** Y. NISHINA (*Phil. Mag.*, 1925, [vi], **49**, 521—537).—The *L*-absorption spectra of all the elements from tin (50) to tungsten (74) are measured. Evidence of fine structure is obtained in the case of the *L*<sub>III</sub> absorption spectra. The values of different energy levels of different atoms are calculated by means of the frequency values of the emission lines. The curves showing the relation between energy levels and atomic number are discussed with special reference to the development of electronic groups due to the appearance, as atomic weights increase, of orbits of new type. C. W. B.

**Semi-optical Lines in the X-Ray Spectra.** E. BÄCKLIN, M. SIEGBAHN, and R. THORÆUS (*Phil. Mag.*, 1925, [vi], **79**, 513—517).—Peculiarities found in the  $K\beta_1$  line of sodium and magnesium are explained by an atomic model proposed by Stoner (this vol., ii, 85). The  $K\beta_1$  line of sodium and magnesium is not a true X-ray line of the *K*-spectrum, since with these elements there is no electron in

the  $M_{II}$  level. The  $K\beta_1$  line is a semi-optical line produced by a transition from a free level of the atom to the  $K$  level. A similar phenomenon is found in the case of the  $K\beta_2$  line for potassium.

C. W. B.

**Semi-optical Lines in the X-Ray Spectra.** L. DE BROGLIE and A. DAUVILLIER (*Phil. Mag.*, 1925, [vi], **49**, 752—753; cf. preceding abstract, also A., 1924, ii, 369).—A claim for priority. The views of the authors on the relations between X-ray lines, the periodic system, and the electronic structure of the elements are illustrated.

R. A. M.

**Absorption of Superposed X-Radiations.** W. H. WATSON (*Proc. Roy. Soc. Edin.*, 1924—5, **45**, 48—58).—Attempts have been made to determine whether the sudden increase in absorption of X-rays, by aluminium, as the rays are hardened and a certain value of the mass-absorption coefficient is reached, is due to some temporary transformation of the aluminium. The influence on the absorption of a second beam of X-rays, when this passes through the affected aluminium at the same time as the original beam, has been studied. No effect of superposition in the first series of experiments was observed, but the results are not conclusive. A second similar series of investigations, suggested by Wilson's photographs of paired  $\beta$ -ray tracks obtained by the passage of X-rays through the air (*Proc. Roy. Soc.*, 1923, **A**, **104**, **1**, 190), gave effects very much smaller than were to be anticipated.

M. S. B.

**Suitability of the Seemann "Edge-method" for Measurements of X-Ray Standards.** A. P. WEBER (*Z. wiss. Phot.*, 1925, **23**, 149—183).—The Seemann "edge-method" is quite suitable for precision measurements, and with other methods, is suitable for use in setting up the planned standard system of X-ray wavelengths. The sources of error in the "edge-method" were fully examined and results compared with results obtained by other methods. This showed that Bragg's method must give a systematic error due to the penetration of the rays in the crystal. The apparatus used was of improved design, giving greater precision, but not suitable for absolute measurements. An instrument for absolute measurements of wave-length has been designed, combining the author's principle of crystal rotation with the arrangement used by Vogel, which is considered to be particularly suitable for absolute measurements.

W. C.

**Energy Levels of X-Ray Spectra of Chemical Elements.** D. COSTER (*Z. Physik*, 1925, **31**, 898—900).—Critical of the conclusions of Walter (*ibid.*, 1924, **30**, 357), who found no irregularities in the energy levels for the iron and palladium groups such as had been suggested as probable by Bohr and Coster (*ibid.*, 1923, **12**, 342).

E. B. L.

**Intensity of Multiplets and their Zeeman Components.** R. DE L. KRONIG (*Z. Physik*, 1925, **31**, 885—897).—The conditions

arising from the application of the principle of correspondence are studied and deductions made which enable the intensities to be calculated in magnetic fields either strong, weak, or vanishingly small. The formula obtained is in agreement with experiment.

E. B. L.

**Glow Electronic Emission at Transition and Melting Points.** A. GOETZ (*Physikal Z.*, 1925, 26, 206—207; cf. *ibid.*, 1923, 24, 377; 1924, 25, 570).—The Richardson emission equation requires a linear relationship between the logarithms of the intensity of electronic glow and of the reciprocal of temperature. The slope of this line is determined by the work of emission, and its position by the number of conducting electrons. A change in the former at a transition or melting point would correspond with a change of direction, and of the latter to a parallel displacement of the intensity-temperature curve. Change of direction, but no displacement, is found at these points. According to the above equation, a displacement is to be expected at the  $A_4$  point of iron owing to the increase of conducting electrons consequent on the change from a face-centred to a space-centred lattice. F. G. T.

**Absorption of Cathode Rays in Aluminium.** B. F. J. SCHONLAND (*Nature*, 1925, 115, 497).—Polemical (cf. *Proc. Roy. Soc.*, 1923, A, 104, 235; Terrill, this vol., ii, 79). A. A. E.

**Primary and Secondary Products of Ionisation in Hydrogen.** H. D. SMYTH (*Physical Rev.*, 1925, [ii], 25, 452—468).—A discussion in greater detail of results already reported (A., 1923, ii, 455). Atomic hydrogen ions are produced by secondary dissociation of diatomic ions, and triatomic ions also appear when the voltage is above 16. The probability of dissociation is considered theoretically. A. A. E.

**Single and Double Ionisation of Argon by Electron Impacts.** H. A. BARTON (*Physical Rev.*, 1925, [ii], 25, 469—483).—Using Smyth's magnetic deflexion method (cf. preceding abstract), the minimum potentials for the production of singly and doubly charged argon ions are 15.2 volts (assumed) and  $45.3 \pm 1.5$  volts, respectively. No trebly charged argon ions or singly charged argon molecules were observed. Possible ways of reconciling the results with spectroscopic evidence for the production of doubly charged ions at 34 volts are discussed. A. A. E.

**Total Ionisation Produced in Air by Electrons of Various Energies.** G. A. ANSLOW (*Physical Rev.*, 1925, [ii], 25, 484—500).—An account of the experimental and theoretical basis of results already published (this vol., ii, 343). The voltages at which the total ionisation shows peaks are interpreted as the ionisation potentials of the *L*-electrons of argon (250) and the *K*-electrons of nitrogen (375) and oxygen (494). A. A. E.

**Ionisation of Potassium Vapour by Light.** R. SAMUEL (*Z. Physik*, 1924, 29, 209—213).—A reinvestigation of the minimum



frequency necessary to excite ionisation, using an apparatus which eliminates secondary effects under the conditions prescribed for its operation. The light source is the arc spectrum of magnesium which contains two unusually strong lines in 2852 and 2804 in the range of the convergence frequency of potassium 2857 Å. By the use of suitable filters, and by using fields too small to produce ionisation by collision, it is established that potassium vapour is ionised by radiation in the range 2893—2804 Å. R. W. L.

**Ionisation of Potassium Vapour under the Influence of Visible Light.** A. ARNULF (*Compt. rend.*, 1925, **180**, 1259—1262).—A discharge tube with a tungsten filament and a plane plate is kept evacuated by a mercury pump, and a little potassium is distilled into the tube. The plate is given a positive potential with respect to the filament. When the filament is heated to incandescence the ammeter registers  $I_1$  milliamp. If now a beam of visible light is allowed to fall on the plate or anywhere inside the discharge tube a higher current is found. With a varying voltage, the following extreme readings are obtained: (a)  $V=3$ ,  $I_1=13.2$ ,  $I_2=15$ ,  $\Delta I/I_1=0.136$ ; (b)  $V=110$ ,  $I_1=650$ ,  $I_2=826$ ,  $\Delta I/I_1=0.271$ . If now the potential difference between plate and filament is reversed, the beam of light exerts no influence on the current. When the plate is again made positive and the beam falls midway between plate and filament, lateral displacement of the pencil of light causes  $\Delta I$  to diminish.

The work indicates that potassium vapour is ionised by visible light and a small number of electrons and positive ions are liberated. The considerable increase in current is due to the accumulation of positive ions until the number of ions recombining every second plus the number per second reaching the filament is equal to the number of ions formed per second under the influence of visible light. Possible objections to this explanation are discussed.

R. A. M.

**$\beta$ -Rays produced in Air by Short-wave X-Rays.** H. IKEUTI (*Compt. rend.*, 1925, **180**, 1257—1259).—Monochromatic X-rays, 0.21 Å., were allowed to enter a Wilson chamber and stereoscopic photographs taken. The  $\beta$ -rays were of two kinds, those arising from high-speed photo-electrons and the fish and sphere tracks from low-velocity electrons. The mean length of trajectory of the first kind was 76 mm. (air pressure 570 mm.); corrected to 18°/760 mm. the value is between 57 and 65 mm. Wilson's data extrapolated according to Whiddington's law lead to a higher value, namely, 67 mm. The maximum trajectory of the (slow electron) fish tracks lay between 3.3 and 3.7 mm. The fish tracks are not due to  $J$ -electrons, but to a new type of radiation. Compton's formula for calculating the energy of recoil electrons arising from the diffusion of X-rays leads to a value 2.9 mm., lower than that found. The trajectory (on the basis of recoil) corresponding with an initial angle  $\theta$  with the direction of exciting rays can be calculated from  $E_m=E(1+1.01 \tan^2\theta)$  for  $\lambda=0.2$  Å.,

where  $E_m$  is the maximum energy and  $E$  the energy of a recoil electron projected at an angle  $\theta$ . This expression of Compton is approximately verified, but there are a few completely anomalous trajectories.

If the small trajectories are due to recoil effects the ratio of absorption coefficients by diffusion and by fluorescence should correspond with the ratio of the number of short with long trajectories. This is 11.0 in both cases. Wilson's work leads to equally good agreement, so that the view that the small trajectories are due to the recoil of diffusing electrons is completely justified. Compton's theory gives 1.3 for the ratio of the number of sphere tracks to fish tracks. Regarding as sphere tracks all below 0.2 mm., experiment leads to a value of 1.1 for this ratio. R. A. M.

**Radiation given out by Gases through which Electric Discharges are passing.** (SIR) J. J. THOMSON (*Phil. Mag.*, 1925, [vi], 49, 761—786).—The suggestion (A., 1924, ii, 646) that ionisation in the negative glow of a discharge tube is due to radiation excited by the cathode rays in the gas through which they pass is confirmed by experiments of several types. The rays so generated have low penetrative powers, less than 1% from the negative glow produced by 3000 volts passing through a celluloid film  $3 \times 10^{-5}$  cm. thick. From measurements of the absorption of these rays by different materials, it is shown that they may have far higher frequencies than any characteristic of the gas from which they are derived. Thus the most penetrative rays generated in hydrogen by the electrons produced by a potential of 1500 volts were of wavelength  $8.1 \times 10^{-8}$  cm. The frequency of these rays thus corresponds with an ionising potential of 1500 volts. These results and the variations of the radiations in their path through the discharge tube indicate that they constitute a continuous spectrum with a maximum frequency proportional to the energy of the exciting electrons. It is concluded from the fact that some of this radiation is absorbable by two or three centimetres of air at 0.01 mm. pressure that the volume in which the energy of this type of radiation is concentrated must be considerably larger than the volume of a molecule of the gas (cf. *ibid.*, 1924, [vi], 48, 737). At a polished zinc surface, up to about 5% of the rays suffer reflexion. An expression is derived for the distribution of energy in a continuous spectrum produced by the passage of electrons through a gas, and it is shown how this continuous spectrum, with a concentration of energy in the longer wave-lengths, may be brought about by the degradation of a homogeneous radiation, the frequency of which fixes the upper limit of the continuous spectrum. F. G. T.

**Electrical Conductivity of Heated Gas.** R. N. GHOSH (*Z. Physik*, 1925, 32, 113—118).—The conductivity is calculated from estimates of the life-period of electrons in heated gases; in the case of stellar material, the value is about 100 times that of copper.

E. B. L.

**Gas Ion Mobilities.** L. B. LOEB (*Phil. Mag.*, 1925, [vi], 49, 517—519).—The ionic mobility equation originally published

(*ibid.*, 1924, [vi], 48, 446) should be multiplied by  $\sqrt{2}$ . The corrected equation is:  $K = (0.104\sqrt{(1+b)/b})/(p/760\sqrt{(D-1)M_0})$  cm./sec./volt/cm.  
C. W. B.

**The Permanent Electret.** M. EGUCHI (*Phil. Mag.*, 1925, [vi], 49, 178—192).—Disc electrets are prepared by solidifying molten mixtures of equal parts of carnaüba wax and resin in a strong electric field. The nature of the free charge is shown to be a permanent internal electrification, the surface density of which is calculated by  $\sigma = CV/\pi r^2$ , where  $C$  is the capacity of condenser system,  $V$  the potential recorded by electrometer, and  $r$  the effective radius of the induction plate. The free charge remains the same over a period of some years, and is only temporarily affected by exposure to  $X$ -rays, solvents, planing with a knife, application of electric forces, etc. Under such treatment, the free charge temporarily disappears and then recovers exponentially according to the law  $V' - V = (V' - V_0)e^{-\lambda t}$ , where  $V$  is the potential at time  $t$ , and  $V'$  the final potential. The intensity of electrification  $E = 4\pi\sigma$  is such that the electric intensity in air in front of the electret takes almost the greatest sustainable value.  
C. W. B.

**Periodic Classification of the Elements from the Point of View of the Study of Isotopes.** S. SCHTSCHUKAREV (*Neue Anschauungen in der Chemie*, 1924, 9, 61—120; from *Chem. Zentr.*, 1924, ii, 1877—1878).—All elements are derived from the disintegration of four parent elements, of which two, namely, thorium and uranium, are known. The nuclei of elements consist of protons, electrons,  $\alpha$ -particles, and helium atoms. The  $\alpha$ -particle is given off as such: the helium atom is given off in three stages, namely, an  $\alpha$ -radiation and two successive  $\beta$ -radiations (the  $\alpha, \beta, \beta$ -transformation which thus results in the formation of isotopes). The  $\alpha$ - and  $\alpha, \beta, \beta$ -transformations can be so arranged as to give all known and some unknown isotopes. There are, for example, between niton and xenon 16  $\alpha$ - and 6  $\alpha, \beta, \beta$ -transformations, between xenon and krypton 9  $\alpha$ - and 3  $\alpha, \beta, \beta$ -transformations, between krypton and argon 9  $\alpha$ - and 3  $\alpha, \beta, \beta$ -transformations, between argon and neon 4  $\alpha$ -transformations, and between neon and lithium 3  $\alpha$ - and 1  $\beta$ -transformations.

The existence of isobares is explained on the theory expressed. It is shown that the outer periodicity of the electron structure appears to be superimposed on the inner periodicity of the nuclear structure. The different changes are represented in tabular form.

G. W. R.

**Attempted Electrolytic Separation of the Isotopes of Chlorine and Magnesium.** J. E. G. PILLEY (*Phil. Mag.*, 1925, [vi], 49, 889—899).—By considering the migration velocity of an ion as made up of a large number of free paths over which there is a component of acceleration due to an electrical force, an expression is deduced for the variation of mobility with the mass of ions otherwise identical. For the isotopic chlorine ions, provided neither

hydration nor association of water molecules occurs, a difference of mobility of between 0.3 and 0.7% is to be expected, according to the value of the coefficient of restitution in the ionic collisions. If the ions are hydrated, and the water molecules polymerised, these limiting differences become 0.2 and 0.4%. The differences for the magnesium ions should be of the same order. Unsuccessful attempts were made to detect such differences in the diffusion of these ions through long tubes filled with agar gel under a potential difference of 300 volts. Careful atomic weight determinations on different layers of the gel after the experiments showed no indication of a separation of the isotopes. Probable causes of the failure of this method are discussed.

F. G. T.

**Rare Earths. XVI. Purification and Atomic Weight of Holmium.** F. H. DRIGGS and B. S. HOPKINS (*J. Amer. Chem. Soc.*, 1925, **47**, 363—369).—Purification was effected by fractionation of the bromates, dividing the series into fractions containing neodymium but no erbium and those containing erbium but no neodymium, followed by partial decomposition of the nitrates. Freedom from yttrium and dysprosium was established by comparison of the observed magnetic susceptibility with that calculated from the equivalent weight. From the ratio chloride: silver the atomic weight of holmium is 163.47.

L. J. H.

**Period of Mesothorium-2.** W. P. WIDDOWSON and A. S. RUSSELL (*Phil. Mag.*, 1925, [vi], **49**, 137—140).—The separation of mesothorium-2 from its parent substance by addition of thorium and precipitation with ammonia is described. From a preparation with  $\gamma$ -ray activity equal to that of 6 mg. of radium bromide, mesothorium-2 is obtained and its half-period determined. Exponential decay to zero is observed and the half-period values are 360, 352, 359, 361, 356, 354, and 356, giving a mean of 357 mins. The period of average life is consequently 8.58 hrs. and the disintegration constant  $\lambda = 0.116$  per hr. The half-value period, having a probable error of 1%, is 4% lower than that obtained by Hahn (A., 1908, ii, 454). No product with a less period is detectable, and the experiments point to the unlikelihood of a product with greater period.

C. W. B.

**Constancy of the Rate of Transformation of Radium Emanation at Different Concentrations.** (MME.) P. CURIE (*Ann. Physique*, 1924, **11**, 405).—The rates of decay of the  $\gamma$ -radiation from similar samples of radium emanation enclosed in small spherical vessels are found to be constant to within 1 part in 10,000 parts. At pressures of about 0.5 atm. the emanation gives  $\gamma$ -rays the rate of decay of which differs by less than 1 part in 2000 parts from that of samples at lower concentrations.

R. W. L.

**Determination of the Ratio of the Velocities of the Two Groups of  $\alpha$ -Particles Emitted from the Active Deposit of Thorium.** S. ROSENBLUM (*Compt. rend.*, 1925, **180**, 1332—1334).—A new experimental arrangement of the photographic method of measuring deflexion in a magnetic field of varying in-

tensity (15,000—18,000 gauss) is described. The distance from radioactive source to photographic plate was also varied. The ratio of the velocities of  $\alpha$ -particles from thorium-*C* and thorium-*C'* is  $1.209 \pm 0.001$ . The value obtained after correction for the increase in mass of high-velocity  $\alpha$ -particles is 1.210, so that the experimental error and the correction are of the same order. The most recent values for the ranges of  $\alpha$ -particles from thorium-*C* and -*C'* are 8.62 cm. and 4.72 cm., respectively, at  $15^\circ$  and 760 mm. (Henderson, A., 1921, ii, 617; Geiger, Z. *Physik*, 1922, 8, 45). The cube root of the ratio of these numbers is 1.217, agreeing with the ratio of velocities to within 0.6%.

R. A. M.

**Increase of the Heating Effect of Radium Preparations Due to Growth of Polonium.** (MME.) M. CURIE and D. K. YOVANOVITCH (*J. Phys. Radium*, 1925, [vi], 6, 33—35).—The heating effect of a preparation of radium chloride, purified  $16\frac{3}{4}$  years ago, has been compared with that of a preparation recently prepared, the actual masses of radium in each preparation being compared by their  $\gamma$ -radiations. The results show that the heating effect has increased by 11% in this period. This is due to the formation of polonium and is very approximately the amount to be expected on present knowledge of the heating effects of radium with its short-lived products, and of polonium, and of the periods of radium, radium-*D*, and polonium. The growth of polonium in preparations of radium is consequently at the rate to be expected on present theory. The calorimetric measurements are not sufficiently accurate to give at this stage a more exact value of the period of radium-*D* than that accepted at present.

A. S. R.

**Quantity of Heat Set Free as  $\gamma$ -Radiation in Radioactive Disintegration.** J. THIBAUD (*Compt. rend.*, 1925, 180, 1166—1169).—The total heat set free per hr. by 1 g. of radium in radioactive equilibrium is 135—137 cal. (Rutherford and Robinson, A., 1913, ii, 269). The kinetic energy of  $\alpha$ -particles and the recoil effects are calculated to be 117.7 cal., or, including the energy of  $\beta$ -radiation, 129.8. The discrepancy is due to the effect of penetrating  $\gamma$ -rays. Kovarik (A., 1924, ii, 447) suggests that each  $\alpha$ -particle emission is accompanied by a single  $\gamma$ -quantum. The complexity of  $\gamma$ -spectra implies that nuclear emission need not be followed by emission of a  $\gamma$ -quantum of constant energy. Radium-*B* would emit several frequencies, some of which would be more likely to occur than others. Their intensities supply a measure of the probability of occurrence. Summation of energy and intensities indicates values for the mean quanta of the  $\gamma$ -radiations of radium-*B* (302,000 volts), radium-*C* (1,010,000 volts) and radium (187,000 volts). Thus,  $\Sigma h\nu = 1.49 \times 10^6$  volts and  $E_\gamma = Z \cdot \Sigma h\nu = 0.841 \times 10^5$  ergs ( $Z$  is  $3.57 \times 10^{10}$ , the number of atoms disintegrating per second). This corresponds with 7.25 g.-cal. per hr., accounting quantitatively for the low calculated heat evolution given above.

The heat in cal./hr. is distributed as follows:  $\alpha$ -particle emission and recoil effect 117.7, primary  $\beta$ -emission 12.1,  $\gamma$ -emission 7.2, total, 136.9. The energy due to  $\gamma$ -rays is by no means negligible;

for radium-*B*+*C*, it attains 16% of the total heat. The success of these calculations supports the hypothesis that each  $\alpha$ -particle emission from the nucleus is followed by emission of a single  $\gamma$ -entity the quantum of which may be variable.  
R. A. M.

**Separation of the Total Radiation of Radium into Groups by Absorption in Platinum.** J. S. LATTÈS (*Compt. rend.*, 1925, **180**, 1023—1026).—The radiation from radium and its disintegration products, which is of four main types, namely, primary  $\beta$ - and  $\gamma$ -radiations and the secondary  $\gamma$ - and  $\beta$ -radiations derived from them, is further divided into ten groups, according to their various coefficients of absorption by platinum. The distributions of the radiation in the various groups are tabulated for thicknesses of platinum up to 1.5 mm. The bearing of the results on medical applications is discussed.  
G. M. B.

**Gold in the Mercury Lamp.** T. RETSCHINSKY (*Physikal. Z.*, 1925, **26**, 280—281).—Since the potential gradient in the Heraeus high-pressure lamp is slightly greater than in the Jaenicke lamp, conditions in the former are more favourable for the penetration of the atomic nuclei by electrons. Slightly modified Heraeus lamps have been constructed to work at a potential gradient of 21 volts/cm. and 150 cm. mercury pressure.  
F. G. T.

**Quantum Radiation.** (SIR) O. LODGE (*Nature*, 1925, **115**, 798).

**Electrical Behaviour of Radioactive Colloidal Particles of the Order of  $10^{-5}$  cm. as Observed Separately in a Gas.** F. EHRENHAF ( *Phil. Mag.*, 1925, [vi], **49**, 633—648).—Largely polemical against Millikan, with a claim for priority in the method of determining the electric charge on individual particles. The author contends that he has proved the existence of fractions of an electronic charge. Microscopic spherical particles of silver of the order of  $10^{-5}$  cm. were examined under a variable electric field  $E$  between two horizontal metal plates. A test-body of constant charge  $e$  would move with a velocity  $(Ee - mg)B$ , where  $B$  is the mobility. Since the observed speed varies linearly with field strength, the mobility is constant and concordant values are given on the basis of Stokes' law, the colour of the light scattered, and the photophoretic maximum. The Einstein theory of Brownian movement in gases leads to an anomalous and untrustworthy value. It was found that for particles of radius less than  $3 \times 10^{-5}$  cm. charges smaller than that on an electron were often carried, the fraction falling below 1/10 and 1/20 of the elementary quantum.

The subdivision of the electron charge has been criticised on the grounds (a) that the test-bodies are not spheres, (b) that the density of the particle is not the same as that of the substance in bulk, (c) that the test-body is surrounded by a gas layer, (d) that the exact form of the law of resistance for small spheres in a gas is not known. The author claims that these objections are all either untenable or irrelevant. If (b) is valid, the density of platinum must fall from 21.4 to 0.2.

Small, spherical, colloidal test-particles of selenium and mercury can be made radioactive by contact with niton or polonium. In a constant electric field they move so as to give the impression of a continuous change of electric charge, whilst the movement of non-radioactive particles is uniform. The radioactive test-bodies must therefore gain or lose charges which are only small fractions of the supposed indivisible electronic charge. These results have an important bearing on the fact that there is no theory to account for the cohesion and stability of the electron.

Observations consistent with subdivision of the electronic charge have been made by other workers and discrepancies are due to interpretation rather than experiment. Lodge adds a note to the effect that Millikan ("The Electron," 1917) has discussed carefully and rejected Ehrenhaft's views, but that, nevertheless, a serious attack on so fundamental a question cannot be ignored.

R. A. M.

**Law of Force within the Atom.** G. GREEN (*Phil. Mag.*, 1925, [vi], 49, 1020—1028).—A law of force is suggested which gives rise to an atomic system essentially in conformity with the Bohr theory of the atom and with quantum theory. The proposed law of force between a positive charge  $e$  and an electron  $e$  is of the form  $f = (e^2/r^2) \cdot \cos(\rho/r)$ , where  $\rho$  represents a radius drawn from the centre of an atom, such that for all distances exceeding a small multiple of  $\rho$  the inverse square law of attraction holds. According to this law, an electron within an atom could remain at rest in stable equilibrium at values of  $r$  given by  $\rho/r = (2n + \frac{1}{2})\pi$ , where  $n$  is an integer. Consideration of the amount of energy radiated in the movement of an electron from one stable position to another shows that this law provides a system in which energy would be radiated in a manner conforming closely to that obtaining for change of orbit in the Bohr atom. By choosing a system of stable states such that  $n=25, 16, 9, 4, 1$ , the Rydberg constant may be derived. It is further shown that, in agreement with the Bohr theory, an orbital motion established by an electron in any one of the stable positions would be nearly permanent, provided the natural radiation loss was small.

F. G. T.

**Problem of the Quantitative Formulation of Bohr's Correspondence Principle.** R. C. TOLMAN (*Phil. Mag.*, 1925, [vi], 49, 130—136).—Six methods of averaging the light intensities emitted by states intermediate between the initial and final quantum states used by Hoyt (A., 1924, ii, 433) are employed to calculate the probability of transitions in three simple quantum systems: the harmonic oscillation, the rotating dipole, and the simplified hydrogen atom. The only method giving zero probability for an electron falling into the hydrogen nucleus from the innermost orbit, is that expressed by  $\log(Q\nu^2) = \int_0^1 \log(C_r r^2 \omega^2) d\lambda$ . This treatment assumes the validity of the inverse square law down to zero distance between nucleus and electron, contrary to the finite mass and energy of the hydrogen atom.

C. W. B.

**Possible Reconciliation of Bohr's Interpenetration Ideas with Sommerfeld's Relativistic Treatment of Electron Orbits.**

R. A. MILLIKAN and I. S. BOWEN (*Phil. Mag.*, 1925, [vi], **49**, 923—935; cf. A., 1924, ii, 710).—A third possibility is suggested as a solution of the dilemma previously discussed. An examination of the data of doublet separation shows that whilst the Sommerfeld relativity equation predicts the fine structure of hydrogen and ionised helium as accurately as is attainable in experimental work, for lithium to nitrogen, and sodium to chlorine series, even for remote orbits which ought to obey the laws of a simple nucleus-electron system, greater discrepancies are obtained by the use of the equation than can be accounted for by experimental error. It is suggested that whilst the fine structure in the cases of hydrogen and ionised helium is due entirely to the relativity effect, in the heavier atoms there is some cause acting by virtue of the difference of the orientation of the two circular orbits  $L_{II}$  and  $L_{III}$ , which increases the energy of the circular orbit  $L_{II}$  to about the amount which it would have had by virtue of relativity, had it been a  $2_1$  orbit. To account for the approximate validity of the relativity equation for these atoms, this postulated force, which may be magnetic or electrostatic or a combination of the two, must demand the same variation with nuclear charge, and with total and azimuthal quantum number, as is required by the relativity principle. The difference of behaviour in weak magnetic fields of hydrogen and helium as compared with lithium and other atoms is adduced in support of this suggestion. The appearance of the Paschen-Back effect in hydrogen is, however, contrary to expectation.

F. G. T.

**Quantum Defect and Atomic Number.**

D. R. HARTREE (*Phil. Mag.*, 1925, [vi], **49**, 390—396; cf. Turner, *ibid.*, 1924, **48**, 384).—The proposal to alter the assignment of the principal quantum numbers to certain terms of atomic number greater than 28 is discussed. It is maintained that the reasons for the change are scarcely adequate. An objection to the newly-proposed scheme of quantum numbers is pointed out. Fresh evidence, afforded by X-ray spectra, which seems to be definitely in favour of Bohr's assignment, is put forward.

C. W. B.

**Quantum Numbers of the Bohr Orbits in the Alkali Atoms.**

R. B. LINDSAY (*Science*, 1924, **60**, 475—476).—Polemical against Turner (A., 1924, ii, 797), whose assignment of quantum numbers 6 and 8 to the outermost orbits of rubidium and caesium, respectively, is held to be unjustified.

A. A. E.

**Quantum Theory of Red Displacement of Spectral Lines.**

J. KUDAR (*Physikal Z.*, 1925, **26**, 207—211).—Mathematical. The Einstein red displacement of the hydrogen series and the Deslandres-Schwartzchild band spectra are deduced on the basis of the equations of electron movement of the general relativity theory, the Sommerfeld quantum condition for hypothetical periodic systems, and the Bohr frequency relation.

F. G. T.



**Balmer Law as an Equation of Motion.** L. PAGE (*Physical Rev.*, 1925, [ii], **25**, 429—443).—An attempt to develop a form of dynamics in which the intra-atomic motions are unifrequentic, the dynamical frequency coinciding with the optical frequency as calculated on Bohr's theory. A. A. E.

**Intensity of Multiplet Lines.** A. SOMMERFELD and H. HÖNL (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 141—161).—A formula is suggested by which the intensity of multiplet lines arising from a given electron transition may be calculated. Where data are available for comparison the agreement is good. The expression embodies the correspondence principle and the summation rule of Burger and Dorgelo (*Z. Physik*, 1924, **23**, 258). F. G. T.

**Rectilinear Diameter of Helium.** E. MATHIAS, C. A. CROMMELIN, H. K. ONNES, and J. C. SWALLOW (*Compt. rend.*, 1925, **180**, 1005—1007; cf. A., 1922, ii, 440).—The density of liquid and gaseous helium has been determined at temperatures between  $-268.38^{\circ}$  and  $-270.79^{\circ}$ . Helium obeys the law of rectilinear diameters, the data agreeing well with those calculated from the equation for the diameter:  $y = -0.40263 - 0.0017616t$ . The following constants are recorded:  $t_c -267.90^{\circ}$ ,  $d_c 0.06930$ , and the critical coefficient  $RT_c d_c / p_c 3.270$  as compared with the value 3.276 for hydrogen. G. M. B.

**Secondary Spectrum of Hydrogen.** J. W. NICHOLSON (*Month. Not. Roy. Astr. Soc.*, 1925, **85**, 449—464).—The Fulcher hydrogen bands are to be regarded as two parts of a single band system, of great complexity, which is probably due to un-ionised hydrogen molecules. The lines of these bands do not show the Zeeman effect. The most characteristic components in the first Fulcher band are in each case arranged in triplets about 100 Å. apart. In addition to the strong lines noted by Fulcher, it is shown that practically all the weak lines in the region 6000—6400, not showing the Zeeman effect, are to be regarded as components of a single scattered band. Similarly, groups of lines in the region 5300—5700 are related to the second Fulcher band, the chief components of which are triplets of mutual separation 120 Å. The wave-numbers of the strongest components in these two bands may be expressed by formulæ of the type  $n = \alpha + \beta(m + \mu)^2$ , in which the values of  $\alpha$  for the two series are approximately equal. The two bands thus possess a common limit. Examination of the lines in the blue region which do not show the Zeeman effect indicates the existence of other widely separated bands analogous to those of Fulcher, and the probability that the number of distinct bands in the secondary spectrum of hydrogen is small. F. G. T.

**Secondary Spectrum of Hydrogen at Very Low Temperatures.** J. C. McLENNAN and G. M. SHRUM (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 177—182).—The secondary spectrum of hydrogen was photographed with the discharge tube at (a) the ordinary temperature, (b)  $-180^{\circ}$ , and (c)  $-252^{\circ}$ . The lines of Fulcher's  $S_3$  group (*Physical Rev.*, 1923, [ii], **21**, 375) were greatly

enhanced at the low temperatures, those of the  $S_2$  unchanged and those of the  $S_1$ ,  $S_0$ , and  $X$  groups all weakened. Tables are given for a large number of lines which are enhanced, weakened, or entirely suppressed at  $-252^\circ$ . J. S. C.

**Regularities in the Secondary Spectrum of Hydrogen.** O. W. RICHARDSON and T. TANAKA (*Proc. Roy. Soc.*, 1925, **A**, 107, 602—623; cf. *ibid.*, 1924, **A**, 106, 640, 663).—It has been found possible to arrange 123 additional lines provisionally in 22 series. Three of these form a  $P$ ,  $Q$ ,  $R$  combination. The present indications are that the moments of inertia of the emitters are spread fairly well over a range extending from the high value deduced from the  $P$ ,  $Q$ ,  $R$  combination found provisionally to a value somewhat below the lowest value which has been deduced from Fulcher's second band. This involves an extreme variation by a factor of almost 6 in the moment of inertia. L. L. B.

**Third Negative Group of Carbon. Spectrum of the Tails of Comets. Extension on the Red Side and Structure of the Bands.** F. BALDET (*Compt. rend.*, 1925, **180**, 820—822).—Previous work (this vol., ii, 180) has been extended by making use of panchromatic plates and a high-dispersion spectroheliograph, and seven new bands are now recorded in addition to the three measured previously. The fine structure can be interpreted in terms of rotational quantum numbers and the combination rules of Heurlinger. Alternative combination rules are given which show better agreement. A more detailed treatment of structure will appear elsewhere.

The measurements of Baldet and Baume-Pluvinel on the Morehouse comet (1908) have now been reproduced in every detail with pure carbon monoxide. Helium need not be present for the production of the first or third negative groups of carbon. R. A. M.

**Influence of Pressure on Carbon Band Spectra in Discharge Tubes. Consequences for the Theory of Comets.** F. BALDET (*Compt. rend.*, 1925, **180**, 1201—1203; cf. preceding abstract).—Pressure plays an essential part in the appearance of the different groups in the carbon monoxide spectrum. The light arises either from impacts of electrons (the speed of which exceeds that corresponding with the ionisation potential) on neutral or ionised molecules, or from collisions of neutral and ionised molecules. Thus, different groups appear. At low pressures, when electron impacts predominate, only the first and third groups occur. At higher pressures, the molecular collisions influence the spectra by exciting new groups. The effect of pressure is also seen on the structure of the bands of the third negative group. At very low pressures, the heads are intense as in the cometary spectra. It is concluded that the carbon monoxide in the tails of comets must be bombarded by electrons from the sun. R. A. M.

**Band of Unusual Structure probably due to a Highly Unstable Calcium Hydride Molecule.** R. S. MULLIKEN (*Physical Rev.*, 1925, [ii], **25**, 509—522).—An isolated band with head at  $3533.6 \text{ \AA}$ . observed in the spectrum of the calcium arc in hydrogen

at 3—20 mm. has been measured and analysed. The emitting molecule is probably a compound of a hydrogen atom with an excited, but not ionised, calcium atom. A. A. E.

**The CuH Molecule and its Band Spectrum.** H. BELL (*Phil. Mag.*, 1925, [vi], 49, 23—32).—The figures of Frerichs and Bengtsson (*Z. Physik*, 1923, 20, 170, 229) for the bands shown by copper in the region 4700 to 4000 are used in the application of a formula for band spectra in the visible region, developed by the author. The presence of the CuH molecule is verified, and the half quantum for its rotation established. The distances between the hydrogen and copper nuclei for the initial and final configurations are calculated, and a diagram is given showing variation of radial force function with distance. C. W. B.

**Budde Effect in Bromine.** E. B. LUDLAM (*Proc. Roy. Soc. Edin.*, 1924, 44, 197—201).—Ordinary pure bromine vapour when illuminated showed an immediate rise in temperature with corresponding volume change. Purified bromine containing no water vapour showed no Budde effect under various conditions of illumination. It is suggested that, as proposed by Perrin (A., 1919, ii, 177), pure bromine radiates in all directions the energy which it absorbs, but that traces of water vapour have a catalytic effect on the dissociation into atoms, which on re-combining effect an increase in temperature with an appropriate volume change.

A. E. M.

**Electrical Excitation of the Band and Line Spectra of Iodine.** G. CARIO and O. OLDENBERG (*Z. Physik*, 1925, 31, 914—919).—The primary object of the work was to find a spectrum of the positively charged iodine molecule,  $I_2^+$ . Only a weak, narrow group of bands was found at about 2700 Å., indicating that the stability of this form is slight. The bands in the blue and near ultra-violet, observed in a narrow capillary, were resolved into a series of single bands. The diffuse band at 3460 Å. was also resolved into a series of single bands. By using a silica tube heated at above 1000°, the line spectrum for atomic iodine was obtained and the wave-lengths were measured as far into the ultra-violet as the strong line at 2062.2 Å.

E. B. L.

**Band Spectrum of Mercury.** E. HULTHÉN (*Z. Physik*, 1925, 32, 32—55).—These bands are obtained when an uncondensed discharge is passed through mercury vapour, but a trace of moisture or hydrogen is necessary. Mercury hydride is considered to be the source of the bands. The bands are classified and tables of wave-lengths given.

E. B. L.

**Emission Band Spectra of Aromatic Compounds. I. Their Connexion with Infra-red Absorption Bands and a Classification.** J. K. MARSH (*Phil. Mag.*, [vi], 1925, 49, 971—980).—Baly's relationship that the frequencies of the heads of absorption bands in the ultra-violet and visible regions are integral multiples of that of a fundamental infra-red band, is made the basis

of a classification of the emission band spectra of a number of aromatic compounds. Of these, one class is characterised by groups of bands at frequency intervals of 102 waves/mm. These are considered to be multiples of the benzene infra-red band at  $9.8\ \mu$ . An aromatic-aliphatic derivative type, exemplified by *p*-xylene, has band intervals of 40 or 80 in the ultra-violet. With the Tesla discharge, these substances give a green glow, consisting of two bands at an interval of 160. A third class, of which benzaldehyde is typical, gives a blue Tesla luminescence characterised by three very strong bands with frequency differences of 172. A fourth, less defined, class of substances containing condensed nuclei shows three or four bands near  $4000\ \text{\AA}$ ., with frequency intervals of 142 for anthracene and its derivatives, and of 47 for naphthalene. Many substances do not give any emission, or only one of a continuous character, and cannot be classified. In the infra-red, bands of absolute frequency equal to the above ultra-violet frequency differences are in each case well-marked and characteristic of the groups.

F. G. T.

**Relation between the Constants of the Infra-red Bands of Triatomic Molecules.** E. FERMI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 386—387).—The theory of infra-red bands leads to the formula  $\Delta\nu = \hbar/4\pi^2 I$ , where  $\hbar$  represents Planck's constant,  $I$  the moment of inertia of the molecule, and  $\Delta\nu$  the constant frequency difference between the lines of the infra-red band. For triatomic molecules, the three atoms must lie in a plane, and the three principal moments of inertia are connected by the expression  $I_1 = I_2 + I_3$ ; hence  $1/\Delta\nu_1 = 1/\Delta\nu_2 + 1/\Delta\nu_3$ . This equation is obeyed closely for water vapour, the molecule of this being the only one for which the necessary experimental data are available.

T. H. P.

**Electrodeless Discharge in the Vapours of Phosphorus and Sulphur.** W. W. SHAVER (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 145—149).—The spectrum of the electrodeless discharge in phosphorus vapour has been investigated in the fluorite region, the frequencies and wave-lengths of 12 lines between  $1859.4$  and  $1671.5\ \text{\AA}$ ., some of which have been previously reported (Saltmarsh, A., 1924, ii, 436), being given. The frequencies and wave-lengths of 9 lines in the corresponding spectrum for sulphur are recorded in the region  $1903.6$ — $1666.5\ \text{\AA}$ .

J. S. C.

**Spectrographic Study of the Iodo-cadmium Complex.** P. JOB (*Compt. rend.*, 1925, 180, 1108—1110).—The existence of  $\text{K}_2\text{CdI}_4$  complex has been shown in several ways, but the author's method of detecting double salts in aqueous solution by absorption spectra measurements gave negative results. Examination of the spectrograms suggested that this was due to complexity of cadmium iodide itself. This view was tested by photographing absorption spectra of cadmium sulphate-potassium iodide mixtures. The ultra-violet absorption was considerable and passed through a sharp maximum at 80% potassium iodide corresponding with the ion  $\text{CdI}_4''$ . A rough idea of the stability of the complex can be obtained

by determining the equilibrium constant of the reaction  $\text{Cd}^{++} + 4\text{I}'' \rightleftharpoons \text{CdI}_4''$ , by using the composition-maxima of solutions of the two iodides at various concentrations. R. A. M.

**Absorption of Ultra-violet Light in Dilute Solutions.** C. J. W. GRIEVESON (*Phil. Mag.*, 1925, [vi], **49**, 1006—1020).—A method is described of comparing the transparency to ultra-violet light of aqueous solutions by measuring the photo-electric effect of the transmitted light. The transmission coefficients at a series of concentrations are given for the chloride, hydrogen carbonate, carbonate, sulphate, and nitrate of sodium, disodium hydrogen phosphate, manganese chloride, copper sulphate, potassium permanganate, and calcium nitrate. Of the sodium salts, the sulphate is very transparent. The presence of the nitrate ion renders a solution highly opaque. The addition of tap water containing 0.3 g. of impurity per litre greatly reduced the transparency of the solutions. The relation between the absorption and the thickness of the solution layer was examined for calcium nitrate. F. G. T.

**Ultra-violet Absorption as a Function of  $p_{\text{H}}$  of some Organic Acids, considered as Ultra-violet Indicators.** F. VLÈS and (MILLE.) M. GEX (*Compt. rend.*, 1925, **180**, 1342—1345; cf. this vol., ii, 292).—The ultra-violet absorption spectrum of certain organic acids is different from that of the corresponding salt;  $p_{\text{H}}$  measurements should therefore be taken into account. If  $\phi$  is the ratio of the extinction coefficients at wave-lengths  $\lambda_1$  and  $\lambda_2$  at a definite  $p_{\text{H}}$  value, the curve  $\phi$  against  $p_{\text{H}}$  will then bear a relation to the changing constituents of the solution. Oxalic acid has a wide absorption band from 350  $\mu\mu$  to the extreme ultra-violet with a succession of breaks near 230, 255, 260, 272, 284, 298, 320, and 345. Taking  $\phi$ =ratio of  $e$  at 260 to  $e$  at 273, and graphing against  $p_{\text{H}}$ , a curve is obtained with a maximum between  $p_{\text{H}}$  0 and  $p_{\text{H}}$  1, a minimum between  $p_{\text{H}}$  1 and  $p_{\text{H}}$  4, an inflexion between  $p_{\text{H}}$  4 and  $p_{\text{H}}$  10, and a steep portion between  $p_{\text{H}}$  10 and  $p_{\text{H}}$  13. There are five possible successive constituents: undissociated acid, two anions, the monosodium ion, and undissociated disodium salt at very strong  $p_{\text{H}}$ . The middle portion of the curve can be calculated from equilibrium data if  $p_{\text{K}}$  is taken as 3.6 (Scudder's conductivity data gives 4.31) and  $p_{\text{K}1}$  as 1.05.

Benzoic acid shows seven bands,  $\lambda$  max. equals 245, 250, 261, 266, 273, 278, and 285  $\mu\mu$ , which vary with  $p_{\text{H}}$ . The bands 272 and 250 increase and the bands 261, 266 decrease with lowered  $p_{\text{H}}$ . The ratios  $\phi_1=273/261$ ,  $\phi_2=273/256$ ,  $\phi_3=273/250$  graphed against  $p_{\text{H}}$  give curves for benzoic acid quite as complicated as for oxalic acid, in spite of its univalency. A middle portion similar in appearance to a neutralisation curve is found near  $p_{\text{K}}$  (constant) and can be calculated from the dissociation equation. The curves for  $\phi_1$ ,  $\phi_2$ , and  $\phi_3$  against  $p_{\text{H}}$  are all similar in type and show maxima and minima. These latter cannot be accounted for on the assumption of three possible constituents, namely, undissociated benzoic acid, benzoate ion, and undissociated sodium benzoate. It seems as if

two other constituents must occur. The idea of supplementary constituents requires recourse to very hypothetical notions, such as modification of the carboxyl group or activation of the benzene ring. It is suggestive that preliminary work indicates that the absorption spectrum of aqueous benzene varies with hydrogen-ion concentration.

R. A. M.

**Relationship of Thyroxin to Tryptophan.** C. S. HICKS (*J. Chem. Soc.*, 1925, **127**, 771—776; cf. Kendall, A., 1919, i, 496).—Measurements of the ultra-violet absorption spectra of thyroxin in  $M/8000$ — $M/40,000$  alkaline solution compared with those of tryptophan in  $M/10,000$ — $M/50,000$  alcoholic solution reveal a definite group resemblance. In thyroxin, the bands are shifted towards the red, owing to the iodine present. Similar relations are shown to hold between the spectra of isatin and iodoisatin. The conclusion is arrived at that the indole skeleton is present in thyroxin.

W. A. C.

**Döppler Effect in the Reflexion of Resonance Fluorescence.** W. RUMP (*Z. Physik*, 1924, **29**, 196—208).—It is shown that a re-emitted line in a resonance fluorescence spectrum shows a greater Döppler effect than that of the incident radiation when the source of secondary radiation is at a higher temperature than that of the primary radiation. The width of a line is unchanged by reflexion from glass, metal, or mercury vapour.

R. W. L.

**Resonance Fluorescence of the Line 1849 Å. of Mercury Vapour.** W. RUMP (*Z. Physik*, 1925, **31**, 901—902).—Light from a quartz mercury vapour lamp crossed a space from which oxygen had been driven out by carbon dioxide and fell on mercury vapour in a quartz tube. The resonance radiation emitted in a direction at right angles to the incident light fell on the slit of a fluorite-quartz spectrograph filled with carbon dioxide, and the photograph showed the line 1849, the plate having been rendered fluorescent by a thin layer of paraffin oil. The production of this line had been predicted as the result of the absorption of the line 2536.7 followed by a further absorption of light by the atom in the  $2p_2$  state.

E. B. L.

**Effect of an Alternating Magnetic Field on the Polarisation of the Resonance Radiation of Mercury Vapour.** E. FERMI and F. RASETTI (*Nature*, 1925, **115**, 764).

**Fluorescence and Channelled Absorption of Bismuth at High Temperatures.** K. R. RAO (*Proc. Roy. Soc.*, 1925, **A**, **107**, 760—762; cf. A., 1924, ii, 804).—The absorption and fluorescence spectra of bismuth vapour at  $1500^\circ$  to  $1600^\circ$  have been photographed and compared. The fluorescence spectrum is practically the exact complement of the absorption spectrum in this region. In contrast to the bands in the ultra-violet, some of the absorption bands show a distinctly fine structure. It is considered that the existence of a fluorescent banded spectrum in the

above region is a criterion for molecular radiation processes, and that in elements which are polyatomic, the radiating systems are molecules instead of atoms.

L. L. B.

**Extinction of Fluorescence of Dyes at High Concentration.** S. J. WAWILOW (*Z. Physik*, 1925, **31**, 750—764).—As the concentration of the solution of the dye is increased a point is reached at which the extinction begins and it increases thereafter in simple exponential relation to the concentration. It is suggested that the critical concentration is related to the life-period of the activated molecule and the Brownian movement to which the molecule is subjected. There appears to be no relation between the extinction and the conductivity of the solutions. The presence of other dyes was found to reduce the fluorescence, but experiments to detect an analogous effect to the Cario and Franck transference of energy have not yet led to a decisive result.

E. B. L.

**Decay and Regeneration of Radio-luminescence.** C. H. VIOL, G. D. KAMMER, and A. L. MILLER (*Nature*, 1925, **115**, 801—802).—It is believed that the decrease with time of the luminescence of phosphorescent zinc sulphide etc. is due to the masking of the radiation luminosity by the colour which the material acquires, due to the action of the radiation.

A. A. E.

**Luminescence of Grignard Compounds. Spectra and Brightness.** R. T. DUFFORD, D. NIGHTINGALE, and S. CULVERT (*J. Amer. Chem. Soc.*, 1925, **47**, 95—102).—In continuation of previous work (A., 1923, ii, 714) the following organometallic halides are reported as chemiluminescent: calcium phenyl iodide, magnesium *p*-fluorophenyl bromide, magnesium *o*-chlorotolyl bromide, magnesium 2-cynyl bromide, magnesium  $\alpha$ - and  $\beta$ -naphthyl iodides. Direct spectrum photographs have been obtained and quantitative measurements of brightness made. Previous conclusions have been quantitatively verified.

L. J. H.

**Emission of Light by Solidified Gases at the Temperature of Liquid Helium and the Origin of the Spectrum of the Aurora.** L. VEGARD, H. K. ONNES, and W. H. KEESOM (*Compt. rend.*, 1925, **180**, 1084—1087; cf. A., 1924, ii, 436, 509, 584, 713, 805).—The study of the light emitted by bombarding solid nitrogen or mixtures of nitrogen and neon with high-velocity cathode rays has been continued at the temperature of liquid helium. The  $N_1$  band of nitrogen has its maximum at 5555 with two secondary maxima; cooling does not result in a diminution in the width of the band. The  $N_2$  band is strong and is divided into two components (5236, 5222). The spectrum shows a regular series of seven bands extending from 3986 to 5770. At higher temperatures, these are broad and diffuse, but on cooling they are each resolved into two fine lines shading off on the red side. In argon containing a trace of nitrogen (at the temperature of liquid hydrogen) the bands are also concentrated into pairs of lines, but their position is different. The

two strongest bands are at 4523, 4473 and 4236, 4211, and they correspond with the bands observed by Rayleigh in diffuse night light. In the region of longer waves, nitrogen, at the temperature of liquid helium, emits 3 or 4 feeble lines 5914, 5952, 6399, and perhaps 6417. These lines probably correspond with feeble ones in the auroral spectrum. Solid neon-nitrogen mixtures show the  $N_1$  band shifted in a similar way as in argon-nitrogen mixtures. Diminishing proportions of nitrogen cause disappearance of the secondary maxima with displacement of the principal maximum towards the red. Qualitatively, the argon-nitrogen and neon-nitrogen mixtures are similar, but the magnitude of the displacement and the law followed are quite different. For both mixtures the wave-length of the principal maximum is a function of the concentration of nitrogen. The shift is due partly to a specific action of the inert gas and partly to a diminution in nitrogen. For argon-nitrogen mixtures, the factors are of the same order, so that a little argon can produce a considerable displacement. The specific effect of neon is very small, so that the shift does not occur until the neon content rises to 70%. As the nitrogen proportion approaches zero, the  $N_1$  band takes the form of a line 5578.6, which nearly coincides with the green line of aurora borealis. The small difference 1.2 Å. is explained by a small specific effect of neon. In neon with traces of hydrogen, the  $N_2$  band is divided into three components (5229, 5220, 5203), of which the first is the strongest. As the proportion of nitrogen increases, the  $N_2$  band has a double line structure, and the spectra show several neon lines. R. A. M.

**Radiation from Non-luminous Flames.** R. T. HASLAM, W. G. LOVELL, and R. D. HUNNEMAN (*Ind. Eng. Chem.*, 1925, **17**, 272—277).—Experiments in which the primary air was varied over a range of 80—150% of the theoretical amount, show that the maximum heat radiated from a flame (when no secondary air is present) is at a maximum when the primary air is at its theoretical amount. Helmholtz's theory that the amount of heat radiated from a flame is equal to the sum of the amounts which would have been radiated if the final products of combustion had been produced by burning hydrogen and carbon monoxide ("Licht u. Wärmestrahlung verbrannter Gase," Berlin, 1890), is not justified.

The maximum energy radiated from methane, illuminating gas, and carbon monoxide with the theoretical amount of air was 14.9, 13.8, and 10.4%, respectively, of the total latent heat. The relative radiation from flames of different depths follows an exponential law indicating that at about 100 cm. the flame becomes opaque to its own radiation.

Increasing the burner tip area by 50% had no appreciable effect. Preheating the primary air decreases the amount of radiation and this may be due either to a shift of the chemical equilibrium or to pre-combustion. The amount of heat radiated has no simple connexion with the flame temperature, and hence the authors suggest that it is intimately connected with the actual chemical reaction taking place in the flame.

M. B. D.



**Phosphors of Boric Acid.** A. MICKWITZ (*Ber.*, 1925, 58, [B], 678—679; cf. Tiede and co-workers, A., 1921, ii, 75; 1922, ii, 8, 245).—The phosphorescence of compounds of boric acid was known at the end of the 18th and beginning of the 19th century.

H. W.

**Ionisation of Iodine Vapour by Ultra-violet Light.** W. WEST and E. B. LUDLAM (*Proc. Roy. Soc. Edin.*, 1924—5, 45, 34—41).—Instead of the quartz windows used in the hitherto unsuccessful attempts to demonstrate the ionisation of iodine by ultra-violet light, an exposure chamber provided with a fluorite window, thus permitting the passage of light of wave-lengths down to about  $120\text{ }\mu\mu$ , has been employed. The aluminium spark gap was placed close to the window to prevent absorption by the oxygen of the air. A stream of nitrogen, which is not ionised by light of the wave-length employed, carried iodine vapour of partial pressure  $0.13\text{ mm.}$  at  $15^{\circ}$ . It has thus been found that, provided the aluminium sparking terminals are kept free from oxide, ionisation takes place, both positive and negative charges being given to the electrometer in approximately equal amounts. The effect ceases when the source of light is removed  $1\text{ cm.}$  in air away from the fluorite. The results show that iodine vapour is ionised by light of wave-length between  $185$  and  $120\text{ }\mu\mu$ . The work of Smyth and Compton (A., 1921, ii, 364) and of Mohler and Foote (A., 1921, ii, 368) on the ionisation potential of iodine indicates a corresponding wave-length of  $123$  or  $131\text{ }\mu\mu$ , whilst the spectrum of the aluminium spark in air shows strong lines between  $170$  and  $180$ , weaker ones at  $150$  and  $160$ , and a group of stronger lines at  $130$ . Many of the molecules of iodine were probably in a state of fluorescence, and the ionisation potential of fluorescing iodine corresponds with a wave-length of  $181\text{ }\mu\mu$  (Smyth and Compton, *loc. cit.*). M. S. B.

**Quantum Equivalent for Photo-electric Conductivity in Sodium Chloride Crystals.** Z. GYULAI (*Z. Physik*, 1925, 32, 103—110).—Rock-salt crystals were coloured yellow by exposure to X-rays, and the ratio of photo-electric conductivity to the light energy absorbed was determined in the visible and near ultra-violet region. This ratio increases with increasing wave-length throughout the absorption band. About  $10,000$  quanta were absorbed for each electron detected, from which it was calculated that the mean path of the electron is  $1/3000\text{ mm.}$  E. B. L.

**Incident and Emergent Velocities of Photo Electrons Emitted from Thin Platinum Films.** C. CHA (*Phil. Mag.*, 1925, [vi], 49, 262—272).—Asymmetry in the velocities of photo electrons emitted from the two sides of thin platinum films is investigated for evaporated and sputtered films. For the former no asymmetry was found over the experimental range of film thickness and wave-length of incident light. The maximum emission energy of a photo electron is given as a linear function of the frequency of light, the slope of the line giving Planck's constant  $h$ ,  $2\%$  lower than the value given by Millikan (*Physical Rev.*, 1916, [ii],

7, 355). With sputtered films, asymmetry occurs, and the ratio of the potentials measuring maximum emission velocities decrease with increasing thickness of film, but are independent of wavelength, confirming the results of Robinson (*Phil. Mag.*, 1913, [vi], 25, 115) and of Stuhlmann (*Physical Rev.*, 1914, [ii], 4, 195). The results point to the asymmetry being due to fundamental differences between the types of film. C. W. B.

**Motion of a Free Electron in the Field of Plane Electromagnetic Waves.** J. FRENKEL (*Z. Physik*, 1925, 32, 27—31).—There can be no photo-electric effect for a free electron: it must be a resonance effect on a bound electron. E. B. L.

**Relation between Energy of Escape of Electrons and Electrochemical Normal Potential.** A. GÜNTHER-SCHULZE (*Z. Physik*, 1925, 32, 186—189).—Examination of existing experimental results shows that there is an empirical relation  $1.3\phi - \epsilon = \text{constant} = \text{approx. } 5$ , where  $\phi$  is the energy needed to enable an electron to escape from a metal and  $\epsilon$  the normal potential of the metal. E. B. L.

**Dielectric Constants of some Liquids and their Variation with Temperature.** I. G. E. BELL and F. Y. POYNTON (*Phil. Mag.*, 1925, [vi], 49, 1065—1072).—Details are given of a method of measuring the dielectric constants of liquids by means of two valve-maintained oscillating circuits, tuned so that the heterodyne note beats slowly with a third valve-maintained circuit oscillating at audible frequency. Measurements were made of the dielectric constants of castor oil, olive oil, and linseed oil between 18° and 185°. The linear relationship between dielectric constant and temperature is expressed by the formula  $K_{\theta} = K_{20} [1 - (\theta - 20)\alpha]$ , where  $\alpha = 0.0015, 0.0008, 0.0009$  for the oils in the above order. The following values, nearest to 20°, were obtained. Castor oil,  $K_{17.5} = 4.86$ , olive oil  $K_{18.5} = 3.21$ , linseed oil  $K_{19} = 3.24$ . F. G. T.

**Proposed Test of the Space Quantisation of Atoms in a Magnetic Field.** A. E. RUARK and G. BREIT (*Phil. Mag.*, 1925, [vi], 49, 504—508).—If properties of matter in bulk may be used as a criterion, the dielectric constant would be the most feasible property for exhibiting an anisotropic nature with respect to the field. The essential condition is that space quantisation shall predominate over a random orientation during an appreciable portion of the time between two collisions. It is shown that this condition is fulfilled with fields of reasonable strength. The feasibility of obtaining anisotropic electric effects by the action of the magnetic field is discussed from the point of view of the reciprocity of action between the two fields. The method of heterogeneous beats is suggested for revealing variations in the dielectric constant. C. W. B.

**Molecular Volumes of Crystals.** F. A. HENGLEIN (*Z. Elektrochem.*, 1924, 30, 5—12).—The molecular volumes in the solid crystalline state can be expressed by an empirical linear equation of

the type,  $\text{mol. vol.} = x'y' + c'$ , provided that the salts have a similar crystalline structure, *e.g.*, halides of the alkali metals. Numerous examples are given to show the validity of the law. H. T.

**Quantum Theory of Optical Phenomena.** J. C. SLATER (*Physical Rev.*, 1925, [ii], **25**, 395—428).

**Molecular Refraction of Natural and of Methyl-rubber.** A. D. MACALLUM and G. S. WHITBY (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 191—193).—The average of several determinations of  $n_D^{20}$ ,  $d_4^{20}$ , and  $[R_L]_D^{20}$  for purified rubber are 1.5219, 0.9237, and 22.46, respectively. Corresponding values for smoked sheet are 1.5208, 0.9217, and 22.44. The results are in accord with the view that, in the polymerisation of isoprene to caoutchouc only one double bond is lost per  $\text{C}_5\text{H}_8$ , the absence of exaltation indicating that there is no conjugation between double bonds in the polymeride. The following quantities were determined for synthetic "methyl-rubber" from dimethylbutadiene;  $n_D^{20}$  1.525,  $d_4^{20}$  0.9292,  $[R_L]_D^{20}$  27.03.

J. S. C.

**Classical Dispersion Formula for Monatomic Gases and Vapours.** K. F. HERZFELD and K. L. WOLF (*Ann. Physik*, 1925, [iv], **76**, 567—570).—Corrected tables and data for the paper of the above title (see this vol., ii, 182).

F. G. T.

**Dispersion of Carbon Disulphide in the Ultra-violet.** G. BRUHAT and M. PAUTHENIER (*Compt. rend.*, 1925, **180**, 1018—1020; cf. A., 1924, ii, 713).—Determinations of the refractive index of carbon disulphide have been made throughout the visible spectrum and as far as 2537 Å. in the ultra-violet, with special attention to the neighbourhood of the absorption band at 3220 Å. The results are compared with the values of absorption previously recorded.

G. M. B.

**Magnetic Rotatory Dispersion of Certain Paramagnetic Solutions.** R. W. ROBERTS (*Phil. Mag.*, 1925, [vi], **49**, 397—422).—Aqueous solutions of certain cobalt and nickel salts show anomalous rotatory dispersion at their principal absorption bands. This is much stronger for cobalt than for nickel solutions. The high-frequency electrons in cobalt solutions, as well as in potassium ferricyanide, give rise to the negative rotation displayed by these salts. The rotatory dispersion in the solutions investigated may be calculated from the formula:  $\delta\lambda^2/n(n^2+2) = x\delta_\omega\lambda^2/n_\omega(n_\omega^2+2) + \Sigma a_s/(1-\lambda^2\lambda_s^2)$ , derived from Drude's molecular current hypothesis, by taking into account the electric polarisation of the liquids.

C. W. B.

**Structure of Molecules in Relation to their Optical Anisotropy.** I. K. R. RAMANATHAN (*Proc. Roy. Soc.*, 1925, **A**, **107**, 684—693).—The view is maintained that the optical anisotropy of molecules is due to the mutual influence of the electric doublets induced by the incident light in the constituent atoms (cf. Raman, A., 1924, ii, 512). It is assumed that each atom by itself is isotropic. Diatomic and triatomic molecules are considered mathematically,

and the expressions  $(1 + \frac{1}{2}R_0k)/(1 - R_0k)$  and  $(2R_1 + R_2 + 31R_1R_2k/8)/(1 - R_1k/8 - 2R_1R_2k^2) \cdot (1 + R_1k/16 - \frac{1}{2}R_1R_2k^2)/(2R_1 + R_2 - 31R_1R_2k/16)$  (where  $R_0$ ,  $R_1$ , and  $R_2$  are atomic refractivities) are deduced for the optical anisotropy in the two cases. From the known refractivity and polarisation of the scattered light in hydrogen, nitrogen, and oxygen, the atomic refractivities and distances between the "optical centres" in the molecules are calculated. These distances are 1.37 Å., 1.90 Å., and 1.46 Å. for hydrogen, nitrogen, and oxygen, respectively, and are consistent with the values of the molecular radius calculated from the kinetic theory. For the triatomic gases, nitrous oxide, carbon dioxide, and carbon disulphide, the imperfection of polarisation of the transversely scattered light is found by calculation to be 14.1%, 10.8%, and 12.5% respectively, these values being in satisfactory agreement with experiment. L. L. B.

### Specific Rotation of Invert-sugar and the Clerget Divisor.

F. W. ZERBAN (*J. Amer. Chem. Soc.*, 1925, **47**, 1104—1111).—From a critical survey of recorded data on the specific rotation of invert-sugar, the following equation is derived, using Vosburgh's data for lævulose (A., 1920, ii, 575), Tollens' for dextrose (A., 1885, 40), and Vosburgh's rule for the rotation of sugar mixtures:  $[\alpha]_D^{20}$  of invert-sugar =  $-(19.415 + 0.07065c - 0.00054c^2)$ . The temperature correction formula is  $[\alpha]_t = [\alpha]_D^{20} + (0.283 + 0.0014c)(t - 20)$ . A value of 32.95 is obtained from the first equation for the negative constituent of the Clerget divisor, using the general factor 0.34657. A redetermination of the latter gave 0.34615, from which the Clerget constant becomes 32.09. F. G. W.

### Configuration of Polyatomic Polar Molecules. II. Molecules consisting of a Negative Ion and Hydrogen Nuclei.

F. HUND (*Z. Physik*, 1925, **32**, 1—18; cf. *ibid.*, 1925, **31**, 81).—The variation of potential with distance is calculated from the position of the bands in the spectra of the halogen hydrides and the course of the potential for the ions O'', S'', Se'', and N''' deduced. The following values are obtained for the shape, size, and energy of the molecules and ions: distance apart of unlike ions  $\times 10^8$  cm., HO' 1.0, H<sub>2</sub>O 1.03, H<sub>3</sub>O' 1.05, HS' 1.5, H<sub>2</sub>S 1.5, HCl 1.27, H<sub>2</sub>Cl' 1.3, H<sub>3</sub>Cl'' 1.3; distance apart of like ions  $\times 10^8$  cm., H<sub>2</sub>O 1.09, H<sub>3</sub>O' 1.11, H<sub>2</sub>S 1.6, H<sub>2</sub>Cl' 1.4, H<sub>3</sub>Cl'' 1.4; energy in kg.-cal. for the complete separation of one hydrogen nucleus from HO' 550, H<sub>2</sub>O 370, H<sub>3</sub>O' 180, HS' 430, H<sub>2</sub>S 310, HCl 316, H<sub>2</sub>Cl' 180.

E. B. L.

**Theory of Metals.** J. FRENKEL (*Z. Physik*, 1924, **29**, 214—240).—By treating the "wandering" of valency electrons which takes place during the condensation of metal vapours as a self-diffusion process, and by evaluating approximately the corresponding diffusion constant, an analysis is advanced leading to an expression for the mobility of the valency electrons and to the electrical conductivity of a metal. The values for the latter quantity and for its temperature variation agree in order of magnitude with those obtained experimentally. In a similar way, an expression is

obtained for the thermal conductivity which is in agreement with Wiedemann and Franz's analysis; it fails, however, to elucidate the mechanism of the process. The analysis also lends itself to a determination of the tensile strength, compressibility, and grating energy.

R. W. L.

**Valency of Ruthenium. Ruthenium Tetroxide and Ruthenium Halides.** O. RUFF and E. VIDIC (*Z. anorg. Chem.*, 1924, **136**, 49—61).—Ruthenium tetroxide may be prepared in a very pure form by distilling at 40—50° in a current of air an acidified solution of the mass obtained by fusing in a silver crucible a mixture of 1 part of ruthenium powder, 2 parts of potassium permanganate, and 20 parts of potassium hydroxide. The tetroxide condenses in a receiver, cooled with ice, in the form of long, golden-yellow needles which are readily soluble in water. The solution is unaffected by addition of hydrofluoric acid, but is reduced with the evolution of the halogen when warmed with the other halogen acids; with dilute hydrochloric acid, the tetroxide is reduced rapidly on warming to the tetrachloride, which slowly decomposes into trichloride and chloride, especially when boiled to expel the chlorine as it forms. A similar reaction occurs with hydrobromic acid, but the second stage of the reduction (to tribromide) is much more rapid. With hydriodic acid, black, insoluble ruthenium tri-iodide is immediately formed. All derivatives of ter- and quadri-valent ruthenium are converted into the sexavalent form by potassium permanganate in alkaline solution; in sulphuric acid solutions, permanganate oxidises ruthenium compounds to the tetroxide.

A. R. P.

**Ruthenium Tetroxide. III. Valency of Ruthenium in the Tetroxide.** F. KRAUSS and H. KÜKENTHAL (*Z. anorg. Chem.*, 1924, **136**, 62—74; cf. A., 1922, ii, 75).—When ruthenium tetroxide is treated with hydrochloric acid and potassium iodide the iodine set free corresponds with a diminution of 5 in the valency of the tetroxide. From the reduced solution, many salts of the type  $M'_2RuCl_5$  were prepared, as well as ruthenium trihydroxide and ruthenium trichloride, thus showing that the metal is tervalent in these compounds and therefore octavalent in the tetroxide. Solutions of potassium ruthenate obtained by fusion liberate three equivalents of iodine from acid iodide solutions, and hence ruthenium is sexavalent in this compound. Pure ruthenium trihydroxide is prepared by heating at 120° in a nitrogen atmosphere the black precipitate obtained by addition of alkalis to solutions containing the trichloride. The latter has been prepared in a pure state for the first time by the interaction of dry ruthenium tetroxide vapour and dry hydrogen chloride at 105—115°, as well as by exposing the pure trihydroxide to dry hydrogen chloride at 105°. Thus formed, the trichloride is a dark violet-brown, deliquescent mass having a metallic lustre.

A. R. P.

**Higher Valencies of Onium Compounds.** W. TSCHELINZEV (*Bull. Soc. chim.*, 1925, [iv], **37**, 176—181).—The heats of formation of ammonium, oxonium, and thionium complexes (with  $EtO \cdot MgI$ )

were determined. They are in the order given. Successive additions (up to a maximum of three) have lower heats of formation. Substituted derivatives were also studied. The order is probably determined by the basicity of the central atom. L. J. H.

**Strengths of the Higher Valencies and their Significance for Assimilation, Catalysis, and other Chemical Processes.** W. TSCHELINZEV (*Bull. Soc. chim.*, 1925, [iv], 37, 181—187).—The ease with which a group may be replaced parallels the heat of formation; this may be applied to the higher valencies of onium compounds. The tendency to form onium compounds progressively diminishes in the order: aldehydes, ketones, esters, acids, alcohols, ethers. These higher valencies may play an important part in assimilation, catalysis, and other chemical processes. A scheme representing the formation of hexoic acid from carbon dioxide and water by the successive formation of oxonium compounds, rearrangement, loss of water, and oxidation is put forward. L. J. H.

**Chemical Affinity and Electronic Structure. I. The Non-polar Band.** B. H. WILSDON (*Phil. Mag.*, 1925, [vi], 49, 354—369).—A quantitative theory to explain the facts of chemical affinity built up on the basis of the constitution of the atom. In order that the free valency orbits of uncombined atoms shall be capable of forming a chemical bond, they must have identical or harmonically related frequencies. An expression is developed by which heats of formation of non-polar compounds can be calculated, using only theoretical values for the frequencies of the atoms in their ground orbits, and without using arbitrary quantum numbers. An insight into the geometrical structure of the molecule is afforded by the theory, and its application to the structural relations of carbon compounds is considered. C. W. B.

**Chemical Affinity and Electronic Structure. II. The Polar Link.** B. H. WILSDON (*Phil. Mag.*, 1925, [vi], 49, 900—911; cf. preceding abstract).—The necessary condition for a stable molecular combination is that the frequencies of the valency orbits concerned shall be synchronised. If  $\nu_1$  and  $\nu_2$  represent the frequencies of the valency electrons of the combining atoms in their ground orbits,  $h(\nu_1 - \nu_2)$  represents a quantum of energy which is termed the available energy of accommodation. This energy is supposed to be responsible for the changes involved in the transfer of a valency electron or electrons from the positive to the negative atom, and for the potential energy of valency electrons and "trunk" in the field of the stripped positive ion. The change in frequency of the valency orbits produced under these conditions, multiplied by the unit of action, must represent the change in kinetic energy. The heat of reaction, which must equal the total energy change, may be calculated if the ratio of the kinetic to the total energy in the field of the molecule is known. This latter ratio has been calculated by Bohr. An analysis of the potential energy change resulting from molecular combination shows that two types of quantum jump should be possible in that process. In the first, the equatorial quantum

number remains unaltered; in the second, it increases by one unit. On this basis, two distinct types of polar compound may be expected. Experimental results support this, the distinction arranging elements into classes which correspond with the A and B sub-groups of the periodic table. A comparison of the experimental heats of formation of the alkali halides, and those of copper, silver, and mercury, with the values calculated by the above theory gives good agreement except for hydrogen fluoride and silver fluoride. F. G. T.

**Electrical Meaning of Chemical Affinity.** M. BORN (*Z. Elektrochem.*, 1924, **30**, 383—386).—A review of recent work and theories. A. R. P.

**Relative Internal Friction.** W. HERZ and A. WEGNER (*Z. anorg. Chem.*, 1925, **144**, 85—86).—Whilst absolute internal friction always diminishes with rising temperature, the coefficient relative to that of water may rise or fall. With formic acid and ethyl and allyl alcohols, the relative value first rises to a maximum and then falls. S. I. L.

**Simple X-Ray Apparatus for the Examination of Powdered Crystals by the Seemann-Bohlin Method, giving Higher Resolution with Shorter Exposure.** H. LANGE (*Ann. Physik*, 1925, [iv], **76**, 455—476).—Full details are given of the construction of a steel X-ray tube embodying low cost, high resolution, low power consumption, and simplicity of manipulation. Water-cooled electrodes are insulated by molybdenum glass from a water-cooled steel tube which carries an aluminium foil window, the junctions being secured by mercury seals. In conjunction with a camera chamber described, an accuracy of 0.05% is attained in lattice measurements, whilst the exposure for a 45-kilovolt tube potential is reduced to 90—100 milliamp.-minutes. In test measurements with this apparatus, the value  $4.036 \pm 0.002$  Å. was obtained for the aluminium lattice constant, and for the difference in the  $K_{\alpha}$  doublet of copper,  $0.00385 \pm 0.00005$  Å. F. G. T.

**X-Ray Spectroscopic Examination of some Alloys by the Seemann-Bohlin Method.** H. LANGE (*Ann. Physik*, 1925, [iv], **76**, 476—492).—Errors in measurements by the apparatus previously described (cf. preceding abstract) are discussed. These arise from errors in plate reading, the influence of the breadth of the slit on that of the lines, and from the existence of inhomogeneity, or predominance of crystals of a particular composition, in a mixed crystal specimen. Diffuse lines arising from such inhomogeneity may be improved by heat treatment of the specimen. The lattice constants were determined for various alloys in the systems copper-nickel and copper-gold. Kirchner's results (*ibid.*, 1922, **69**, 59) for the latter system are confirmed. Except for slight deviations attributable to the inhomogeneity of the alloy specimens, the lattice constants in each case are linear functions of the molar percentage composition of the alloys, in agreement with Vegard's rule.

Measurements were made of the lattice constants of duralumin during the process of hardening. This phenomenon is shown to

be accompanied by the development of a second lattice in the crystal, with a constant slightly greater than the first. This behaviour is in agreement with the theory of Konno (*Sci. Rep. Tôhoku Imp. Univ.*, 1922, **11**, 269) that the hardening is due to the reciprocal action of the compounds  $\text{Mg}_2\text{Si}$  and  $\text{Al}_2\text{Cu}$  with the aluminium. According to this theory, the hardening accompanies the partial separation of  $\text{Mg}_2\text{Si}$  from a solution of  $\text{Al}_2\text{Cu}$  in aluminium. On the other hand, the theory of Fraenkel and Scheuer (*Naturwiss.*, 1924, **13**, 145) does not account for the appearance of this second lattice. F. G. T.

**Application of X-Ray Diffraction to the Determination of the Transformation Temperature of Thallium.** G. ASAHARA (*Sci. Papers, Inst. Phys. Chem. Res.*, 1924, **2**, 125—137).—Earlier work (Nishikawa and Asahara, *Physical Rev.*, 1920, [ii], **15**, 38) showed that the transformation of  $\alpha$ - into  $\beta$ -thallium was accompanied by an abrupt change in the X-ray pattern. The transformation temperature measured in this way had the mean value  $227^\circ$ . Various investigators have reported values between  $225^\circ$  and  $238^\circ$ , based on thermal analysis. A new method has been devised whereby a series of photographs is obtained as the metal is heated through the transformation temperature and cooled. The value  $231.9^\circ$  was obtained on heating and  $230.7^\circ$  on cooling. The metal used contained 99.74% Tl (0.11% Al, 0.14% Ca, 0.13% Mg), and  $231.3^\circ$  is given as the transformation temperature. R. A. M.

**Focussing Method in Crystal Powder Analysis by X-Rays.** J. BRENTANO (*Proc. Physical Soc.*, 1925, **37**, 184—193).—The locus of all powder particles from which X-rays from a point source are reflected to a definite point is a toroid surface. Since in practice a plane surface coated with powder is used, sharply-defined spectral lines can only be obtained within a small angular region, such that  $\sin \alpha / \sin \beta = a/b$ , where  $a$  is the distance source to powder,  $b$  the distance powder to film, and  $\alpha$  and  $\beta$  are the glancing angles of incidence and emergence with respect to the powdered surface. The extreme angular broadening  $\omega_2$  of any spectral line due to the substitution of a flat plane for a toroid is expressed by  $\omega_2 = 0.25\epsilon^2 \cot \beta$ , where  $\epsilon$  is the angular width of the incident beam. At the same time, since for a given position of the powdered surface only one point on the film corresponds with correct definition, the lines will broaden unless the film is screened off save for this one point. The angular broadening thus effected is given by  $\omega_1 = [a/2(a+b)]\epsilon \cot \beta$ , where  $\eta$  is the angular stretch of film exposed. A spectrometer designed to minimise these errors and a hot-cathode X-ray tube giving only the  $K\alpha$  and  $K\alpha'$  copper rays are described. The (100) spacing of nickel oxide is thus found to be  $4.172 \text{ \AA}$ . W. A. C.

**Theory of the Width of the Modified Spectrum Lines in the Compton Effect.** G. E. M. JAUNCEY (*Phil. Mag.*, 1925, [vi], **49**, 427—433).—The increase in width of modified spectrum lines, in excess of that accounted for by the change in direction of the rays, is given by the formula  $\delta\lambda\phi = 4\lambda_0 \sin \phi / 2\sqrt{2h/mc\lambda}$ . Calculated and observed values agree for the scattering of molybdenum  $K\alpha$  rays



by the  $L$  electrons of carbon. For aluminium the calculated values are too great. The formula only seems applicable for small values of the binding energy of the electron. C. W. B.

### Structure of Solid Nitrous Oxide and Carbon Dioxide.

J. DE SMEDT and W. M. KEESOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 839—846).—A method has been worked out for obtaining the X-ray spectra of solidified gases at low temperatures, by means of which the structures of nitrous oxide and carbon dioxide are compared. Nitrous oxide crystallises cubically ( $a=5.72$  Å.), the distance between the neighbouring nitrogen and oxygen atoms being 1.15 Å. Assuming 4 mols. in the unit cube, the calculated density is 1.55, whereas at the m. p. the liquid has  $d$  1.299. Carbon dioxide also crystallises in the cubic system, with ( $a=5.63$  Å.), and the distance between a carbon and an oxygen atom is 1.05 Å.; the calculated  $d$  is 1.63, which agrees with the value found by Dewar at the temperature of liquid air.

L. L. B.

### Crystal Structure of Magnesium Fluoride.

H. E. BUCKLEY and W. S. VERNON (*Phil. Mag.*, 1925, [vi], **49**, 945—951).—The substance was examined in powdered form by the copper  $K_\alpha$  radiation. It crystallises on a structure possessing the symmetry  $D_{2h}^{14}$ . The unit cell is a tetragonal prism with  $a=4.660$  Å.,  $c=3.078$  Å., and  $a:c=1:0.660$ . The distance of closest approach of magnesium to fluorine is 2.07 Å., which agrees with the value 2.08 Å. calculated from Bragg's radii.

F. G. T.

### Crystal Structure of Mercuric Sulphide. II.

N. H. KOLKMEIJER, J. M. BIJVOET, and A. KARSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 847—850).—The striking agreement between the Debye-Scherrer photographs of the cubical (black) and trigonal (red) mercuric sulphide is caused by the complete equality of their dimensions in the octahedral or basis plane. The difference between the two modifications consists only in the manner in which these planes are piled up, at least as regards the arrangement of the centres of the particles. None of the different modifications, including  $\beta'$ -HgS, mentioned by Allen and Crenshaw, were found by X-ray analysis to contain crystals different from those of the ordinary black and red forms.

L. L. B.

### Two Crystal Forms of Zinc Hydroxide.

R. FRICKE (*Z. anorg. Chem.*, 1924, **136**, 48).—The thin needles of zinc hydroxide prepared by Goudriaan's method (A., 1920, ii, 113) from zinc sulphate are metastable; when kept in contact with the mother-liquor for some time, they slowly change into the short, thick, apparently rhombic crystals described by Fricke and Ahrndts (A., 1924, ii, 681).

A. R. P.

**Orthorhombic Space Group Criteria and their Application to Aragonite.** R. W. G. WYCKOFF (*Amer. J. Sci.*, 1925, [v], **9**, 145—175).—Spectrum and Laue photographic data for aragonite are recorded. It is shown that the space group must be  $2D_{16}$  if

aragonite possesses holohedral symmetry. The nature of this group is briefly discussed. S. K. T.

**Crystal Structure of Barite.** L. PAULING and P. H. EMMETT (*J. Amer. Chem. Soc.*, 1925, **47**, 1026—1030).—The crystal unit of orthorhombic barite contains 4 mols. and has  $d_{100}=8.846$  Å.,  $d_{010}=5.430$  Å., and  $d_{001}=7.10$  Å. The crystal belongs to the space group  $V_h^{16}$ ; its structure is based on the simple orthorhombic lattice  $\Gamma_o$ . The two parameters determining the exact positions of the barium atoms were not evaluated. S. K. T.

**Space Group of Barite ( $\text{BaSO}_4$ ).** R. W. G. WYCKOFF and H. E. MERWIN (*Amer. J. Sci.*, 1925, [v], **9**, 286—295).—Laue and spectrum photographs were taken with plates of barytes cut parallel to (010) and (001). For the spectrum photographs the plate was rotated to and fro through  $25^\circ$  about a crystallographic axis. The results agree with a unit cell containing 4 mols. of  $\text{BaSO}_4$  and of dimensions  $a=8.89$ ,  $b=5.45$ ,  $c=7.17$  Å., corresponding with the axial ratio  $a:b:c=1.633:1:1.316$ . The symmetry is orthorhombic holohedral, the lattice  $\Gamma_o$ , and the space-group  $2Di-16$ . L. J. S.

**Space Group of Diopside.** R. W. G. WYCKOFF and H. E. MERWIN (*Amer. J. Sci.*, 1925, [v], **9**, 379—394).—From the X-ray spectra given by the rotating crystal and the Laue photographs, the dimensions of the unit cell of diopside containing 4 mols.  $\text{CaMg}(\text{SiO}_3)_2$  are deduced as  $X=5.24$ ,  $Y=9.71$ ,  $Z=8.89$  Å. (Here the usual orientation is changed;  $X=-c$ ,  $Y=a$ ,  $Z=b$ ;  $\beta=74^\circ 10'$ .) The lattice is  $\Gamma'_m$  and the space-group  $2Ci-6$ . L. J. S.

**Influence of X-Rays on the Crystallisation of Bismuth.** E. ADINOLFI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 382—386).—X-Rays exert on the arrangement of bismuth during solidification an effect similar to, but distinct from, a debasing effect, and varying in nature with the hardness of the rays used. T. H. P.

**Calculation with Pole-systems: Crystal Groups and Crystal Dynamics.** E. WAELSCH (*Ann. Physik*, 1925, [iv], **76**, 534—560).—Mathematical. F. G. T.

**Connexion between Thermo-electric Power and Space Lattice for Pure Iron.** A. GOETZ (*Physikal. Z.*, 1925, **26**, 260—264; cf. this vol., ii, 187).—The change from  $\beta$ - to  $\gamma$ -iron at the A3 point is accompanied by a change from the space-centred cubic lattice to the surface-centred cube, together with a great decrease in  $dE/dT$  (Richardson equation). This ratio increases in the  $\gamma$  to  $\delta$  transformation. The space-centred lattice is thermo-electrically positive with respect to the other form.  $E$  is proportional to the capacity of the negative component for absorbing electrons, which itself depends on the crystal structure. In spite of its greater density,  $\gamma$ -iron has a smaller capacity for holding electrons than the  $\beta$ -modification. The author considers the thermo-electric processes to be governed by the atomic force-fields. Each atom has its own sphere of force, and between atoms there is a free space

where these are small. The free space determines the power of retaining electrons and the thermo-electric properties.

It is assumed that the radius of the force-field is half the smallest distance between atoms in the lattice. This leads to the conclusion that this distance does not change at the transformation point. The assumption is justified within the limits of error by experiment on the thermo-electric power near the transformation point. Moreover, the behaviour of iron under dilatation and compression, together with the trifling change in the temperature-resistance curve at this point, can all be harmonised with the conception. The iron crystal lattice which is capable (in the thermo-electric sense) of retaining most electrons, possesses (in the sense of the Richardson equation) the largest number of free electrons.

R. A. M.

**Physical Properties of Nacreous Sulphur.** H. WHITAKER (*J. Physical Chem.*, 1925, **29**, 399—405).—When sulphur condenses on a glass plate in droplets it is found that these droplets gradually assume various crystalline structures. Nacreous sulphur forms six-sided plates having the three pairs of opposite sides parallel. The colours shown by these plates are due to interference. The plates gradually disintegrate on ageing, probably into the more stable octahedral variety.

M. B. D.

**Structure of Quenched Carbon Steels.** B. D. ENLUND (*J. Iron and Steel Inst.*, May, 1925 [Advance proof]; 10 pages).—The structure of quenched carbon steels as ascertained from measurement of changes in electrical resistivity and specific volume with annealing temperature is described. The results confirm the view that martensite is transformed into troostite at 100—200° and also that austenite, retained after quenching, is decomposed at about 260°. In this way, it may be shown that even low-carbon steels contain some untransformed  $\gamma$ -iron after quenching. [Cf. *B.*, 1925, 404.]

M. E. N.

**Artificial Magnetic Anisotropy of Nickel. Phenomena of Large Discontinuities.** R. FORRER (*Compt. rend.*, 1925, **180**, 1253—1255).—Nickel can be obtained in a state showing new magnetic properties. Barkhausen amplified the currents induced by progressive magnetisation of a substance and found discontinuities. Van der Pol found 6500 discontinuities using a sample of iron, and 5000 with ferro-nickel. He further found that discontinuities could be observed with nickel even without amplification. This is confirmed for ordinary nickel wire, but if the same wire is drawn out the magnetisation discontinuities disappear. If this drawn specimen is wound round a cylinder, the phenomenon reappears in an intensified form. The cycles have been studied by means of a magnetometer under different field limits. With nickel stretched almost to breaking point, the cycle is wide and regular. When the same wire is wound round a cylinder, the results indicate sudden irregularities comparable in magnitude with the total magnetisation. This sudden increase in magnetisation occurs in spite of the gradual

decrease in the field under the experimental conditions. The property persists over long periods of time. Heating for a few seconds above  $1000^{\circ}$  causes the cycles observed to revert to those ordinarily found. Heating at  $500^{\circ}$  does not effect the reversion, whilst heating at temperatures between  $500^{\circ}$  and  $700^{\circ}$  causes progressive diminution in the discontinuities. About  $720^{\circ}$  the crystalline lattice probably undergoes rearrangement. R. A. M.

**Temper-brittleness of Steels : Susceptibility to Temper-brittleness in Relation of Chemical Composition.** R. H. GREAVES and J. A. JONES (*J. Iron and Steel Inst.*, May, 1925 [Advance proof]; 25 pages).—Phosphorus and manganese increase the susceptibility to a marked extent, silicon and vanadium have only a slight effect, and tungsten has practically none. Molybdenum has a very pronounced reducing effect. Temper-brittleness in certain steels may be overcome by cooling in water, or preferably in oil, or by cooling in water to  $400^{\circ}$  and then air-cooling. [Cf. B., 1925, 405.] M. E. N.

**Anhyseretic Magnetostrictive Effects in Iron, Nickel, and Cobalt.** P. McCORKLE (*Physical Rev.*, 1925, [ii], 25, 541—549).

**Effect of a Superposed Alternating Field on Apparent Magnetic Permeability and Hysteresis Loss.** T. SPOONER (*Physical Rev.*, 1925, [ii], 25, 527—540).

**Modified Reflexion in Metallography.** J. CZOCHRALSKI (*Z. anorg. Chem.*, 1925, 144, 131—141).—The reflexion of light from the etched surface of a metal is governed by the degree of attack of the etching agent, which varies with the inclination of the exposed crystal faces to the crystal axes. The directions of maximum reflexion, which may be determined experimentally, suffice to fix the orientation of the crystal, and hence are of assistance in the examination of the structure of a metal or alloy. Methods of arriving at these directions are described. S. I. L.

**Thermal Expansion of Binary Mixed Crystal Systems.** C. H. JOHANSSON (*Ann. Physik*, 1925, [iv], 76, 445—454).—Measurements have been made by the double-mirror dilatometer (this vol., ii, 27) of the expansion coefficients at a series of temperatures between  $35^{\circ}$  and  $-180^{\circ}$  of the systems silver-gold, copper-nickel, gold-palladium, silver-palladium, copper-palladium, and copper-gold. The coefficients for all mixtures are less than those calculated by the simple mixture rule. The deviations are attributed to distortion of the atomic lattices owing to differences of atomic volume and of atomic force-field between the pairs of components. The magnitude of the maximum deviation runs parallel with the difference of atomic volume of the components. Since the well-developed peaks which characterise the diagrams of the electrical properties of the systems copper-palladium and copper-silver do not occur in the above curves, these properties are not related.

F. G. T.

**Plastic Extension and Fracture of Aluminium Crystals.** G. I. TAYLOR and C. F. ELAM (*Proc. Roy. Soc.*, 1925, **A**, 108, 28—51).—A physical and mathematical paper in which the distortion and fracture of crystals are considered and a theory of fracture is outlined.

J. S. C.

**Martensite and Troostite.** J. H. WHEATLEY (*J. Iron and Steel Inst.*, May, 1925 [Advance proof]; 24 pages).—A consideration of the origin of the different forms of martensite and troostite and their behaviour on tempering as ascertained from a microscopical examination of the quenched specimens. The different types of martensite and troostite are described in detail and the formation of martensite is discussed. [Cf. *B.*, 1925, 404.]

M. E. N.

**Increase in Strength of Single Crystals by Alloying and Cold-drawing.** P. ROSBAUD and E. SCHMID (*Z. Physik*, 1925, **32**, 197—225).—The rigidity of metallic crystals is expressed quantitatively by the shearing force in the plane of slip which is necessary to produce plastic change of shape. The critical value is independent of such force as may be perpendicular to the plane; for zinc containing 0.03% of cadmium at the ordinary temperature it is 94 g./mm.<sup>2</sup> Single crystals of zinc containing 0.53% of cadmium show 9 times the strength, with 1.03% of cadmium 12.2 times; extrapolating for pure zinc the value 40 g./mm.<sup>2</sup> is obtained. Zinc containing more than 0.1% of tin solidifies with inclusions of zinc-tin eutectic; with 0.5% of this eutectic the strength is 3 times that of the crystal free from tin. The increase of strength produced by cold-drawing the zinc-cadmium crystals rises with increase of the cadmium content. Photomicrographs are reproduced.

E. B. L.

**Metal Crystals. III. Thermal Expansion of Zinc and Cadmium.** E. GRÜNEISEN and E. GOENS (*Z. Physik*, 1924, **29**, 141—156).—Henning's expansion apparatus has been modified for determinations at temperatures in the neighbourhood of that of liquid hydrogen. The mean coefficients of expansion parallel to and perpendicular to the hexagonal axis have been determined over the range +100° to -253° for single crystals of cadmium and zinc having axes approximately perpendicular to the hexagonal axis. The values observed for the two directions are not identical; their temperature variation is extraordinary and has considerable bearing on the theory of the solid state. An analysis is developed on the basis of the theories of Börn and Debye which leads to values of the expansion coefficients agreeing well with the values obtained experimentally.

R. W. L.

**Heat of Formation of Calcium Hypochlorite.** B. NEUMANN and G. MÜLLER (*Z. angew. Chem.*, 1925, **38**, 193—195).—The heat evolved in the chlorination of calcium hydroxide moistened with 4% excess water is 100.1 cal. per g. of lime, or 247.5 cal. per g. of chlorine. More or less water yields an inferior product. Perfectly dry chlorine and lime will not react.

S. K. T.

**X-Ray Study of Fatty Acids and Dibasic Acids.** J. J. TRILLAT (*Compt. rend.*, 1925, **180**, 1329—1332; cf. this vol., ii, 195).—The orientation of fatty acid molecules on glass is very regular if a small quantity of alcoholic solution is allowed to evaporate. The invisible films give clear X-ray spectra corresponding with the length of the side-chain, and diffuse effects due to thicker, uneven layers of crystals are eliminated. The maximum distances for the fatty acids are: stearic 39.1 Å., palmitic 35.13, myristic, 31.14, lauric 27.24, decolic 23.30, hexoic 19.30. Thus  $\Delta\lambda$  for  $C_{n+2}-C_n$  is 3.94 (mean). A supposed  $C_{17}$  acid gave two series corresponding with a mixture of stearic ( $C_{18}$ ) and palmitic ( $C_{16}$ ) acids, an interesting analytical application. Thin layers of fused dibasic acids were prepared on glass. The spectra, although feeble, are similar. Succinic acid, maximum distance 4.5 Å.; adipic, 7.0; suberic, 9.3; sebacic, 11.4;  $\Delta\lambda$  for  $C_{n+2}-C_n=2.3$  Å. Two acids with odd numbers of carbon atoms were examined, pimelic ( $C_7$ ) and azelaic ( $C_9$ ), with distances of 7.6 and 9.6 Å., respectively,  $\Delta\lambda=2.0$ . The length of side-chain for an acid with an odd number of carbon atoms is not midway between the two acids with even numbers on either side. Neither are the melting points midway. Thus the  $\text{CH}_2$  groups in a chain are not evenly spaced. The distance between  $C_{2n+1}$  and  $C_{2n}$  is smaller than that between  $C_{2n}$  and  $C_{2n-1}$ .  
R. A. M.

**Tensimetric Determination of Molecular Weight with Liquid Ammonia as Solvent.** A. STOCK and E. POHLAND (*Ber.*, 1925, **58**, [B], 657—661).—The apparatus consists of two tubes one of which contains liquid ammonia, whereas the other is provided with an electro-magnetically operated stirrer and contains the solution of the substance under investigation in liquid ammonia. The tubes are connected with the two arms of a differential mercury gauge and, by means of mercury valves, to the vacuum apparatus. The molecular weight ( $M$ ) is calculated from the formula  $M=17Sp/L\Delta p$ , in which  $S$  and  $L$  are the weights of solute and solvent,  $p$  and  $\Delta p$  the vapour tension of the solvent and the difference between the vapour tensions of solvent and solution, respectively.

The additive compound of diborane and ammonia (cf. A., 1923, ii, 408) contains the simple molecule  $\text{B}_2\text{H}_6$  in the solution.

H. W.

**Variation of the Molecular Condensation of Tin with Temperature.** A. JOUNIAUX (*Bull. Soc. chim.*, 1925, [iv], **37**, 67—84).—The molecular weight of tin is calculated for various temperatures, from its boiling point, heat of vaporisation, and Trouton's rule; from cryoscopic measurements in various metals and in iodine; from vapour-pressure measurements of its amalgams; and from surface tension measurements of the liquid. The molecule is approximately triatomic at 100°, the mean molecular weight decreases linearly with temperature until the molecules are monatomic at about 620° and then remains constant until the b. p., 2270°. Some anomalous cryoscopic results are considered.

L. J. H.

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**Explosion Potential in Carbon Dioxide at High Pressures.** C. E. GUYE, P. MERCIER, and J.-J. WEIGLÉ (*Compt. rend.*, 1925, 180, 1251—1253).—Summary of data. R. A. M.

**Thomson Effect in Copper, Iron, and Carbon Steels.** J. YOUNG (*Proc. Physical Soc.*, 1925, 27, 145—157).—Measurements over a range of 40—300° in annealed wires show that  $(\sigma_{Fe} - \sigma_{Cu})/T$ , where  $\sigma$  is the Thomson effect coefficient, and  $d^2E/dT$ , where  $E$  is the thermo-electric difference of potential, when respectively plotted against temperature give parallel curves (theory requiring congruence) both of which have a minimum at 180°. The Thomson effect in steel wires increases with their carbon content and passes through a minimum value near 250°. Different quantitative results are obtained according as the current is sent along or against the temperature gradient; this is ascribed to structural asymmetry due to the direction in which the wire was drawn through the die.

W. A. C.

**Allotropy of Mercuric Iodide.** S. C. BOKHORST and H. VAN DER ZEE (*Bull. Soc. chim.*, 1925, [iv], 37, 153—157).—Polemical against Damiens (*ibid.*, 1924, [iv], 35, 87).

L. J. H.

**Allotropy of Mercuric Iodide.** A. DAMIENS (*Bull. Soc. chim.*, 1925, [iv], 37, 157—162).—Polemical against Bokhorst and van der Zee (cf. preceding abstract).

L. J. H.

**Calorimetric Researches. VIII. The Paraffin Oil Method: an Aid in the Determination of the Heats of Combustion of Difficultly Combustible and Hygroscopic Substances.** P. E. VERKADE, J. COOPS, and H. HARTMAN (*Rec. trav. chim.*, 1925, 44, 206—216).—The technique of the combustion of organic substances in the calorimetric bomb is described in detail and discussed. Methods of ignition with or without such auxiliary substances as naphthalene are sometimes unsatisfactory, but success is always attained when a porous pellet of the substance is drenched with paraffin oil, and the results are accurate in spite of the use of a relatively large proportion of auxiliary substance of high heat of combustion. Comparative determinations are recorded by this and other methods for a number of compounds. The difficult cases which have been successfully dealt with include substances of low heat of combustion, substances of high melting point, substances which form voluminous masses of crystals, and hygroscopic substances. The following heats of combustion are recorded: *i*-tartaric acid 1845·8, *d*-*N*-benzyltartramide 5602, tetraethylsuccinic anhydride 7639, *s*-*N*-diethyl-*i*-tartramide 5219·5, *trans*-1:2:3:4-tetrahydronaphthalene-2:3-dibenzoate 7521·5, acetone compound of hydrobenzoin 8434, anhydrous oxalic acid 678·0, ammonium hydrogen *d*-tartrate 2050·6, isophthalic acid 4629·5, *d*-*N*-phenyltartramide 5245·7, *s*-diphenylsuccinic acid 6691·8, *r*-diethylsuccinic anhydride 6375·8 cal./g.

G. M. B.

**Physical Properties of Nitro Derivatives.** L. DESVERGNES (*Mon. Sci.*, 1925, 15, 73—78).—*p*-Chloronitrobenzene obtained by

purification of the technical product has m. p.  $83.19^\circ$  (literature,  $83^\circ$ ); its solubility in water at  $17^\circ$  is 0.0028; at  $50^\circ$ , 0.0125; at  $100^\circ$ , 0.0153. 1-Chloro-2:4-dinitrobenzene has m. p.  $50.08^\circ$  to  $50.12^\circ$  (Post and Naumann give  $50^\circ$ ; Ullmann,  $51^\circ$ ; Würtz,  $53^\circ$ ). It is stated in the literature to be insoluble in water, but at  $15^\circ$  the solubility was found to be 0.008, at  $50^\circ$  0.041, at  $100^\circ$  0.159. The solution of chloro-2:4-dinitrobenzene is brown and after some time a violet-black substance, m. p.  $170^\circ$ , separates (cf. Vongerichten, A., 1900, i, 51). Alkalis convert the substance into pyridine dinitrophenate (deep red) (cf. Spiegel, A., 1900, i, 51) from the alcoholic solution of which 2:4-dinitrophenol is precipitated by hydrochloric acid. 1-Chloro-2:4:6-trinitrobenzene, pale straw-coloured crystals when pure, has m. p.  $81.64$ — $81.67^\circ$  (literature gives  $83^\circ$ ). Its solubility in water (g. substance per 100 g. water) is 0.0178 at  $15^\circ$ , 0.053 at  $50^\circ$ , 0.346 at  $100^\circ$  (literature states insoluble in water). Some hydrolysis takes place with water, yielding picric acid, particularly at  $100^\circ$ . 1-Chloro-2:4:6-trinitrobenzene gives an intense black coloration with pyridine in the cold. Evaporation of the solution leaves an amorphous substance from which hot benzene extracts picric acid; the residue on treatment with cold chloroform yields a yellowish-orange, crystalline substance, the alcoholic solution of which gives ruby-red crystals, m. p.  $129$ — $130^\circ$ , the composition of which appears to correspond with the formula  $2C_6H_2(OH)(NO_2)_3 \cdot 5C_5H_5N$ . The undissolved reddish, amorphous residue softens at  $100^\circ$ . The solubilities of the substances in several organic solvents have been determined. A. C.

**Thermal Data on Organic Compounds. I. Heat Capacities and Free Energies of Methyl, Ethyl, and *n*-Butyl Alcohols.** G. S. PARKS (*J. Amer. Chem. Soc.*, 1925, 47, 338—345).—From thermal measurements extending to very low temperatures the specific heats of the crystalline and liquid forms of methyl, ethyl, and *n*-butyl alcohols were measured and also their heats of fusion. Methyl alcohol has two crystalline forms with a transition point at  $161.1^\circ$  Abs., the second form melting at  $175.3^\circ$  Abs., the heat of fusion being 23.7 cal./g. The heats of fusion of ethyl and *n*-butyl alcohols are respectively 25.76 and 29.93 cal./g. Using the third law of thermodynamics and the formula of Lewis and Gibson (A., 1920, ii, 585), up to  $90^\circ$  Abs. the entropies per mol. at  $298^\circ$  are 32.6, 42.3, and 60.2 and the free energies of formation are -44500, -44000, and -44100 cal. The entropy of super-cooled ethyl alcohol exceeds that of the crystalline form by 3.7 units per mol. at  $87^\circ$  Abs. L. J. H.

**Ratio of Specific Heats for Liquids.** F. A. SCHULZE (*Physikal. Z.*, 1925, 26, 153—155).—The values of  $C_p - C_v$  and  $C_p/C_v$  for 37 unassociated and for 16 associated liquids are tabulated. The difference between the molar heat capacities at constant pressure and constant volume lies between 10 and 11 for all unassociated liquids. For associated liquids the value is considerably lower.

F. G. T.



**Specific Heats and Latent Heats of Fusion of Ice and of Several Organic Compounds.** O. MAASS and L. J. WALDBAUER (*J. Amer. Chem. Soc.*, 1925, **47**, 1—9).—An apparatus is described for measuring the heat capacity of substances between 16.5° and various temperatures ranging from -180° to 0°. From this the specific heat is calculated and the latent heat of fusion if the solid melts below 16.5°. The specific heat of ice may be represented by  $c = 0.485 + 0.000914t - 0.00000546t^2$ . The latent heats of fusion of water, benzene, acetone, and methyl alcohol are 79.42, 30.56, 19.60, and 16.40, respectively. Where the specific heat of a compound varies greatly with the temperature the atomic heat is a highly constitutive property. L. J. H.

**Trouton's Ratio at the Absolute Zero.** N. PERRAKIS (*Compt. rend.*, 1925, **180**, 579—580; cf. *ibid.*, 1924, **179**, 562).—As the temperature falls, Trouton's ratio varies according to an exponential function of the temperature and tends to a limiting value, at the absolute zero, equal to  $1.5R$ , the specific heat at constant volume of a monatomic gas. G. M. B.

**Heats of Formation of Phenol-Water Solutions at 75°.** J. B. FERGUSON and W. B. HOPE (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 121).—The maximum heat effect occurs at approximately 61% phenol by weight and is 5.0 cal./g. of solution (heat absorbed). J. S. C.

**Cooling of Hot Bodies in Gases and Liquids.** R. SEELIGER (*Physikal. Z.*, 1925, **26**, 282—295).—A review and bibliography of the hydrodynamic and gas film theories of cooling. F. G. T.

**Temperature-Entropy Diagrams for Nitrogen and Oxygen.** W. H. RODEBUSH, J. W. ANDREWS, and J. B. TAYLOR (*J. Amer. Chem. Soc.*, 1925, **47**, 313—319).—A method of determining the heat content of superheated liquids depending on the proportion vaporised on adiabatic expansion is described and applied to nitrogen and oxygen. The temperature-entropy diagrams are given for these elements, as liquids under their own vapour pressure, from the boiling to the critical points. L. J. H.

**Entropies of the Vapours of Zinc and Lead.** W. H. RODEBUSH and A. L. DIXON (*J. Amer. Chem. Soc.*, 1925, **47**, 1036—1043).—The vapour pressure of zinc, measured by the method described previously (A., 1923, ii, 738), is expressed by the relation:  $\log p(\text{mm.}) = -6967/T - 2.162 \log T + 2.298 \times 10^4/T + 15.1817$ , which also includes Braune's figures (A., 1920, ii, 491). The measurements for lead, which entailed some experimental difficulty, are given by the following equations, which include Egerton's results (*Phil. Mag.*, 1917, [vi], **33**, 33):  $\log p(\text{mm.}) = -9854/T + 7.822$  between 900° and 1600° Abs., and  $\log p(\text{mm.}) = -10100/T - 0.65 \log T + 10.05$  between 600° and 900° Abs. The entropies of the vapours calculated by means of these equations agree with the values predicted by Tetrode (*Ann. Physik*, 1912, [iv], **38**, 434). S. K. T.

**Specific Gravity of Solid Binary Compounds.** U. PANICHI (*Atti R. Accad. Lincei*, 1924, [v], 33, 572—579).—With minerals (cf. this vol., ii, 64) and a number of solid binary compounds examined, as the ratio of the atomic volume to the valency of the element combined with the non-metal decreases, the excess of the calculated density (*loc. cit.*) over the actual density tends first to assume maximum positive values and then to diminish gradually.  
T. H. P.

**Vapour-pressure Curves of Salts.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1925, 143, 336—342).—Lorenz (A., 1924, ii, 654) has shown that the constant  $q$  in Dühring's vapour-pressure formula  $(T_2 - T_1)/(\theta_2 - \theta_1) = q$  is in many cases equal to  $T_1/\theta_1$ . Values of  $q$  and of  $T_1/\theta_1$  have now been evaluated for a considerable number of halides for which vapour-pressure data are available, water and hexane being used as reference substances. The value of  $q$  is reasonably constant over a range of temperatures; the agreement between  $q$  and  $T_1/\theta_1$  is less good, but is considered as close as could be expected for substances so different in character as halides and water or hexane. Tantalum fluoride is an exception,  $q$  not being constant, whereas cuprous chloride, bromide, and iodide and thallium fluoride give constant values for  $q$ , but much lower or higher values for  $T_1/\theta_1$ .  
A. G.

**Partial Pressure of Water Out of Aqueous Solutions of Sulphuric Acid.** C. H. GREENEWALT (*Ind. Eng. Chem.*, 1925, 17, 522—523).—A series of curves showing vapour pressures plotted against concentrations for even temperatures was prepared, and from these curves others correlating  $\log p$  with  $1/T$  were plotted. The parameters for the equations of these curves are given in a table. [Cf. B., July 3rd.]  
D. G. H.

**Germanium. VIII. Physical Properties of Monogermene.** R. B. COREY and A. W. LAUBENGAYER [with L. M. DENNIS] (*J. Amer. Chem. Soc.*, 1925, 47, 112—117).—One litre of monogermene,  $\text{GeH}_4$ , under standard conditions weighs 3.420 g. (theoretical 3.416), the composition being confirmed by analysis; m. p.  $-165^\circ$ , b. p.  $-90^\circ$ ,  $d$  at  $-142^\circ$  1.523. It decomposes into its elements at  $280-285^\circ$ . The vapour pressures from  $-145^\circ$  to  $-90^\circ$  are given. The results differ from those of Schenck (A., 1922, ii, 855), but are probably more trustworthy since the  $\log P-1/T$  curve is linear.  
L. J. H.

**Saturation Pressure of Mercury up to 2000 kg./cm.<sup>2</sup>** F. BERNHARDT (*Physikal. Z.*, 1925, 26, 265—275).—The saturation pressure of mercury was measured up to a temperature of  $1435^\circ$  and a pressure of 2020 kg./cm.<sup>2</sup> For low pressures, an electrically heated glass capillary tube was used. For higher pressures and temperatures, a Des Coudres bomb with a quartz window was employed. For the highest pressures, the window was omitted. In the latter case, the mercury was contained in a quartz vessel, and the boiling point determined by changes of resistance of a mercury thread in a capillary tube forming part of the quartz vessel. An

investigation of the strengths of glass capillary tubes showed that at equal temperatures the strength of ordinary Jena glass is greater than that of hard glass. The saturation pressures at temperatures up to  $850^{\circ}$  are slightly less than those found by Cailletet. The following pressures, in kg./cm.<sup>2</sup>, are typical of higher temperatures:  $1000^{\circ}$ , 260;  $1100^{\circ}$ , 425;  $1200^{\circ}$ , 665;  $1300^{\circ}$ , 1025;  $1400^{\circ}$ , 1600;  $1435^{\circ}$ , 2020. The Hertz-Knudsen formula holds satisfactorily up to  $1000^{\circ}$ . The author's values are consistently higher than those calculated from the density measurements of Bender (A., 1915, ii, 673). Taking Bender's value of  $1650^{\circ}$  as the critical temperature of mercury, extrapolation gives a critical pressure of 3000–3500 kg./cm.<sup>2</sup> F. G. T.

**Vapour Pressures of Solid and Liquid Benzophenone between  $0^{\circ}$  and  $48^{\circ}$ .** M. VOLMER and P. KIRCHOFF (*Z. physikal. Chem.*, 1925, **115**, 233–238).—The vapour pressures of the equilibrium forms were determined by a modification of Knudsen's method (*Ann. Physik*, 1909, [iv], **29**, 179); the apparatus employed is described. The vapour pressures of super-cooled liquid benzophenone were obtained by the method of Volmer and Estermann (A., 1922, ii, 193). The measured value of the vapour pressure of solid benzophenone at  $40^{\circ}$  is about 11% too low; this error, however, probably decreases at lower temperatures. L. F. G.

**Vapour Pressures and Boiling Points of Mono- and Dimethylanilines and Mono- and Di-ethylanilines.** O. A. NELSON and H. WALES (*J. Amer. Chem. Soc.*, 1925, **47**, 867–872).—The vapour pressures of mono- and di-methylanilines and mono- and di-ethylanilines were measured at  $5^{\circ}$  intervals from  $40^{\circ}$  to  $220^{\circ}$ . The latent heats  $L$  and vapour pressures  $P$  at various temperatures  $T$  are given by the following equations: monomethylaniline, b. p.  $195.70^{\circ}/760$  mm.,  $L=17369.0-12.933T$ ;  $\log P=28.1580-(3706.4/T)-6.504 \log T$ ; dimethylaniline, b. p.  $193.50^{\circ}/760$  mm.,  $L=12953.0-4.62T$ ;  $\log P=15.14437-(2828.5/T)-2.3234 \log T$ ; monoethylaniline, b. p.  $204.72^{\circ}/760$  mm.,  $L=13248.0-3.9T$ ;  $\log P=14.1910-(2892.9/T)-1.9613 \log T$ ; diethylaniline, b. p.  $216.27^{\circ}/760$  mm.,  $L=1412.6-5.3081T$ ;  $\log P=16.40076-(3102.3/T)-2.6693 \log T$ . F. G. W.

**Temperatures of Corresponding Densities.** W. HERZ (*Z. anorg. Chem.*, 1925, **144**, 40–44).—The ratios of the temperatures at which the density of a fluid is a definite fraction of the critical density, to the critical temperatures, have been calculated for a great number of fluids, both temperatures being absolute. The ratio  $T/T_k$ ,  $T$  being the temperature at which the density is one-half of the critical density, is very close to 0.978, the maximum divergence in 39 cases being only about 1%; for lower ratios of the density, the divergence increases, the ratio being 0.830 with a maximum divergence of 6% for one-tenth of the critical density, and 0.697 with a maximum divergence of 11.5% for one-fiftieth of the critical density. Ratios of temperatures at which the densities are 2 and 2.75 times the critical density are also compared; the agreement is not so good. S. I. L.

**Equation of State of Liquids and Solids at High and Low Temperatures.** J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, 27, 897—913).—The quantity  $b$  in the van der Waals' equation is assumed to be a function of  $v$ , equal to  $b_g/[1+(b_g-b_0)/v]$ . Certain consequences of this assumption are discussed and the equation of state is derived from thermodynamic relations.

L. L. B.

**Definition of a Perfect Gas.** A. L. CLARK (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 293—311).—Four criteria are usually applied to define a perfect gas. These may be expressed mathematically:

as I  $Pv = f(T)$ ; II  $v = kT$ ; III  $\lambda = T \left( \frac{\delta P}{\delta T} \right)_T - P = 0$ ,

and IV  $\mu = [T \left( \frac{\delta v}{\delta T} \right)_P - v]/Cp = 0$ . ( $P$  = pressure,  $v$  = volume,  $T$  =

Abs. temperature,  $\lambda$  = internal pressure,  $\mu$  = the change in temperature on expansion without doing external work.) The above are not independent, and it is shown mathematically that if any two are satisfied the others are also. The best method of defining a perfect gas depends on the purpose at hand. A definition free from all uncertainty and applicable to all experimental work is that "a perfect gas is one which obeys the laws of Boyle and Joule."

J. S. C.

**Entropy and Probable State of Ideal Gases.** F. VON HAUER (*Physikal. Z.*, 1925, 26, 281—282).—Consideration of the heat exchange between a mass of gas and a gas reservoir at a very much higher temperature shows that the probable state of the gas at a given temperature and volume, calculated by the application of Maxwell's distribution law alone (*Ann. Physik*, 1915, [iv], 47, 365), is related to the entropy by an equation identical in form with the Boltzmann equation  $S = k \log W + \text{constant}$ .

F. G. T.

**Quantising of Monatomic Gases.** M. PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 49—57).—Mathematical. An investigation as to whether, in view of the conclusions of Stern and Gerlach (*Z. Physik*, 1922, 9, 349), quantum statistical methods may be applied to the theory of gases. Previous conclusions (A., 1920, ii, 414) are modified by regarding each state of a gas system of  $N$  molecules as characterised by  $N!$  different phase points, since two phase points in which two or more atoms have exchanged coordinates or velocity components are to be regarded as in identical states. Each quantum cell is thus defined by  $N!$ -congruent cells in generalised space. To each "nuclear cell" the space  $h^{3N}$  is ascribed. On this basis, expressions are developed for the free energy, entropy, and energy content of a monatomic gas. Gas degradation at low temperatures and high densities is predicted by these expressions, which are compared with those deduced by Einstein (cf. following abstract).

F. G. T.

**Quantum Theory of the Monatomic Perfect Gas.** A. EINSTEIN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 3—14).—Mathematical. Continuation of previous work (*ibid.*, 1924, 261—

267). In the earlier paper the conditions necessary for a perfect gas to have its entropy, statistical, and thermodynamic character in accordance with Boltzmann's hypothesis were investigated and the classical gas equation was discussed. In the present paper, the theory of the deviation of the gas equation is extended. At any temperature a saturation density of perfect gas is postulated such that the molecules in excess of this density do not take part in thermal agitation. The statistical properties (density and vibration frequencies) are considered mathematically. The following approximation for the equation of state is given:  $p = RT\eta[1 - 0.186h^3N^4\eta/(2\pi MRT)^{3/2}]$ , where  $\eta$  = molecular concentration,  $N$  = number of molecules per mole,  $M$  = molecular weight. R. A. M.

**Entropy of Perfect Gases at Absolute Zero.** N. DE KOLOSOWSKY (*J. Chim. phys.*, 1925, **22**, 77—78).—Theoretical. Planck's equation  $\log p = -U_0/ART + \alpha/AR + C_p/AR \cdot \log T$  (1) combined with the equation for the entropy of a perfect gas,  $S_g$ , gives the relation (2)  $S_g = U_0/T + C_p$ , from which Planck ("Vorlesungen über Thermodynamik") concluded that the entropy of a gas at absolute zero is  $+\infty$ . Equation (1) is identical with empirical formulae of the type  $\log p = A + B/T + C \log T$ , in which  $C$  is found experimentally to be negative. The proof adopted by Planck thus involves the assumption that  $C_p$  is negative, which is contrary to experimental fact. The proof is therefore unjustifiable, although the conclusion that  $S_g = +\infty$  at the absolute zero is possibly correct. W. H. R.

**Validity of Gas Equations. I.** W. HERZ (*Z. Elektrochem.*, 1924, **30**, 604—607).—Nernst's gas equation  $p(v - v_1) = RT(1 - p/p_c)$ , where  $p, p_c$  are the pressures and critical pressures,  $v, v_1$  the volumes of gases and liquids respectively at absolute temperature  $T$ , and  $R$  is the molecular gas constant, is tested for various organic and inorganic substances from  $T = 273^\circ$  upwards, using values given in the Landolt-Börnstein tables. Apart from inaccuracies due to interpolation, the value of  $R$  is found, in general, to be correctly given up to temperatures of 0.8 to 0.9 of the critical temperatures. It is suggested that deviations may be attributed to molecular association. C. H. D. C.

**Surface Tension : Interpretation of the Eötvös Expression.** L. BRILLOUIN (*Compt. rend.*, 1925, **180**, 1248—1251).—Theoretical interpretations of the Eötvös expression  $-\delta A/\delta T \cdot V_m^{2/3}$  = constant are inadequate. ( $A$  = capillary constant of a liquid,  $V_m$  = molecular volume; the constant for very different liquids is 2.1—2.25 C.G.S.) Two factors are considered: waves of capillarity setting in motion the molecules of the surface layer and penetrating little into the interior of the liquid, and compression waves agitating the interior. The velocity  $W$  of capillarity waves is given by  $W = [2\pi A\nu/(\rho_1 - \rho_2)]^{1/3}$ , where  $\nu$  is frequency and  $\rho_1, \rho_2$  are the densities of liquid and vapour, respectively. If  $\bar{S}_m$  is the area of a unimolecular film of 1 g.-mol. of liquid there are  $N/\bar{S}_m$  mols. per unit area; since each has three degrees of freedom the number per unit area is  $3N/\bar{S}_m$ . The energy of agitation (Debye) will then be  $\epsilon = 3N \cdot KT/\bar{S}_m = 3RT/\bar{S}_m$ .

This energy is partitioned among frequencies extending from 0 to an upper limit  $\nu_e$  with an accumulation near the limit. These waves exert on unit length a force  $\omega = W_g \epsilon / 2W = 3\epsilon/4$ , where  $W_g$  represents the velocity of the group  $\delta\nu/d(\nu/W)$  and is equal to  $3W/2$ . This force will diminish the static surface tension  $A_0$  (that obtained in the absence of thermal agitation) so that the surface tension coefficient at temperature  $T$  will be  $A_T = A_0 - 3\epsilon/4 = A_0 - 9RT/4S_m$ , an expression closely resembling that of Eötvös when differentiated:  $-\delta A/\delta T \cdot S_m = 9R/4 = \text{constant}$ .

If  $d$  is the mean distance separating molecules in the liquid (i.e.,  $Nd^3 = V_m$ ), and  $\delta$  is the mean distance in the surface layer  $N\delta^2 = S_m$ , and if  $d$  and  $\delta$  are equal,  $S_m = N^{1/3}V_m^{2/3}$ . Hence  $-\delta A/\delta T \cdot V_m^{2/3} = 9/4 \cdot RN^{-1/3} = 2.2$ , since  $R = 8.31 \times 10^7$  and  $N = 61 \times 10^{22}$ . The agreement justifies the assumptions made, and in particular that  $d = \delta$ , i.e., that the distance separating molecules in the surface layer is little different from that in the bulk of liquid, although the distances between the first and second layers may be very different.

R. A. M.

**Determination of Surface Tension from the Rise in Capillary Tubes.** S. SUGDEN (*J. Amer. Chem. Soc.*, 1925, **47**, 60—64).—Mathematical.

L. J. H.

**Compressibilities of Gases at 0° and below one Atmosphere, and the Divergence from Avogadro's Law. III. Ethylene, Nitrous Oxide, Nitric Oxide, and Methyl Ether.** T. BATUECAS (*J. Chim. phys.*, 1925, **22**, 101—115).—A continuation of previous work (cf. Guye and Batuecas, A., 1922, ii, 617). The following values are found for the divergence from Avogadro's law ( $1 + \lambda$ ) and the compressibility at 0°. Ethylene,  $1.00780$  and  $102 \times 10^{-6}$ ; nitrous oxide,  $1.00739$  and  $97.8 \times 10^{-6}$ ; nitric oxide,  $1.00112$  and  $14.7 \times 10^{-6}$ ; methyl ether,  $1.02540$  and  $326 \times 10^{-6}$ . The results for ethylene give 12.000 as the atomic weight of carbon, and those for nitrous and nitric oxides give, respectively, 14.003 and 14.006 as the atomic weight of nitrogen. The results for methyl ether are not in such good agreement, and in this case the compressibility diminishes as the pressure is lowered.

W. H.-R.

**Compressibilities of Gases at 0° and below one Atmosphere, and the Divergence from Avogadro's Law. IV.** T. BATUECAS, G. MAVERICK, and C. SCHLATTER (*J. Chim. phys.*, 1925, **22**, 131—141; cf. Guye and Batuecas, A., 1922, ii, 617, and preceding abstract).—A new apparatus has been constructed generally resembling that used by Guye and Batuecas (*loc. cit.*), but differing in dimensions and minor details. For oxygen, the divergence from Avogadro's law is determined as  $1 + \lambda = 1.00087$ , in good agreement with the value 1.00085 found with the old apparatus, and indicating that for oxygen the errors due to adsorption on the glass surfaces are negligible.

W. H.-R.

**Compressibility of some Organic Liquids.** K. SCHMIDT (*Ann. Physik*, 1925, [iv], **76**, 571—589).—The compressibilities of *n*-hexane, nitrobenzene, bromobenzene, chlorobenzene, chloroform, toluene, *o*-nitrotoluene, *o*-toluidine, and *m*-toluidine were

measured at 18° and 8° by Röntgen's method. The measurements were comparative, with Röntgen's value for water as a standard. A full discussion is given of the corrections applied to the results, which are estimated as correct to within 0.6%. F. G. T.

**Relation between the Viscosities of Liquids and their Molecular Weights.** D. B. MACLEOD (*Trans. Faraday Soc.*, 1925, 27 [Advance proof]).—The viscosities of liquids are best compared at temperatures at which the free space is a definite fraction of the total volume. Since the expression  $\eta_t x_t^A = c$ , where  $\eta_t$  and  $x_t$  are the viscosity and free space at temperature  $t$ , does not contain the temperature, it is more simple to calculate the free space at 0° for all liquids, and then to adjust the viscosity by calculation to a fixed value of the free space. The free space at 0° ( $x_0$ ) can be calculated from the viscosities at 0° and 10° by the relation  $\eta_0/\eta_{10} = (x_0 + V_{10} + 1)/x_0 V_{10}$ , where  $V_{10}$  is the volume at 10° of 1 c.c. at 0°. When the molecular weights are plotted against the viscosities of each liquid with the free space adjusted to a fixed ratio 1/10th of the total volume, normal substances lie approximately on a straight line, whilst associated substances are removed from this line. The factors by which the molecular weights must be multiplied in order to make associated substances lie on the normal line (see above), are in general agreement with the association factors found by other means. The viscosity of a liquid may therefore be expressed in the form  $\eta = KMa/x$ , where  $K = 0.5492$ ,  $M$  is the molecular weight in the gaseous phase,  $a$  the degree of association in the liquid, and  $x$  the relative amount of free space. W. H.-R.

**Physical Properties of Water.** D. B. MACLEOD (*Trans. Faraday Soc.*, 1925, 27 [Advance proof]; cf. preceding abstract).—In most liquids, association causes a loss both of volume and of free space, but viscosity and density data indicate that in water association results in a loss of free space but a gain in volume, owing to the bulky nature of the associated molecule. As the temperature is raised from 0°, the bulky molecules dissociate, causing a decrease in volume which is counteracted by the ordinary thermal expansion, and this causes a minimum volume to occur at 4°. The viscosity, however, decreases continuously with rise of temperature because the dissociation causes a decrease in molecular weight and an increase in free space, both of which diminish the viscosity (*loc. cit.*). When water is compressed, the bulky molecules dissociate and hence water has an added compressibility, but whilst the dissociation increases the free space, further compression reduces the volume and also the free space, and hence the viscosity shows an initial sag with application of pressure followed by a continual rise with further pressure. W. H.-R.

**Variation of Viscosity of Fluids as a Function of Volume.** J. DUBIEF (*Compt. rend.*, 1925, 180, 1164—1166).—According to the kinetic theory, the coefficient of internal friction,  $\eta_0$ , is proportional to the mean path,  $L$ , and to the mass,  $M^1$ , of gas traversing unit surface in unit time, i.e.,  $\eta_0 = 2M^1L$  (1). But  $M^1 = N_1 mu/6$  (2), and  $L = \lambda^3/\pi\sqrt{2\rho^2}$  (3) (where  $N_1$  is the number of molecules in unit

volume,  $m$  the mass of a molecule,  $u$  its mean velocity,  $\lambda$  the mean distance, and  $\rho$  the diameter of collision). In their application to actual fluids, these relations require correction. For a spherical molecule of a real gas  $M'_1 = M'v/(v-b_0)$ , where  $M'_1$  is the mass of real gas traversing unit volume in unit time,  $v$  the volume, and  $b_0$  the co-volume of van der Waals. Since  $L$  requires no correction,  $n = 2M'_1L = 2M'Lv/(v-b_0) = n_0v/(v-b_0)$  (4). For carbon dioxide (cf. A., 1912, ii, 832),  $b_0 = 0.002363$  and the relations are well verified. Beyond  $v = 12b_0/\pi$ ,  $b_0$  should diminish. This conclusion is verified. The van der Waals equation can be written:  $v/(v-b_0) = (p + a/v_2)v/RT$  and from (4)  $n/n_0 = v/(v-b_0)$ , thus  $n/n_0 = (p + a/v_2)v/RT$ . The degree of agreement is as good for this expression as for the van der Waals equation itself. Similarly, the Dieterici equation leads to  $n/n_0 = v/(v-b_0) = (pv/RT)e^{clv/RT}$ . The agreement is improved, but discrepancies persist, due, it is suggested, to the lack of an exact equation of state.

R. A. M.

### Measurements of Viscosity by the Ostwald Viscosimeter.

F. MARTIN (*Bull. Soc. chim. Belg.*, 1925, **34**, 81—116).—An investigation of conditions necessary to obtain accurate viscosities with a simple type of viscosimeter. The values of Thorpe and Rodger for water, ethyl ether, carbon tetrachloride, benzene, and ethylene bromide were taken as standards and a comparison was made of the values found for the viscosities of these liquids in seven viscosimeters of various dimensions at 15° and 30°. Variations of from 3 to 10% were found, the magnitude of the error being roughly proportional to the speed of outflow. By modifying the Ostwald viscosimeter so that the end of the capillary tube projected into a subsidiary bulb lying slightly above and to the side of a larger bulb, a constant level was obtained below the capillary tube. This reduced considerably the variations in viscosities measured in apparatus of different dimensions. An investigation of the effect of hydrostatic pressure showed that there is a critical velocity of outflow beyond which Poiseuille's law does not hold. Data are given for the construction of viscosimeters by the use of which viscosities may be determined to 1% by the application of a formula containing a simple correction term.

F. G. T.

**Viscosity of Ethyl Ether near the Critical Point.** A. L. CLARK (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 329—338).—Previous experiments (A., 1916, ii, 16), the results of which were interpreted as supporting the view that the liquid state persisted above the critical temperature, have been repeated and are shown to confirm the classical theory of Andrews. The results of the earlier paper are to be interpreted as due to the inability of the density to distribute itself within the experimental tube except after a long period of time.

J. S. C.

**Viscosity of Cotton Cellulose.** J. O. SMALL (*Ind. Eng. Chem.*, 1925, **17**, 515—517).—Factors influencing viscosity are origin of the plant and conditions of growth, and the subsequent purification treatment of the cellulose. Viscosity may be determined and



consistent results obtained by a modification of Joyner's "cuprammonium" solution method (T., 1922, **121**, 1511), and the viscosity of the nitrated products may thus be controlled. It is necessary in the case of low-viscosity types of cotton lint to use a solvent containing approximately 3% of copper. [Cf. B., July 3rd.] D. G. H.

**Diffusibility of Helium through Crystalline Septa.** A. PIUTTI and E. BOGGIO-LERA (*Atti R. Accad. Lincei*, 1924, [v], **33**, 532—537; cf. A., 1924, ii, 42, 105).—At 480°, helium cannot traverse thin sheets of mica or thin sections of quartz cut either parallel or perpendicular to the optic axis, although it is able to pass through both ordinary and silica glasses. According to recent views, such glasses are considered to be composed of liquids of high viscosity. T. H. P.

**Diffusion of Carbon through Tungsten and Tungsten Carbide.** M. R. ANDREWS and S. DUSHMAN (*J. Physical Chem.*, 1925, **29**, 462—472; cf. A., 1923, ii, 327).—The rate of decarbonisation of tungsten wire at temperatures of about 2000° Abs. is fast until all the tungsten carbide,  $W_2C$ , has been decomposed, when a slower rate sets in which depends on the carbon dissolved in the tungsten. In carbonisation, a shell of the second carbide, WC, is formed before the core is completely converted into  $W_2C$ , so that the minimum conductivity of the wire is not reached. M. B. D.

**Self-diffusion in Solid Metals.** G. HEVESY and A. OBRUT-SHEVA (*Nature*, 1925, **115**, 674—675).—Lead foil was pressed in a vacuum against lead containing thorium-B in homogeneous mixture; on heating, diffusion of the active into the inactive lead took place, the  $\alpha$ -particles due to the diffused atoms or their successive products of disintegration producing scintillations on a screen. The rate of self-diffusion increased from  $6 \times 10^{-7}$  cm.<sup>2</sup> day<sup>-1</sup> at 260° to  $1.4 \times 10^{-4}$  at 324°. Further experiments just below the m. p. indicated that the coefficient of diffusion in a single crystal of lead is less than  $10^{-8}$  cm.<sup>2</sup> day<sup>-1</sup>. A slowly-cooled lead bar gave a low, and a suddenly-cooled bar a high, coefficient of diffusion. Comparable results were obtained for the diffusion of similar metals, e.g., thallium and lead, into one another, but in the case of the diffusion of polonium into lead, the coefficient is approximately the same for the foil and the crystal, the atoms of polonium thus loosening the lattice of the individual lead crystals, and diffusing as if through amorphous lead. A. A. E.

**Effect of Molecular Attractions on the Total Pressure of a Gas.** O. MAASS and D. M. MORRISON (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 49—55).—The changes in pressure consequent on the mixing of a number of gases, ranging from gases which for experimental purposes may be regarded as ideal (hydrogen, helium, etc.) to gases of the type of ammonia and methyl ether, have been measured, using the apparatus already described (A., 1923, i, 892). The experimental numbers are interpreted in favour of the view that in a two-component gas mixture three distinct forces of attraction come into play, two between the same species and one

between the different species of molecules. The total pressure depends on the magnitude of these attractions and on the extent to which the forces can come into play. At high pressures the influence of the volumes of the molecules becomes very marked. The results of the investigations of Masson and Dolley (A., 1923, ii, 462) on mixtures of argon, ethylene, and oxygen over the pressure range 5—125 atm. may be interpreted by means of the above hypothesis. J. S. C.

**Concentration of Ammonia in a Compressed Mixture of Hydrogen and Nitrogen over Liquid Ammonia.** A. T. LARSON and C. A. BLACK (*J. Amer. Chem. Soc.*, 1925, **47**, 1015—1020).—The volume percentages of ammonia in a compressed mixture of hydrogen and nitrogen over liquid ammonia increase with increasing temperature ( $-22.5^{\circ}$  to  $18^{\circ}$ ) and decreasing pressure (1000 to 50 atm.). A definite equilibrium exists. The values are much higher than those calculated from the vapour pressure of liquid ammonia; possible explanations are given. S. K. T.

**Separation of Gas Mixtures by Diffusion.** R. LORENZ and A. MAGNUS (*Z. anorg. Chem.*, 1924, **136**, 97—113).—The separation under ideal conditions of a mixture of two gases by diffusion through a porous cell has been calculated from considerations based on the kinetic theory. If  $y$  is the percentage by volume of a gas of molecular weight  $M_1$  in admixture with a gas of molecular weight  $M_2$  after diffusion and  $x$  the volume percentage of the first gas in the mixture before diffusion, then  $y = (100x\sqrt{M_2/M_1})/[100 - x(1 - \sqrt{M_2/M_1})]$ . The degree to which it is possible to separate the gases by diffusion varies with the composition of the mixture and is at a maximum when  $x = 100/(1 + \sqrt{M_2/M_1})$ . For mixtures of hydrogen and carbon monoxide, maximum separation is obtained when the mixture contains 34.08% of hydrogen; the gas after diffusion then contains 65.9% of hydrogen. An apparatus is described for testing the efficiency of porous earthenware cells in separating gases by diffusion, the efficiency of a cell being defined as the ratio of the actual enrichment of the lighter gas after passing through the cell to the theoretical enrichment calculated from the above equation. The results obtained showed that the efficiency of a cell depends on the size of its pores, the rate of passage of the gas mixture over the cell, and the rate of removal of the diffused gas from the interior of the cell. The greatest efficiency observed in the tests was 97%, but only a very small amount of enriched gas was obtained in this case. A. R. P.

**Vapour Pressures of Solutions of Phenol and Water at  $75^{\circ}$ .** J. B. FERGUSON and W. S. FUNNELL (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 122—123).—The vapour pressure of mixtures of phenol and water (7—60% phenol) at  $75^{\circ}$  is found to be almost independent of the composition of the mixture. J. S. C.

**Composition of Liquid and Vapour Phases of Glycerol-Water Mixtures.** M. IYER and F. L. USHER (*J. Chem. Soc.*, 1925, **127**, 841—844).—Mixtures of glycerol and water of known

composition were distilled in a vacuum and the distillates analysed refractometrically. For liquid phases, which contain 75, 98, and 99% of glycerol, the vapour phases contain 0.2, 1.7, and 17.0%, respectively.

W. A. C.

### **Solid Solutions of the Alkali and Ammonium Halides.**

R. J. HAVIGHURST, E. MACK, jun., and F. C. BLAKE (*J. Amer. Chem. Soc.*, 1925, **47**, 29—43).—Solid solution may be due to substitution in the space lattice of the solvent by the solute atoms, but this is possible only if the atoms are chemically similar and do not differ greatly in molar volume. The effect on the space lattice is additive. Another type of solid solution is interstitial, the solute atoms being packed between the solvent atoms enlarging the unit cell whatever the atomic volumes. X-Ray measurements are given for solid solutions of a number of binary systems of the alkali and ammonium halides. They are of the first type, are completely miscible at the ordinary temperature, and obey the law of additivity until the difference in the cube sides of the pure components exceeds 5% of the mean of the two, after which the law does not hold strictly. For completely miscible systems, each solid solution behaves towards X-rays as though it were a pure substance, the reflecting power and volume of the compound atom being determined additively by the atomic numbers and volumes of the constituent atoms.

L. J. H.

**Structure of Alloys.** A. WESTGREN and G. PHRAGMÉN (*Koll.-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 86—91).—An ideal solid chemical compound is defined by the chemical identity of the structurally equivalent atoms. In an ideal solid solution all the atoms are structurally equivalent. These two types of structure are to be regarded as limiting cases; most metallic phases represent intermediate stages. Many alloys can be regarded as solid solutions in intermetallic compounds, the formulæ of which may be obtained by means of the X-ray-spectrograph. Certain structural types are found in several different alloys. Thus the X-ray spectrograms (by the powder method) for certain phases of the copper-zinc, silver-zinc, gold-zinc, silver-cadmium, silver-aluminium, copper-tin and silver-tin systems correspond with the interference forms of the lattice with the closest possible hexagonal packing of spheres. Agreements of this type bring out important relationships between different systems of alloys.

E. M. C.

**Silver-Tin Amalgams.** G. TAMMANN and O. DAHL (*Z. anorg. Chem.*, 1925, **144**, 16—39; cf. Joyner and Knight, T., 1911, **99**, 195; 1913, **103**, 2247; 1914, **105**, 639).—Amalgams prepared by grinding powdered silver-tin alloys with excess of mercury in a mortar and expressing the excess of mercury under constant pressure vary in composition and properties with the age and previous history of the powdered silver-tin alloys; freshly prepared alloys retain more mercury than old or previously heated powder, the difference being greatest for an alloy containing 73% of silver corresponding with the composition  $\text{Ag}_3\text{Sn}$ , and disappearing for

pure silver and tin, respectively. At the same composition, the amount of mercury retained is a maximum. The limits within which the components of the ternary system are the compound  $\text{Ag}_3\text{Sn}$ , mixed crystals of tin and mercury, and mixed crystals of  $\text{Ag}_3\text{Hg}_4$  and tin are plotted, and tables for hardness, breaking strain, and volume change given. The amalgams obtained from an alloy of the composition  $\text{Ag}_3\text{Sn}$  are the hardest, most easily broken, and show the greatest volume increase; those prepared from old silver-tin powder show contractions in all cases. The ageing effect of the silver-tin alloys is accompanied by increase in density and reluctance to take up mercury. S. I. L.

**Thermal and Electric Conductivities of some Aluminium Alloys.** H. MASUMOTO (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **13**, 229—242).—The thermal and electrical conductivities of several aluminium alloys were determined by the method previously described (*ibid.*, 1917, **6**, 111). The alloys were examined in the chill-cast and annealed states, after quenching, and after cold-drawing and annealing. Both conductivities decreased with increase in the amount of other constituents in the alloy, the effect being greatest for manganese and chromium, and least for tin. The conductivities were increased by annealing the cast specimens, but reduced by quenching. The cold-drawn and annealed specimens had the highest conductivities. The product of the electrical resistance and thermal conductivity was practically constant ( $6.91 \times 10^{10}$  C.G.S. units) for all the alloys, the lower values corresponding with the lower conductivities. C. S.

**Constitution of Technical Iron.** F. WEVER (*Z. Elektrochem.*, 1924, **30**, 376—382).—The parameter of the iron lattice in austenitic steels containing manganese is a function of the carbon and manganese content and may be expressed by the formula  $(3.578 + 0.0005\text{Mn} + 0.00645\text{C}) \text{ \AA.}$ ; the specific volume is given by the expression  $v = 0.1246 + 0.0004\text{Mn} + 0.0041\text{C}$ , the proportion of manganese and carbon in each case being expressed in atomic percentage. The lattice parameter of  $\alpha$ -iron is  $2.861 \text{ \AA.}$  and is increased to  $2.87\text{—}2.88 \text{ \AA.}$  in hardened steel, but is practically unchanged in annealed steel. Carbon therefore appears to fill spaces in the lattice of  $\alpha$ -iron and not to replace iron in the lattice structure. [Cf. *B.*, 1925, 403.] A. R. P.

**Viscosity Measurements with Glass.** V. H. STOTT, E. IRVINE, and D. TURNER (*Proc. Roy. Soc.*, 1925, **A**, **108**, 154—171).—The viscosities of thirteen glasses have been determined at various temperatures. Very high viscosities ( $10^9\text{—}10^{17}$  C.G.S. units) are measured by applying torsional forces to the two ends of a circular rod of the glass to be examined. For viscosities lower than these values, the glass is held in a cylindrical container and a cylindrical co-axial rod, made from a nickel-iron-chromium alloy, is plunged into the glass and rotated. In each case the time required for the moving portion of the apparatus to rotate through a given angle under the influence of a known torque is a measure of the viscosity.

The shape of the temperature-viscosity curves can be determined accurately, but the absolute values depend largely on the circularity and uniformity of diameter of the rods. Viscosity determinations at high temperatures have been made by measuring the rate of fall of a partly counterpoised platinum-iridium ball through the glass.

J. S. C.

**Mutual Solubilities of Cetene (Hexadecene) and Liquid Sulphur Dioxide.** W. F. SEYER and J. L. HUGGET (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 213—216).—The critical solution temperature is in the region of  $42.7^{\circ}$ . The freezing point of cetene ( $3.5^{\circ}$ ) is lowered to  $-2.2^{\circ}$  in presence of sulphur dioxide. It is shown that under ordinary working conditions diolefines are soluble and mono-olefines insoluble in liquid sulphur dioxide. This difference may be utilised with advantage in the refining of mineral lubricating oils. [Cf. *B.*, 1925, 388.]

J. S. C.

**Mutual Solubility of Sulphur Dioxide and *n*-Hexane.** W. F. SEYER and A. F. GILL (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 209—211).—Above  $10.1^{\circ}$ , the two liquids are completely miscible. *n*-Hexane freezes at  $-93.7^{\circ}$ , this temperature being lowered to  $-96^{\circ}$  in presence of sulphur dioxide. The f. p. of sulphur dioxide,  $-72.8^{\circ}$ , is lowered to  $-73.5^{\circ}$  in presence of hexane. The solubility curve is very similar to that found for sulphur dioxide-cyclohexane (*A.*, 1923, i, 313). At temperatures in the region of  $-10^{\circ}$ , the solubilities of the two hydrocarbons differ but slightly, and assuming the two substances to be typical of the class of compounds to which they belong it does not appear possible to separate naphthenes from paraffins by means of liquid sulphur dioxide (cf. Moore, Morrell, and Egloff, *A.*, 1918, i, 285).

J. S. C.

**Supersaturation of Gases in Liquids.** K. S. WYATT (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 127).—An aqueous solution of nitrogen saturated at a pressure of above 100 atm. at the ordinary temperature was brought to atmospheric pressure without the immediate formation of bubbles in the body of the liquid. The phenomenon has not yet been reproduced.

J. S. C.

**Solubilities of Rare Earth Salts.** I. M. D. WILLIAMS, H. C. FOGG, and C. JAMES (*J. Amer. Chem. Soc.*, 1925, 47, 297—301).—The solubilities of the hexahydrated trichlorides of yttrium, samarium, and neodymium in water are, respectively, 217.0, 218.4, and 243.0 parts of the hydrate in 100 parts of water at  $20^{\circ}$ . Values at other temperatures from  $10^{\circ}$  to  $50^{\circ}$ , and similar values for the solubility in hydrochloric acid (*d* 1.1051) are also given, together with the solubility of ytterbium trichloride hexahydrate in the latter solvent. The melting points are  $124^{\circ}$ ,  $142.5^{\circ}$ ,  $161$ — $163^{\circ}$ , and  $153$ — $155^{\circ}$  for the hydrates in the order named.

L. J. H.

**Supersaturated Solutions of Uric Acid.** R. STERN (*Klin. Woch.*, 1924, 3, 1583; from *Chem. Zentr.*, 1924, ii, 1925).—Colloidal solutions of monosodium urate may be obtained by simple dispersion in water. The solubility of uric acid in a 1% solution of sodium

salicylate is twice as great, and in 0.1% solution of the sodium compound of "atophane" three times as great as in water.

G. W. R.

**Solubility of the Double Fluorides of Zirconium and Hafnium.** G. VON HEVESY, J. A. CHRISTIANSEN, and V. BERGLUND (*Z. anorg. Chem.*, 1925, **144**, 69—74).—The solubilities of the ammonium and potassium double fluorides,  $(\text{NH}_4)_2\text{RF}_6$ ,  $(\text{NH}_4)_3\text{RF}_7$ , and  $\text{K}_2\text{RF}_6$  ( $\text{R}=\text{Zr}, \text{Hf}$ ) in water, and in solutions of ammonium fluoride and hydrofluoric acid have been determined. The first are more soluble than the second, and the hafnium compounds more soluble than those of zirconium, the difference being most marked with the salts  $(\text{NH}_4)_2\text{RF}_6$  and  $\text{K}_2\text{RF}_6$ . The solubilities are higher in presence of ammonium fluoride and hydrofluoric acid. S. I. L.

**Solubility of Ferrous Hydroxide and its Effect on Corrosion.** W. G. WHITMAN, R. P. RUSSELL, and G. H. B. DAVIES (*J. Amer. Chem. Soc.*, 1925, **47**, 70—79).—The solubility of ferrous hydroxide in pure water is  $6.7 \times 10^{-5}$  mol./litre and its dissociation constant is  $6.8 \times 10^{-10}$ , the ionisation in saturated solution at  $25^\circ$  being 30%. The solubility in various salt solutions is also given, affording data from which the solubility in any non-oxidising salt solution in which the ionic strength does not exceed unity may be calculated. The free energy of formation of ferrous hydroxide is  $-57,200$  cal. The precipitation of colloidal ferric hydroxide in salt solution has no direct connexion with the rate of corrosion. The rate of corrosion in salt solutions parallels the solubility of ferrous hydroxide in these solutions. It is suggested that this is due to changes in film protectivity with the solubility of the ferrous rust. L. J. H.

**Solutions in 100% Sulphuric Acid. Solvolysis and Double Decomposition Reactions.** A. W. DAVIDSON (*J. Amer. Chem. Soc.*, 1925, **47**, 968—981).—The solubilities of aluminium, zinc, and lead sulphates in 100% sulphuric acid are not increased by the presence of sodium sulphate, showing that soluble additive compounds are not formed. Salts are readily "solvolysed" in sulphuric acid solution; salts of metals of which the sulphates are insoluble in the acid, or of insoluble acids, are either themselves insoluble or are largely solvolysed to form insoluble products and *vice versa*. Additive products of salt and solvent could not be isolated. With potassium ferrocyanide pale yellow plates of  $\text{H}_4\text{Fe}(\text{CN})_6 \cdot \text{H}_2\text{SO}_4$  were obtained, and with calcium phosphate,  $\text{CaSO}_4 \cdot \text{H}_2\text{SO}_4$ . Qualitative solubility data for a number of salts are recorded. Double decomposition occurs readily between ionised salts in sulphuric acid solution, though not always instantaneously, probably because of the high viscosity of the solvent. S. K. T.

**Equilibrium in the System: Carbamide, Methyl Alcohol.** J. H. WALTON and R. V. WILSON (*J. Amer. Chem. Soc.*, 1925, **47**, 320—323).—From saturated solutions of carbamide in methyl alcohol at  $0^\circ$ , solvated crystals, of composition  $\text{CO}(\text{NH}_2)_2 \cdot \text{MeOH}$ , separate. Solubility data for this and for unsolvated carbamide are given, and the transition point is  $19.25^\circ$ . L. J. H.

**Theory of Extraction.** M. FRENC (*Z. angew. Chem.*, 1925, **38**, 323—324).—A short account of the methods for separating quantitatively two substances by shaking out with immiscible liquids, with a mathematical treatment of the different methods. [Cf. *B.*, 1925, 429.] P. M.

**Partition of Silver between Lead and Zinc.** W. A. NAISH (*Trans. Faraday Soc.*, 1925, **27** [Advance proof]).—The partition of silver between lead and zinc has been determined at temperatures from 550° to 850°. For mixtures containing more than 5% of silver, no consistent values can be found for the partition coefficient, but for dilute solutions the results may be expressed by the relation  $C_{Zn} = KC_{Pb}$ , where  $C_{Zn}$  and  $C_{Pb}$  are the weight concentrations of silver in the zinc and lead layers, respectively, and the partition coefficient  $K = 301.9$  at 550°, rising to (approximately) 342, 388, and 415 at 650°, 750°, and 850°, respectively. The values of  $K$  are independent of the proportion of lead to zinc and when expressed in volume concentrations, substitution in the van't Hoff equation  $d \log K / dT = -Q / RT^2$ , leads to the value  $Q = 2048$  cal. approximately. W. H.-R.

**Partition Phenomena.** N. DE KOLOSSOWSKY (*Bull. Soc. chim.*, 1925, [iv], **37**, 372—381).—The partition data for hydrogen peroxide and propionic acid between water and ethyl ether at 18° are represented satisfactorily over a large range of concentration by empirical equations of the type,  $C^{a+bS} / C' = \text{constant}$ , in which  $C$  and  $C'$  are respectively the concentrations of the dissolved substance in the aqueous and ethereal layers,  $a$  and  $b$  constants and  $S = C + C'$ . The purely empirical supplementary term  $bS$  compensates for the deviations from the simple Nernst formula consequent on changes in the total concentration of the solute. The data for acetic acid require a more complex expression involving  $S^2$ . No simple algebraic equation can be applied to the partition numbers for ferric chloride, the value of the ratio  $C / C'$  varying from 470 to 1.85 when the concentration of ferric chloride in the aqueous phase is increased from  $N$  to  $3.6N$ . J. S. C.

**Absorption of Water by Dried Films of Boiled Starch.** F. D. FARROW and E. SWAN (*J. Text. Inst.*, 1923, **14**, t, 465—474).—Two methods are described for determining the moisture relations of thin films of boiled starch. In one, the material was allowed to come to constant weight at 20°, in an atmosphere controlled by sulphuric acid solutions, and in the other a vacuum vessel was used in which the film could be periodically treated with measured quantities of water. With the latter method, temperature was controlled to  $20 \pm 0.05^\circ$  and pressures reproduced to about 0.05 mm. The absorption curve is sigmoid and not considerably affected by the type of starch used or the mode of cooking the paste. Prolonged heating of the film reduces its capacity for water. Starch persistently retains more moisture in a given atmosphere if introduced from a wetter atmosphere than from a dryer. The dehydration curve of starch, however requires further study. J. C. W.

**Sorption by Cotton.** H. F. COWARD, L. SPENCER, and F. C. WOOD (*J. Text. Inst.*, 1925, **14**, T, 529—533).—Using the centrifuge to remove interfibrillar liquid (A., 1923, i, 305), the amounts of water and various reagents absorbed by bleached cotton at the ordinary temperature have been determined. 100 g. of cotton absorb about 50 c.c. of water, saturated sodium chloride, dilute sodium hydroxide (below  $N/20$ ), or dilute sulphuric acid (below  $N/25$ ). A solution is taken up as a whole, except that a small but easily measurable preferential absorption of solute takes place with alkali or acid. With more concentrated solutions of sodium hydroxide, the volume taken up is very much greater and the preferential absorption of alkali is considerable. A similar example of high preferential absorption is observed with dilute solutions of copper oxide in ammonia solution; cotton becomes much bluer in these solutions than the corresponding baths. It appears that preferential absorption is a necessary antecedent to both swelling and solution of cotton. J. C. W.

**Adsorption. VIII. Adsorptive Capacity of Air-dried Manganese Dioxide Hydrate.** P. N. PAVLOV (*Kolloid-Z.*, 1924, **35**, 375—377; cf. A., 1924, ii, 594, 732, 733, 833).—The adsorption of silver by freshly precipitated air-dried hydrated manganese dioxide from silver nitrate solution has been studied. The solution, when neutral before adsorption, becomes afterwards strongly acid. The adsorption of silver ions is a chemical process and can be explained by the amphoteric character of the manganese dioxide, which in this case acts as an acid. D. C. J.

**Experimental Investigation of the Dynamical Equation of the Process of Gas Sorption.** D. H. BANGHAM and W. SEVER (*Phil. Mag.*, 1925, [vi], **49**, 935—944).—The sorption of carbon dioxide by glass-wool has been determined over long periods. Over a considerable range the equation previously obtained (A., 1924, ii, 392)  $\log s = \log t/m + c$  is obeyed. Time-sorption data beyond this range are satisfactorily represented by the formula  $\log [\sigma/(\sigma - s)] = kt^{1/m}$ , where  $\sigma$  is the limiting value of the sorption  $s$ , as  $t$  approaches infinity. It is shown that the form of the time-sorption curve in the latter stages of sorption cannot be reconciled with the normal laws of diffusion. F. G. T.

**Influence of Rate of Flow on the Adsorption of Gases.** R. LORENZ and E. WIEDBRAUCK (*Z. anorg. Chem.*, 1924, **136**, 147—148).—When a mixture of hydrogen and carbon monoxide is passed over charcoal the rate of flow has little effect on the adsorption at the beginning, but as the charcoal becomes nearly saturated with the gas, the adsorption decreases with increase in the rate of flow, complete saturation being effected in a shorter time with a slow stream of gas. The ratio by volume of the gases adsorbed is the same as that in the original gas mixture. A. R. P.

**Adsorption Experiments with Solutions.** E. BERL and E. WACHENDORFF (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 36—40).—The adsorption of crystal-violet from water and "tetralin"



solutions, of brucine from water and toluene solutions, and of iodine from aqueous potassium iodide and toluene solutions by a number of charcoals shows a general agreement with the integral heats of wetting with water and benzene. A silica gel adsorbed much greater amounts of crystal-violet from "tetralin," and of brucine from toluene than did the charcoals, but it did not adsorb iodine from a solution in toluene.

E. M. C.

**Adsorption Phenomena in the Vicinity of the Critical Temperature.** W. A. PATRICK, W. C. PRESTON, and A. E. OWENS (*J. Physical Chem.*, 1925, 29, 421—434).—The adsorption isotherms for carbon dioxide and nitrous oxide on silica gel at 0°, 20°, 30°, and 40° at pressures below 1 atm. do not show any discontinuity at the critical temperature. The adsorption equation deduced from the capillary theory (cf. A., 1920, ii, 417; 1922, ii, 262) does not apply if the experimental values of the surface tension are used. By assuming that the surface tension is correct at the lower temperatures it is possible to calculate what it should be near the critical temperatures. The results show that capillarity lowers the vapour pressure of the liquid, increases its surface tension, and raises the critical temperature.

M. B. D.

**Adsorption from the Gas Phase at a Liquid-Gas Interface.** III. T. IREDALE (*Phil. Mag.*, 1925, [vi], 49, 603—627).—It is shown by two independent methods of measuring the surface tension of mercury, when the mercury surface is exposed to vapours of different pressures, that these vapours adsorb on the surface to give films which are probably only 1 mol. thick. In the saturated state, under special conditions, it is possible to form films which are of much greater thickness; but it is argued on thermodynamical grounds that such condensation is impossible under strictly isothermal conditions, if the tension of these films is not less than the tension of the unimolecular films. The mercury surface is easily contaminated by traces of impurities. Such contamination is irreversible, and the adsorbed impurities cannot be removed at the ordinary temperature under the highest vacua. The adsorption of organic vapours is largely reversible, except for such compounds as methyl iodide which are known to form a definite compound with mercury. It is suggested that a distinction must be drawn between a "surface compound" and a "surface solution."

C. W. B.

**Solution of Solids in Liquid Surfaces, and the Properties of the Resulting Films.** M. VOLMER and P. MAHNERT (*Z. physikal. Chem.*, 1925, 115, 239—252).—Experiments in which solid benzophenone was brought into contact with a mercury surface show that the adsorption of the former is direct, and not determined by vaporisation and subsequent adsorption of the vapour, nor by preliminary true solution followed by concentration at the surface. On decreasing the mercury surface, benzophenone separates out. The thickness of the adsorbed film has been determined between -9° and 25°, and in all cases is less than unimolecular. Langmuir's equation of state  $(\sigma_0 - \sigma)\Omega = RT$  (A., 1917, ii, 25) is modified

to the form  $(\sigma_0 - \sigma)(\Omega - \beta) = RT$ , in which  $\beta$  is a correction for the close packing of the molecules. L. F. G.

**Photographic Action of Methylene-blue as an Adsorption Effect.** J. EGGERT and J. REITSTÖTTER (*Koll.-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 298—305).—The addition of methylene-blue at the rate of  $10^{-6}$  g. per c.c. to silver bromide-gelatin emulsion causes fogging on alkaline development and a reduction of light-sensitivity to one-half. The adsorption of methylene-blue by silver bromide is complete under these conditions and corresponds with about 5000 mols. of methylene-blue per silver bromide crystal. The effect of the methylene-blue is regarded as a heterogeneous catalysis and is ascribed to the sulphur atom, since dimethyl-*p*-phenylenediamine is not adsorbed and gives no fogging. There is a general similarity between this catalysis and that of the silver produced by exposure to light, but the two effects are not additive. [Cf. *B.*, June 26th.] E. M. C.

**Property of Very Small Bubbles of Gas in Water.** H. A. McTAGGART (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 129—131).—Microscopical observations of the movements of minute globules of oil on the surface of small gas bubbles in water point to the existence of electric repulsive forces between the globules. J. S. C.

**Upper Limit for the Thickness of the Adsorption Layer on Silica.** D. C. JONES (*J. Physical Chem.*, 1925, 29, 369—375).—Powdered silica glass passing through a 100—120-mesh sieve was added to a solution of nitrobenzene in kerosene. No change in concentration of the nitrobenzene could be detected with an interferometer. On the assumption that the particles of silica were cubes, the layer of nitrobenzene molecules adsorbed on the surface of the silica must be less than three or four molecules thick. M. B. D.

**Capillary Adsorption.** W. A. PATRICK (*Koll.-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 272—277).—The author reviews his earlier experimental work on the adsorption of vapours by silica gel. The presence of small quantities of permanent gases plays an important part in the hysteresis phenomena. The application of the usual laws of capillarity to the very narrow capillaries postulated in porous adsorbents is criticised. E. M. C.

**Capillary-Chemical Reaction in Spot-tests.** F. FEIGL (*Kolloid-Z.*, 1924, 35, 344—345).—A collected account, with references, of a number of instances of the application of spot-tests on filter-paper to inorganic qualitative separations (cf. *A.*, 1921, ii, 278; 1923, ii, 508). D. C. J.

**Flow of Starch Paste through Capillary Tubes.** F. D. FARROW and G. M. LOWE (*J. Text. Inst.*, 1923, 14, T, 414—440).—The work was undertaken in order to define the method and the nature of the measurements which are required to specify the fluid properties of starch pastes. The factors considered were temper-

ature, method of preparation, concentration and age of the paste, type of viscosimeter used, and origin of the starch. To avoid effects due to gelation, the measurements were made and the pastes stored at 90°. The pastes were prepared by blowing steam into a suspension of the starch in water contained in an asbestos-jacketed cylindrical separating funnel, steam being admitted for a definite time (usually 2 hrs.) after reaching 100°. The apparent viscosity of farina paste gradually rose until a concentration of 0.7% was reached and thereafter rapidly, the upper limit studied being 5%. The viscosity rapidly decreased, however, on storage at 90°. With maize pastes, the rapid increase in viscosity set in at 1.5%, and decrease with time was only slight. Maize pastes, therefore, were used in further studies on the effect of the design of the instrument on the apparent viscosity and it was soon found to be necessary to take into account the rate of flow. Experiments were therefore made in an Ubbelohde viscosimeter which could be fitted with capillaries of known dimensions and in which the driving pressures could be varied. The apparent viscosity was found to be less as the driving force was increased, thus accounting for variations from one instrument to another. By altering the usual equation to  $[\eta] = P^N \pi r^4 t / 8l \cdot V$ , however, an expression was obtained which took this effect into account, and also the nature of the paste;  $P$  is the pressure in absolute units,  $r$  and  $l$  are the dimensions of the capillary, and  $V$  is the volume flowing in time  $t$ . The exponent  $N$  was determined by plotting the logarithm of the rate of flow against the logarithm of the pressure and measuring the tangent of the angle between the graph and the log.  $P$  axis;  $N$  is unity for water and purely viscous liquids, but greater for starch pastes, increasing with increasing concentration. The number  $[\eta]$  was then found by calculation; it is designated the "coefficient of flow," and is regarded as a provisional, practical number which summarises the influence of unknown factors on the apparent viscosity. The values of  $[\eta]$  and  $N$  fully describe the way in which the pastes will flow through capillary tubes;  $N$  is probably an expression of the fact that in two-phase systems the viscosity varies instantaneously with the rate of shear, which in a capillary tube rises from zero at the axis to a maximum at the wall.

J. C. W.

**Surface Tensions of Water-Phenol Mixtures.** A. K. GOARD and E. K. RIDEAL (*J. Chem. Soc.*, 1925, 27, 780—787).—The surface tensions against air of phenol-water mixtures have been redetermined by the drop-weight method. With rising temperature, the surface tensions of the two phases in contact differ by amounts which diminish regularly up to the critical temperature of miscibility, without any inversion at 40—45°. With two-liquid systems in general the difference between the surface tensions of the conjugate solutions is greater the more remote the systems are from the critical solution temperature.

W. A. C.

**Heat of Wetting of Oils and Metal and its Relationship to Lubricating Power.** W. BACHMANN and C. BRIEGER (*Koll. Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 142—154).—Oils of high lubricating

power have much higher heats of wetting against finely-divided copper than oils of low lubricating power. From experiments in which the oil was diluted with half its weight of benzene, which has a low heat of wetting, the heats of wetting in calories per 100 g. of copper, calculated for the pure oil, were castor oil 12.1, linseed oil 13.8, and liquid paraffin 3.85. Petroleum without benzene gave 5.7 and the addition of 1% oleic acid increased the value to 21.3. [Cf. *B.*, 1925, 435.] E. M. C.

**Adsorption. X. Coagulation of Diluted Sols by Electrolytes, Acclimatisation, and Behaviour towards Mixed Electrolytes.** S. GHOSH and N. R. DHAR (*J. Physical Chem.*, 1925, 29, 435—461; cf. *A.*, 1924, ii, 394, 733, 737).—The precipitation value for all electrolytes decreases as a sol is diluted. The behaviour of negatively charged mastic sol is abnormal, since the precipitation values for potassium chloride and barium chloride increase as the sol is diluted. The coagulating power of the barium ion is seven times that of the potassium ion with this sol, whereas normally it is about fifty times greater. The coagulation by potassium chloride of Prussian-blue on dilution gives abnormal results, contrary to the experience of Weiser and Nicholas (*A.*, 1922, ii, 266). The precipitation values of a mixture of two electrolytes on antimony sulphide, Prussian-blue, and mastic sols are abnormal in that they are greater than the additive values of the salts alone. The influence of the rate at which the electrolyte is added on the precipitation value (acclimatisation) is more pronounced with mastic sol than with negatively charged ferric hydroxide. The amount of electrolyte required to precipitate arsenic sulphide sol decreases with the age of the sol. The authors consider that the abnormality of sols with respect to dilution, in their behaviour towards mixtures of electrolytes and in respect of acclimatisation, is mainly due to adsorption of ions carrying the same charge as the sol. Negatively charged stannic hydroxide sol has been prepared. M. B. D.

**Molecular Association of Furfuraldehyde.** F. H. GETMAN (*J. Physical Chem.*, 1925, 29, 395—398).—Furfuraldehyde gives a normal lowering of the freezing point of benzene and water in dilute solutions. The molecular lowering of the freezing point rises to a maximum at about 0.1 mol. per 1000 g. of solvent and then decreases. The degree of association of freshly-distilled furfuraldehyde is slightly less than that of a sample which had been exposed to light and when calculated from three empirical formulæ is found to be slightly greater than unity. M. B. D.

**Nature of the Undissociated Acids.** H. VON HALBAN (*Z. Elektrochem.*, 1924, 30, 601—604).—A reply to criticisms of the author's theory made by Hantzsch (*ibid.*, 194). The question as to whether the process of electrolytic dissociation has an influence on light absorption is discussed, in relation to the alternative views of Hantzsch and Bjerrum. Hantzsch's hypothesis is found to lead to such difficulties that it is regarded as untenable. C. H. D. C.

**Nature of Undissociated Acids.** A. HANTZSCH (*Z. Elektrochem.*, 1925, **31**, 167—172).—An answer to the criticisms of von Halban (see preceding abstract). The latter's conception of solvate formation is held to be physico-chemical to such a degree that it is incompatible with chemical observations on the alteration of many substances by solvents. N. H. H.

**Dissociation of Polyatomic Salts. II.** N. SASAKI (*Z. anorg. Chem.*, 1925, **144**, 114—116).—The dilution of a solution of a salt of a multivalent metal, *e.g.*, ferric chloride, increases the concentration of the simplest ions ( $\text{Fe}^{+++}$ ,  $\text{Cl}^-$ ); the intermediate ions ( $\text{FeCl}^+$ ,  $\text{FeCl}_2^+$ ) first increase in concentration and then diminish. S. I. L.

**Viscosimetric Neutralisation of Monobasic Acids by Alkalis. Comparison of Alkali Chlorates and Bromates with Nitrates.** L.-J. SIMON (*Compt. rend.*, 1925, **180**, 1169—1171; cf. A., 1924, ii, 335, 455).—Measurements of the viscosities of aqueous solutions of constant molecular concentration demonstrate sharply when neutralisation of monobasic acids occurs. The present work does not substantiate the connexion between viscosity and isomorphism noted previously for polybasic acids. When viscosity is plotted against the proportion of acid or alkali, the experimental points lie on straight lines intersecting exactly at equimolecular proportions. The viscosities of chloric, bromic, and nitric acids are quite different from one another, whilst those of the salts are quite near. For sodium chlorate and bromate the viscosity is proportional to the concentration, a relation which does not hold for the nitrate. Since the correlation of viscosity with isomorphism fails, it is suggested that an examination of sodium metaphosphate would test whether the formal similarity between sodium nitrate, bromate, and chlorate has any bearing on the matter. R. A. M.

**Dielectric Constants of Solutions of Electrolytes.** P. WALDEN, H. ULICH, and O. WERNER (*Z. physikal. Chem.*, 1925, **115**, 177—202; cf. *ibid.*, 1924, **110**, 43; A., 1924, ii, 648, 824).—An apparatus is described for determining these constants by a resonance method, somewhat similar to those employed by Theodorschick (*Physikal. Z.*, 1922, **23**, 344) and Lattey (A., 1921, ii, 426). Errors due to damping of waves are eliminated. Theoretical considerations show that with the short wave-length employed (4·5 metres) the conductivity of the dielectric has only a slight effect on the measurements; this was confirmed experimentally and is not in agreement with Lattey (*loc. cit.*). L. F. G.

**Light Scattering in Salt Solutions.** C. W. SWEITZER (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 125—126).—Solutions of sodium chloride, ammonium chloride, and sodium sulphate have been rendered dust-free by the method of envelopment using aluminium and cadmium hydroxides as precipitates. The observed light scatterings in the solutions are much smaller than those calculated by the Smoluchowski-Einstein-Cabannes formula. J. S. C.

**Theory of Concentrated Aqueous Solutions of Strong Electrolytes.** E. HÜCKEL (*Physikal. Z.*, 1925, 26, 93—147).—Equations are derived on the basis of the Debye theory for electrode potentials and the electromotive force of simple cells. Activity coefficients of sodium chloride calculated from electromotive force measurements of the cell  $\text{Hg}|\text{Na}|\text{NaCl}|\text{HgCl}_2|\text{Hg}$  (T., 1919, 115, 1020), fall with increasing concentration, pass through a minimum, and then rise. The decrease at lower concentrations is explained by the action of interionic forces in solution. Each positive ion will on the average be surrounded by more negative than positive ions, and *vice versa*. For each ion this inequality of distribution will occur over a characteristic range which will depend largely on the dielectric constant of the solvent. This distribution gradient and therefore its effect on the interionic forces will increase with concentration. A formula for the activity coefficient derived on this basis reproduces the fall in activity at lower concentrations, but the minimum occurs at a much higher concentration than the experimental value.

The effect of the interionic forces on the ions is to cause a deformation of their electron orbits with the development of polarity. This, on the close approach of two ions in water, establishes a repulsive force between them, which may overcome the ordinary attraction and so increase the activity coefficient (*i.e.*, a result comparable with hydration of the ion). Owing to the very steep potential gradient at the surface of an ion the water dipoles at that surface will be strongly oriented, "electrically saturated," and thus the imposition of an external field (due to other ions) will not cause a polarisation proportional to its strength (*i.e.*, to the dielectric constant of the water), but a much smaller one. In effect the dielectric constant of the water will have been lowered by the ions. The magnitude of this decrease depends on the polarising tendency, volume, and the radius of the "saturation sphere" of the ions. Taking the fall in dielectric constant as a linear function of the ion concentration (cf. Blüh, A., 1924, ii, 824) the Debye calculation of the activity coefficient (A., 1924, ii, 386) is modified on this basis. The expression so obtained consists of two parts, one expressing the electrical work due to the ionic force field in the transfer of ions from a weak to a stronger solution, the other the electrical work arising from the change of dielectric constant during this concentration change. An approximate expression for a univalent electrolyte is given as  $\log f = -0.354\sqrt{2\gamma}/(1 + A\sqrt{2\gamma}) + C2\gamma$ , where  $A = a \cdot 0.232 \times 10^8$  ( $a$  = ionic radius),  $\gamma$  = molar concentration, and  $C$  = a constant, which for a univalent ion is a determined function of the lowering of dielectric constant of the solvent.

Owing to the lack of data for dielectric constants of solutions, the assumption has been made that the increase of activity coefficients at high concentrations is due entirely to the lowering of dielectric constant. By using electromotive force determinations of the activity coefficients of the chlorides of lithium, sodium, and potassium to evaluate the lowering of dielectric constant in these cases, the values 20, 9, and 6 for normal solutions were obtained.

Values of the same order may be calculated from Blüh's results, and indirectly from the refractive indices of the salt solutions on the assumption that the polarising tendency of water molecules is unaffected by the presence of ions. The activity coefficients for a series of hydrochloric acid solutions were calculated on the assumptions that (1) all the  $H^+$  ions exist free in solution, (2) hydration is practically complete to  $H_3O^+$ . The agreement between calculated and observed results is so close in each case that no decision between these views is possible. The activity coefficient in low concentrations is lowered by the addition of a salt with a common ion, but in stronger solutions is considerably raised, the more so the greater the increase of activity coefficient with concentration of the pure salt.

F. G. T.

**Partial Pressures of Aqueous Solutions of Hydrochloric Acid at 50°.** N. C. YANNAKIS (*Bull. Soc. chim.*, 1925, [iv], 37, 389—404; cf. A., 1923, ii, 611).—Methods for the determination of the partial pressures of aqueous solutions of the halogen acids are reviewed and the effect of errors of experiment on the pressure values obtained is considered. The partial pressures of water and hydrogen chloride over aqueous solutions of hydrochloric acid (6.65—35.9% HCl) have been measured by the distillation method at 50°. A cooled receiver serves to arrest all the water in the distillate, together with a small percentage of acid, the bulk of which is, however, absorbed in U-tubes containing metallic zinc. The partial pressure of hydrogen chloride remains small until the acid concentration reaches 25% and then increases rapidly with increasing concentration, 97% of the total pressure of the 35.9% acid solution being due to hydrogen chloride. A reply is made to the criticisms of Dunn and Rideal (*J.*, 1924, 125, 676).

J. S. C.

**Temperature of Vapour above Boiling Salt Solutions.** W. H. BAHLKE and R. E. WILSON (*Chem. Met. Eng.*, 1925, 32, 327—328).—A solution of zinc chloride boiling at 152° was vigorously boiled in a large flask, the vapour passing through screens of wire gauze to a thermometer, and then returning to the bottom of the flask by a reflux condenser. The thermometer readings depend on the outside temperature and varied from 126° to 150°, the latter value being obtained with an outside temperature of 152°. The temperature of the vapours evolved from boiling salt solutions when correctly measured is thus the same as that of the solution, in contradiction to the work of Schreiber, whose results are contrary to the second law of thermodynamics.

W. H.-R.

**Importance of Colloid Chemistry in Mineralogy and Geology.** C. DOELTER (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 95—103).

E. M. C.

**Silver Iodide Hydrosol. Method of Formation of Hydrosols and Gels.** IV. A. LOTTERMOSER, W. SEIFERT, and W. FORSTMANN (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 230—244; cf. A., 1907, ii, 851; 1908, ii, 364; 1910, ii, 278).—In the titration of rapidly stirred potassium iodide and silver nitrate solutions the

point of complete flocculation and clearing of the silver iodide sol coincides with the equivalent point only in extremely dilute solutions. In solutions of medium concentration, clearing takes place in both cases before the equivalent point is reached, owing to the flocculating action of the potassium nitrate formed. With less rapid stirring of very dilute solutions of potassium iodide, more than the equivalent amount of silver nitrate is required for complete clearing. The interval between the commencement and the completion of flocculation is greater for the addition of silver nitrate to potassium iodide than for the addition of potassium iodide to silver nitrate. The positive silver iodide hydrosol is thus less stable than the negative one. Pure silver iodide may be prepared by titrating potassium iodide with silver nitrate to the point of clearing and removing potassium iodide from the precipitate by repeated washing and prolonged shaking with water. The positive and negative hydrosols show marked flocculation when equal amounts are mixed and some flocculation when the positive hydrosol is in slight excess. Positive silver thiocyanate hydrosol is much less stable than the negative hydrosol. By analogy with the gold value, a silver iodide value is defined as the amount, in mg., of a protective colloid which serves to prevent complete flocculation during the titration with 0.1*N*-silver nitrate of 25 c.c. 0.1*N*-potassium iodide, diluted to a definite volume. For a series of decreasing potassium iodide concentrations, the silver iodide values of a commercial dextrin were found to decrease exponentially and asymptotically to a constant value. Potassium iodide solution containing dextrin required more than the equivalent amount of silver nitrate for complete clearing; the excess increased regularly with the amount of dextrin up to a maximum value. On the other hand, silver nitrate containing dextrin required less than the equivalent amount of potassium iodide, the numerical relationships being more complicated.

E. M. C.

**Dispersoid Study of Cellulose.** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 103—109).—A lecture, outlining the work in progress in the author's laboratory on the dispersion of cellulose in concentrated salt solutions.

E. M. C.

**Wool as an Amphoteric Colloid. II. Chemical Theory of Dyeing.** J. B. SPEAKMAN (*J. Soc. Dyers and Col.*, 1925, 41, 172—179; cf. *B.*, 1925, 38).—The dyeing of wool is regarded as a typical case of the combination of an acid or base with an amphoteric colloid, the isoelectric point being about  $p_H$  4.8. De-aminated wool combines with acid dyes in virtue of the  $-CO-NH-$ groups. The electric charge on wool is ascribed to membrane equilibrium and this charge may be the immediate cause of dyeing with colloidal dyes. Thus the electrical theory, as also the adsorption theory, is regarded as a particular case of the chemical theory of dyeing. [Cf. *B.*, July 3.]

A. G.

**Lyophile Colloids and Poiseuille's Law.** H. R. KRUYT (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 218—230; cf. de Jong, A., 1923, ii, 132).—When the ratio of the hydrostatic



pressure to the length of the capillary was varied from 0.23 to 1.08, it was found that the viscosity remains constant and Poiseuille's law is obeyed by sols of agar and gelatin, above their gelatinising temperatures, and also by starch, gum arabic, casein, cerium oxide, and silica sols. Agar and gelatin sols below their gelatinising temperature do not obey Poiseuille's law. An "aged" vanadium pentoxide sol showed deviations. Gelatin and cerium sols, which are normal in the Ostwald viscosimeter, are also normal in the Hess viscosimeter. Deviations from Poiseuille's law occur when the particles are not spherical.

E. M. C.

**Physico-chemical Studies on Gold Hydrosols.** A. GALECKI (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 154—184).—Gold hydrosols prepared in several ways have been examined with respect to their viscosity and catalytic activity towards hydrogen peroxide. During the ageing and flocculation of gold hydrosols prepared by Zsigmondy's method, the viscosity falls to a minimum value and then increases. During flocculation by the addition of salts the minimum viscosity corresponds with the first change from red to violet. On prolonged ageing, the gold hydrosols give a constant viscosity which is lower than the initial values owing to some precipitation. Exposure of the hydrosols to light increases the viscosity by an amount proportional to the amount of incident light. The catalytic decomposition of hydrogen peroxide by gold hydrosols prepared by Zsigmondy's formaldehyde method decreases with the age of the hydrosol and is increased by the addition of alkali. For gold hydrosols prepared by Zsigmondy's nuclear method, the catalytic activity increases in a linear manner with the dispersion. Gold hydrosols prepared by Doerinckel's method are inactive in neutral solutions and have an optimum concentration of alkali. They inhibit the catalytic activity of the Zsigmondy hydrosols. Gold hydrosols prepared by the Gutbier and Varádi method of reduction with hydroxylamine are more active in neutral solution when prepared at 50° than at other temperatures. There is an optimum alkali concentration for hydrosols prepared below 50°, but no such optimum for those prepared above 50°. It is suggested that the two broad divisions of colloids should be termed the "gold type" and the "protein type."

E. M. C.

**Water-combination in Colloids.** G. F. HÜTTIG (*Kolloid-Z.*, 1924, 35, 337—339).—Four general types of water-combination in solid substances can be distinguished. The first type (A) is exemplified by the crystalline hydrates in which the chemically combined water molecules occupy fixed positions in the crystal lattice. For such systems, the vapour pressure-composition curve has the well-known step-like form. In type B, a portion of the water is chemically combined—fixed in the crystal lattice—whilst another portion is free to move in the crystal lattice. A kinetic equilibrium is suggested between these two kinds of attracted water molecules. The vapour pressure-composition curves show strong deviations from the step-like curve of type A. Of the very few cases that have been thoroughly studied, yellow tungstic acid,  $\text{WO}_3 \cdot \text{H}_2\text{O}$ , and

$\text{K}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$  ( $\beta$  salt) are instances in which most of the water is held as in type A, whereas in the zeolites the greater portion of the water is free to move in the crystal lattice. The palladium-hydrogen system is of this type.

In type C most of the water is free and conditions are obtained to which the osmotic laws are applicable. For such systems, the vapour pressure is given by the equation  $\log_e p_0/p = k/n$  where  $p_0$  is the vapour pressure of pure water at a free surface,  $k$  is a constant for the particular system,  $p$  is the observed vapour pressure, and  $n$  is the adsorbed amount of water. White tungstic acid ( $\alpha$ ) is an instance of this type, in which case  $k = 3.0$ . This type occupies a position midway between the purely chemical and the purely colloidal systems.

For colloidal systems the vapour pressure is a function of the radius of the capillary as expressed in the relation of Zsigmondy and Anderson (cf. A., 1914, ii, 632). This is type D, of which silica gels afford an example. Type C differs from type D only in that the capillaries in the former are of molecular size. Various combinations of these different types exist.

D. C. J.

**Colloidal Properties of Soap Solutions.** L. GURWITSCH (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 196—199).—Solutions of soaps of the naphthenic acids dissolve considerable amounts of mineral oil. The amount of oil dissolved per unit weight of soap increases with increasing concentration of the soap solution and with increasing molecular weight of the soap. The solubility of the oil decreases with increasing temperature. The interfacial tension of slightly acid mineral oils against water decreases slightly with increase of temperature, but that against sodium hydroxide solutions increases considerably. In dilute alcohol, the soaps are unimolecular and dissolve only traces of oil. These observations are interpreted in terms of the size of the soap micelles; greater amounts of oil are dissolved by soaps with larger micelles.

E. M. C.

**Electrical Behaviour of Radioactive Colloidal Particles of the Order of  $10^{-5}$  cm. as Observed Separately in a Gas.** F. EHRENHAF. — (See ii, 465.)

**Colloid-chemistry of Linseed Oil.** H. VOLLMANN (*Z. angew. Chem.*, 1925, 38, 337—339).—A survey of the evidence in favour of regarding linseed oil as a colloidal solution, although there is no indication to show which constituents of the oil form the disperse phase. Its colloidal character is shown by its stabilising action on suspensions of finely-divided pigments. Suspensions of Milori-blue, chrome-yellow, ivory-black, and zinc-white were made in equal concentrations in linseed oil and in a paraffin oil of slightly higher viscosity, and in every case the suspension in linseed oil showed a markedly higher stability, this difference being greatest in the case of Milori-blue, and least in the case of chrome-yellow.

P. M.

**New Type of Silica Gel.** H. N. HOLMES and J. A. ANDERSON (*Ind. Eng. Chem.*, 1925, **17**, 280—282).—It is more satisfactory to wash silica gel free from chlorides after drying and not before in order to prevent collapse of the capillary walls. Silica gel was precipitated together with ferric oxide. After keeping for 2—3 days, the sludge was filtered and allowed to dry very slowly in thick masses. It was then broken up, washed free from chlorides, and activated at about 140° for 12 hrs. This gives a very active gel and the activity can be increased by dissolving out the ferric oxide with hydrochloric acid. Nickel chloride may be substituted for ferric chloride.  
M. B. D.

**Electrolyte-free, Water-soluble Proteins. IV. Acid-Protein Compounds. I.** F. MODERN and W. PAULI (*Biochem. Z.*, 1925, **156**, 482—505).—Highly purified solutions of glutin (1.2%), serum-albumin (1.0%), and ovalbumin (1.57%) prepared by a process of dialysis followed by electrodialysis, are shown to give characteristic reproducible values for hydrogen-ion concentration ( $C_H = 7.88 \times 10^{-6}$ ,  $3.3 \times 10^{-6}$ ,  $1.67 \times 10^{-5}$ , respectively) and for chlorine ion activity, with mercurous chloride ( $C_{Cl} = 1.27 \times 10^{-4}$ ,  $1.82 \times 10^{-4}$ ,  $3.17 \times 10^{-4}$ , respectively). The behaviour of these solutions towards acids is studied and from the  $C_H$ ,  $C_{Cl}$  data an insight is gained into the constitution of acid-protein compounds. Preliminary determinations of the isoelectric points of these solutions have been made using conductivity measurements and the alcohol precipitation method. The  $C_H$  for optimum precipitation for ovalbumin is slightly, and for serum-albumin and glutin appreciably higher than the  $C_H$  of the corresponding pure protein solutions. The value of  $C_H$  for ovalbumin given above is slightly higher than Sørensen's figure ( $1.574 \times 10^{-5}$ ).  
P. W. C.

**Proteins. VII. Coagulation of Proteins by Heating.** M. SØRENSEN and S. P. L. SØRENSEN (*Compt. rend. Trav. Lab. Carlsberg*, 1925, **15**, (9), 1—26).—Mainly the text of a lecture delivered before the American Chemical Society on 3rd October, 1924.  
C. I. B. V.

**Casein.** K. KONDO (*Compt. rend. Trav. Lab. Carlsberg*, 1925, **15**, (8), 1—39).—When casein is shaken with aqueous hydrochloric acid, it is found that the amount of protein dissolved decreases as the amount of casein in contact with the solution increases. In explanation, it is suggested that the chlorine ions are bound partly as a complex in the solutions and partly with the hydrogen ions in the solid phase. Calculations show that the casein in solution binds about  $2 \times 10^{-4}$  g.-equiv. of chlorine ions. The observations of Loeb are confirmed by the osmotic pressure and membrane potential measurements of casein solutions with varying quantities of hydrochloric acid. Results in agreement with those of Loeb and of Pauli for the viscosity and conductivity of alkali caseinate solutions are also obtained, except that the casein solutions do not alter their condition in the course of time so long as the quantity of base added is small. The influence of sodium chloride on the

osmotic pressure and membrane potential of sodium caseinate in alkaline solutions is accompanied by a marked increase in the concentration of the hydrogen ions. A theory closely allied to that of Donnan is put forward, and on this basis it would appear that the molecular weight of casein is high. C. I. B. V.

**Elasticity of Gelatin Jellies and its Bearing on their Physical Structure and Chemical Equilibria.** H. J. POOLE (*Trans. Faraday Soc.*, 1925, 27; Advance proof).—The behaviour of cylinders of gelatin jellies under tensile stress has been examined. The strain produced by a steady stress is not a function of the stress alone, but is also governed by a time factor or "creep." If  $E$  is the extension of a cylinder of jelly after time  $T$ , the graph connecting  $E$  and  $dE/dT$  consists of two portions, the first being a straight line and the second curved, in agreement with equations deduced from the assumption that jellies are liquid-solid structures, where the solid phase has the form of a mesh of fine fibrils, and in which the "creep" is due chiefly to a reversible flow of the liquid phase in the interstices of the solid, and, to a lesser extent, to an irreversible plastic deformation of the solid. For this type of structure the elasticity at constant temperature should vary approximately with the square of the volume concentration of the solid phase, and this is approximately the case for temperatures from  $5.7^{\circ}$  to  $27^{\circ}$ . The elasticity varies greatly with temperature and this is attributed to changes in the equilibrium constant of a reversible reaction, either hydration or hydrolysis, which removes part of the protein substance from the solid to the liquid or *vice versa*. W. H.-R.

**Determination of the Elasticity of Gelatin Gels.** E. SAUER and E. KINKEL (*Z. angew. Chem.*, 1925, 38, 413—421).—Methods are described for the determination of the modulus of elasticity of gelatin gels against a shearing force. Such a gel if formed within a glass cylinder adheres firmly to the glass and the deformation of the longitudinal axis under a given air pressure can be measured. For pure gelatin Leik's observation, that it varies as the square of the concentration, is confirmed. [Cf. *B.*, June 26th.] C. I.

**Second Isoelectric Point of Gelatin.** E. O. KRAEMER (*J. Physical Chem.*, 1925, 29, 410—413).—From the experimental evidence available, the second isoelectric point of gelatin at  $p_H$  7.8 cannot be the isoelectric point of the sol form postulated by Wilson and Kern (*A.*, 1923, i, 68). The author suggests that the behaviour of gelatin is analogous to that of ferric hydroxide sol (cf. Kruyt and Spek, *A.*, 1919, ii, 498). When ferric hydroxide sol is treated with dilute sodium hydroxide it is found to have two regions of stability, corresponding with charges of different signs, and two precipitation zones. The two regions of instability correspond with the two isoelectric points. M. B. D.

**Periodic Precipitation in Dilute Gelatin Gels.** G. W. SCOTT-BLAIR (*Phil. Mag.*, 1925, [vi], 49, 90—96).—The phenomenon of the formation of Liesegang rings is investigated with silver nitrate and 0.019% potassium dichromate in 0.5 and 1% gelatin.

The age of the gel influences the distance from the surface of the last ring formed. It is suggested that a change in the structure of the gel accounts for this. The effect of exposure to light of different wave-lengths is investigated and there is a fundamental difference in the behaviour with visible and ultra-violet light. As a modification of Ostwald's theory, it is suggested that no sharp metastable region exists, but one of concentration where precipitation becomes probable. Experimental evidence is put forward in support of this view. C. W. B.

**Thermolability of Collagen.** A. W. THOMAS and M. W. KELLY (*J. Amer. Chem. Soc.*, 1925, **47**, 833—836).—Comparison of the fixation of gallotannin and wattle bark extract by collagen at 40°, in aqueous solution with that at 25° indicates that at 40° collagen is converted into a "sol" form, the isoelectric point of which is approximately  $p_H$  8. [Cf. *B.*, 1925, 370.] F. G. W.

**Heat Changes of the Globulins.** M. ADOLF (*Kolloid-Z.*, 1924, **35**, 342—344; cf. this vol., ii, 199; see also A., 1924, ii, 831, 728; i, 101; 1923, i, 396). D. C. J.

**Theory of Swelling and Reversibility Phenomena of Colloids.** W. BILTZ (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 49—52).—In crystalline hydrates and ammoniates the molecular heat of formation and the volume contraction decrease with successive additions. By analogy with such systems, it is suggested that the swelling of colloids is associated with the possession of relatively low lattice-energy. Anhydrous minerals have high lattice energy, as shown in their hardness, and do not swell. Hysteresis effects in the dehydration of hydrated oxides may be due to the formation of some of the anhydride. Protective colloids oppose the action of the lattice forces by preventing sufficiently close contact between the colloidal particles. E. M. C.

**Method for Measuring Small Changes of Swelling.** P. A. THIESSEN and C. CARIUS (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 245—252).—Changes in the thickness of thin solid discs on treatment with liquids or atmospheres of known humidity are magnified optically. A rod suspended from one pan of an analytical balance rests lightly on the disc and the other pan is connected to the pan of a smaller balance, carrying a mirror on its beam. E. M. C.

**Swelling-promoting Effect of Alcohol.** F. LOEBENSTEIN (*Kolloid-Z.*, 1924, **35**, 345—353).—The swelling effects of acids such as hydrochloric and sulphuric acids and a series of organic acids, e.g., acetic, propionic, lactic, etc., in the presence and absence of alcohol, on hide-powder have been determined. Measurements were also made using various protein hydrolysis products such as carbamide, alanine, and glycine and also putrefactive decomposition products. The swelling velocity was also approximately determined. It is shown that in many cases alcohol increases enormously the swelling of the protein. Especially is this the case with carbamide, *n*-butyric, phenylacetic, and phenylpropionic acids.

In these cases, a large increase in swelling velocity was also noticed. The effect of the sugars on this phenomenon is of considerable physiological interest. Sucrose and maltose produce a slight volume diminution, which was largely increased on increasing alcohol concentrations. Lactose produced a slight swelling increase both with and without alcohol, whilst dextrose produced scarcely any change in aqueous solution and a slight decrease in alcohol.

D. C. J.

**Cell Permeability. I. Swelling of Gelatin under the Influence of Carbamide.** F. CHODAT (*Bull. Soc. Chim. biol.*, 1925, 7, 113—123).—When cylinders or discs of 90% gelatin (neutral, or faintly alkaline to litmus) are immersed in solutions of carbamide at various concentrations, swelling of the gelatin, as measured by the quantity of liquid absorbed, increases with increasing concentration of carbamide up to the point of complete dispersion. At all  $p_H$  values there is greater swelling in the presence of carbamide than with water alone, the effect being at a minimum with gelatin at the isoelectric point ( $p_H$  4.7) and increasing on both sides of this point. Glycine, biuret, and hydroxylamine do not show the same phenomena. It is considered that the specific action of carbamide is entirely a physical one and is due to the reduction of surface tension of the liquid caused by its presence.

A theory explaining the course of the swelling of gelatin in weak acids, based on Donnan's theory of membrane equilibrium, is put forward.

C. T. G.

**Physico-chemical Analysis of Oxide Sols.** A. LOTTERMOSER [with F. FRIEDRICH, H. M. HÜBNER, and A. SZABÓ] (*Z. Elektrochem.*, 1924, 30, 391—393).—The ultrafiltration of sols of chromic, ferric, or aluminium hydroxide peptised with the corresponding chloride gives an ultrafiltrate that contains only hydrochloric acid and the hydrogen ion concentration of which is the same as that of the sol; the micelles therefore retain chloride ion, the negative charge on which compensates the positive charge on the colloid particles and the original sol may be formulated as  $[(xFe_2O_3, yHCl, zH_2O)H^+]_n + nCl^-$ . The specific conductance of the sol is higher than that of the ultrafiltrate, the difference being the true conductivity of the micelles which may thus be considered as complex electrolytes, the equivalent conductivity of which at infinite dilution may be calculated from the equation,  $\Lambda_{m\infty} = 1000K_m/c_K$ , where  $K_m$  is the conductivity of the micelles and  $c_K$  that of the free chloride ion. The mobility of the micelle cation,  $1000K_m/c_K - l_a$ , rises abnormally with increasing dilution in sols containing little chlorine owing to displacement of the adsorption equilibrium, but in sols containing much chlorine  $\Lambda_{\infty}$  approaches a constant as the sol more nearly approximates to a true electrolyte.

A. R. P.

**Constitution of Silicic Acid Sols. I.** W. PAULI and E. VALKÓ (*Kolloid-Z.*, 1925, 36 [*Zsigmondy-Festschr.*], 334—340).—Graham's silicic acid sol gives a well-defined specific conductance which remains constant after dialysis. Its constitution may be

represented as  $[x(\text{SiO}_2 + n\text{H}_2\text{O}) \cdot y\text{SiO}_3\text{H}^-] + y[\text{H}^+ \text{ or } \text{Na}^+]$ . In the sol obtained by simple dialysis hydrogen and sodium ions are present in varying proportions. The sodium ions may be replaced by hydrogen ions by electrodialysis. In such purely acidoid sols, there is a close agreement between the values for the hydrogen-ion activity obtained potentiometrically, by conductimetric titration, and from the conductivity. Electrodialysis provides a suitable method for preparing highly concentrated from dilute sols. Although such sols set to fairly hard jellies, they may be redispersed in water and show the same composition as the more dilute sols. In a series of sols the ratio  $x : y$ , or the number of neutral molecules associated with one ion, varied from 320 to 1200. E. M. C.

**Organic Sols of Arsenic Trisulphide.** J. J. BIKERMAN (*Z. physikal. Chem.*, 1925, **115**, 261—272).—The cataphoresis of colloidal solutions of arsenic trisulphide in nitrobenzene and ethyl acetoacetate, in the presence of dissolved salts, has been investigated. Precipitation takes place at a definite potential which is practically independent of the solvent and of the concentration of the sol. The rule connecting the precipitating power of ions with their valency holds in these non-aqueous solutions. L. F. G.

**Electrosynthesis of Sulphide Hydrosols.** F. V. VON HAHN (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 277—286).—The synthesis of hydrosols of sulphide minerals by means of electrical disintegration was studied. Galena and molybdenite gave stable sols on cathodic disintegration and antimonite gave a very slight turbidity. The disintegration of molybdenite took place only when the temperature exceeded  $53^\circ$ ; the value of this critical temperature varied by a few degrees according to the source of the mineral. This is the first case of a critical temperature in the electrical synthesis of colloidal solutions. The molybdenite sol showed a striking increase in the amplitude of its Brownian movement when a current was passed through it. The oscillatory discharge gave colloidal solutions with antimonite, sphalerite, chalcocite, and molybdenite; galena and iron pyrites gave only coarsely dispersed systems. Disintegration in the electric arc gave stable sols with galena, chalcocite, iron pyrites, and molybdenite. E. M. C.

**Influence of Agitation on the Coagulation of Hydrophobic Sols.** H. FREUNDLICH and S. K. BASU (*Z. physikal. Chem.*, 1925, **115**, 203—223).—The effect of agitation on the coagulation of arsenic trisulphide, ferric oxide, vanadium pentoxide, cupric oxide, and gold sols has been investigated. Acceleration is observed especially with comparatively large electrolyte concentrations and strongly coagulating ions; with the last three sols, retardation is observed and this is attributed to peptisation which becomes more effective the lower the concentration of electrolyte and the weaker the coagulating power of the ions. Coagulation velocity curves, without agitation, of cupric oxide sols show an initial induction period which is reduced on increasing the electrolyte concentration or on agitating. These effects, and the temperature effect, are in agree-

ment with Smoluchowski's theory. The formula of Schalek and Szegvari (A., 1924, ii, 115) expresses the influence of electrolyte concentration on slow coagulation.

L. F. G.

**Ultramicroscopy and Coagulation.** A. DE G. ROCASOLANO (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 80—82).—It is suggested that ultramicroscopic observation of the cessation of Brownian motion affords a satisfactory criterion of the occurrence of flocculation in all types of systems.

E. M. C.

**Stability of Suspensions. I. Rate of Sedimentation of Kaolin Suspensions.** W. O. KERMACK and W. T. H. WILLIAMSON (*Proc. Roy. Soc. Edinburgh*, 1924—25, **45**, 59—70).—A comparison has been made of the rates of sedimentation of a kaolin suspension in presence of varying concentrations of electrolyte at different  $p_H$  values. Contrary to the general behaviour observed, sodium chloride, and, to a less extent, sodium sulphate, inhibit precipitation in acid solution, possibly due to chemical reaction with the kaolin. Monocalcium phosphate, and still more "superphosphate," have an abnormally large precipitating action above a certain concentration in alkaline solution. This is ascribed to precipitation of basic phosphate on the kaolin particles. In acid solutions, the trivalent aluminium, ferric, and lanthanum ions have very little effect, but a zone of very marked flocculation occurs at  $p_H$  7—8, separating an alkaline region within which the unsedimented particles are negatively charged, from an acid region in which they are positively charged. Similar behaviour has been observed with ordinary colloidal sols such as gold or gum benzoin (Kermack and Voge, following abstract), and also with soil clays (Comber, A., 1922, i, 212). [Cf. B., June 26th.]

M. S. B.

**Action of Salts with Multivalent Cations on Colloidal Solutions of Gold and Gum Benzoin.** W. O. KERMACK and C. I. B. VOGÉ (*Proc. Roy. Soc. Edinburgh*, 1924—25, **45**, 90—101).—The precipitating action of beryllium sulphate and calcium, ferric, aluminium, and lanthanum chlorides on gold and gum benzoin sols has been examined at different  $p_H$  values. There is a marked difference between the behaviour of bivalent and trivalent cations, for, not only do the latter precipitate at very much lower concentrations than the former, but with increasing concentration of the trivalent ions the charge on the colloid changes from negative to positive, and between these regions lies a precipitating zone of concentration. The salts hydrolysed in a greater degree, for example ferric chloride, confer a positive charge in more acid solution than those hydrolysed to a less degree, *e.g.*, lanthanum chloride. The phenomenon appears, therefore, to be related to the presence of hydroxide. Too large an increase in the amount of hydroxide, however, decreases stability, so that probably a certain concentration of metallic ions is necessary. Possibly, therefore, a complex between colloid and hydroxide is formed, associated with a positively charged trivalent ion. The trivalent ions may have a more powerful atomic field of force than the bivalent ions, and thus be



able to form such associated complexes more easily. By testing the non-precipitated, positively-charged, colloidal solutions, protected regions were observed in the case of gold sol with aluminium chloride and of gum benzoin sol with ferric chloride. This should be the region where the highest number of positively charged metallic ions exist simultaneously with sufficient hydroxide to form a surface layer.

M. S. B.

#### **Influence of Neutral Salts on some Properties of Gelatin.**

E. STIASNY (*Kolloid-Z.*, 1924, **35**, 353—358).—It has been shown (cf. A., 1923, ii, 301) that sodium thiocyanate not only causes swelling in collagen but peptises it to a considerable extent; the thiocyanate has no hydrolysing action. Similar effects are found with gelatin. The hydrolytic effect was determined by the formol titration method and by a determination of the Van Slyke value. The peptising effect was determined by ultrafiltration experiments, mutarotation measurements, and viscosity measurements on the dialysed solutions. Sodium thiocyanate produces the same effect in decreasing the specific rotatory power of gelatin at 15° as does a rise of temperature to 35°. Further heating produces no change in the value of the constant. The effectiveness of other salts in decreasing the specific rotatory power follows the Hofmeister series for anions. The effects of sodium thiocyanate on the viscosity of gelatin solutions are traced to a swelling effect which increases the viscosity and a peptising effect which decreases it. It is possible to follow these two effects by observing the viscosity before and after dialysis, because the swelling effect is completely reversible while the peptising effect is not. The peptising effect is not attributable to the rupture of principal valencies but rather to a breaking down of the protein molecule, composed of aggregates of peptone molecules into simpler groups and finally into the peptone molecules themselves.

D. C. J.

#### **Action of Colloidal and Semi-colloidal Ferric Hydroxide on Aqueous Gelatin Solutions. I.**

R. WINTGEN and E. MEYER (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 369—379).—When constant amounts of ferric hydroxide sol are mixed with increasing amounts of gelatin solution and water to give constant final volumes, two types of flocculation are obtained according as the necessary amount of water is added to the ferric hydroxide or the gelatin solution. When the water is added to the gelatin solution, flocculation commences at a well-defined point and the amount of precipitate increases to a maximum. Irregularities are shown when the water is added to the ferric hydroxide. For increasing amounts of gelatin, there is a well-marked commencement of flocculation, followed by an increase to a rather indefinite point of maximum flocculation, a sudden fall to a point of no flocculation and a renewal of increasing flocculation. The amount of gelatin required for the first flocculation decreases with increase in the concentration and the age of the initial gelatin solution. For a series of dilutions of ferric hydroxide sols of different origin, the amount of gelatin required for flocculation decreases in a linear manner with the dilution for typical colloidal

sols, but decreases in a linear manner with the concentration of semi-colloidal sols, containing much hydrochloric acid. The first case is regarded as a simple mutual flocculation and the second as involving, in addition, an increasing dispersion of the gelatin with increasing amounts of hydrochloric acid. E. M. C.

**Influence of Gelatin on the Stability of a Colloidal Solution of Cholesterol and on the Charge on the Particles.** W. O. KERMAK and P. MACCALLUM (*Proc. Roy. Soc. Edinburgh*, 1924—25, 45, 71—89).—The stability of a cholesterol sol, prepared by the addition of an alcoholic solution of commercial cholesterol to distilled water, and subsequent filtration, has been examined in solutions of varying  $p_H$  value. The minimum amount of sodium chloride required to produce precipitation increases at first with increasing  $p_H$  value, reaches a maximum at  $p_H$  7—8, remains constant up to  $p_H$  12, and then returns to zero, indicating that the cholesterol is precipitated by the alkalinity of the solution alone. An examination of the effect of gelatin on the sol, combined with a study of the cataphoretic potential difference (*P.D.*) between the cholesterol particles and the medium, in the presence of gelatin of varying concentration and  $p_H$ , shows that gelatin brings about precipitation through a range of  $p_H$  values which varies in position for varying concentrations of gelatin and exactly separates the region of positively charged from that of negatively charged colloid. When sufficient gelatin is present the cholesterol particles show a zero potential at  $p_H$  4.7, the isoelectric point of gelatin. On decreasing the  $p_H$  the particles acquire a positive charge which increases until a *P.D.* of about 14 mv. is reached, when it remains approximately constant or decreases. Similarly, above  $p_H$  4.7 the *P.D.* becomes negative up to values of about 25 mv. The effect of sodium chloride in the presence of gelatin is to widen the zone of precipitation. The gelatin, however, exerts a protective action against precipitation by sodium chloride, which probably reaches a minimum at the isoelectric point. The amount of gelatin required to protect against precipitation by sodium chloride is approximately that necessary to cover the particles of the sol with a unimolecular layer of gelatin from one to two atoms in thickness. This is also sufficient to keep the particles in suspension even when the *P.D.* is zero. The protective action of gelatin against precipitation by acid and alkali has also been studied. M. S. B.

**Effect of Dielectrics on the Stability of Colloids.** D. DEUTSCH (*Magyar orvosi Archivum*, 1924, 25, 511—514).—The concentrations of dielectrics which are able to annul the colloid coagulating action of ammonium sulphate are in the order of their (low) dielectric constants. Organic acids with low dielectric constants are in the same order. By suitable combination of electrolytes and dielectrics, blood-serum, casein, and albumose could be brought into a globulin-like phase. CHEMICAL ABSTRACTS.

**Peptisation of Bismuth Hydroxide.** A. KUHN and H. PIRSCH (*Kolloid-Z.*, 1925, 36 [*Zsigmondy-Festschr.*], 310—318).—By repeated washing or dialysis of bismuth hydroxide precipitates a

point is reached at which the precipitate forms a sol, stable for a day or two. Sucrose and mannitol act as peptising agents and have maximum effects in 0.05*N*-solutions. With glycerol and lactose the amount of bismuth hydroxide in solution increases regularly with the concentration until the whole of the precipitate is peptised; the peptisation appears to be followed by the formation of chemical complexes.

E. M. C.

#### **Protective Action of Soaps for Zsigmondy Gold Hydrosols.**

B. PAPACONSTANTINOU (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 329—333).—The protective action of soaps towards gold hydrosols, as measured by the reciprocals of their gold values, decreases in the order oleate, palmitate, stearate, myristate, and laurate at the ordinary temperature. Increase of temperature increases the protective action of these soaps, presumably by decreasing the micelle size. Linoleates have about the same protective action as oleates at the ordinary temperature, but the protective action decreases with increase of temperature. The potassium and sodium soaps of lauric, myristic, and palmitic acids have approximately equal actions. At high temperatures, potassium stearate and linoleate are more active than the sodium salts, but sodium oleate is much more active than potassium oleate.

E. M. C.

**Protection in a Colloidal Solution by Addition of an Electrolyte in Quantities too Small to Effect Flocculation.** A. BOUTARIC and (MLLE.) G. PERREAU (*Compt. rend.*, 1925, **180**, 1337—1340; cf. A., 1924, ii, 595).—Addition of small amounts of an electrolyte to a colloidal solution can prevent its flocculation by a much larger quantity of the same electrolyte than is normally necessary. If the time which elapses before flocculation occurs is graphed against the quantity of electrolyte added the curve shows an asymptote parallel to the time axis, of which the abscissa  $\alpha$  measures the maximum amount of electrolyte which can be added without causing flocculation. A small amount of sulphuric acid was added to a gamboge suspension which was then left to stand. Redetermination of the graph time/amount of coagulating electrolyte (sulphuric acid), indicated a uniform increase in stability of the suspension. The higher value ( $\beta$ ) of the abscissa for the asymptote is a measure of the maximum amount of electrolyte which cannot effect coagulation, and  $\beta - \alpha$  indicates the degree of protection.

Using an arsenic sulphide sol treated with lithium chloride and kept for 11 days, the value of  $\beta - \alpha$  has been found for various quantities of lithium chloride. The protective effect at first increases with increasing lithium chloride, passes through an optimum and then diminishes. Using the optimum concentration, the variation of  $\beta - \alpha$  with the time which elapses between addition of protecting agent and testing its efficiency has been plotted. At first the protection increases with time, then passes through a maximum and diminishes.

In other cases, e.g., gamboge and sulphuric acid, the protective effect increases steadily with the amount of electrolyte added. This

can be reconciled with the preceding case by supposing the maximum protection to be effected by an amount of electrolyte greater than the maximum quantity which may be added to the untreated suspension without causing flocculation. In all cases, the curve showing variation of protective effect with time (that elapses after introduction of the electrolyte) passes through a maximum.

R. A. M.

**Sensitisation and Protection by Lipoids.** W. BECK (*Biochem. Z.*, 1925, 156, 471—481).—Both the positive ferric oxide sol and the negative molybdic oxide sol can be rendered much more sensitive to precipitation by electrolytes by the addition of pure lecithin-sol or cholesterol-sol, the action of the latter being somewhat less than that of the former. Lecithin retains its sensitising property on admixture with serum albumin. Congo-red sols containing lecithin are more sensitive than lecithin sols, whereas Congo-red sols containing cholesterol are less sensitive than cholesterol sols. Congo-red sols containing a mixture of 0.5% lecithin and 0.5% cholesterol sols are less sensitive than the original lipid mixture.

P. W. C.

**Dispersion and Base Exchange (Ion Exchange).** G. WIEGNER (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 341—369; cf. this vol., ii, 36).—The general significance of base exchange in dispersoid chemistry is illustrated by reference to clay. The charge on clay particles is ascribed to the presence of a complex silicate anion, holding by weak residual electrostatic forces a sheath of cations in dynamic equilibrium. The attractive force on these cations increases with increased valency and decreases with increased hydration. Ultramicrons with heavily hydrated cations, e.g., lithium and sodium, are bulky and viscous and resemble hydrophilic colloids; those with less hydrated cations, e.g., caesium and calcium, are less viscous and resemble hydrophobic colloids. Simple effects of added electrolytes are obtained only if the added cation is the same as that in the outer sheath of the colloid particle; in other cases flocculation effects always include the effects of a base exchange. An extensive series of experiments with clays containing a single alkali or alkaline-earth metal led to the following conclusions. Ultramicroscopic and viscosimetric measurements show that clays are more stable, more hydrated, more viscous, and less sensitive to electrolytes the greater the hydration of their cations. The less hydrated the cation of an added salt, the more rapidly does it flocculate a clay. Increased concentrations of added salt, for dilute solutions and slow coagulation, increases the size of the aggregates formed, as shown in increased viscosities. For equal concentrations of the added electrolyte, the least hydrated flocculating cation forms the largest aggregates and gives the highest viscosity. For more concentrated salt solutions, the viscosity decreases with increasing salt concentration, owing probably to the removal of water from the ultramicrons by the dissolved salts. The viscosity is higher for coagulated clays with heavily hydrated cations than for those with less hydrated cations. Owing to base exchange, a

small amount of potassium chloride, added to a large amount of a calcium clay, has the same flocculating effect as an equivalent amount of calcium chloride, and the Schulze law is thus invalid. The changes in the relative flocculating powers of uni- and bi-valent ions with varied concentrations of colloid probably depend on changes in the amounts and relative importance of the exchanged bases.

E. M. C.

**Application of the Diffusion Coefficient to the Determination of the Molecular Size of Heavy, Amphoteric Hydrated Oxides in Alkaline Solution.** G. JANDER and H. SCHULZ (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 109—118).—In the alkali tantalates the ratio  $M_2O : Ta_2O_5$  is 7 : 5 and the basicity of the tantalic acid is at least six, according to the variation of the conductivity with the dilution. Potassium tantalate may be represented as  $K_7[Ta(TaO_4)_4]$  with a molecular weight of about 1440. An estimate of the molecular weight was made by comparing its diffusion coefficient with that of a salt of similar molecular weight. The technique employed resembled that of Öholm (*A.*, 1905, ii, 147). 0.05*N*-Sodium hexamolybdic periodate,  $Na_5[MoO_4)_6]$ , with molecular weight of 1202, had a diffusion coefficient of 0.29 at 10° in 0.1*N*- and 0.5*N*-sodium nitrate solutions, but gave much higher values in water and in *N*-sodium nitrate solution. 0.05*N*-Potassium tantalate had a diffusion coefficient of 0.24 in 0.1*N*-potassium hydroxide and 0.1*N*-potassium nitrate solutions, but a higher value in water. The molecular weight of the potassium tantalate was thus 1750.

E. M. C.

**Centrifuging, Diffusion, and Sedimentation Equilibria of Colloids and Substances of High Molecular Weight.** T. SVEDBERG (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 53—64).—A mathematical treatment of the determination of the size-distribution of colloidal particles by means of the ultra-centrifuge and measurements of diffusion.

E. M. C.

**Theory of Membrane Equilibria.** E. HÜCKEL (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 204—217).—An exact thermodynamic theory of membrane equilibria is given for ideal and actual solutions of completely ionised electrolytes. Allowance is made in the case of ideal solutions for the diffusion of the solvent through the membrane. Debye's theory of electrolytes is used for the treatment of the equilibria and leads to equations which are in harmony with the experiments of Donnan and Allmand (*T.*, 1914, **155**, 1941) on the potassium ferrocyanide-potassium chloride equilibria.

E. M. C.

**Use of Tap Water as the Outer Liquid in Dialysis.** E. WILKE-DÖRFURT and M. DEKER (*Kolloid-Z.*, 1925, **36** (*Zsigmondy-Festschr.*), 305—310; cf. Gutbier, Huber, and Schieber, *A.*, 1923, ii, 131).—Silicic acid sol takes up calcium when dialysed against tap water. The calcium is readily removed by dialysis against distilled water provided that some of the original salts

still remain in the sol. After complete removal of the original salts by tap water, the subsequent removal of calcium is very difficult. Tap water containing iron should not be used, since ferric hydroxide is formed in the silicic acid sol and cannot be removed. E. M. C.

### Physical-chemical Studies of Synthetic Colouring Matters.

W. KOPACZEWSKI (*Rev. gén. Mat. Col.*, 1925, 39, 34—35, 105—106).—The rates of diffusion of 53 dyes in 1% aqueous solution at 25° through a collodion membrane prepared under carefully defined conditions were measured, and the results, which differ from those obtained by other workers, are tabulated. Resorcin-yellow, eosin, malachite-green, acridine-yellow, and methyl-violet diffuse rapidly; tropæolin, helianthine, gentian-violet, sudan-G, and direct-brown diffuse easily; but direct-grey, hæmoglobin, direct-violet-J, and direct-green do not diffuse. It is suggested that the osmotic pressure of dyes in solution is due to the anions and non-dissociated molecules rather than to the cations (*e.g.*, sodium). The results of investigations by other workers on the behaviour of dyes in solution are summarised. [Cf. *B.*, 1925, 348.] A. J. H.

### Ultrafiltration of Non-aqueous Solutions. H. BECHHOLD

and V. SZIDON (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 259—271).—Membranes for the ultrafiltration of non-aqueous solutions may be prepared in Bechhold and König ultrafiltration vessels by coagulating the impregnating material by means of an organic liquid. The best results are obtained with solutions of collodion in ether, coagulated by benzene or toluene. Light petroleum, carbon tetrachloride, and “tetralin” may also be used for the coagulation and cellulose triacetate in acetone for the impregnation. The relative porosities of the membranes may be compared either by replacing the benzene or toluene by alcohol and water and filtering hydrosols of known degrees of dispersion, or by means of the air-bubble method (*A.*, 1908, ii, 823). Oil sols of a number of dyestuffs were found by ultrafiltration and by diffusion in jellies of aluminium oleate and caoutchouc in benzene to be very finely divided and probably in the molecular state. Oil sols of copper and iron oleates were also very finely divided. Successful fractionations were made with sols of cadmium sulphide, zinc sulphide, iron oxide, and graphite in oil and of asphalt in petroleum. E. M. C.

### Ultrafiltration under Pressure. B. BRUCKNER and W. OVER-

BECK (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 192—196).—The rate of ultrafiltration under high pressures is considerably increased by providing constant stirring immediately above the filtering membrane. Two forms of electromagnetic stirrers are described. In one, an iron stirrer is driven by a rotating electromagnet above the ultrafilter. In the other, a hollow iron cylinder is lifted and dropped by means of an annular water-cooled electromagnet actuated by an intermittent current. This is obtained by passing the current through a heating coil in a hydrogen vessel and arranging that the alternate expansion and contraction of the gas

moves a mercury column which breaks and makes the electrical circuit.

E. M. C.

**Mechanism of Ultrafiltration.** J. DUCLAUX and J. ERRERA (*Rev. gén. Colloid.*, 1925, 3, 97—103).—The rate of passage of different liquids through membranes of cellulose nitrate is approximately proportional to their viscosity (*B.*, 1924, 815). This relation has been confirmed under conditions which minimise changes in the membrane during use, and it is shown that membranes of the cellulose type behave as rigid assemblages of fine capillary tubes towards all liquids which exert no solvent action on them. The bearing of these results on the structure of irreversible gels is briefly considered.

F. G. T.

**Methylene-blue Test. Evaluation of Active Charcoals.** W. MECKLENBURG (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 132—142).—Considerable errors may be introduced by assessing the relative values of decolorising charcoals on the basis of the amounts of methylene-blue which are adsorbed by equal weights of charcoal. The time ( $t$ ) in seconds required by different weights ( $m$ ) in mg. of charcoal, dried at  $120^\circ$ , to decolorise 20 c.c. of 0.15% methylene-blue solution were found to be connected by the equation  $(m - a)Z = K$ , where  $a$  and  $K$  are constants. A charcoal was separated into six fractions and the outer specific surfaces ( $O$ ) were determined microscopically. The constant  $a$  was found to decrease gradually with increasing specific surface and the product  $K \cdot O^{1.5}$  remained constant throughout the series of fractions.

E. M. C.

**Theory of Liesegang Rings.** WO. OSTWALD (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 380—390).—In all reacting systems giving typical periodic precipitates there are three principal diffusion waves. The added electrolyte diffuses into the gel, the electrolyte in the gel diffuses outwards and that produced by the reaction may diffuse in both directions. In many cases, the product of the reaction has a higher rate of diffusion than one or both of the reactants. Many and probably all reactions giving typical periodic precipitates are balanced reactions and the precipitation may be prevented by changes of dissociation or hydrolysis and the formation of complex and double salts. The precipitation depends on certain critical mixture ratios of the concentrations of reactants which vary over wide ranges through the interference of diffusion waves. The following facts are advanced in support of the theory. Many Liesegang rings may be destroyed by the subsequent introduction by diffusion of the electrolyte produced in the reaction. Rings may sometimes be produced from a continuous precipitate in a gel, *e.g.*, a uniform precipitate of lead sulphate in a gelatin gel containing ammonia is converted into rings by the diffusion of concentrated ammonium chloride. Replacing one component by a compound not giving a balanced reaction results in a continuous precipitate. The distribution of chloride ions in a gelatin gel containing magnesium chloride was found after the diffusion of

ammonia to show a periodic variation between values much higher and much lower than those in the original gel. E. M. C.

**Iodine as an Emulsifying Agent.** H. N. HOLMES and H. A. WILLIAMS (*J. Amer. Chem. Soc.*, 1925, **47**, 323—325).—By shaking ethyl ether, ethyl acetate, amyl acetate, or amyl alcohol with water containing iodine in solution emulsions of the oil-in-water type are produced. Adsorption films of iodine at the liquid-liquid interface are formed, the change in the iodine concentration being very marked. L. J. H.

**Theory of Mordanting. II.** E. ELÖD (*Z. angew. Chem.*, 1925, **38**, 199—201).—The mordanting of wool by means of an aluminium bath is a chemical and not a physical process. The production of deleterious hydrochloric acid is avoided by using baths of aluminium formate or by adding sodium formate and formic acid to the aluminium chloride bath. In the case of silk, the production of the acid is surmounted by the use of suitable complex tin salts of organic acids, e.g.,  $\text{Na}_2[\text{Sn}(\text{HCO}_2)_6] \cdot 5\text{H}_2\text{O}$ , which is produced within the fibres by soaking the fabric successively in sodium formate solution containing free formic acid and in stannic chloride. S. K. T.

**Mutual Action of Charged Particles in Liquid Media.** E. F. BURTON and J. E. CURRIE (*Phil. Mag.*, 1925, [vi], **49**, 194—209).—A theoretical discussion is given of the Helmholtz double layer theory in conjunction with Smoluchowski's assumptions of mutual attraction of particles in close proximity, and Gouy's explanations of the effect of electrolytes on the ions in the outer layer. Smoluchowski's assumptions are replaced by postulating that (1) particles are drawn together by capillary action when very close to one another, (2) failure to combine under normal conditions is due to mutual repulsion by the effective charges when particles approach one another within the limits of the diffuse outer layer, (3) electrolytes by suppressing the diffusiveness of the outer layer reduce the effective distance of the repulsive action, (4) electrolytes by discharging the particles destroy the source of the force which kept them apart. Experimental evidence is given of scattering of particles due to charge, proving the existence of mutual repulsion. Scattering coefficients for lead shot in water, turpentine, alcohol, ether, and benzene are given, and the scattering is shown to be proportional to the viscosity of the medium.

C. W. B.

**Applications of the Kinetic Theory of Gases.** N. DE KOLOSSOWSKY (*J. Chim. Physique*, 1925, **22**, 79—82).—On the assumption that  $C_p$  is a linear function of the number ( $n$ ) of atoms in the molecule of a gas, the kinetic theory leads to the relations (1)  $C_p = 2n + 3$ , and (2)  $C_v = 2n + 1$ . These equations give a much closer agreement with experimental data than the equation  $C_p = 3.5 + 1.5n$  given by Nernst (*Gött. Nachr.*, 1906, **1**, 12).

Combination of the equation of Laplace for the velocity ( $U$ ) of sound in a gas with the kinetic theory equation for the arithmetic



mean velocity ( $u$ ) of translation of the molecules, leads to the relation  $U/u=0.627\sqrt{(2n+3)/(2n+1)}$ , which is in good agreement with experimental data.

W. H. R.

**Equilibrium Pressures of Individual Gases in Mixtures and the Mass-action Law for Gases.** L. J. GILLESPIE (*J. Amer. Chem. Soc.*, 1925, **47**, 305—312).—A mathematical discussion of the law of mass action for real gases. No equation of state yet proposed permits a complete solution. The rule of Lewis and Randall for calculating the fugacity of a gas in a mixture is made exact by the addition of a term involving the integral of  $(\partial v/\partial n_1 - V/n_1)dp$  between zero and the total pressure. Exactness of the Lewis-Randall rule, additivity of volumes and activity of heat content are interdependent. A method of experiment employing solid phases to fix the fugacities of the gases in the mixture is outlined.

L. J. H.

**Representation of the Haber Equilibrium Data by an Equation.** L. J. GILLESPIE (*J. Math. Phys. Mass. Inst. Tech.*, 1925, **4**, 84—96).—The equation  $\log K_p = (2679.35 + 1.1184p)/T - (5.8833 + 0.001232p)$  is shown to represent within the errors of experiment the values of the equilibrium constant determined by the Fixed Nitrogen Research Laboratory (cf. Larson and Dodge, A., 1924, ii, 104; Larson, *ibid.*, ii, 331) for the temperature range 325—500° and from 100 atm. to the lowest pressure. For higher pressures the equation  $\log K_p = (2172.26 + 1.99082p)/T - (5.2405 + 0.002155p)$  yields better results.

J. S. C.

**Equilibrium Proportions in the Formation of Methane from Carbon Monoxide and Hydrogen, and from Carbon Dioxide and Hydrogen.** B. NEUMANN and K. JACOB (*Z. Elektrochem.*, 1924, **30**, 557—576).—The equilibrium relations and conditions of maximum yield of methane according to the equations (a)  $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$  and (b)  $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$  are investigated experimentally and theoretically. Mixtures of the reacting gases in (a) and (b) were led over reduced nickel with porous porcelain or magnesia as carriers at different temperatures, and the resulting gas mixtures analysed. Above the temperature at which the yield of methane is a maximum there is a rapid diminution as the temperature rises. In the carbon monoxide reaction, the following changes appear to be involved:  $\text{C} + \text{CO}_2 = 2\text{CO}$ ,  $\text{C} + 2\text{H}_2 = \text{CH}_4$ , and  $\text{CO} + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$ , the equilibrium constant for the reaction (a) calculated from the known constants for the partial reactions agreeing satisfactorily with that derived from the experimentally found partial pressures. The equilibrium is also considered from the point of view of the van't Hoff isochore, the integration constant being deduced from the experimental measurements and from the chemical constants of the individual gases. Similar considerations are applied to reaction (b).

C. H. D. C.

**Influence of Intensive Drying on Inner Equilibrium.** A. SMITS (*J. Amer. Chem. Soc.*, 1925, **47**, 794—795).—An exactly similar explanation as that suggested by Lewis (A., 1924, ii, 98)

concerning Baker's experiments on intensive drying was previously put forward by the author (A., 1922, ii, 358). A short statement regarding the results obtained in recently published investigations (T., 1924, 125, 1068) is appended. J. S. C.

**Equilibrium between Creatine and Creatinine in Aqueous Solution. Effect of Hydrogen Ion.** G. EDGAR and H. E. SHIVER (*J. Amer. Chem. Soc.*, 1925, 47, 1179—1188).—The conversion of creatine into creatinine proceeds, in aqueous solution, to an equilibrium, the ratio of the molecular concentration of creatinine to that of creatine being 0.54 at 25°, 1.02 at 50°, 1.59 at 70°, and 2.89 at 100°. In buffer solutions, the above ratio at 50° is as follows:  $p_H$  1, 36.72;  $p_H$  3, 4.01;  $p_H$  4, 1.33;  $p_H$  5, 1.05; and  $p_H$  6, 1.03. At 25°, about 10% of the material is lost by hydrolytic decomposition before equilibrium is reached. The results are discussed mathematically from the point of view of the ionisation of the two bases (cf. Hahn and Barkan, A., 1921, i, 515) and equations are derived for the influence of temperature and hydrogen-ion concentration on the equilibrium. F. G. W.

**Equilibrium Diagram of the Binary Alloys of Antimony and Bismuth.** B. OTANI (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, 13, 293—297).—The equilibrium diagram for the binary alloys of antimony and bismuth was determined by the method of Konno and Ishara (*ibid.*, 1921, 10, 57; 1924, 13, 75). The form of the curves for both solidus and liquidus indicates a continuous series of solid solutions, confirming the results of Gautier. The horizontal form of the solidus suggested by Cook (*J. Inst. Met.*, 1921, 26, 421) is not confirmed. C. S.

**Equilibrium Diagrams and the Heats of Formation in some Binary Organic Systems. I.** B. E. KITRAN (*Far-maceutski vjesnik*, 1924, 14, 583—590, 617—620, 668—674, 702—704, 748—751, 777—783).—The equilibrium relations in binary systems with trichloroacetic acid as the first component ( $C_1$ ) have been studied by the cooling curve method. In the following summary, the composition of characteristic mixtures is expressed in moles % ( ) of the second component ( $C_2$ ).  $C_2$ =*p*-Toluidine: two eutectic points at 18.2° (15) and at 32.7° (65), and a maximum at 84.0° (33.3), corresponding with the compound  $\text{Me}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot 2\text{CCl}_3\cdot\text{CO}_2\text{H}$ .  $C_2$ =Diphenylamine: two eutectic points at 19.6° (15) and at 51.3° (95), and a maximum at 114.2° (66.6) corresponding with the compound  $2\text{NHPh}_2\cdot\text{CCl}_3\cdot\text{CO}_2\text{H}$ .  $C_2$ = $\beta$ -Naphthylamine: two eutectic points at 15.0° (12) and at 98.6° (65) and a maximum at (50). It was not possible to determine the m. p. of the equimolecular compound owing to the decomposition of the trichloroacetic acid. Results with phenol confirmed those previously obtained by Kendall (A., 1916, i, 599). Quinol: two eutectic points at 49.5° (2) and at 77.5° (35), and a maximum at 84.9° (25) corresponding with the compound  $\text{C}_6\text{H}_4(\text{OH})_2\cdot 3\text{CCl}_3\cdot\text{CO}_2\text{H}$ . Pyrocatechol, resorcinol, pyrogallol, and naphthalene form no compounds. The data for the respective eutectic points are:

pyrocatechol,  $34.7^{\circ}$  (25); resorcinol,  $25.0^{\circ}$  (30); pyrogallol,  $40.2^{\circ}$  (12); naphthalene,  $35.2^{\circ}$  (23).  $C_2$ =Camphor: two eutectic points at  $6.7^{\circ}$  (30), and at  $22.3^{\circ}$  (67) and a maximum at  $62^{\circ}$  (50) corresponding with an equimolecular compound. The formation of this compound is significant as it accounts for the difference in the results for the heat of combustion of trichloroacetic acid as determined by Berthelot and Matignon (*Ann. Chim. Physique*, 1893, [6], 28, 565) and those obtained by the author. In the second part of the paper binary systems with phenacetin ( $C_1$ ) have been investigated.  $C_2$ =Urethane gives a eutectic at  $45.0^{\circ}$  (93.5);  $C_2$ =acetaniline, a eutectic at  $75.0^{\circ}$  (78.4);  $C_2$ =benzoic acid, a eutectic at  $86.7^{\circ}$  (65.7). The third part of the memoir deals with various binary systems. Naphthalene ( $C_1$ ) gives with *m*-dinitrobenzene ( $C_2$ ) a eutectic at  $51.0^{\circ}$  and 44 mol. % of *m*-dinitrobenzene. The different results of Kremann (A., 1905, ii, 77) are attributed to supercooling, to which the mixture is strongly inclined. Phenol ( $C_1$ ) and *p*-toluidine ( $C_2$ ) form an equimolecular compound, which exist in two forms, the metastable modification crystallising at  $28.6^{\circ}$  and the stable at  $29.4^{\circ}$  (cf. Philip, T., 1903, 83, 828); the eutectic points are at  $9.1^{\circ}$  (25) and at  $20.8^{\circ}$  (69). *m*-Chloronitrobenzene ( $C_1$ ) and *m*-bromonitrobenzene ( $C_2$ ) yield only a continuous series of solid solutions as previously found by Küster (A., 1892, 396) and Hasselblatt (A., 1913, ii, 484). S. S. M.

**Transformation Points of Solid Solutions of Alumina or Chromic Oxide in Ferric Oxide.** H. FORESTIER and G. CHAUDRON (*Compt. rend.*, 1925, 180, 1264—1266; cf. A., 1924, ii, 617).—It has been shown earlier by a dilatometric method that ferric oxide undergoes a reversible transformation at  $675^{\circ}$ . The influence of the addition of the corresponding oxides of aluminium and chromium has now been investigated. Mixtures of hydroxides not ignited above  $400^{\circ}$  show no lowering of the transition point, indicating mere juxtaposition of the oxides. Heating at  $700^{\circ}$  affords evidence of solid solution formation which is completed on heating for 2 hrs. at  $900^{\circ}$ . Addition of alumina causes a linear decrease in the transformation point up to 12%  $Al_2O_3$ . Further addition has no effect, the point remaining fixed at  $575^{\circ}$ . Addition of chromic oxide causes a similar linear decrease ( $40\%$   $Cr_2O_3$  corresponds with  $230^{\circ}$ ), but no sharp break in the curve of temperature against chromium content is observed. At high percentages, the influence of chromium oxide on the transition point is much smaller. The oxides of iron and chromium are miscible in all proportions. This conclusion is supported by the fact that the ratio of their molecular volumes is practically equal to unity. R. A. H.

**Hydrated Ferric Oxide and Iron Oxides.** A. SIMON and T. SCHMIDT (*Kolloid-Z.*, 1925, 36 (*Zsigmondy Festschr.*), 65—80).—The water lost by hydrated ferric oxide, prepared in several ways, was determined at a series of temperatures and a constant pressure of 10 mm. The isobars were quite smooth and gave no evidence of the existence of definite hydrates. A sample prepared by the dialysis of ferric nitrate held water more strongly than those pre-

precipitated from ferric nitrate or chloride. The form of the isobars suggests that at low temperatures the water obeys the osmotic law for amorphous systems with capillaries of molecular size (cf. Huttig, *Fortschritte der Chem.*, **18**, 1), and that at higher temperatures the water is held within and affects the lattice structure of the ferric oxide. An X-ray analysis showed that the lattice structure of the heated residue was slightly different from that of the ignited oxide. The 10 mm. isobar for the decomposition of ferric oxide showed a sharp break at 1300°, corresponding with a complete conversion to ferrosferric oxide without the formation of any intermediate oxide. On X-ray analysis the interference lines of ferric oxide were of an unknown type, those of ferrosferric oxide of the spinel type, and those of a partly decomposed ferric oxide were a mixture of those of the two separate oxides and included no other lines. Neither mixed crystals nor intermediate oxides are formed by the decomposition of ferric oxide by heat.

E. M. C.

**Equilibrium States of the Ternary Alloys.** I. K. IWASE (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **13**, 311—354).—The author discusses the equilibrium states for more complicated cases of ternary systems. The conditions for equilibrium are stated in terms of the Gibbs' function  $\Sigma = \epsilon - T\eta + Pv$  which has a minimum value in the equilibrium state. Each case is dealt with graphically on a triangular base, the  $\Sigma$  values being represented by the height of the vertical ordinates. The discussion refers to systems in which (1) solid solutions are not formed, (2) solid solutions are formed. In each group, special types are dealt with. The method can be used to determine the equilibrium in more complex cases. C. S.

**Graphic Representation of Ternary Iron-Carbon Alloys.** A. VON VEGESACK (*Stahl u. Eisen*, 1925, **45**, 458—461).—The representation of ternary iron-carbon alloys on an equilateral triangular diagram confines the results to a small strip remote from the carbon apex. To overcome this disadvantage, the use of the method of Goerens is recommended, in which an isosceles triangle is employed, the distance of the carbon apex being proportional to the increased carbon scale chosen. This method fulfils the requirement that the coordinates of all points on the diagram should add up to 100. [Cf. *B.*, 1925, 405.]

T. H. B.

**Lead-Zinc-Antimony Alloys.** G. TAMMANN and O. DAHL (*Z. anorg. Chem.*, 1925, **144**, 1—15).—Of the three binary systems involved, zinc-antimony alone forms compounds; the most stable,  $\text{ZnSb}$ , m. p. 537°, decomposes into  $\text{Zn}_3\text{Sb}_2 + \text{Sb}$ . The space model for the ternary system is divided by a ridge corresponding with the binary system  $\text{Pb-Zn}_3\text{Sb}_2$  into two regions,  $\text{Pb-Zn}_3\text{Sb}_2\text{-Zn}$  and  $\text{Pb-Zn}_3\text{Sb}_2\text{-Sb}$ , respectively. The ridge has a eutectic at 312°, corresponding with 2%  $\text{Zn}_3\text{Sb}_2$  and 98% Pb, which gives the maximum temperature for the univariant system,  $\text{Pb} + \text{Zn}_3\text{Sb}_2 + \text{liquid}$ , the ternary eutectics for the regions on the zinc and antimony sides of the ridge being lower; that on the zinc side contains

very little zinc, and the structure can scarcely be distinguished from that of the  $\text{Pb-Zn}_3\text{Sb}_2$  eutectic. The eutectic on the antimony side is at  $244.5^\circ$ , with the composition 87.1% Pb, 12.5% Sb, 0.4% Zn; in this region miscibility in the liquid state is complete, whilst on the zinc side two immiscible layers are obtained. S. I. L.

**System Molybdenum-Nickel-Tin.** H. PFAUTSCH (*Z. Metallk.*, 1925, 17, 122—124).—The solid solution region at the nickel corner of the ternary diagram of the molybdenum-nickel-tin alloys is bounded by a slightly curved line joining the point corresponding with 34% Mo on the molybdenum side with that corresponding with 15% Sn on the tin side. There are no ternary compounds or eutectics. The alloys consisting of nickel-rich solid solutions are harder than the corresponding alloys in which silicon replaces the tin (cf. this vol., ii, 298), but can be easily worked; they are all relatively easily attacked by acid and alkaline liquids. [Cf. *B.*, June 26th.] A. R. P.

**System Aluminium-Molybdenum-Nickel.** H. PFAUTSCH (*Z. Metallk.*, 1925, 17, 125—127).—The system aluminium-molybdenum-nickel contains no ternary compounds or ternary eutectics, and there is only a small region of homogeneous mixed crystals at the nickel corner of the diagram. This includes all alloys containing 89% Ni or more and extends along the molybdenum side of the diagram to the 30% Mo alloy and along the aluminium side to the 12% Al alloy. The Brinell hardness of alloys consisting of solid solutions of molybdenum and aluminium in nickel varies from 200 to 286; these alloys, although inclined to be porous are fairly resistant to attack by alkali metal hydroxides, but are somewhat readily corroded by ammonia and mineral acids. [Cf. *B.*, June 26th.] A. R. P.

**Ternary System : Silver Perchlorate, Pyridine, and Water.** R. MACY (*J. Amer. Chem. Soc.*, 1925, 47, 1031—1036; cf. *A.*, 1924, ii, 679).—Pyridine forms a set of compounds with silver perchlorate similar to the corresponding aniline compounds, viz.,  $\text{AgClO}_4 \cdot 4\text{C}_5\text{H}_5\text{N}$  ( $-43^\circ$  to m. p.  $68^\circ$ ; unstable);  $4\text{AgClO}_4 \cdot 9\text{C}_5\text{H}_5\text{N}$  ( $68^\circ$  to m. p.  $95.6^\circ$ ; unstable);  $\text{AgClO}_4 \cdot 2\text{C}_5\text{H}_5\text{N}$  (m. p.  $147^\circ$ ; stable). Above  $130^\circ$ , metallic silver is deposited; most aromatic amines are oxidised by silver perchlorate. The solubility of silver perchlorate varies from 20% in pure pyridine to less than 0.5% when much water is present; pyridine is practically insoluble in aqueous solutions of the silver salt. Above  $30^\circ$  conjugate solutions appear in the ternary system. Pure pyridine melts at  $-40.3^\circ$ . S. K. T.

**Equilibria between Metals and Fused Salts.** R. LORENZ (*Trans. Amer. Electrochem. Soc.*, 1925, 47, 243—258).—The author has investigated the equilibria for a number of fused electrolytes of the type  $\text{Cd} + \text{PbCl}_2 \rightleftharpoons \text{CdCl}_2 + \text{Pb}$  and  $\text{Cd} + \text{TiCl}_2 \rightleftharpoons \text{CdCl}_2 + 2\text{Ti}$ . The equilibrium is only slightly affected by temperature in the range  $600\text{--}700^\circ$ . The influence of diluents was examined in respect of both phases. No salt was found which is

without effect on the fused chlorides, sodium and potassium chlorides forming complex salts, although taking no part in the reaction. The addition of potassium chloride with sodium chloride shifts the equilibrium with increasing additions until a maximum is reached, further additions producing no effect. Bismuth is an entirely indifferent diluent in the metal phase and produces no shift in the equilibria. Antimony forms compounds with cadmium, but not with lead, and shifts the equilibria to a maximum position as with potassium chloride. In the second case, the equilibrium may be written  $\text{Cd} + \text{Tl}_2\text{Cl}_2 \rightleftharpoons \text{CdCl}_2 + 2\text{Tl}$ , or  $\text{Cd} + 2\text{TlCl} \rightleftharpoons \text{CdCl}_2 + 2\text{Tl}$ . The addition of potassium chloride with sodium chloride would affect the second, but not the first case, and the first scheme is therefore preferred. Similarly it is deduced that the metal is monatomic if cadmium is monatomic. The law of mass action is not applicable to such condensed systems, and a new equation is developed for these cases. C. S.

**Molten Electrolytes.** R. LORENZ (*Z. Elektrochem.*, 1924, 30, 371—375).—The paper summarises the earlier work of the author and his collaborators on the equilibrium between molten metals and salts. Tammann's theory is applied to the study of the equilibrium of the system  $\text{Pb} + \text{CdCl}_2 \rightleftharpoons \text{Cd} + \text{PbCl}_2$ , and is shown to be in good agreement with previous experimental results. A new formula derived from van Laar's work is employed to represent the equilibrium between thallium, cadmium, and their chlorides. A. R. P.

**System Sodium Palmitate-Sodium Chloride-Water.** J. W. MCBAIN and G. M. LANGDON (*J. Chem. Soc.*, 1925, 127, 852—870; cf. McBain and Burnett, T., 1922, 121, 1320).—Isotherms derived from solubility determinations have been drawn up for 60°, 90°, 120°, and 150°. Nearly half the triangular diagram is occupied by the field of isotropic solutions of soap and salt, which are partly colloidal and partly crystalloidal. There is a large field of "wet curds" in which salt solutions are in heterogeneous equilibrium with anisotropic soap solutions; also a number of small fields representing equilibria of the above phases with curd fibres and with two distinct forms of anisotropic soap solution. Of these latter the more concentrated form (about 63% of fatty acid) appears to be a liquid crystal, whilst the other, which occurs in concentrations of 2.5 to 3.0  $N_w$ , is considered to be a conic anisotropic liquid. W. A. C.

**Heterogeneous Dissociation Equilibria of Water Vapour and of Carbon Dioxide over Iron and its Oxides.** K. HOFMANN (*Z. Elektrochem.*, 1925, 31, 172—176).—The dissociation constants for water vapour over the phase pairs  $\text{Fe}_3\text{O}_4$ -FeO (a) and FeO-Fe (b) have been recalculated from Eastman's values (A., 1922, ii, 506) for the corresponding carbon dioxide constants, Eastman's own results in this operation being considered unsatisfactory. The values obtained are  $\log K_a = -3237/T + 3.509$  and  $\log K_b = -834/T + 0.636$ . In addition, the constant for the carbon dioxide equi-

librium over the phase pair  $\text{Fe}_3\text{O}_4\text{--Fe}$  has been calculated from Wöhler and Günther's equation for the corresponding water-vapour dissociation, the value obtained being  $\log K = +261/T - 0.325$ . The results are compared with those of other workers. Since the degree of gaseous dissociation in the systems  $\text{Fe--O--C}$  and  $\text{Fe--O--H}$  is small, equilibrium is practically independent of pressure. The presence of four phases should therefore cause invariance. In the blast furnace, a fourth phase, viz., carbon as coke, is continually added so that application of the equilibrium diagrams to this process is uncertain. N. H. H.

**Equilibria in Systems in which Phases are Separated by a Semi-permeable Membrane. III.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, 28, 42—51).—A mathematical discussion of the membrane diffusion pressure and the osmotic attraction in ternary systems, in which one or more solid phases occur and water is the diffusing substance. L. L. B.

**Differential Methods and Apparatus for the Determination of Dissociation Isochores. Thermal Dissociation of Cadmium Carbonate.** L. ANDRUSSOW (*Z. physikal. Chem.*, 1925, 115, 273—288; cf. Centnerszwer and Andrussov, A., 1924, ii, 665; Mazzetti, A., 1924, ii, 853).—An apparatus is described which was used to determine velocities of reaction and equilibrium constants for the system cadmium carbonate—cadmium oxide—carbon dioxide. The equation for the reaction isochore is in agreement with the Nernst equation. L. F. G.

**Activity Coefficients of Hydrochloric Acid in Solutions of Ethyl Alcohol.** H. S. HARNED and M. H. FLEYSHER (*J. Amer. Chem. Soc.*, 1925, 47, 82—92).—From the *E.M.F.* of the cells,  $\text{H}_2|\text{HCl}(\text{M})|\text{AgCl}|\text{Ag}$ , in ethyl alcohol and mixtures of ethyl alcohol and water at 25°, the relative activity coefficients of the acid in these solutions have been determined and the absolute activity coefficients approximately estimated. L. J. H.

**Activity Coefficient and Ionic Concentration Product of Water in Sodium and Potassium Chloride Solutions.** H. S. HARNED (*J. Amer. Chem. Soc.*, 1925, 47, 930—940).—From previously recorded measurements of the *E.M.F.* of certain concentration cells containing no liquid junctions (Harned, A., 1920, ii, 664; 1922, ii, 255), the activity coefficients of water in solutions of sodium and potassium chlorides have been calculated and also values for the product  $\gamma_{\text{H}}\gamma_{\text{OH}}/a_{\text{H}_2\text{O}}$ ,  $\gamma$  being the activity coefficient and  $a$  the activity. From this it is shown that water passes through a maximum state of ionisation with progressive addition of salts, sodium chloride producing a higher dissociation than the potassium salt. All weak electrolytes yielding ions with high activity coefficients probably produce a similar effect. S. K. T.

**Free Energy of Sulphuric Acid in Aqueous Sulphate Solutions.** H. S. HARNED and R. D. STURGIS (*J. Amer. Chem. Soc.*, 1925, 47, 945—953).—The activity coefficients of sulphuric

acid in sulphate solutions are calculated from the *E.M.F.* of cells of the type  $\text{H}_2|\text{M}_2\text{SO}_4(c_1), \text{H}_2\text{SO}_4(c_2)|\text{Hg}_2\text{SO}_4|\text{Hg}$ , where  $\text{M}=\text{Na}$  or  $\text{K}$ , and  $\text{H}_2|\text{MgSO}_4(c_1), \text{H}_2\text{SO}_4(c_2)|\text{Hg}_2\text{SO}_4|\text{Hg}$ , where  $c_1$  is  $0.1N$  to  $1N$  and  $c_2$  is  $0.1N$  and  $0.01N$ . Measurements are also made with the former cells in which  $c_1+c_2=0.1N$ . S. K. T.

**Activity of the Hydroxyl Ion in Concentrated Lyes on the Basis of Electrode and Liquid Potential Measurements.** R. FRICKE (*Z. Elektrochem.*, 1924, 30, 580—587).—Measurements of liquid potentials, hydrogen electrode potentials, and mercuric oxide electrode potentials lead to fairly consistent results for the activity of the hydroxyl ion in alkali hydroxides at  $30^\circ$  with concentrations up to about  $15N$ . It is found that the activity increases relatively slowly up to about  $10N$ , after which it increases very rapidly. When the concentrations are referred to *N*-solutions, potassium hydroxide is more active than sodium hydroxide of the same concentration. The increasing activity is attributed in part to lower hydration of hydroxyl ions at higher concentrations.

C. H. D. C.

**Affinity.** T. DE DONDER (*Compt. rend.*, 1925, 180, 1334—1337).—A mathematical treatment of affinity from the point of view of thermodynamics. In the Clausius equation,  $dA = TdS - dQ \geq 0$  ( $S$  is entropy,  $T$  abs. temperature,  $dQ$  heat absorbed during a given transformation),  $dA$  is identified with affinity. On this basis, the van't Hoff and Le Chatelier theorems are deduced in a generalised form. R. A. M.

**Thermodynamic Deductions from the Equation of State for Adsorbed Substances.** M. VOLMER (*Z. physikal. Chem.*, 1925, 115, 253—260).—By means of a cyclic process Gibbs' equation is derived, and by combining this with the corrected equation of state (cf. preceding abstract) further equations are derived, similar to those already obtained from kinetic considerations by Langmuir (*A.*, 1918, ii, 430). L. F. G.

**Thermodynamics of Surface Actions.** L. GAY (*J. Chim. Physique*, 1925, 22, 115—130).—Theoretical. A description of the general principles underlying the application of thermodynamics to surface actions.

The phase rule as usually formulated involves the assumption that the phases in equilibrium are all at the same pressure, which is not necessarily the case when curved interfacial boundaries are present. If the pressure of each phase is considered as a separate variable, the number of degrees of freedom of a system, in which all the phases are in contact, is independent of the number of phases, and equals  $(n+1)$ , where  $n$  is the number of components. W. H.-R.

**Relation between Deviations from Raoult's Law and the Partial Heats of Solution.** J. A. V. BUTLER (*J. Amer. Chem. Soc.*, 1925, 47, 117—122).—In those cases for which data exist, there is an almost exact proportionality between the deviations



and the partial heats of solution. From statistical theory it is suggested that this linear relation between the two quantities would be explained if the heat of solution is divided between the passage from the interior to the surface and the escape from the surface in definite proportions for each system. L. J. H.

**Proposal to Establish a Secondary Thermochemical Standard.** W. SWIENTOSLAWSKI (*Bull. Soc. chim.*, 1925, [iv], 37, 84—89; cf. A., 1924, ii, 39).—A protest against the use of any thermochemical standard (for the combustion of organic substances) other than that accepted internationally, *i.e.*, benzoic acid, except as an auxiliary to prove the purity of the benzoic acid employed in the calibration. L. J. H.

**Thermal Method for the Study of Gaseous Systems.** G. PICCARDI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 226—229).—The results of experiments on dry air and on nitrogen tetroxide show that the method previously described (A., 1924, ii, 537, 600) gives at least qualitative indications of the changes in the gas which are produced by a rise of temperature. T. H. P.

**Heats of Solution of Glycerol.** N. DE KOLOSSOWSKY (*J. Chim. Physique*, 1925, 22, 83—93).—Using 99% glycerol and a Berthelot calorimeter, the following values have been determined for the molecular heats of solution of glycerol. In water, +1335 cal. for dilutions from 1/140 to 1/200 mol.; in methyl alcohol —370 cal. for a dilution of 1/50 mol.; in an equimolecular mixture of water and methyl alcohol, —417 cal. for a dilution of 1 mol. glycerol to 86 mols. of mixed solvent; in mixtures of water and ethyl alcohol containing 30, 33.83, and 62% ethyl alcohol (by weight), 0, —412, and —337 cal., respectively. The heats of dilution in water and pure or aqueous methyl alcohol are comparatively small. The most probable value for the heat of solution of 1 mol. of anhydrous glycerol in 200 mols. of water is +1450 cal. W. H.-R.

**Heats of Solution of Phenols in Water.** N. DE KOLOSSOWSKY and A. KRAEFF (*J. Chim. Physique*, 1925, 22, 94—96).—The following molecular heats of solution in water have been determined, using a Berthelot calorimeter. Phenol, —2762 cal.; *o*-cresol, —3126 cal.; resorcinol, —3636 cal.; quinol, —4446 cal.; pyrogallol, —3911 cal. W. H.-R.

**Heats of Solution of Barium Chloride in Aqueous Alcohol.** N. DE KOLOSSOWSKY (*J. Chim. Physique*, 1925, 22, 97—100).—The heats of solution of anhydrous barium chloride in aqueous solutions of ethyl alcohol containing 20.36 and 33.83% alcohol, are —130 and —944 cal., respectively; the corresponding values for the hydrated salts  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  are —6718 and —7416 cal. The heats of hydration are thus +6588 and +6472 cal. in the two cases, indicating that the addition of alcohol to water lowers the heat of hydration, which in the case of pure water is +7465 cal. W. H.-R.

**Theory of Electrolytic Conductivity.** O. REDLICH (*Physikal. Z.*, 1925, 26, 199—205).—The range of applicability of the Debye and Hückel equations (A., 1923, ii, 724) without the introduction of arbitrary constants is considerably extended by the introduction of a single universal constant, which, although possessing a theoretical basis, has to be evaluated from experimental data. This constant, 0.694, is obtained as a correction factor in calculating the ionic radius by means of a modified Stokes' law (Redlich, *ibid.*, 1925, 26, 155), and is evaluated from conductivity data for potassium chloride. It is valid for all binary electrolytes. An application of Ohm's law to the inter-ionic forces leads to an expression which includes the previously neglected second term in  $\sqrt{c}$  of the Debye and Hückel equation, contains no arbitrary constants although it includes the above universal one, and satisfactorily reproduces the conductivities of binary electrolytes up to 0.1N concentration.

F. G. T.

**Conductivity of Electrolytes.** C. W. DAVIES (*J. Physical Chem.*, 1925, 29, 473—481).—For concentrations below 0.002N conductivity data agree with the relation:  $\lambda_{\infty} - \lambda_c = K\sqrt{c}\lambda_{\infty}$ , where  $K$  is a constant,  $c$  the concentration in g. equivalents per litre, and  $\lambda_{\infty}$ ,  $\lambda_c$  the equivalent conductivities of univalent ions. M. B. D.

**Precision Determination of the Electrical Conductivities of Concentrated Aqueous Solutions of Calcium Chloride.** M. CROWE (*Trans. Roy. Soc. Canada*, 1924, [iii], 18, III, 339).—Determinations of the electrical conductivities of aqueous solutions of calcium chloride at concentrations from 25% to 50% for temperatures between 10° and 30° have been made, the accuracy being estimated as about 0.05%. Details will be published later.

J. S. C.

**Theory of Electrolytic Ions. XXIX. Method of Measuring Conductivity by the Use of an Amplifying Tube.** R. LORENZ and H. KLAUER (*Z. anorg. Chem.*, 1924, 136, 121—146).—In the ordinary Wheatstone bridge arrangement for the determination of the conductivity of dilute solutions, the use of an amplifying tube in series with the telephone permits of a much sharper determination of minimum tones. Small changes in the potential of the grid are more highly amplified when the potential approximates to zero, so that a very sudden fall in the intensity of the tone is noticeable as the potential actually reaches zero. When the system contains an unbalanced capacity there must be a compensating condenser in the circuit and the electrodes used should be slightly platinised. Some curves obtained by the use of the apparatus with and without the amplifier are reproduced and a device for comparing tone intensities is described and illustrated.

A. R. P.

**Electrical Conductivity of Films.** G. TAMMANN and H. BREDEMEIER (*Z. anorg. Chem.*, 1925, 144, 64—68).—The growth of films on metal surfaces may proceed in accordance with either

a parabolic or an exponential law. In the former case, the concentration of the attacking agent (halogens) falls uniformly throughout the film, and the films show electrolytic conduction, as indicated by polarisation effects; in the second case, the concentration of the attacking agent (oxygen or nitrogen) varies exponentially with the thickness, and the film shows metallic conduction. S. I. L.

**Conductivities in Liquid Hydrogen Sulphide Solutions.** G. N. QUAM and J. A. WILKINSON (*J. Amer. Chem. Soc.*, 1925, **47**, 989—994).—The conductivities of saturated solutions of substances in liquid hydrogen sulphide (sp. cond.  $< 1 \times 10^{-11}$  ohm $^{-1}$ ) at the temperature of solid carbon dioxide are recorded. Some solutions will not conduct, e.g., those of many organic compounds, ammonium and bismuth chlorides; the latter forms an insoluble thio-compound. The halides of the phosphorus group of elements exhibit better conductivities the higher the atomic weight; halogen acid is probably not formed in these solutions. Halogen solutions conduct well; observations with iodine confirm Walden's explanation of this phenomenon (A., 1903, ii, 408). Progressive introduction of alkyl radicals in ammonium chloride causes a corresponding increase in the conductivity of the solution. Solutions of acetic acid only conduct at the ordinary temperature, whilst the anhydride, the acid chloride and thioacetic acid show a maximum conductivity, and reaction with the solvent occurs. S. K. T.

**Transference Numbers of Hydrochloric Acid in Solutions of Ethyl Alcohol.** H. S. HARNED and M. H. FLEYSHER (*J. Amer. Chem. Soc.*, 1925, **47**, 92—95).—By comparing the data previously obtained (cf. this vol., ii, 538) with measurements of cells of the type  $\text{Ag}|\text{AgCl}|\text{HCl}(m_2)|\text{HCl}(m_1)|\text{AgCl}|\text{Ag}$ , the transference numbers of the hydrogen ion are obtained at 25° for solutions of hydrochloric acid in ethyl alcohol and in 50% ethyl alcohol–water mixtures. L. J. H.

**Transport Numbers by the Moving-boundary Method. III. Novel Form of Apparatus.** D. A. MACINNES and T. B. BRIGHTON (*J. Amer. Chem. Soc.*, 1925, **47**, 994—999).—A transport apparatus is described in which two sharp boundaries are very simply obtained. Results should not be calculated from the ratios of the boundary movements in very accurate work. S. K. T.

**Transport Numbers by the Moving-boundary Method. IV. Transport Numbers of some Chloride Solutions.** E. R. SMITH and D. A. MACINNES (*J. Amer. Chem. Soc.*, 1925, **47**, 1009—1015).—An apparatus is described similar to, but smaller than, that previously used (Smith and MacInnes, A., 1924, ii, 727) by means of which correct values for transport numbers are obtained throughout wider ranges of indicator concentrations. Values obtained at 25° in 0.1N-chloride solutions were:  $N_{\text{Na}^+}=0.3865$ ,  $N_{\text{H}^+}=0.8320$ ,  $N_{\text{K}^+}=0.492$ ; in 0.2N-potassium chloride solution,  $N_{\text{K}^+}=0.4900$ . The product of the transport number of the chloride ion and the corresponding equivalent conductivity for the 0.1N-

solutions is constant, which shows that these salts have the same degree of ionisation at  $25^{\circ}$ . This also holds at  $18^{\circ}$  (MacInnes, A., 1921, ii, 619). This ionisation is considered to be complete, so that the influence of concentration on equivalent conductivity is due to change in mobility rather than in the numbers of ions.

S. K. T.

**Transport of Electrolytes. Mobilisation of Ions by Inter-molecular Exchanges.** W. MESTREZAT and (MLLE.) Y. GARREAU (*Compt. rend.*, 1925, **180**, 1266—1268).—Certain ions have been shown to possess enhanced mobilities under physiological conditions. It is suggested that a mobile ion may be replaced by another of the same sign, taken from the solute on the other side of the membrane. If the salts NaX and NaCl are on either side of a membrane which is penetrated more easily by the anions than the cations, it would seem possible to have chains of the ions of these salts moving in opposite directions with penetration of the membrane by the anions only. Once through the membrane, the anions are temporarily liberated from the electrostatic forces of the molecule; a rearrangement of forces occurs and fresh anions reinforce the chains. Thus, diffusion occurs in cascade fashion. This method of representation combines the concept of the molecular unit (electrostatic forces) with mobility of ions in the living organism. Side by side with small changes in the diffusion of the less mobile ions, it establishes a circulation of the more mobile ions of the same sign, tending towards complete exchange on either side of the membrane. The presence of molecular systems capable of exchanging ions in this way gives a simple conception of rapid transport of anions and of selective effects in the organism.

R. A. M.

**Transport of Electrolytes. Velocity of Diffusion through a Membrane and Ionic Selection.** W. MESTREZAT and (MLLE.) Y. GARREAU (*Compt. rend.*, 1925, **180**, 1069—1071).—A study has been made of the rates of diffusion of the anions when 0.25*N*-solutions of sodium iodide, sodium nitrate, magnesium sulphate, disodium hydrogen phosphate, and potassium ferrocyanide are dialysed through animal or collodion membranes against distilled water or dilute solutions of sodium chloride (0.01*N*—0.25*N*). The presence of sodium chloride in general increases the velocity of diffusion to an extent of more than 100% and in the case of the ferrocyanide of 1268%. The maximum effect is observed with concentrations of NaCl, which vary inversely as the valency of the anion involved: 0.14*N* for univalent, 0.08*N* for bivalent, 0.05*N* for trivalent, and 0.01*N* for the quadrivalent ions. The observed maximum of diffusion also varies approximately inversely as the valency of the diffusing ion, the concentration of the diffusate being after 2 hrs. 0.043*N* for  $I^{-}$  and  $NO_3^{-}$  and 0.023*N* for the  $SO_4^{--}$  ion. The large effect produced by a relatively small amount of sodium chloride can only be explained by a concentration of the salt on the outer face of the membrane which modifies the potential difference between it and the liquid and so hinders the passage

backwards of the anions through the membrane. It is significant that the concentration of sodium chloride in the body fluids is close to that found to be the optimum concentration for the diffusion of uni- and bi-valent ions.

G. M. B.

**Electrode Potentials and the Free Energy of Solvation.** J. HEYROVSKÝ (*J. Physical Chem.*, 1925, 29, 406—409; cf. this vol., ii, 404).—The electrode potential depends, not only on the number of ions in solution, but also on their degree of solvation and therefore on the vapour pressure of the solution. The activity coefficient is therefore expressed mathematically by means of the free energy of solvation.

M. B. D.

**Electromotive Behaviour of Magnesium.** A. SMITS (*Z. Elektrochem.*, 1924, 30, 223—230).—The values of the potential of magnesium against solutions of its salts, as measured by other workers, are discussed from the point of view of the author's theory of allotropy, and it is shown that the too negative value of the results cannot be accounted for by the formation of a film on the surface of the metal which resists the passage of electrons. It is deduced mathematically that the hydrogen in the hydrogen film on the metal is still in process of formation and that its solubility product is greater than if it were in internal equilibrium. The potential of an amalgamated magnesium electrode against a *M* solution of magnesium sulphate is  $-1.85$  volt.

A. R. P.

**Influence of Finely Porous Materials at the Liquid Boundaries on Liquid Potential.** R. FRICKE (*Z. Elektrochem.*, 1924, 30, 577—580).—Experimental evidence is adduced that the presence of porous materials, such as the filter-paper pads used by Müller at the liquid boundaries in concentration cells, has an appreciable effect on potential measurements. The measured values are lower than those obtained with a pure liquid boundary, and a time factor is introduced, the *P.D.* gradually increasing over many hours. It is noted that Müller has recently overcome the difficulty connected with his arrangement.

C. H. D. C.

**Potential Differences between Liquids and Air.** A. FRUMKIN (*Kolloid-Z.*, 1924, 35, 340—342; cf. A., 1924, ii, 462).—Inorganic electrolytes charge the water-air interface either not at all or negatively, the greater the charge the less hydrophile the anion. Organic substances charge the water-surface according to their capillary activity. Comparing concentrations of different substances which correspond with equal adsorptions, it is found that the charge produced per adsorbed molecule varies but slightly with the number of adsorbed molecules. For homologous series, this quantity is independent of the length of the carbon chain. An explanation is based on the Langmuir-Harkins theory of orientation.

The Kenrick method of measurement (cf. A., 1896, ii, 460), although convenient and accurate, has its limitations. A new apparatus has been devised capable of measuring the potential difference when the liquid surface is still. The liquid is placed in a rectangular glass vessel and connected to earth through a

calomel electrode. A variable *E.M.F.* is interposed between the calomel electrode and earth; 4—6 mm. distance from the liquid surface is a platinum wire 0.1 mm. thick connected to a quadrant electrometer. The wire is heated to white heat by a very small (2 mm. long) gas flame. Care is taken completely to insulate the gas flame. When the liquid surface is charged the electrometer deflection can be brought back to zero by the introduction of an *E.M.F.* between the calomel electrode and earth. This gives directly the value of the required potential difference. The readings obtained in the course of 1 hr. show variations of less than 10 millivolts and the absolute values agree with those obtained by Kenrick's method. The potential difference between air and water when a unimolecular layer of a substance such as oleic acid or olive oil covers the water-surface has been measured. By varying the surface area a curve is obtained showing the variation of the potential difference with the area occupied per molecule or with the film thickness. As the area occupied by the oil film is decreased, the value suddenly rises sharply to a new value, the curve being very similar to that obtained in investigations on the variation of surface tension with the thickness of the oil film. The author does not accept Langmuir's suggestion of the existence of a "liquid" and "vapour" condition of the film, but suggests that the "liquid" condition of Langmuir corresponds with the formation of molecular complexes or micelles. D. C. J.

**Mechanism of the Development of a Potential Difference at the Boundary of Two Phases.** D. REICHINSTEIN (*Z. Elektrochem.*, 1924, 30, 238—246).—Assuming that the partition coefficients of all the ions and electrons are of equal value, the author deduces the following generalisations: a necessary condition for the development of a potential difference at the phase boundary is the existence of a single asymmetry in the homogeneous phase; a symmetrical equilibrium is produced when a solid which sets up a chemical equilibrium between ions and electrons in a finite time is introduced into a solution in which a non-asymmetrical equilibrium is maintained, and, finally, a potential difference is set up at the boundary of two phases if different degrees of asymmetry prevail in both phases in relation to the same electrolytic or electronic dissociation process. A. R. P.

**Thermo-electricity of Electrolytes.** J. THIELE (*Physikal. Z.*, 1925, 26, 321—329; cf. Schmidt, A., 1924, ii, 727).—When long strips of quartz are coated with solid salts and heated at one end, suitable contacts being applied at the extremities, the thermo-electric difference of potential is measurable by means of an electrometer. With halides of cadmium, lead, thallium, silver, and copper, also sodium and potassium nitrates, from 300° downwards, the difference of potential is directly proportional to the temperature difference and ranges from  $20 \times 10^{-5}$  volt to  $136 \times 10^{-5}$  volt per 1°. The temperature gradients in successive series of measurements on a given salt, however, show some divergences. In all cases,

the hot end becomes positive, in agreement with the view that cations alone migrate, whilst heavy complex anions remain stationary. Mercuric chloride and iodide show no thermo-electric effect. Similar measurements with aqueous solutions of electrolytes confirm the known fact that the current in that case flows in the opposite direction, the temperature gradients being again linear.

W. A. C.

**Decomposition Potentials of Non-aqueous Solutions.** W. FINKELSTEIN (*Z. physikal. Chem.*, 1925, **115**, 303—329).—Current-voltage data, between 0 and 9 volts, were obtained for the following solutions: iodine trichloride in bromine, liquid sulphur dioxide, arsenic trichloride, nitrobenzene, dichloroacetic acid, acetic acid; iodine bromide in bromine, liquid sulphur dioxide, arsenic trichloride, nitrobenzene, acetic acid; phosphorus pentabromide in bromine, liquid sulphur dioxide, arsenic trichloride, nitrobenzene; phosphorus oxychloride in bromine; ether tribromide in ether, bromine, chloroform; acetamide in bromine; benzamide in bromine; antimony tribromide in bromine. No polarisation was observed with any of these solutions, *i.e.*, each series of data when plotted gives a straight line passing through the origin. Critical decomposition potentials were observed with the following solutions: dimethylpyrone ditrichloroacetate in benzene and chloroform; dimethylpyrone in liquid sulphur dioxide and arsenic trichloride; arsenic tribromide in ethyl alcohol, liquid sulphur dioxide, nitrobenzene; arsenic trichloride in nitrobenzene; antimony tribromide in nitrobenzene and ethyl acetate; bismuth tribromide in nitrobenzene; phosphorus trichloride in nitrobenzene. As the nature of the solvent had very little effect on the decomposition potential, it was assumed that heats of solution were small. The temperature coefficients of the decomposition potentials of the last-mentioned series of solutions (trihalides in various solvents) were calculated by the Helmholtz formula; experimentally found values for arsenic trichloride in nitrobenzene and antimony tribromide in ethyl acetate were in good agreement. Yellow phosphorus, antimony, and bismuth, respectively, precipitate arsenic from solutions of arsenic trichloride in nitrobenzene. L. F. G.

**Reduction Potential of Dicyan-quinhydrone.** E. K. RIDEAL (*Trans. Faraday Soc.*, 1925, **27**; Advance proof).—The *E.M.F.* of a cell of the type substituted quinhydrone in 0.1*N*-HCl|0.1*N*-HCl|benzoquinhydrone in 0.1*N*-HCl has been determined. For 1:2-dicyanoquinhydrone, the *E.M.F.* is 0.27374 and 0.27224 volt at 0° and 25°, respectively, giving a temperature coefficient of -1.5 mv. for 25°. The corresponding reduction potential of 1:2-dicyanoquinhydrone is  $\pi_{0.250}=0.9712$  volt, a much higher value than those obtained for the 1:4-dichloro or 1:4-dibromo substituted compounds. W. H.-R.

**Relation between Energy of Escape of Electrons and Electrochemical Normal Potential.** A. GÜNTHER-SCHULZE.—(See ii, 477.)

**Electrolytic Deposition of Calcium from Solutions of Calcium Hydroxide in Water, and Calculation of the Normal Potential of Calcium.** A. EILERT (*Z. Elektrochem.*, 1925, **31**, 176—180).—An amalgam containing up to 2.4% of calcium may be obtained by the electrolysis of a saturated solution of calcium hydroxide in water, using a platinum anode and a mercury cathode, provided that traces of water are previously removed from the mercury and that the electrolyte is free from suspended particles. The discharge potential of calcium ( $\epsilon_h$ ) in saturated calcium hydroxide solution is found to be  $-1.81$  volts, and from this and other data the normal potential is calculated. The value obtained,  $-2.57$  volts, is in good agreement with Wilsmore's figure,  $-2.56$  volts.  
N. H. H.

**Transfer Resistance.** A. L. FERGUSON and G. VAN ZYL (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 145—160).—The concept of "transfer resistance" and in particular the work of Newbery are attacked. A large number of experiments on decomposition potentials have been carried out by both the direct and commutator methods, the influence of such factors as the concentration of the electrolyte, speed of commutator, current density, and the size and nature of the electrode surfaces being studied. The effect of time on the polarisation was largely eliminated by making the measurements several hours after potential was applied or increased. The conclusion is that the differences between the various potentials measured by the two methods are due to sources of error in the commutator method. The discharge potential of an electrode would be the same as the charge potential if the two could be measured at the same instant by the commutator method and both would be the same as the value measured by the direct method. The existence of "transfer resistance" is therefore denied.  
N. H. H.

**Electrical Overvoltage.** A. SMITS (*Z. Elektrochem.*, 1924, **30**, 214—223).—A theoretical and mathematical discussion of the application of the author's theory of allotropy to overvoltage is given. The theory assumes that the origin of overvoltage is to be found in the electrodes themselves, which are assumed to consist of molecules, atoms, ions, and electrons in a state of equilibrium and that, when an electrode is placed in contact with an electrolyte, its surface is covered with a liquid film with which the metal is in equilibrium. As an illustration of the theory the case of a cell with electrodes of hydrogen and platinum or palladium is considered.  
A. R. P.

**Effect of Surface Condition on Overvoltage.** M. KNOBEL (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 139—144).—Measurements have been made at different current densities of the hydrogen overvoltages for smooth and spongy surfaces of lead, copper, gold, cadmium, platinum, silver, and palladium, and oxygen overvoltages for smooth and spongy nickel and platinum. Arguments are put forward to show that the lowering of overvoltage on the



spongy surfaces is due to the changed nature of the surface and not to the greater magnitude of the area alone. For example, a roughly crystalline surface of silver showed nearly the same over-voltage as a smooth surface whilst a true sponge gave a much lower value.

N. H. H.

**Anode Effect.** C. S. TAYLOR (*Trans. Amer. Electrochem. Soc.*, 1925, 47, 161—171).—An analysis of previous observations of the anode effect in the electrolysis of fused electrolytes and its causes is presented. Any combinations of conditions which permit local overheating at any point of the anode surface may produce the effect. At this point, a gas film is formed and by the diversion of current to other parts of the anode area, which are already in a metastable state, these become overloaded and the result is the practically instantaneous spread of the film over the whole anode surface. For example, a high-resistance film of solid impurity or of frozen electrolyte on certain portions of the anode surface may start overheating at other points. The combination of factors which lead to the effect may, however, differ widely.

N. H. H.

**Effect of Small Alternating Currents on Some Polarised Electrodes.** S. GLASSTONE (*J. Amer. Chem. Soc.*, 1925, 47, 940—945).—The previously recorded potentials indicating the influence of a small alternating current on cathodic and anodic overvoltages are probably doubtful, mainly owing to the use of a direct method of measurement. By the use of superimposed direct and alternating currents for certain metals in normal sulphuric acid and sodium hydroxide solutions, it is found that the polarisation is reduced in a few cases only. It is suggested for these cases that rapid variation of the current strength, due to the superimposition, causes a diminution in the tension at the metal-gas-electrolyte interfaces, thus favouring bubble formation and retarding the accumulation of active material. The results of Grube and Dulk (*A.*, 1918, ii, 348) and of Goodwin and Knobel (*Trans. Amer. Electrochem. Soc.*, 1920, 37, 617) are probably not valid.

S. K. T.

**Effect of Alternating Current on Polarisation during Metal Deposition.** N. ISGARISCHEV and S. BERKMANN (*Z. Elektrochem.*, 1925, 31, 180—187).—The effect of an alternating current on the cathodic and anodic polarisation of nickel during the electrolysis of solutions of nickel ammonium sulphate and of nickel sulphate, with and without the addition of sulphuric acid and of gelatin, has been studied. From the character of the cathodic polarisation curves, it is concluded that there are at least two effective processes, the deposition of the nickel and the evolution of hydrogen. It is highly probable that the alternating current influences strongly only one of these processes and that this influence is largely affected by the frequency. The concentration of hydrogen ions and of gelatin has a considerable effect on the curves. The effect of the alternating current on the anodic polarisation of nickel and on the cathodic polarisation of zinc in solutions of zinc sulphate is not so marked.

N. H. H.

**Polarisation and Concentration Changes at the Cathode during Electrolysis of Copper Salts.** A. R. GORDON (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 116—117).—The observed polarisation values are much greater than those predicted by theory. On starting the current there is an instantaneous initial polarisation  $\pi_0$ , over and above the *CR* drop; during electrolysis the polarisation increases up to the moment at which hydrogen is evolved, in accordance with the equation,  $\pi = \pi_0 + 0.188 \log z_0/z$ , where  $z_0$  is the concentration of copper in the body of the electrolyte and  $z$  its concentration at the cathode. The value of  $\pi_0$  is apparently dependent on the nature of the surface and previous treatment of the cathode. J. S. C.

**Electrolysis with Gas Cathodes.** A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1925, **31**, 187—189).—Experiments are described in which solutions of (a) copper sulphate, (b) copper sulphate and sulphuric acid, (c) copper sulphate and sodium sulphate, (d) potassium cuprocyanide, (e) silver nitrate, (f) mercurous nitrate, and (g) lead nitrate were electrolysed at low pressures by using the vapour above the solution as the cathode, electrical contact being made by means of a platinum dish suspended 1—2 cm. above the surface of the solution. The anode consisted of a wire of the metal under consideration. The products received on the platinum dish were: (a) and (c) copper hydroxide, (e) silver oxide, (g) lead oxide, (b), (d), and (f) nothing. No metal was deposited and therefore no confirmation of Gubkin's results with silver nitrate (*Pogg. Ann.*, 1887, **33**, 114) was obtained. The phenomena are explained by the theory that the electrons streaming from the cathode with much greater velocity than the cations do not discharge these, but ionise the water molecules. The hydroxyl ions then react with the cations forming, e.g., copper hydroxide. If the solution is acid this neutralises the base and no deposit is formed. An extension of the theory explains the absence of deposit in (d) and the deposit of copper hydroxide in (c).

N. H. H.

**Surface Phenomena in Photo-electric Elements with a Fluorescent Liquid.** A. GRUMBACH (*Compt. rend.*, 1925, **180**, 1102—1105; cf. A., 1923, ii, 108).—The cell Pt|fluorescent or absorbing solution|Pt, under illumination shows an *E.M.F.* due to a modification of the electrode-surface by adsorption of molecules changed by light. Radiation causes two effects, the Becquerel *E.M.F.* and the adsorption *E.M.F.* In aqueous solutions, the latter is always at first opposed to the former; it persists in the dark and finally reaches a value which remains constant until diffusion intervenes. The adsorption effect is independent of electrical conditions, for the variation of electrode potential is a function of illumination and the nature and concentration of the solution. This is shown by experiments with solutions of potassium fluorenesulphonate ( $3.84 \times 10^{-6}$  g./litre), in which the same limiting *E.M.F.* is observed whether the cell is connected in open circuit or short-circuited during the period of illumination. The

view that the phenomenon is due to the transformation of molecules in the bulk of the liquid under illumination, followed by adsorption, is confirmed by the observation that the same *E.M.F.* is obtained when the light from a mercury vapour lamp is focussed directly on the electrode or on to the liquid above it. R. A. M.

**Electronic Theory of the Anodic Behaviour of Metals, especially those exhibiting Passivity Phenomena.** U. SBORGI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 315—318).—On the basis of the most recent views concerning the distribution of the electrons in the atoms of different elements (cf. Lewis, "Valence and the Structure of Atoms and Molecules," and Bohr, "Les spectres et la structure de l'atome"), the author shows that each large period of the periodic system may be divided into three portions: (1) Elements preceding the transition elements. The configuration of the kernel is that of the initial noble gas, the kernel and valency are fixed, and the ionisation is of the metallic type, taking place with simultaneous loss of all the valency electrons. (2) Transition elements, with which the kernel and valency are variable, and the ionisation is usually metallic. (3) Elements subsequent to transition elements: pre-metalloids and metalloids. These have fixed kernels with the configuration of that of the final noble gas. The valency is fixed in the elements of the first kind (Zn, Cd), but variable in the remainder, for which also the ionisation is metalloid in type, taking place by partial loss of the valency electrons. The constancy of the valency of zinc and cadmium may be a particular case of the phenomenon that the alteration of valency for all elements of this category usually occurs in double steps, so that for bivalent elements the only ordinary ionisation possible is total ionisation and these elements are thus of fixed valency.

T. H. P.

**Electronic Theory of the Anodic Behaviour of Metals, especially of those exhibiting Passivity Phenomena. II.** U. SBORGI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 388—392; cf. preceding abstract).—An electronic interpretation is suggested for various anode phenomena.

T. H. P.

**Behaviour of Diaphragm Electrolysers with Circulation of the Alkali Chloride. IV.** F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], 30, 135—149).—For the current yield of circulating diaphragm electrolysers in its dependence on the alkali concentration of the cathodic effluent, the author (*ibid.*, 1922, [iii], 28, 142) derives the expression,  $R = 1 - n / (1 + \chi_1 / \chi_2) + 0.0103 \chi_{1.2} / (U_{OH} + U_M)(1 + \chi_1 / \chi_2) C_2$ , where  $n$  indicates the transport number of the cation of the alkali,  $\chi_1$  and  $\chi_2$  the respective partial conductivities of the chloride and alkali in the catholyte,  $\chi_{1.2}$  the total conductivity of the catholyte,  $U_{OH}$  and  $U_M$  the respective effective velocities of the hydroxyl and metal ions per 1 volt of potential gradient, and  $C_2$  the concentration of the alkali in the catholyte. Results obtained with electrolysers fed with sodium chloride are now given, and correspond qualitatively, but not

quantitatively, with the above formula; this is doubtless attributable to the uncertainty attending the determination of the ratio  $\chi_1/\chi_2$ .  
T. H. P.

**Behaviour of Diaphragm Electrolysers with Circulation of the Alkali Chlorides.** V. F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], 30, 181—188).—From data obtained for catholytes from an electrolyser fed with saturated sodium chloride solution, the author calculates the values of the velocity of the hydroxyl ion in the catholyte and of the total linear velocity with which the liquid is displaced normally to the diaphragm. The results show that, in counter-current electrolysers, no loss in yield should be incurred owing to migration of the ions, the losses being due solely to diffusion phenomena; the reason for the great influence of the type of diaphragm on the yield is thus evident. Experiments made with small glass electrolysers containing asbestos diaphragms, the anode being of Acheson graphite and the cathode of iron gauze, show that almost theoretical yields are obtainable, even when the molecular concentration of the sodium hydroxide is comparatively high.  
T. H. P.

**Chemico-physical Investigations on the Catholyte of Diaphragm Electrolysers with Circulation of the Sodium Chloride.** F. GIORDANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1924, [iii], 30, 150—165).—The results are given of determinations at various temperatures of density, viscosity, and conductivity measurements of (1) sodium chloride solutions of concentrations ranging from *N* to saturation, (2) sodium hydroxide solutions ranging from *N* to 6.72*N*, and (3) solutions containing both the chloride and the hydroxide in proportions varying in accordance with the decomposition occurring in an electrolytic cell supplied with saturated sodium chloride solution. Contrary to theoretical anticipation, the equivalent conductivities of sodium hydroxide solutions, corrected for the viscosity, increase with the concentration of the solution; this result suggests considerable hydration of the ions, the degree of which diminishes as the concentration is augmented. The experimental values of the conductivity of the solutions containing both chloride and hydroxide are in good agreement with those calculated from the values for the separate components. The accord is less satisfactory when the values of the conductivity corrected for the viscosity are compared, owing partly to the anomalous behaviour of the hydroxide referred to above.

In general, the results furnish abundant indication of the great influence of the viscosity of the ions and confirm the observation that the low mobility of the hydroxyl ions in the cathode liquids, in comparison with the value calculated for infinite dilution, is largely responsible for the high current yields given by circulation electrolysers containing diaphragms.  
T. H. P.

**Electrolytic Preparation of Potassium Bromate with Carbon Electrodes.** D. T. EWING and H. W. SCHMIDT (*Trans. Amer. Electrochem. Soc.*, 1925, 47, 133—137).—Potassium bromide

solutions were electrolysed using carbon electrodes in place of platinum. Since untreated carbon electrodes disintegrate rapidly the pores were filled with paraffin wax. A depolariser such as potassium dichromate is essential for high yields. The optimum yield was obtained with an anodic current density of 7 amp./dm.<sup>2</sup>

N. H. H.

**Critical Increment of Chemical Reactions.** W. E. GARNER (*Phil. Mag.*, 1925, [vi], 49, 463—465).—In the usual interpretation of the Arrhenius constant  $A$ , the assumption that the experimental velocity constant  $K$  corresponds with the velocity constant of the activation process is unsound. Assuming the momentary formation of complexes between the reacting molecules, it is shown that the activation energy of the reactants may be either greater or less than  $A$ . Thus the critical increment is not necessarily the same as the activation energy, and  $\nu$  calculated therefrom may not coincide with the actual absorption bands of the reactants. C. W. B.

**Kinetics of Reactions.** [BARON] JÜPTNER (*Kolloid-Z.*, 1925, 36 [*Zsigmondy-Festschr.*], 185—191).—The fundamental distinction between uni- and multi-molecular reactions is discussed and it is shown that the application to gas reactions of Bjerrum's views (*Z. Elektrochem.*, 1911, 17, 732) gives only approximate agreement with experimental results. The velocity of reactions between gases and solids is shown, by consideration of the reduction of carbon dioxide by different forms of carbon, to depend, not only on the surface density and porosity, but also on the atomic distances in the solid. E. M. C.

**Termolecular Collisions resulting from Bimolecular Collisions considered from the Physical and Chemical Points of View. I. Formation of Nitrosyl Chloride.** M. TRAUTZ and H. SCHUETER (*Z. anorg. Chem.*, 1924, 136, 1—47).—The empirical identity of the chemical (formation of an intermediate compound) and the physical (duration of impact) conceptions of ter- and multi-molecular collisions is proved from theoretical considerations. The reaction between nitric oxide and chlorine, which is purely termolecular within wide ranges of temperature and concentration, is shown to proceed in two stages in accordance with the impact duration law, thus:  $\text{NO} + \text{Cl}_2 = \text{NOCl}_2$  and  $\text{NOCl}_2 + \text{NO} = 2\text{NOCl}$ . The velocity constants for each stage of the reaction are in agreement with those deduced from the law of mass action, and the temperature coefficients agree with the requirements of the reaction velocity isochore. The compound  $\text{NOCl}_2$  cannot be formed by the interaction of nitrosyl chloride and chlorine, but only from nitric oxide and chlorine; it is extremely unstable, and the equilibrium of the reaction by which it is formed lies very close to the left-hand side of the equation above. The heat of formation of nitrosyl dichloride is 7000 cal. ( $\pm 700$ ) and its formation and decomposition velocity constants are  $1.5 \times 10^{-5}$  and  $4 \times 10^{-3}$ , respectively. The results of this investigation show that all reactions of a higher order than the second which take place in dilute systems of liquids or

gases may be considered as superimposed reactions of the first or second order.

A. R. P.

**Chemical Reactions in the Glow Discharge.** A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1924, **30**, 386—391).—The normal cathode fall in mixtures of gases which do not interact can be calculated by the mixture rule, but in gases which react with each other the curve has a pronounced hump above the line joining the values for each individual gas. The height of this hump in mixtures of oxygen and hydrogen and of oxygen and nitrogen is proportional to the reaction velocity, which is itself proportional to the strength of the current and is independent of the gas pressure. This is explained in the case of the oxygen-hydrogen reaction by the assumption that the reaction is induced by the hydrogen which is decomposed into reactive  $H^+$  and  $H^-$  atoms by the discharge; the critical potential of this decomposition is 17.2 volts in the discharge zone and about 8.8 volts outside it. Nitrogen and oxygen react only slightly in the glow discharge, whilst nitrogen and hydrogen do not react at all; in fact, ammonia is completely decomposed by the discharge.

A. R. P.

**Thermal Theory of Gas Ignition by Electric Sparks.** J. D. MORGAN (*Phil. Mag.*, 1925, [vi], **49**, 323—336).—Ignition depends on the raising of a sufficient volume of the combustible gas to a sufficiently high temperature. The incendivity of capacity sparks is, in general, greater than that of inductance sparks. The incendivity of capacity sparks depends on the shape and relative position of the electrodes in a manner to be expected. The energy required for ignition of a given gas by low-voltage inductance sparks is constant over a wide range of values of self-inductance and current, so long as the deviation of the spark is constant. There is no difference between the incendivity of inductance sparks produced in direct and alternating current circuits. Experiments on the ignition of highly inflammable solids by means of short, hot wires shows that the energy required for ignition increases with diminution of rate of heating. Over a wide range, a linear relation exists between the energy and the time during which it is supplied.

C. W. B.

**Limits for the Propagation of Flame in Inflammable Gas-Air Mixtures. III. Effect of Temperature on the Limits.** A. G. WHITE (*J. Chem. Soc.*, 1925, **127**, 672—684).—On the assumption that the ignition temperature of a gas mixture at lower-limit concentrations is practically independent of the concentration of the inflammable gas, the lower composition limits for the downward propagation of flame in certain mixtures of air and combustible gas have been determined as previously described (T., 1922, **121**, 1244). The temperature-concentration curves for the upper and lower limits are practically linear, but for acetylene and ethylene the upper-limit concentration figures increase very rapidly at the higher temperatures. Except for hydrogen, the theoretical flame temperature remained approximately constant throughout the whole temperature range at the lower concentration

limit. The upper limits for mixtures of methane and air determined in a narrow tube increase less rapidly with temperature than those determined in a wide tube; this mixture, also, yields practically the same results for horizontal as for downward propagation of flame. S. K. T.

**Movement of Flame in Closed Vessels.** O. C. DE C. ELLIS and R. V. WHEELER (*J. Chem. Soc.*, 1925, 127, 764—767).—By means of the apparatus already described (this vol., ii, 590) the assumptions made by Wheeler (T., 1918, 113, 840) and by Mallard and Le Chatelier (*Ann. Mines*, 1883, [viii], 4, 379) regarding the propagation of flames in closed spherical vessels are confirmed experimentally. The rate of development of pressure in such experiments is retarded when ignition takes place at the bottom of the sphere instead of the centre; the maximum pressure attained, also, is less. S. K. T.

**Thermal Decomposition of Nitrogen Pentoxide.** H. S. HIRST (*J. Chem. Soc.*, 1925, 127, 657—671).—The thermal decomposition of nitrogen pentoxide is shown to be probably a true unimolecular reaction. The measured velocity coefficient agrees with that obtained by Daniels and Johnston (A., 1921, ii, 249); the values found at low initial pressures are not in accordance with Bodenstein's theory (A., 1923, ii, 303). No inhibitor of the reaction was discovered; the temperature coefficient is very large (300% velocity increase for 10° rise) so that there is probably no wall effect. The decomposition of pure nitrogen pentoxide at 80° is practically instantaneous (cf. Daniels, Wulf, and Karrer, A., 1923, ii, 24). S. K. T.

**Velocity of Reaction in Mixed Solvents. VIII. Velocity of Formation of certain Quaternary Ammonium Salts.** H. MCCOMBIE, H. M. ROBERTS, and H. A. SCARBOROUGH (*J. Chem. Soc.*, 1925, 127, 753—759).—Measurements of the velocity of formation,  $k$ , of quaternary ammonium salts in three different solvent pairs confirm the authors' previous suggestion that when  $k$  is a discontinuous function of the composition of the solvent the solvent complex undergoes further complex formation with one of the reactants or reaction products. Addition of that solvent in which the reaction proceeds more slowly causes a large decrease in  $k$  except in the case of mixtures of acetone and benzene. S. K. T.

**Bromometric Investigations.** H. P. KAUFMANN and E. HANSEN-SCHMIDT (*Arch. Pharm.*, 1925, 263, 32—50).—In addition to a general review of the literature, the following new observations are recorded. The stability of bromine solutions (0.1N) depends on the nature of the solvent. Thus, in carbon tetrachloride there is a loss of only 1% after 56 days; in acetic acid the decrease in strength is slightly greater; in carbon disulphide or chloroform it is about 22% in the same time; in methyl or ethyl alcohol, the strength falls rapidly at first, but afterwards less quickly, so that ultimately no further change takes place. In the two alcohols, 7.4% and 67%, respectively, of the active bromine disappears in

the first day. These rates are for the anhydrous solvents; when water is present the action is more rapid. The formation of acid inhibits further action, and, in the case of the alcohols, the addition of certain bromides has the same effect. Thus, if sodium or lithium bromide (12 equivalents) be added to a 0.1*N* solution of bromine in methyl alcohol a very stable preparation is obtained, only 3% of the active bromine having disappeared after 56 days. Calcium bromide is not so active; zinc and stannous bromides are almost indifferent; ferric bromide facilitates the interaction of the bromine and the alcohol. Ethyl alcohol solutions are similarly stabilised, but not so effectively. It is recommended, therefore, to use as a standard a 0.1*N*-solution of bromine in methyl alcohol saturated with sodium bromide.

Various substitutive and additive reactions were investigated. Hexane is not attacked by bromine (0.1*N*-solution) in darkness in carbon tetrachloride, carbon disulphide, or methyl alcohol (as above), and in daylight with measurable rapidity only in carbon tetrachloride. With salicylic acid, substitution takes place (the dibromo derivative being formed) slowly in carbon tetrachloride either in daylight or darkness, more rapidly in methyl alcohol, but here again exposure to daylight or to the light of a mercury vapour lamp scarcely accelerates the interaction.  $\alpha\beta$ -Di-iodoethylene (Kaufmann and Utzel, A., 1922, i, 213) reacts rapidly with bromine in carbon tetrachloride when the mixture is illuminated, but in darkness scarcely at all. Cinnamic acid takes up two atomic proportions of bromine (from a 0.1*N*-solution) in 1 hour in carbon tetrachloride, 3 hours in carbon disulphide, 24 hours in acetic acid, and 24 hours in methyl alcohol (containing sodium bromide). The rate of addition is affected by the presence of water in the methyl alcohol, and by light, particularly in the case of the carbon tetrachloride. Linseed oil takes up bromine additively only in darkness from carbon tetrachloride solution; when the solution is illuminated substitution reactions also take place. In methyl alcohol, however, there is only addition, and no substitution, either in light or darkness.

The application of these findings to the determination of the enol in keto-enol mixtures, and to the determination of "iodine-numbers" is discussed.

W. A. S.

### Hydrolysis of Iodine as Measured by the Iodine Electrode.

H. D. MURRAY (*J. Chem. Soc.*, 1925, 127, 882—885).—The diatomic iodine molecule is assumed to give two oppositely charged ions; hydrolysis then follows from the reaction  $I^+ + H_2O = H^+ + HIO$ . There is in the solution between the iodine and hypoiodous acid molecules and the ions  $H^+$ ,  $I^+$ ,  $I^-$ , and  $I_3^-$ , an equilibrium which is derivable from the mass-action laws:  $[I^+][I^-]/[I_2] = K_1$ ;  $[I^-][I_2]/[I_3^-] = K_2$ ;  $[I^+][OH^-]/[HIO] = K_3$ . Hence under conditions where any hydrogen iodide formed is largely dissociated,

$$K_1 = ([I^+]^2/[I_2])(1 + 1/K_2 \cdot [I_2]) / (1 + K_4/K_3 \cdot 1/[H^+]).$$

The value of  $K$  was measured by means of an iodine-iodide electrode. The normal potential of the iodine electrode at 25° was found to be



0.6204 volt; the value in 0.1*N*-sulphuric acid was 0.6829 volt. At 25° the value of  $K_1$  was  $0.97 \times 10^{-8}$ , and  $K_3$   $3.2 \times 10^{-10}$ . W. T.

**Velocity of Ester Formation.** P. PETRENKO-KRITSCHENKO, W. BOGATSKY, and N. LUBMAN (*Z. physikal. Chem.*, 1925, **115**, 289—302).—The velocity constants of the reactions between the following alcohols and acids, in benzene solution, at 100°, have been determined: ethyl alcohol, isopropyl alcohol, *tert.*-butyl alcohol, benzyl alcohol, benzhydrol, triphenylcarbinol; acetic acid, trichloroacetic acid, hydrochloric acid. The generally accepted view that the velocity is greatest with primary and least with tertiary alcohols is correct only for the reactions with acetic acid. In each series of alcohols, the velocity constant for the reaction with trichloroacetic acid is greatest with primary and least with secondary alcohols; with hydrochloric acid the velocity constant is greatest for tertiary and least for primary alcohols. L. F. G.

**Thermal Decomposition of Derivatives of Ethyl Oxalacetate. A Unimolecular Reaction.** D. L. WATSON (*Proc. Roy. Soc.*, 1925, **A**, **108**, 132—153).—The thermal decomposition of ethyl ethoxyoxalacetate, oxalpropionate, and oxalsuccinate between 140° and 200° as represented by the equation,  $\text{CO}_2\text{Et} \cdot \text{CO} \cdot \text{CHR} \cdot \text{CO}_2\text{Et} = \text{CO} + \text{CO}_2\text{Et} \cdot \text{CHR} \cdot \text{CO}_2\text{Et}$ , follows the unimolecular law. Ethyl oxalacetate itself also loses carbon monoxide in accordance with this equation, but a simultaneous condensation process occurs at the temperatures investigated. The decomposition of ethyl phenyl-oxalacetate is autocatalytic. The above changes are practically unaffected by solvents or acids. These investigations are shown to afford no evidence in support of the radiation theory as developed by Lewis and Perrin. Various theoretical considerations are discussed. J. S. C.

**Kinetics of the Reaction between the Halogens and Saturated Aliphatic Ketones in Dilute Aqueous Solution.** F. O. RICE and C. F. FRYLING (*J. Amer. Chem. Soc.*, 1925, **47**, 379—384).—Chlorine, bromine, and iodine react with acetone in dilute aqueous solution with the same velocity and have the same temperature coefficient of velocity, supporting the view that the mechanism of the reaction consists of a slow reaction between acetone and hydrogen ion followed by a rapid reaction involving the halogen. Pinacolin and iodine react with less than half this velocity but all other ketones investigated react at the same, or at a greater rate. This does not support the hypothesis that the slow change is an enolisation of the ketone. The reactions between different ketones and iodine all have the same temperature coefficient. L. J. H.

**Velocity of the Addition of Hydrogen Chloride to Quinone in Methyl Alcohol.** EBERT (*Z. Elektrochem.*, 1925, **31**, 209; cf. this vol., ii, 408).—A correction;  $\log k = 1.160 + \log [\text{H}^+] + \log [\text{Cl}^-] - 1.61([\text{H}^+] + [\text{Cl}^-])^{\frac{1}{2}}$ . N. H. H.

**Kinetics of Hæmoglobin. III. Velocity with which Oxygen combines with Reduced Hæmoglobin.** H. HARTRIDGE and F. J. W. ROUGHTON (*Proc. Roy. Soc.*, 1925, **A**, **107**, 654—683).—The investigation deals with (1) the order of the reaction, (2) the relation between the velocity-coefficients and the equilibrium-constant, and (3) the effect of  $p_{\text{H}}$ , temperature, light, and salt content upon the reaction-velocity. The methods adopted were similar to those used in studying the rate of dissociation of oxy-hæmoglobin (cf. *A.*, 1923, ii, 746). The velocity of reaction was independent of the methods of preparation of the solutions. The measurement, at different cross-sections of the velocity apparatus, was made by means of the reversion spectroscope. The time for half completion of the reaction was between 0.01 and 0.001 second. By comparing the results obtained with two widely different rates of flow, the velocity apparatus was shown to be adequate for dealing with such high velocities. The velocity coefficients with different concentrations of reactants at  $p_{\text{H}}$  7 and at  $p_{\text{H}}$  10 to 11 showed the reaction to be bimolecular. A further test of the correctness of the equation  $d(\text{O}_2\text{Hb})/dt = k_1(\text{O}_2)(\text{Hb}) - k(\text{O}_2\text{Hb})$  was obtained by comparing the value of the equilibrium constant, as calculated from the dissociation curve, with that obtained from the ratio of the two velocity coefficients. The experiments showed that the dissociation curve, in dilute solution, is of a hyperbolic character, and that the quotient of the velocity coefficients is equal, within the limits of error, to the equilibrium constant. Change of salt concentration, hydrogen-ion concentration, or of temperature was found to have no marked effect on the reaction velocity. The low temperature coefficient both at  $p_{\text{H}}$  7 and  $p_{\text{H}}$  10 (little more than unity for  $10^\circ$  rise) suggested that the reaction might be a photochemical one, but experiment showed that this is not so. In view of the small effect of  $p_{\text{H}}$  on  $k_1$ , the effect of  $p_{\text{H}}$  on the equilibrium constant must be mainly ascribed to its influence on the reduction velocity coefficient. The possible existence of aggregates in solution is discussed, and it is concluded that the presence of such aggregates will not affect the velocity of oxygen uptake so long as the part of the hæmochromogen grouping which combines with oxygen is sharply localised and far removed from the part of the grouping which forms aggregates. The low temperature coefficient of the reaction may be explained by assuming that every collision of oxygen with this localised portion results in combination. L. L. B.

**Space Velocity of Transformation of the Modifications of Sulphur.** W. FRAENKEL and W. GOEZ (*Z. anorg. Chem.*, 1925, **144**, 45—59).—Assuming that transformation originates at a number of points and spreads outwards from them with constant linear velocity (at the same temperature and for the same substance), it is shown that the amount of substance changed in unit time increases with the square of the time, until the boundaries of the changed areas meet; the transformation velocity becomes constant and finally diminishes. The curve for total amount of substance changed thus rises at first with the third power of the time, gradually

flattens, and then falls; the **S**-curve is accepted as the characteristic of a true transformation in and throughout the solid phase. The volume-time diagrams, plotted by aid of the air dilatometer, for the change monoclinic to rhombic sulphur at temperatures somewhat above normal and for rhombic to monoclinic at  $100^{\circ}$ , conform to this curve. The temperature for maximum formation of transformation centres in supercooled monoclinic sulphur was found to be  $-20^{\circ}$ ; the change to the rhombic form was also observed microscopically, being inaugurated by means of carbon disulphide or rhombic crystals, and the linear velocity measured. S. I. L.

**Transformation Velocity of Ammonium Nitrate.** A. SIEVERTS (*Z. anorg. Chem.*, 1925, **144**, 60—63).—The characteristic **S**-curve for transformation throughout a solid (cf. preceding abstract) was obtained, and the transformation temperature of  $32.1^{\circ}$  observed by Early and Lowry confirmed (T., 1919, **115**, 1387).

S. I. L.

**Theoretical Force and Co-volume of Explosives.** E. BURLOT (*Compt. rend.*, 1924, **179**, 968—970).—The experimental values of  $f$  do not agree with those calculated from the formula  $f = P_0 V_0 T / 273$ , the discrepancy being as great as 22% in the case of ballistite. The differences are attributed to the cooling of the gas by the walls of the bomb and the fact that a given pressure which is developed within a few thousandths of a second has not the same crushing effect as when the pressure is developed slowly.

H. J. E.

**Theoretical Force of Explosives.** H. LE CHATELIER (*Compt. rend.*, 1924, **179**, 971—972; cf. Mallard and Le Chatelier, A., 1883, ii, 542, 844; 1884, ii, 549).—Burlot's experiments show that the values determined by Mallard and Le Chatelier for some specific heats should be modified, but sufficient data are not yet available for fixing the new values. The errors are in part due to the assumption that the specific heat of a gas is independent of the pressure, but at low temperatures, when internal pressures are not negligible, this is not the case. Errors in the methods of pressure measurement are also indicated, but these to some extent counteract each other.

H. J. E.

**Rate of Dehydration in the System Water-Alumina.** M. GUICHARD (*Bull. Soc. chim.*, 1925, [iv], **37**, 381—389).—Determination of the constitution and nature of hydrates, by determination of constant weight at constant temperature, is inapplicable in the case of the hydrates of alumina and other gelatinous substances in which some or all of the contained water is adsorbed. However, curves showing the rate of dehydration with constantly increasing temperature differentiate between combined and adsorbed water. Alumina obtained by precipitation in the cold undoubtedly contains chemically combined water, and evidence is obtained for the existence of the hydrates  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  and  $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ . Alumina from boiling solutions contains only adsorbed water. The catalytic activity of alumina in promoting chemical processes involving the

removal of the elements of water appears to be purely an adsorption phenomenon. J. S. C.

**Rapidity of Dehydration at Increasing Temperature.** M. GUICHARD (*Bull. Soc. chim.*, 1925, [iv], 37, 62—67).—On dehydrating precipitates at a slowly increasing temperature, a period of constant weight is obtained for a time for each definite hydrate, whilst adsorbed water is driven off continuously. The method is superior to that of dehydration at constant temperature in that it avoids recording false equilibria due to the rate of loss in water decreasing with the water content in cases of absorbed water.

L. J. H.

**Decomposition of Malic Acid by Sulphuric Acid.** E. L. WHITFORD (*J. Amer. Chem. Soc.*, 1925, 47, 953—968).—The decomposition of active and inactive malic acid by 100% sulphuric acid is a unimolecular reaction and is uninfluenced by the nature of the walls of the containing vessel. The reaction is greatly inhibited by water, many sulphates (especially those of sodium, potassium, and silver), acetic acid, dimethylpyrone, and large amounts of sulphur trioxide; dissolved hydrogen chloride and copper sulphate have no influence. The logarithm of the velocity constant is a linear function of the "molality" of the inhibitor, as is also the case for formic and oxalic acids (cf. Schierz, A., 1923, ii, 230; Lichty, A., 1907, ii, 445; 1909, ii, 38). The temperature coefficient of the reaction is large (3.72) and falls off slightly when water is added in increasing amounts (cf. Dhar, A., 1924, ii, 746). It is suggested that the reaction proceeds as follows:  $C_4H_6O_5 + H_2SO_4 \rightleftharpoons C_4H_6O_5 \cdot H_2SO_4 \rightleftharpoons H_2SO_4 + CO + H_2O + C_3H_4O_3$  (formylacetic acid). The action of inhibitors is completely explained on Taylor's theory of negative catalysis (A., 1923, ii, 399).

S. K. T.

**Velocities of Crystallisation of Gypsum and Preparation of a Plaster of Great Resistance to Compression.** L. CHASSEVENT (*Compt. rend.*, 1925, 180, 1029—1031; cf. A., 1924, ii, 483).—By means of measurements of the electrical conductivity of the solution, the velocities of crystallisation of  $CaSO_4 \cdot 2H_2O$  from supersaturated solution have been determined at temperatures from 16° to 80°. The velocity of crystallisation falls as the temperature approaches 60°, above which temperature seeding the solution with the dihydrate is practically without effect. If the solution is supersaturated with respect to  $CaSO_4 \cdot 0.5H_2O$  at these temperatures, crystallisation is rapid to a point between the solubilities of the two hydrates and then proceeds extremely slowly. A plaster of high density (2.18) and great hardness is obtained by mixing plaster of Paris with the amount of water theoretically necessary for production of the dihydrate, compressing the mass at 80°, and then allowing it to set at laboratory temperature.

G. M. B.

**Effect of Various Factors upon the Velocity of Crystallisation of Substances from Solution.** J. D. JENKINS (*J. Amer. Chem. Soc.*, 1925, 47, 903—922).—The velocity of crystallisation at 0° of solutions of carbamide and of naphthalene in methyl

alcohol was investigated by a thermometric and by a rapid refractometric method. The presence of collodion strongly inhibits the crystallisation of naphthalene and converts it from a process of the first into one of the second order; it also suppresses deposition on the (110) faces of the crystals, thus causing elongation to a needle form. Addition of water (up to 13%) and of benzene (7%) has practically no influence. No inhibitors were found for the crystallisation of carbamide from methyl alcohol; above a certain point, increase in the amount of initial supersaturation causes an increase in the rate of crystallisation, possibly because of the spontaneous formation of fine crystals at the time of seeding.

The velocity coefficient  $k$ , for the crystallisation of carbamide from mixed and pure solvents is related to the viscosity,  $\eta$ , of the latter by the relation:  $k\eta^{0.59} = \text{constant}$ ; this expression is not in harmony with the diffusion explanation of crystallisation. The results, generally, indicate that the influence of inhibitors is not due to capillary action, but to the formation of stable adsorption complexes (cf. Marc, A., 1912, ii, 336). The influence of temperature on the velocity of crystallisation of acetanilide from two different solvents is accounted for by the lower viscosities of the media at the higher temperature.

Lactose hydrate crystallises only slowly from water because of its slow formation in solution; the process is greatly accelerated by a little ammonia. Preliminary experiments with ammonium nitrate in various solvents indicate that the velocity of solution tends to be more susceptible to the viscosity of the medium than the velocity of crystallisation, though other factors also intervene.

A solvate compound of carbamide,  $(\text{NH}_2)_2\text{CO} \cdot \text{CH}_3 \cdot \text{OH}$ , was isolated as rhomb-shaped plates, unstable above  $10^\circ$ , which rapidly lost methyl alcohol in the air. S. K. T.

**Kinetics of Cellulose Production.** S. ARRHENIUS (*Z. Elektrochem.*, 1924, 30, 375—376).—Comparative tests on the solubility of the cellulose and encrustants of wood in the usual technical solvents—sodium hydroxide, sodium sulphide, and “sulphate liquor”—show that the reactions are unimolecular. The cellulose and the encrustants appear to be converted into soluble intermediate compounds with great velocity and the reaction constants of these depend on the concentration of the solution and on the temperature, the encrustants dissolving much more rapidly than the cellulose at the lower temperatures. Sodium sulphide retards solution of the cellulose and increases the rate of solution of the encrustants. [Cf. B., 1925, 395.] A. R. P.

**Corrosion Phenomena in Aluminium.** E. MAASS and W. WIEDERHOLT (*Z. Metallk.*, 1925, 115—121).—Aluminium is more readily attacked by alkaline solutions than by acids of equivalent strength, but in neither case is the rate of solution dependent on the concentration of the hydroxyl or hydrogen ions, although it is markedly influenced by the nature of the other ions present as it is in solutions of neutral salts. Of the cations, potassium has the

greatest accelerating action, followed by sodium, ammonium, calcium, and magnesium. Of the anions, chloride is the most corrosive, producing generally a loosely-adherent oxide deposit and severe local pitting. Sulphates and nitrates, on the other hand, have only a slight corrosive action as a more tenacious deposit of hydroxide is usually formed in these solutions. Carbonates are almost as strongly corrosive as the corresponding hydroxides. The rate of attack of aluminium by 0.1*N*-acids decreases with the acid in the following order: sulphurous, hydrochloric, nitric, sulphuric, oxalic, acetic, tartaric acids; except in the case of sulphurous acid, where no action is visible, the corrosion is uniformly accompanied by the evolution of hydrogen from the surface of the metal. With alkalis, the gradual formation of a protective coating slowly retards corrosion. Pure water has no action on aluminium, but a slight attack occurs when a current is passed between two aluminium electrodes. Hydrogen peroxide rapidly destroys a sheet of the metal. [Cf. *B.*, June 26th.] A. R. P.

**Reaction between Potassium Persulphate and Potassium Iodide in Gelatin Sols.** S. O. RAWLING and J. W. GLASSETT (*J. Physical Chem.*, 1925, **29**, 414—420).—The reaction between potassium persulphate and potassium iodide to give potassium sulphate and iodine is accelerated by the presence of gelatin. Some of the iodine liberated reacts with the gelatin. The accelerating effect is not due to the influence of catalysts present as impurities in the gelatin. The acceleration is increased to a maximum by acids and decreased by alkalis. Acceleration still occurs when the gelatin is at its isoelectric point and also when the solutions are kept at 39°, so that the effect is not due to the gel form. The acceleration is either caused by an organic catalyst in the gelatin or by adsorption of the reacting ions on the gelatin particles. M. B. D.

**Autoxidation and Anti-oxygenic Action. XVI. Location of the Catalytic Property in the Oxidisable Part of the Molecule of the Catalyst.** C. MOUREU, C. DUFRAISSE, and P. LOTTE (*Compt. rend.*, 1925, **180**, 993—998; cf. *A.*, 1924, ii, 841).—Comparative experiments on the autoxidation of furfuraldehyde, acraldehyde, heptaldehyde, benzaldehyde, styrene, and turpentine in the presence of small quantities of various sulphur compounds show that in general the catalytic action of a molecule  $R\cdot S\cdot R'$  is greatly diminished or entirely suppressed if the oxidised form  $R\cdot SO_2\cdot R'$  be substituted. Thus the autoxidation of furfuraldehyde is inhibited by traces of methyl, ethyl, or phenyl sulphides, or of propane- $\beta$ -diethylthiol, whilst dimethyl- and diethyl-sulphones, diphenyl sulphoxide, sulphonol, and trional have no such effect. On the other hand, in the case of the autoxidation of acraldehyde, the positive catalytic action of methyl and ethyl sulphides and the negative action of propane- $\beta$ -diethylthiol are both practically suppressed when the corresponding sulphones are substituted for the parent sulphides. The conclusion is reached that the catalytic activity is due to the oxidisability of the sulphur atom in the active substances. G. M. B.

**Classification of Reactions Taking Place in the Presence of a Contact Substance.** W. SWIENTOSLAWSKI (*J. Chim. phys.*, 1925, 22, 73—76).—Theoretical. Reactions in the presence of a contact substance are divided into two classes according as equilibrium is attained or not. If the reacting substances are in contact with the catalyst for a time sufficient to establish equilibrium, the final state is independent both of the nature of the catalyst and of the series of reactions by which the equilibrium is established. If, however, the substances are removed from the catalyst before equilibrium is attained, the products of reaction may differ both qualitatively and quantitatively according to the particular catalyst and the exact nature of the intermediate reactions. W. H.-R.

**Theory of the Catalytic Surface.** H. S. TAYLOR (*Proc. Roy. Soc.*, 1925, A, 108, 105—111).—Previous investigations (A., 1924, ii, 668) lead to the conclusion that some modification of the Langmuir concept (A., 1922, ii, 629) is necessary. The concept of the catalytic surface to which the varying capacity of the surface to adsorb and to promote catalytic change has led is set forth in reference to the action of metallic nickel in effecting catalytic hydrogenation. Whilst X-ray examination shows that metallic catalysts possess the definite lattice structure of the crystalline material, there are, on the surface, groups of atoms in which the crystallisation process is incomplete. The surface is to be regarded as composed of atoms in varied degrees of saturation by neighbouring metal atoms; varying from those one degree less saturated than interior atoms to those which are held to the solid surface by a single constraint only, and it is by this constraint alone that these outermost atoms differ from gaseous metal atoms. These atoms can attach to themselves or adsorb three molecules, the linking between which and the nickel atom is identical with that obtaining in nickel carbonyl. This concept introduces a mechanism whereby both constituents of a hydrogenation process may be attached to one nickel atom and obviates the necessity, inherent in the Langmuir scheme, of having both reactants adsorbed on adjacent elementary spaces. The idea of metallic atoms detached to varying extents from the normal crystal lattice is in harmony with observations on such catalytic surfaces. The phenomenon of catalyst-poisoning is discussed. The amount of surface which is active catalytically is determined by the nature of the catalysed reaction. J. S. C.

**Catalytic Actions at Solid Surfaces. XII. Particles of a Catalyst which participate in Chemical Change.** E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1925, A, 108, 111—120).—The results of investigations on the toxic action of the mucilaginous and other impurities of whale oil on nickel catalyst during hydrogenation accord excellently with the views of Taylor (preceding abstract). The points at which isolated or semi-isolated nickel atoms are supposed to exist correspond with the "active patches" previously suggested by the present authors (*Trans. Faraday Soc.*, 1922, 17, 670). The inactivation of the catalyst by means of impurity depends on the covering up of the active

particles by toxic material, the active patches being thus rendered inaccessible to unsaturated compound or hydrogen. Taylor's views are critically discussed and extended. The attraction between the unsaturated organic molecule and unsaturated nickel atom is held to be strong enough to loosen the nickel atom from its adjacent atom or atoms so that when catalytic change actually occurs the nickel atom loses all contact with its neighbours. For the moment, there may exist, actually apart from the solid surface, a combination of nickel, unsaturated compound, and probably hydrogen as well. This is a much more definite conception of the "intermediate complex" than has yet been advanced. The relative rôles played by unsaturated compound and hydrogen are discussed, and it is shown that the theoretical postulates advanced are in agreement with experiment.

J. S. C.

**Catalytic Reactions at Solid Surfaces. XIII. Some Factors Controlling Selective Hydrogenation: Terpene Derivatives.**

E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1925, **A**, 108, 121—131).—Previous work on the subject is reviewed in an attempt to connect the process of selective hydrogenation with some determining factor relative to the association between unsaturated compound and the acting atom of the metal (cf. preceding abstract). The normal course is the complete hydrogenation of any unsaturated system which has become definitely associated with an active atom of metal, and hence when selective hydrogenation of a diethylenic substance occurs one unsaturated centre only is associated with the metal at the moment catalytic change occurs. The extent to which factors other than unsaturation itself control the selective nature of the process is indicated by observations on the hydrogenation of acids instead of esters, the predominating affinity between the acid radical and the metal exerting a marked influence on the development of association between the latter and the ethylene groups. The work of Lebedev, Kobliansky, and Yakubchik (this vol., i, 350) shows that the rate of hydrogenation of various ethylene derivatives depends on the degree of substitution, and that in binary mixtures of substances each containing an ethylene linking, the less highly substituted is hydrogenated in preference to the other. Applying the latter generalisation to previous observations on the course of hydrogenation of various terpene derivatives (*A.*, 1922, ii, 41), the positions of the ethylene linkings in a number of these substances have been fixed.

J. S. C.

**Synthesis of Water over Nickel and Copper Catalysts.**

A. T. LARSON and F. E. SMITH (*J. Amer. Chem. Soc.*, 1925, **47**, 346—355; cf. Pease and Taylor, *A.*, 1922, ii, 148, 701).—The synthesis of water over reduced nickel is essentially similar to that over copper. In each case, a stable oxide is formed which retards the catalytic action. The essentially catalytic reaction appears to be of the nature of an alternate oxidation and reduction.

L. J. H.

**Activity of Contact Substances. I. Catalytic Synthesis of Water by the Platinum Metals and their Alloys.** H. REMY and B. SCHAEFFER (*Z. anorg. Chem.*, 1924, **136**, 149—183).—The catalytic



activity of the platinum metals and their binary alloys with each other has been compared by passing a volume of a diluted mixture of 2 vols. of hydrogen and 1 vol. of oxygen over the metal until a visible amount of water was produced. The activity of the catalyst was markedly influenced by previous treatment with oxygen or hydrogen alone. After exposure to oxygen, the activity of the metals decreased in the order: iridium, palladium, platinum, whilst osmium, ruthenium, and rhodium were inactive. After exposure to hydrogen, the activity with mixtures of oxygen and hydrogen diluted with excess of hydrogen decreased in the order: osmium, iridium, platinum, rhodium, whilst ruthenium and palladium were inactive, whereas when the diluent was nitrogen the corresponding order was: osmium, platinum, palladium, rhodium, whilst ruthenium and iridium were inactive. On the other hand, alloys of the metals behaved quite differently; thus in the last-named case osmium-platinum alloys were only very slightly active, although each metal separately was very active, and rhodium-ruthenium alloys were exceedingly active, although rhodium itself was only slightly active and ruthenium, alone, inactive. Addition of ruthenium to palladium or iridium and exposure of the alloys to hydrogen results in greatly increased activity.

A. R. P.

**Influence of Gas Content on Catalysis with Platinum.** G. KÄB (*Z. physikal. Chem.*, 1925, **115**, 224—232).—A method of forming deposits of platinum-black by electrical dispersion of the metal in atmospheres of different gases is described. The rate of catalytic decomposition of formic acid was studied. The activity was inhibited if the atmosphere in which dispersion took place contained hydrogen, carbon monoxide, or oxygen, the inhibiting effect due to oxygen being greatest and that due to hydrogen least; nitrogen has no effect on the activity. Platinum-black prepared in a hydrogen or carbon monoxide atmosphere can be activated by pumping away the gas, or, in the case of hydrogen, by the action of atmospheric oxygen or of ozone. The electrode potentials, against dilute sulphuric and formic acids, of specimens of platinum-black saturated with hydrogen are displaced in the noble direction if the metal is inactive, the displacement being the greatest with the most inactive preparations (cf. Hofmann and Ebert, A., 1917, ii, 25). L. F. G.

**Interaction of Hydrogen and Carbon Dioxide on the Surface of Platinum.** C. R. PRICHARD and C. N. HINSHELWOOD (*J. Chem. Soc.*, 1925, **127**, 806—811).—The interaction of carbon dioxide and hydrogen has been investigated from 870° to 1122°. The reaction was made irreversible by the absorption of the water formed, and was shown to go to completion; the product consisted entirely of carbon monoxide. With a constant pressure of carbon dioxide, the rate was found to be proportional to the pressure of hydrogen, at least up to 300 mm. When the pressure of hydrogen is kept constant, the rate is at first proportional to the pressure of carbon dioxide, and then passes through a maximum when the pressure of carbon dioxide is about double that of hydrogen. Carbon monoxide has only a slight retarding influence. The course of the

reaction is nearly unimolecular when the gases are present in equimolecular proportions. The rate of reaction increases 2.85 times for 100° rise in temperature. The poisoning effect of carbon dioxide at high pressure points to its strong adsorption, which, however, is not the case, hydrogen being much more strongly adsorbed. It is therefore assumed that the catalytic activity is localised in certain active points, and the relative adsorbability of the gases on the active points bears no relation to that on the total surface. The results obtained are in accordance with the equation  $d[\text{CO}]/dt = k[\text{H}_2]\sigma(1-\sigma)$ , where  $\sigma$  is the fraction of the active surface covered with carbon dioxide.

W. T.

**Catalytic Oxidation of Ammonia.** P. PASCAL and E. DECARRIÈRE (*Mém. Poudres*, 1924, 21, 68—86).—The temperature at which oxidation begins depends on the form of the platinum catalyst, but not on the ammonia content or velocity of the gas. These temperatures are 145° for corrugated platinum foil, 170° for foil crumpled into pellets, 240° for wire gauze, and 240° for wire in plug form. The yield of nitrogen oxides increases to a maximum with increasing temperature, then falls, and is negligible above 900°. With increasing curvature of the catalytic surface, the optimum temperature rises steadily from 650° to 775°, and the maximum yield sinks from 100% to 75—80%. Thus, pellets of crumpled foil are better than wire, and spongy platinum on a soluble support is the least advantageous. In the case of pellets, the yield is slightly increased by increasing the proportion of oxygen in the air, an optimum content being about 25% of oxygen. Ammonia losses are due principally to formation of nitrogen, apart from cases in which oxidation is only partial owing to too low a temperature or imperfect contact with the catalyst.

W. T. K. B.

**Influence of Gaseous Impurities on the Yield in the Catalytic Oxidation of Ammonia.** P. PASCAL and E. DECARRIÈRE (*Mém. Poudres*, 1924, 21, 87—105).—Hydrogen sulphide causes a progressive decline in activity of the platinum catalyst proportional to the quantity of the impurity present, the activity gradually increasing again when the impurity is removed. Acetylene differs from hydrogen sulphide and hydrogen phosphide (cf. *J.S.C.I.*, 1922, 214A, 291A) in causing a momentary increase in yield followed by a decrease depending in extent on the absolute quantity of impurity that has passed over the catalyst. The yield continues to decrease even when the actual proportion of acetylene present is diminished and for some time after all acetylene has been eliminated. The main cause of the decreased yield with hydrogen sulphide and acetylene is the rise in temperature due to the combustion of the impurity.

W. T. K. B.

**Catalytic Oxidation of Ammonia by Air in Contact with Platinum-Palladium Alloys.** E. DECARRIÈRE (*Bull. Soc. chim.*, 1925, [iv], 37, 412—421; cf. A., 1919, ii, 463; 1924, ii, 169).—The catalytic oxidation of ammonia by air in presence of platinum-palladium alloys containing 0.5% and 5%, respectively, of palladium has been investigated at various temperatures. Although the

efficiencies of the alloys as catalysts are somewhat reduced after their first employment, the effect is fairly small in the case of high (8–10%) concentrations of ammonia; the alloy containing 0.5% of palladium is preferred to platinum. [Cf. *B.*, 1925, 352.]

J. S. C.

**Efficiency of Catalysts [in Oxidation of Ammonia].** A. T. SCHLÆSING (*Mém. Poudres*, 1924, **21**, 106–126).—The yield is expressed by the ratio of the quantity of nitric acid produced to that theoretically obtainable from the ammonia in the gas before passing over the catalyst, both being expressed in terms of the same volume of nitrogen present. Samples may be taken before and after being passed over the catalyst by means of evacuated bottles, but a better arrangement is to remove a steady stream of gas continuously over a period of time and concurrently at both points. A special type of absorbing vessel is described, the gas before the catalyst being drawn through one absorber containing *N*-sulphuric acid and a second containing potassium pyrogallate, and the gas after the catalyst being drawn through three absorbers, the first two with sodium hydroxide (slightly weaker than *N*) and the third with potassium pyrogallate. In both cases, the volume of residual nitrogen is measured. There is no loss of accuracy if the second alkaline absorber in the nitric acid determination and the pyrogallol absorber in the ammonia determination are omitted, the volume of nitrogen in the latter case being calculated from that of the air collected. Various corrections and precautions are discussed.

W. T. K. B.

**Synthesis of Nitric Acid by Ostwald's Process.** P. PASCAL (*Mém. Poudres*, 1924, **21**, 1–67).—Calcium cyanamide does not suffer loss of nitrogen on storage, but there is a gradual absorption of atmospheric moisture accompanied by incipient polymerisation to dicyanodiamide. When heated in autoclaves with an alkali, dicyanodiamide liberates ammonia, although not so readily as calcium cyanamide, and the final reaction products include tri-cyanotriamide and ammeline melanurate. A maximum liberation of ammonia and minimum formation of nitrogenous secondary products is obtained by using in the autoclave a solution containing 16 g. of sodium hydroxide per litre, the average yield being 96%. The oxidative efficiency of the platinum catalyst depends on the ammonia content of the gas, a sharp maximum being observed. It also deteriorates with age, gaseous impurities (*e.g.*, hydrogen phosphide and hydrogen silicide) and, particularly, dust being detrimental. There is also an optimum value for the velocity of the gas passing over the catalyst, and it is important to maintain a low temperature in the absorbing towers. Losses may be reduced to almost zero by using an alkaline spray in the towers, sodium nitrite and nitrate being formed in about equal quantities as long as the liquid is alkaline and sodium nitrate alone occurring when it becomes acid. On the three stages of the process, a net yield of 87% should be attainable with the plant described. [Cf. *B.*, 1925, 444.]

W. T. K. B.

**Catalytic Decomposition of Nitrous Oxide on the Surface of Gold: a Comparison with the Homogeneous Reaction.**

C. N. HINSHELWOOD and C. R. PRICHARD (*Proc. Roy. Soc.*, 1925, **A**, **108**, 211—215).—The decomposition occurring on the surface of heated gold wires follows the simple unimolecular law and is shown to be a true surface reaction rather than a reaction occurring in a small zone of heated gas. The value of  $E$  in the expression  $d \log k/dT = E/RT^2$  is 29,000 cal./g.-mol. The mechanism of the process is discussed and compared with that of the homogeneous reaction (A., 1924, ii, 751) and of the reaction at the surface of platinum (this vol., ii, 310).  
J. S. C.

**Reaction Velocity of Oxygen with Solutions of some Inorganic Salts. III. Catalytic Oxidation of Sulphites.**

W. REINDERS and S. I. VLES (*Rec. trav. chim.*, 1925, **44**, 249—268; cf. this vol., ii, 308).—The results of Titov (A., 1904, ii, 113) have been confirmed and extended. An examination of the velocity of oxidation at various hydrogen-ion concentrations showed that cupric and ferric ions exert catalytic activities between  $p_H 4$  and  $p_H 12$ , reaching a maximum within this range, whilst nickel and cobalt are only active in alkaline solutions. In ammoniacal solutions, no oxidation occurs except in presence of copper salts; under these conditions, the reaction is unimolecular, the concentration of oxygen having very little influence, and the velocity being proportional to the concentration of the copper catalyst. Without addition of any catalyst, the reaction velocity is a maximum for  $p_H 10$ , but this is probably due to presence of traces of copper; by extrapolation from the results obtained with increasing quantities of copper, the amount of the latter in the distilled water used was found to be  $3.2 \times 10^{-7}$  mol. per litre, a probable proportion. The catalytic activity of nickel and cobalt in alkaline solutions is ascribed to the hydroxides, but no regularities could be observed.  
S. I. L.

**Effect of Water and of Carbon Dioxide on the Catalytic Oxidations of Carbon Monoxide and Hydrogen by Oxygen.**

A. B. LAMB and W. E. VAIL (*J. Amer. Chem. Soc.*, 1925, **47**, 123—142).—The retarding effect of water vapour on the catalytic oxidation of carbon monoxide and hydrogen by the oxygen of the air in contact with "hopcalite" (manganese dioxide and cupric oxide) was measured over a considerable range of temperatures and partial vapour pressures of water and compared with the water content of "hopcalite" in equilibrium with moisture under the same conditions. The activity is only slightly dependent on the temperature, being mainly determined by the equilibrium water content of the catalyst. The temperature coefficient of activity of very dry "hopcalite" for the oxidation of carbon monoxide is also small, and the initial activity of the very dry material for the oxidation of hydrogen is very high. Larger amounts of water vapour, carbon dioxide, and nitrogen affect the two reactions (oxidation of hydrogen and carbon monoxide) equally for each gas and to about the extent expected from the relative absorptibilities of the three gases.  
L. J. H.

**Organic Reactions at the Surface of Titania. Adsorption of certain Gases by Titania.** F. BISCHOFF and H. ADKINS (*J. Amer. Chem. Soc.*, 1925, **47**, 807—826; cf. A., 1924, ii, 159).—Mixtures of acetic acid with varying proportions of formic acid were passed over titania at 300—350°. The formation of acetaldehyde (cf. Sabatier and Mailhe, A., 1912, i, 238) was not observed. The catalytic activities of various samples of titania in decomposing butyl alcohol (at 430°), ethyl alcohol (at 400°), ethyl ether (at 430°), and ethyl acetate (at 450°) were compared. Those derived from titanium chlorides and from alkyl titanates by hydrolysis are reproducible as regards catalytic activity, whilst those from sodium titanate behave irregularly. The results obtained are in accord with the hypothesis previously advanced to explain the mechanism of catalysis at the surface of alumina (A., 1924, ii, 159), the surface state of the titania being influenced by the size and shape of the groups previously attached to the titanium atom. The decomposition of ethyl alcohol into ethylene at the surface of titania does not take place through the intermediate formation of ether. The formation of saturated hydrocarbons by the decomposition of alcohols or ether at the surface of titania is due to auto-oxidation and reduction, which takes place either between two molecules of alcohol or between two parts of the ether molecule, with simultaneous formation of an aldehyde. The decomposition of formic acid at the surface of titania dried below 300° proceeds with formation of carbon monoxide and water exclusively, whilst ignited titania gave considerable proportions of carbon dioxide and hydrogen. The total rate of decomposition of the acid was the same with the two catalysts, and it is concluded that the latter reaction is due to secondary adsorption. The adsorption of carbon dioxide, ethylene, ethane, and hydrogen by various samples of titania was determined at 20° and 97°, and was found to be independent of the relative catalytic activities of the samples. No relationship was observed between the relative activities of a catalyst for different reactions and its absolute activity as measured by the amount of material undergoing decomposition. F. G. W.

**Carbon Monoxide, a Product of Electrolysis.** A. F. O. GERMANN (*Science*, 1925, **61**, 70—71).—The specific conductivity of carbonyl chloride at 25° is  $0.007 \times 10^{-6}$ . Electrolysis of a solution of aluminium chloride in carbonyl chloride results in the evolution of carbon monoxide and chlorine. A. A. E.

**Pseudohalogens.** I. L. BIRCKENBACH and K. KELLERMANN (*Ber.*, 1925, **58**, [B], 786—794).—Measurement of the decomposition potentials of the corresponding potassium salts in aqueous solution allows the halogen and pseudohalogens to be arranged in the sequence, TeCN, SeCN, I, SCN, CN, Br, N<sub>3</sub>, Cl, OCN, F, in which there does not appear to be any direct relationship between affinity and atomic or molecular weight. In absolute ethyl-alcoholic solution the values found are those appropriate to the corresponding halogen or pseudo-halogen acids, the cation not appearing to exert any influence.

Electrolysis of solutions of potassium cyanate in the lower alcohols with a flowing mercury cathode yields a solution containing *oxycyanogen* ( $\text{OCN}$ )<sub>2</sub>. The compound has not been isolated in the homogeneous state, but its solution has a halogen-like odour, liberates iodine from potassium iodide, and dissolves copper, zinc, and iron without evolution of gas. The action of oxycyanogen on methyl alcohol gives formaldehyde and cyanic acid; the latter compound yields with methyl alcohol methyl carbamate, which is converted by cyanic acid into methyl allophanate. Preliminary experiments establish the possibility of isolating oxycyanogen by the action of a halogen on silver cyanate in an organic solvent at a low temperature.

*Selenocyanogen*,  $(\text{SeCN})_2$ , cannot be obtained by the electrolysis of solutions of potassium selenocyanate in methyl alcohol, since such solutions decompose with precipitation of selenium. It is prepared by shaking a solution of iodine in ether, chloroform, or carbon tetrachloride with an excess of pure silver selenocyanate at a temperature not exceeding 10° and evaporation of the filtered solution in a vacuum. It is a yellow, crystalline powder which can be preserved in a vacuum, but becomes red in a few hours when exposed to air. It exhibits the properties typical of halogens. Pure potassium selenocyanate is prepared by heating a mixture of potassium cyanide and selenium with anhydrous ethyl alcohol for several hours and subsequently evaporating the alcoholic solution in a vacuum; it is transformed into silver selenocyanate by means of silver acetate.

H. W.

**Electrolytic Production of Magnesium (from Fused Mixtures containing the Oxide).** O. RUFF and W. BUSCH (*Z. anorg. Chem.*, 1925, **144**, 87—113).—The solubilities of magnesium oxide in fused mixtures of the chlorides, sulphides, and fluorides of the alkali and alkaline-earth metals have been examined; only the fluorides dissolve it freely, and of these only the lithium, calcium, and magnesium compounds can be employed. The ternary diagram for these three was constructed from experimental data, the ternary eutectic being found to melt at 665° and to have the composition,  $\text{LiF}$ , 56.2;  $\text{CaF}_2$ , 15.2;  $\text{MgF}_2$ , 28.6%. To meet the necessary temperature conditions for electrolysis, this eutectic must be employed; the solubilities of magnesium oxide in this are 0.16% at 700°, 0.07 at 800°, 0.17 at 900°, and 0.12% at 1000°. The solubilities of lithium oxide and calcium oxide in the same eutectic were also determined; the first is almost insoluble, the latter more soluble than magnesium oxide. Addition of oxides, sulphides, chlorides, or other fluorides did not raise the solubility of magnesium oxide in the fused mass. Electrolysis of the oxide dissolved in the molten eutectic was investigated; below 725° compact metal could not be obtained, above 775° the metal diffused in the mass. Between 725° and 775° a compact rod of magnesium was obtained, the current efficiency reaching 90% with a density of 1000 amp./dm.<sup>2</sup> and a potential of 6—8 volts; the accumulation of oxygen in the cathode chamber reduced the efficiency greatly in other cases. S. I. L.

**Production of Metallic Magnesium from Fused Salts.**

W. G. HARVEY (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 229—241).—The electrolytic production of magnesium from the chloride and oxide is described. The chloride hexahydrate is dehydrated by heat, an equal quantity of sodium chloride and a little ammonium chloride being added to prevent the formation of oxychloride. The fused mass contains 10% of magnesium oxide and melts at 620°. Electrolysis is carried out at 675—725° in steel pots (cathodes) using graphite anodes. Metallic sodium is not formed if the electrolysis is stopped when the concentration of the magnesium chloride falls to 10%. Metallic magnesium floats on the electrolyte, a thin film of which protects it from oxidation. The metal is purified by remelting, but cannot be freed entirely from the chloride, which leads to subsequent corrosion of the metal. The oxide process overcomes this difficulty. Magnesium oxide dissolves (0.1%) in a fused mixture of equal parts of magnesium and barium fluorides containing sufficient sodium fluoride to give fluidity at 950°. The primary reaction is electrolysis of the fluoride, but this is reformed by reaction between the fluorine and dissolved magnesium oxide. The latter is added from time to time to maintain the concentration. The metal after remelting contains 99.9% Mg, and is permanent owing to the absence of hygroscopic impurities. [Cf. *B.*, 1925, 406.] C. S.

**Zinc Arc as a Means of Reduction.** A. STOCK, A. BRANDT,

and H. FISCHER (*Ber.*, 1925, **58**, [B], 643—657; cf. Stock and Praetorius, A., 1913, ii, 46).—The apparatus consists of a very thin-walled glass flask the stopper of which supports two brass rods which carry the lower, fixed and the upper, movable electrodes and a glass T-piece serving for the introduction of an indifferent gas and a resistance thermometer. The arc is formed beneath the liquid under investigation. The apparatus is immersed in a cooling bath which is kept stirred by a mechanical agitator, figured and described in the original. The behaviour of zinc and graphite electrodes in the presence of carbon disulphide is described in detail. The optimum yield of carbon subsulphide,  $C_3S_2$ , amounting to almost 50% of that obtainable according to the scheme  $3CS_2 + 4Zn \rightarrow C_3S_2 + 4ZnS$  is secured by the use of a zinc anode and carbon cathode at 0°. The reaction is not merely a thermal change between carbon disulphide and zinc vapour in which the arc serves as a source of heat, since carbon subsulphide is not produced with an alternating current arc. With silicon tetrachloride, the best conditions are found in the use of a stationary aluminium cathode and movable zinc anode at -55° to -15°. The main reaction consists in the production of zinc chloride and silicon, whereas a minor portion of the silicon tetrachloride is converted into hexachlorodisilane, m. p. +2.5° (instead of -1° as recorded previously). Under similar conditions at -60° to +10°, phosphorus trichloride yields mainly yellow phosphorus and zinc chloride, phosphorus dichloride,  $P_2Cl_4$ , m. p. -28°, being formed in minor quantity (cf. Besson and Fournier, A., 1910, ii, 121). Boron trichloride is converted chiefly into boron; to a small extent

a new *chloride*,  $B_2Cl_4$ , b. p.  $0^\circ/44$  mm., m. p. about  $-100^\circ$ , is produced which could not be freed completely from silicon tetrachloride present to a small extent in the initial boron trichloride. It decomposes slowly at the atmospheric temperature into boron and boron trichloride, is decomposed by sodium hydroxide according to the equation,  $B_2Cl_4 + 3H_2O = B_2O_3 + 4HCl + H_2$ , and with water yields a moderately stable compound in which the B·B group remains intact.

The action of sodium amalgam on the chlorides of silicon, boron, or phosphorus leads almost exclusively to the production of the respective non-metal. Phosphorus trichloride appears to react slowly with mercury with intermediate formation of the dichloride, by which the metal is greatly attacked. H. W.

**Preparation of Electrolytic Mercurous Chloride in Saturated Potassium Chloride for Use in the Calomel Electrode.** W. W. EWING (*J. Amer. Chem. Soc.*, 1925, 47, 301—305).—Mercurous chloride is made electrolytically in saturated potassium chloride solution, the stirrer being arranged to sweep the surface of the mercury, thus removing the calomel as formed. The saturated potassium chloride solution of the anolyte is connected to the catholyte by inverted U-tubes containing *N*-potassium chloride solution, the open ends bearing semi-permeable membranes made from filter-paper soaked with collodion. The cathode is of copper, and the catholyte is saturated cupric chloride solution. The method gives a dependable quality of calomel mixed with finely divided mercury and avoids washing and shaking. The *E.M.F.* of the cell  $Hg + HgCl | HgCl$  in satd.  $KCl | HgCl$  in *N*- $KCl | HgCl + Hg$  is 0.0388 volt at  $25^\circ$ . The electrode potential of the saturated potassium chloride calomel half-cell is  $-0.2446$  volt on the hydrogen scale at  $25^\circ$  and its temperature coefficient is 0.0002 volt per degree from  $20^\circ$  to  $30^\circ$ . L. J. H.

**Electrolytic Reduction of Tungstic Acid in Hydrochloric Acid Solution.** O. COLLENBERG and J. BACKER (*Z. Elektrochem.*, 1924, 30, 230—238).—At a platinum cathode solutions of alkali tungstates in concentrated hydrochloric acid (containing the oxychloride  $WO_2Cl_2$ ) are reduced quantitatively to derivatives of quinquivalent tungsten, whereas reduction proceeds further at a mercury, lead, or tin cathode. Above  $16^\circ$ , sodium tungstate gives quantitative yields of tervalent tungsten derivatives at the base metal cathode, but below  $16^\circ$  reduction is not so complete; potassium tungstate is completely reduced only at a lead cathode. During reduction, the colour of the solution changes first to blue when the tungsten is in the quinquivalent form, and this colour slowly fades on further reduction, yielding eventually a yellowish-green or red solution of tervalent tungsten. The yellowish-green solution is always obtained above  $35^\circ$ ; it contains compounds of the type  $R'_3W_2Cl_9$ . The red solution is obtained at  $16^\circ$  and contains compounds of the type  $R'_2(WCl_5, H_2O)$  which are unstable, changing on keeping or warming to compounds of the first-named type.

A. R. P.



**Photosensitive Formation of Water from its Elements in the Presence of Chlorine.** R. G. W. NORRISH and E. K. RIDEAL (*J. Chem. Soc.*, 1925, **127**, 787—797).—The formation of water in the gaseous system hydrogen–chlorine–oxygen on illumination by visible radiation is governed by the relationship  $d[\text{H}_2\text{O}]/dt = k[\text{Cl}_2][\text{O}_2]$ . It is independent of the partial pressure of hydrogen between the limits tested (0.16–0.9 of the total pressure). The result is consistent with the hypothesis that activation of the oxygen is first brought about by contact with chlorine molecules activated by absorption of light. The activated oxygen molecules then combine with hydrogen molecules to form water. The anticatalytic effect of oxygen on the formation of hydrogen chloride is regarded as due to the direct intervention of oxygen in the hydrogen–chlorine reaction chains, resulting in the formation of water. With the photosensitive decomposition of ozone by chlorine, and the activation of hydrogen by resonating mercury atoms, this reaction falls into the simplest class of photochemical sensitisation. W. T.

**Photodecomposition of Chlorine Water and of Aqueous Hypochlorous Acid Solutions.** A. J. ALLMAND, P. W. CUNLIFFE, and R. E. W. MADDISON (*J. Chem. Soc.*, 1925, **137**, 822—840).—Chlorine in water is considerably hydrolysed according to the equation  $\text{Cl}_2 + \text{H}_2\text{O} = \text{HClO} + \text{H}^+ + \text{Cl}^-$ . The addition of chlorides, and especially of hydrochloric acid (which suppress the hydrolysis), retards its photodecomposition; this indicates that the hypochlorous acid molecule is more photosensitive than the chlorine molecule. The hypochlorous acid decomposes to give hydrogen chloride and oxygen. The production of molecular oxygen and of chloric acid would then be due to secondary reactions, the latter being formed as a result of the hypochlorous acid molecules acting as acceptors for oxygen atoms. The addition of sodium acetate and disodium hydrogen phosphate (salts of acids the dissociation constants of which, though small, are appreciably greater than those of hypochlorous acid) suppress the concentration of hydrogen ion but form no hypochlorites. The effect of these salts (especially the latter) was to increase the yield of chloric acid from 61 to 83%, supporting the idea of the primary product of photolysis being oxygen atoms and that these with hypochlorous acid formed chloric acid. The suppression of chlorine ions by the addition of mercuric chloride (to form  $\text{HgCl}_4^{2-}$ ) was not found effective. The addition of hydrochloric acid, which would decrease hydrolysis, should considerably decrease the yield of chloric acid; the yield decreased, but much less rapidly than expected if solely produced by the interaction of the primarily formed oxygen and hypochlorous acid (calculation based on Jakowkin's hydrolytic constant, A., 1899, ii, 736). Hence hypochlorous acid is probably one of the intermediate products of reaction of photoactivated chlorine molecules and water, this then acting as an acceptor for the oxygen. Chlorides and sulphuric acid also lower the yield of chloric acid. Their effects vary and various ions seem to have specific effects. Manganous sulphate and cobalt sulphate gave side reactions. The evolution

of oxygen in the reaction is subject to marked supersaturation effects. W. T.

**Action of Light on Chlorine Dioxide.** H. BOOTH and E. J. BOWEN (*J. Chem. Soc.*, 1925, 127, 510—513).—Dry gaseous chlorine dioxide on exposure to light is converted into chlorine heptoxide to the extent of about 60%; the latter forms a red liquid, b. p. about 80°, which becomes colourless on continued exposure. Chlorine monoxide and another unknown oxide are probably intermediate products. Dry chlorine dioxide (diluted with carbon dioxide) prepared in the dark is stable towards heat; after the addition of chlorine monoxide it gives thermal decomposition curves identical with those obtained with illuminated gas. S. K. T.

**Action of Ultra-violet Light on Carbon Dioxide and Water.** C. W. PORTER and H. C. RAMSPERGER (*J. Amer. Chem. Soc.*, 1925, 47, 79—82).—Experiments on the formation of formaldehyde by the action of ultra-violet light on mixed water vapour and carbon dioxide gave negative results. L. J. H.

**Photochemical Studies. III. Reaction between Nitrogen and Hydrogen in Presence of Mercury Vapour: Resonance Radiation of Mercury.** W. A. NOYES, Jun. (*J. Amer. Chem. Soc.*, 1925, 47, 1003—1009).—Gaseous hydrogen and nitrogen combine to form ammonia in presence of mercury vapour with the possible formation of traces of hydrazine also; the reaction is probably of the first order with respect to hydrogen. The important factor appears to be the dissociation of hydrogen caused by the first resonance radiation of mercury (cf. Compton and Turner, A., 1924, ii, 639). Kuhn's results were qualitatively confirmed (A., 1924, ii, 249). The number of molecules of ammonia formed is of the same order as the number of quanta in the incident radiation (cf. Moore and Noyes, A., 1924, ii, 748). S. K. T.

**Photochemistry of Silver Compounds.** J. EGGERT and W. NODDACK (*Z. Physik.*, 1925, 31, 942—948).—The absorption of pure silver chloride emulsion was determined with particular attention to the reflected light, using an Ulbricht hollow sphere photometer. For 365  $\mu\mu$  1 mol. of silver chloride was decomposed by one quantum. For Valenta printing-out-paper emulsion, the same quantum relation was found to be probable. The sensitivity of this emulsion for green light is greatly increased by previous exposure to blue light, whereby an adsorption compound of silver and silver chloride is formed which in turn is decomposed by the green light. The behaviour of emulsions of silver chloride, bromide, and iodide is compared. E. B. L.

**Silver Halide Emulsions and the Law of Photochemical Equivalence.** J. EGGERT and W. NODDACK (*Z. Physik*, 1925, 31, 922—941).—A critical examination of the divergence between the results of other workers and those contained in the previous paper (cf. preceding abstract), particularly as regards the shape of the curve relating amount of silver reduced and time of exposure

of the Valenta emulsion. The initial portion of the curve is found to be straight and not S-shaped.

E. B. L.

**Leptology of the Silver Bromide Grain.** T. T. BAKER (*Brit. J. Phot.*, 1925, **72**, 248).—The X-ray crystal patterns of (1) silver bromide made by direct precipitation in water, (2) silver bromide precipitated in presence of iodide, *i.e.*, the so-termed silver iodobromide, (3) silver bromide precipitated from silver ammonium nitrate, and (4) silver bromide emulsified in gelatin and the crystals grown to be about 500 times their original sensitivity, are identical. There is no indication of silver iodide in the silver iodobromide. The change in spectral sensitivity of silver iodobromide compared with that of pure silver bromide may be due to the presence of silver iodide, which need not, however, take part in the photochemical change. It is suggested that in a sensitive emulsion the silver iodide is adsorbed in a colloidal form on the surface of the silver bromide grains. In certain types of photographic emulsion the presence of iodide retards growth of the silver bromide crystals. Whatever the function of the iodide may be, the evidence is stated to support the view that photographic sensitisation is due to substances deposited on the grain surfaces.

W. C.

**[Photographic] Ripening Process.** LÜPPO-CRAMER (*Z. wiss. Phot.*, 1925, **23**, 137—144; cf. *B.*, 1925, 150).—Both acid and basic dyes exert a protective action on silver bromide, as can be shown by their preventing the ripening of a highly disperse silver bromide-gelatin emulsion by ammonia. The effect is independent of the charge on the silver bromide. Bromo-chloride emulsions are very resistant to fogging on warming. The effect is probably due to the small grain-size and consequent greater protective action of the gelatin. Emulsions prepared by adding the silver salts to the halide solution give a higher speed than emulsions prepared in the reverse order, but they develop an intense fog in a digestion time which gives no trace of fog in emulsions prepared by adding the halides to the silver salts. The effect is due to the different environment during precipitation, the grains prepared in excess of halide solution containing less gelatin than those prepared in the reverse manner. The grain size in each emulsion pair is the same. If the amount of colloidal silver adsorbed by silver bromide is increased above a certain limit, no more silver is adsorbed, and the protecting power of the silver bromide for the silver already adsorbed is decreased, owing to the excess silver preventing the silver bromide shrinking and protecting the silver (cf. *Kolloid-Z.*, 1911, **8**, 97). This explains the greater effect of oxidising agents in decreasing the sensitivity of an emulsion after exposure to light. [Cf. *B.*, June 26th.]

W. C.

**Action of Light on Silver Bromide.** H. STOCK (*Z. wiss. Phot.*, 1925, **23**, 132—136).—A criticism of results obtained by Stromberg (*J.S.C.I.*, 1923, 953A), showing that no valid conclusions can be reached from them, and indicating certain essential factors for experiments of this nature. [Cf. *B.*, June 26th.]

W. C.

**History and Theory of the Latent Image. II.** LÜPPOCRAMER (*Z. wiss. Phot.*, 1925, **23**, 122—132; cf. *B.*, 1925, 151).—The three important new reactions which depend on the complicated colloid-chemical nature of the latent image are: the “Keimblosslegung” (nucleus exposure), dependent on the part of the silver of the latent image occluded in the silver halide grains, which is uncovered and made active by treatment with solvents for silver halide; “nucleus isolation,” which is due to an adsorption replacement of the soluble part of the latent image as a result of treatment with acid-bromide-dye mixtures, and “nucleus activation,” which is due to peptisation of the soluble portion of the latent image by treatment with alkali. [Cf. *B.*, June 26th.] W. C.

**Blackening of a Photographic Film by X-Rays.** J. K. ROBERTSON and J. T. THWAITES (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 99—102).—The degree of blackening produced on a photographic plate may be expressed by an expression of the type  $I t^p$ , where  $I$  is the intensity of the light,  $t$  the time of exposure, and  $p$  a constant. For ordinary visible light,  $p$  has the value 0.86. By means of a wedge method the value of  $p$  has been determined for X-rays and has been found to be of the order of unity. J. S. C.

**Kinetics of Photochemical Processes in Dyes.** A. PREDWODITELEFF and N. NETSCHAJEWA (*Z. Physik*, 1925, **32**, 226—235).—The initial rates of the bleaching of cyanine and pinacyanol in collodion show a periodicity which is dependent on concentration. This does not apply if the solutions are sufficiently dilute, for which the rate of bleaching is in accordance with the formula for a unimolecular reaction. E. B. L.

**Photolysis of Dibasic Acids.** VOLMAR (*Compt. rend.*, 1925, **180**, 1172—1173).—Berthelot (*A.*, 1914, ii, 602) showed that photolysis of one carboxyl group in oxalic acid occurs with radiation of  $0.3\mu$  and that shorter waves,  $\lambda=0.2\mu$ , were required for the decomposition of the product. The changes are expressed better by the schemes  $R(CO_2H)_2 \rightarrow CO_2 + RH(CO_2H)$ ;  $RH(CO_2H) \rightarrow CO_2 + RH_2$  than by  $R(CO_2H)_2 \rightarrow 2CO_2 + RH_2$ . The latter reaction requires radiations of wave-length  $0.18\mu$ , since the radiations not absorbed by quartz do not effect the change. Near ultra-violet radiation causes partial photolysis. Using  $0.01M$ -solutions of dibasic acids subjected to the light of a quartz mercury lamp, oxalic and malonic acids yielded formic and acetic acids, respectively. Succinic acid gave a trace of propionic acid, whilst glutaric acid gave no butyric acid. In the last case, only 0.13 c.c. of carbon dioxide was set free in 4 hrs. Thus the active wave-length is greater the nearer the carboxyl groups. Oxalic acid, by reason of its special constitution, has the maximum sensitivity towards light. As the side-chain lengthens the mutual influence of the carboxyls diminishes, so that from succinic acid onwards the groups behave as if they were single, and photolysis only occurs at wave-lengths shorter than  $0.21\mu$ , as in monobasic acids. The results are in accord with the law of photochemical equivalence. R. A. M.

**Photochemistry of Complex Compounds. I.** R. SCHWARZ and H. WEISS (*Ber.*, 1925, 58, [B], 746—755).—Hexaminecobaltic chloride, nitropentamminecobaltic chloride, *cis*- and *trans*-dinitrotetramminecobalt, the two forms of trinitrotriamminecobalt, and *cis*-tetranitrodiamminecobalt are hydrolysed in aqueous solution at a rate which is inappreciable in the dark, but is greatly accelerated by light. The cobalt separates, except from dilute solutions, in which it remains as sol, as brownish-black cobaltic hydroxide, whereas the nitrito residue passes into the ionic form. Attempts to determine the latter iodometrically in an atmosphere of carbon dioxide gave results which were not sufficiently reproducible for measurements of the kinetics of the change, which is therefore followed by determination of the electrical conductivity of the solution. Sodium hexanitritocobaltate is too unstable in solution to yield accurate measurements. For hexaminecobaltic chloride, the conductivity method is unsuitable, since there is not a considerable difference between the conductivity of the complex and that of the products of its hydrolysis; in this case, therefore, the reaction is studied in acid solution, in which the acid titer gradually diminishes in consequence of the ammonia liberated. The photochemical decomposition of the nitritoamminecobalt compounds is an irreversible action of the first order in which the maximum action of light is observed in all cases in the ultra-violet at  $366\text{ }\mu\text{m}$ . Increase in the number of nitro groups in the nucleus diminishes the photochemical stability; trinitrotriamminecobalt occupies an intermediate position by reason of its electrically neutral nucleus. Among stereoisomeric salts, the *trans* compound is photochemically the more stable. The velocity of reaction is about  $1\frac{1}{2}$  times as great in acid as in neutral solution and is largely independent of the hydrogen-ion concentration. H. W.

**Chemistry of High Temperatures.** H. VON WARTENBERG (*Z. Elektrochem.*, 1924, 30, 351—356).—Chiefly speculative. After reviewing some of the principal reactions of compounds of the commoner elements between  $2000^{\circ}$  and  $3000^{\circ}$ , the author speculates on the probable course of certain reactions above  $5000^{\circ}$ . A. R. P.

**Induced Reactions and Diabetes from the Point of View of Induced Oxidation.** N. M. MITTRA and N. R. DHAR (*J. Physical Chem.*, 1925, 29, 376—394).—Although mercuric chloride is not reduced by solutions of sodium arsenite alone, yet in the presence of another reducing agent such as sodium sulphite, sodium phosphite, or formic acid, it is reduced by both simultaneously. Similarly, it is possible to oxidise solutions of sodium nitrite, potassium oxalate, sodium arsenite, or nickelous hydroxide by air or oxygen when in the presence of sodium sulphite, which in its turn is itself oxidised. The amount of oxidation of nickelous hydroxide induced by the presence of cobaltous hydroxide increases with the concentration of sodium hydroxide to a maximum and then falls with further increase in alkali. Dextrose can be oxidised by passing air through solutions which also contain sodium sulphite. These induced oxidations are due to the formation of active oxygen

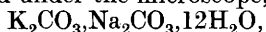
molecules in one reaction, which are then capable of reacting with the second substance present. Diabetes is due to insufficient oxidation of dextrose and fat in the human body, and the action of insulin etc. is to induce this oxidation in a similar manner to the reactions which have been investigated. The author suggests that iron preparations should be helpful in the treatment of diabetes.

M. B. D.

**Reduction of Metals from their Salts by Means of Other Metals in Liquid Ammonia Solution.** C. A. KRAUS and H. F. KURTZ (*J. Amer. Chem. Soc.*, 1925, **47**, 43—60).—When a metallic salt is added to a solution of a more electropositive metal in ammonia, precipitation of the metal (from the salt), either alone or as a compound with the other, may occur. The theory of the various possible cases is fully discussed. Salts of mercury, cadmium, zinc, tin, lead, antimony, bismuth, and thallium reduced thus by sodium all give compounds with sodium, but silver is precipitated alone. Some of the intermediate compounds of sodium with mercury, tin, and lead are not stable in contact with the solutions, but decompose to compounds poorer in sodium. Mercuric ethyl chloride, by the same treatment (with excess of sodium), gives the compound NaHg, identical with that obtained by reducing ordinary mercury salts. Data are also given for the reduction of some salts by calcium, compounds being obtained. Numerical data suggest the formation of compounds having the formulæ NaCd, NaZn<sub>4</sub>, Na<sub>4</sub>Sn, Na<sub>4</sub>Pb, Na<sub>3</sub>Tl<sub>2</sub>, CaAg, Ca<sub>7</sub>Zn, Ca<sub>3</sub>Hg<sub>2</sub>, Ca<sub>2</sub>Pb<sub>3</sub>, Ca<sub>5</sub>Sn.

L. J. H.

**Double Salts formed by Sodium and Potassium Carbonates.** J. W. BAIN (*Univ. Toronto, Sch. Eng. Res. Bull.*, 1925, **5**, 123—124).—Attempts to prepare crystals of the supposed double salt, K<sub>2</sub>CO<sub>3</sub>.3Na<sub>2</sub>CO<sub>3</sub>.10H<sub>2</sub>O (cf. Bain and Oliver, A., 1917, ii, 87), by the evaporation of solutions of varying concentration at temperatures above 35° have proved unsuccessful, and the isothermal diagram of the solubilities of potassium and sodium carbonates at 40° exhibits no indication of a double salt, unless the intersections are very obtuse. When heated under the microscope, the double salt,



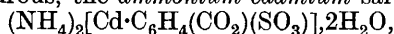
yields small needles at 35°, but these appear to consist of Na<sub>2</sub>CO<sub>3</sub>.2H<sub>2</sub>O.

T. H. P.

**Interaction of Sodium Chloride and Alumina.** F. H. CLEWS (*J. Chem. Soc.*, 1925, **127**, 735—739).—The following reactions occur when sodium chloride and alumina are heated together: (a)  $4x\text{NaCl} + y\text{Al}_2\text{O}_3 + x\text{O}_2 = 2x\text{Na}_2\text{O} + y\text{Al}_2\text{O}_3 + 2x\text{Cl}_2$ ; (b)  $2x\text{NaCl} + y\text{Al}_2\text{O}_3 + x\text{H}_2\text{O} = x\text{Na}_2\text{O} + y\text{Al}_2\text{O}_3 + 2x\text{HCl}$ ; (c)  $4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$ . Reaction (b) always predominates, the chlorine being due to (c) rather than (a). The yield of hydrogen chloride and chlorine passes through a maximum as the proportion of sodium chloride increases. Reaction (b) is practically complete above 1000° when water is continuously supplied. Equilibrium in the solid phase at 830° is imperfectly attained when the quantities of water and hydrogen chloride are varied. The stability of sodium aluminate

with reference to hydrogen chloride decreases rapidly when the molecular ratio  $\text{Al}_2\text{O}_3:\text{Na}_2\text{O}$  is less than 10:1 at  $1045^\circ$  or 12:1 at  $830^\circ$ . For the complete interaction of alumina and sodium chloride in the presence of water excess of the first-named is more important than excess of water. S. K. T.

**Complexes with Two Unsymmetrical Co-ordination Valencies.** F. L. HAHN and H. WOLF (*Z. anorg. Chem.*, 1925, 144, 117—127).—It is proposed to substitute for the phrase "having the co-ordination number  $n$ " the description " $n$ -numbered." A four-numbered complex should give rise to *cis-trans* isomerism or optically active isomerides, according to the disposal of the co-ordination linkings. In this class, the following double salts have been examined: *ammonium copper o-sulphobenzoate*, bluish-green rosettes, anhydrous, the *ammonium cadmium salt*,



and the *ammonium zinc salt* ( $+1\cdot5\text{H}_2\text{O}$ ); *dipyridine copper sulphoacetate*, and the *diammonium sulphoacetates* of copper, zinc, nickel, and cobalt; the *manganese* and *cadmium* salts of this series partly dissociate in solution. The simple *sulphoacetates* of potassium, sodium, and ammonium (anhydrous), *magnesium*, *zinc*, *cadmium*, *cobalt*, and *nickel* (with  $3\text{H}_2\text{O}$ ), *copper* ( $+1\text{H}_2\text{O}$ ), and *manganese* ( $+2\text{H}_2\text{O}$ ) are described. Determinations of molecular weights by the cryoscopic method in aqueous solution indicate that copper sulphobenzoate and the sulphoacetates of zinc, cadmium, and manganese are all considerably dissociated; the apparent absence of dissociation of copper sulphoacetate is attributed to equilibrium between association and dissociation. The equivalent conductivities of some of the simple sulphoacetates are recorded.

A number of *compounds* of 2-acetamidopyridine with the sulphates, chlorides, and nitrates of bivalent heavy metals have been prepared. S. I. L.

**Effect of Colloids in the Displacement of Lead and Copper from their Salts by Zinc.** L. T. M. GRAY (*J. Chem. Soc.*, 1925, 127, 776—780).—In the presence of colloids (gelatin, gum arabic, and glue) the size of the lead crystals deposited diminishes fairly steadily throughout, but the cohesive power increases up to a certain point and then diminishes; this maximum was not shown in the case of gum arabic. This effect on the cohesive power is ascribed to a film of adsorbed colloid. The same results were obtained in the case of copper and gelatin. In the experiments on copper with glue, the decrease in the size is apparently the decisive factor. The deposit deteriorates with time of contact owing to the continued adsorption of the colloid. The best deposits were obtained with a concentration of 0.0020—0.0026*M* copper sulphate and in the presence of 0.6—0.8% of boric acid. Mechanical cleaning of the zinc strip with fine emery paper gave better results than treatment with acid or alkali. W. T.

**Ageing of Metallic Hydroxides.** R. FRICKE (*Z. Elektrochem.*, 1924, 30, 393—396).—Gallium hydroxide, precipitated by the calculated amount of alkali, always retains more water than corresponds

with  $\text{Ga}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , even after prolonged drying in the air. The actual proportion of water retained varies with the method and conditions of preparation; less water is retained the higher the temperature of precipitation and the longer the precipitate is washed. The solubility of the compound in alkali hydroxide solutions decreases with decreasing water content and with increasing alkali concentration of the solution. A cold saturated solution of freshly-precipitated gallium hydroxide in alkali hydroxide solution slowly deposits gallium hydroxide on keeping. Potassium hydroxide dissolves less gallium hydroxide than does sodium hydroxide and a greater proportion of the gallium is precipitated on keeping. The colour of ferric hydroxide varies considerably with the method of precipitation; this is apparently due to the varying amounts of water retained by the precipitate, light coloured precipitates retaining a greater proportion of water than those more deeply coloured.

A. R. P.

**Lanthanum Thallous Sulphates.** F. ZAMBONINI and G. CAROBBI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 278—283; cf. this vol., ii, 222).—Investigation of the system lanthanum sulphate-thallous sulphate-water shows the existence at  $25^\circ$  of the compounds:  $\text{La}_2(\text{SO}_4)_3 \cdot 4 \cdot 5\text{Tl}_2\text{SO}_4$ ;  $\text{La}_2(\text{SO}_4)_3 \cdot 3\text{Tl}_2\text{SO}_4$ ;  
 $\text{La}_2(\text{SO}_4)_3 \cdot \text{Tl}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .

T. H. P.

**Transformations of Carbon Monoxide under the Influence of the Silent Electric Discharge.** E. OTT (*Ber.*, 1925, 58, [B], 772—775).—The primary change of carbon monoxide under the influence of the silent electric discharge proceeds according to the scheme  $4\text{CO} = \text{C}_3\text{O}_2 + \text{CO}_2$ . The carbon suboxide subsequently becomes polymerised to a degree which depends on the intensity of the discharge; in a 10-tube Siemens ozoniser it yields an ochre-yellow deposit, whereas in a single tube the deposit is dark brown and resembles that obtained by the thermal decomposition of carbon monoxide.

H. W.

**Interaction of Carbon Dioxide and Hydrogen in the Corona due to Alternating Currents of High Frequency.** R. W. LUNT (*Proc. Roy. Soc.*, 1925, A, 108, 172—186).—With a frequency  $1 \cdot 5 \times 10^7$ , approximately equimolecular mixtures of carbon dioxide and hydrogen interact in the corona to give a water-gas equilibrium. The same result is obtained by exposing mixtures of carbon monoxide and water vapour to the discharge. Experiments in which the carbon dioxide content of the initial gas mixture was varied over the range 11—100% show that in the range  $\text{CO}_2 < 50\%$  some of the carbon monoxide is reduced to methane, but in no case was it possible to detect formaldehyde or formic acid.

J. S. C.

**Oxides, Metals, and Carbides at High Temperatures.** O. RUFF (*Z. Elektrochem.*, 1924, 30, 356—364).—A review of the reactions of oxides and carbides of some of the commoner and rarer metals such as thorium, zirconium, calcium, silicon, and tungsten, together with speculations on the probable behaviour of some of these compounds at very high temperatures. **Alumina**



and zirconia are more resistant to reduction above  $2000^{\circ}$  than are thorium and silica, but both are readily attacked by lime and magnesia at this temperature. Lists of m. p. of refractory oxides, carbides, and metals are given and the mechanism of the formation of calcium carbide and of its reactions at high temperatures is discussed.

A. R. P.

**Silicates.** W. EITEL (*Z. Elektrochem.*, 1924, **30**, 364—370).—A review of the work of other investigators on the systems  $\text{SiO}_2\text{--Al}_2\text{O}_3$ ,  $\text{MgO--SiO}_2$ ,  $\text{CaO--SiO}_2$ ,  $\text{CaO--Al}_2\text{O}_3\text{--SiO}_2$ , diopside-anorthite-albite, anorthite-forsterite-quartz,  $\text{SiO}_2\text{--K}_2\text{SiO}_3\text{--H}_2\text{O}$ ,  $\text{CaCO}_3\text{--nepheline}$ . A bomb furnace for the examination of the equilibrium between carbonates and silicates under pressure is described and illustrated.

A. R. P.

**Silicates. III. Action of Magnesium, Calcium, and Barium Oxides on Silicates at High Temperatures and the Preparation of Metallic Iron from Silicates.** G. TAMMANN and C. F. GREVEMEYER (*Z. anorg. Chem.*, 1924, **136**, 114—120).—Orthoclase, leucite, nepheline, hornblende, and willemite were heated at temperatures up to  $1000^{\circ}$  with magnesium, calcium, and barium oxides equivalent to the silica content of the mineral. Magnesium oxide had no action on any of the minerals, calcium oxide reacted slowly above  $500^{\circ}$  with all, the reactions with leucite and nepheline being the most energetic. Barium oxide attacked silicates containing alumina at  $275^{\circ}$  and those free from alumina at  $350^{\circ}$ ; the action was much more energetic when the barium oxide contained a small proportion of water, but in no case was complete decomposition obtained and in no case did fusion ensue at  $1000^{\circ}$ , the particles of mineral simply becoming coated with a protective layer of partly fused barium compound. Fusion of hornblende at  $1400^{\circ}$  with barium oxide equivalent to the silica content and with carbon sufficient to reduce the iron resulted in the production of 62% of the theoretical quantity of iron together with a fluid barium silicate slag.

A. R. P.

**Fusion of Rare-metal Ores. I. Pyrosulphate Fusion of Titanium Ores.** G. W. SEARS and L. QUILL (*J. Amer. Chem. Soc.*, 1925, **47**, 922—929).—Complete decomposition of rutile and dissolution of the titanium content are only obtained when at least 12.5 parts of sodium pyrosulphate are used to 1 part of ore. A higher ratio is required when elements with high-melting sulphates are present. Sufficient pyrosulphate must be used to keep the fused mass below  $700^{\circ}$ , since above this temperature normal titanium sulphate is converted into an insoluble basic salt; this behaviour is probably common to all the less basic rare metals. Sodium pyrosulphate is somewhat more efficient than the potassium salt.

S. K. T.

**Rare Earths. XVIII. Preparation and Properties of Cerium-free "Misch Metal."** A. P. THOMPSON and H. C. KREMERS (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 207—212).—Cerium-free "misch metal" was prepared by removing cerium from

a rare-earth mixture by precipitation as  $\text{CeO}_2$  and electrolysing the fused chlorides of the remaining metals in iron cells with carbon anodes. Two products, *A* and *B*, were obtained, the percentages of iron being 11.8 and 32.0, respectively. The metal is white, tarnishes in air, and is brittle; m. p. *A*,  $975^\circ$ ; *B*,  $1050^\circ$ ;  $d^{15}$ , *A*, 6.96; kindling temperature, *A*,  $195^\circ$ ; *B*,  $280^\circ$ . The metal is pyrophoric and *A* shows a lower kindling temperature than a sample of commercial "misch metal," despite the absence of cerium. N. H. H.

**Rare Earths. XIX. Preparation and some Properties of Metallic Cerium.** H. C. KREMERS and H. BEUKER (*Trans. Amer. Electrochem. Soc.*, 1925, **47**, 213—230).—Cerium free from iron was prepared by electrolysing the fused chloride in graphite cells with carbon anodes. The metal corrodes easily in dry air. It is highly malleable and ductile. The following physical constants were redetermined:  $d^{15}$  (in absolute alcohol) 6.77; Brinell hardness (500 kg. weight) 21; heat of combustion 1.661 cal./g.; kindling temperature,  $165^\circ$ . The pure metal is moderately pyrophoric; it shows promise as a means of removing oxygen from partially evacuated tubes. N. H. H.

**Dehydration of Ammonium Nitrate.** T. L. DAVIS and A. J. J. ABRAMS (*J. Amer. Chem. Soc.*, 1925, **47**, 1043—1045).—The results of Pelouze's experiments on heating ammonium nitrate with sulphuric acid (*Ann. Chim. Phys.*, 1841, [iii], **2**, 47) may be explained by assuming the intermediate formation of nitroamide. Further experiments are described in support of this view; lower yields of nitrous oxide are obtained when meta- or ortho-phosphoric acid is used in place of sulphuric. S. K. T.

**Interaction of Nitrogen Sulphide and Sulphur: Nitrogen Persulphide.** F. L. USHER (*J. Chem. Soc.*, 1925, **127**, 730—735).—Sublimation of nitrogen sulphide containing free sulphur over silver gauze at about  $125^\circ$  yields a film of a ruby-red compound which turns deep blue on keeping ( $\frac{1}{2}$  hr.—2 days) or on warming at  $50^\circ$ , and behaves like blue nitrogen sulphide (Burt, T., 1910, **97**, 1171). Nitrogen sulphide free from sulphur yields directly the blue compound, from which the ruby compound could never be obtained. These modifications are considered to be produced from different intermediate volatile nitrogen sulphides, the one giving rise to the ruby compound being formed by the decomposition of *nitrogen persulphide*,  $\text{NS}_2$ , by silver. Nitrogen persulphide is obtained as a dark red liquid, resembling bromine, and solidifying to a pale yellow solid at the temperature of solid carbon dioxide, by subliming nitrogen sulphide with sulphur at  $125^\circ$  in the absence of silver gauze. It has a penetrating odour like that of iodine and can be distilled unchanged in a vacuum. At the ordinary temperature it decomposes slowly into sulphur and yellow nitrogen sulphide. Water decomposes it into ammonium salts and free sulphur. It is more volatile than the sulphide  $\text{N}_4\text{S}_4$ ; hydrogen sulphide decolorises an ethereal solution with probable formation of a thio-acid of nitrogen. S. K. T.

**Synthetic Praseodymiferous Chlorovanadinite.** G. CAROBBI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 311—315).—Fusion of a mixture of 10 g. of lead vanadate, 2 g. of lead chloride, and 1 g. of praseodymium vanadate results in the formation of a crystalline chlorovanadinite containing praseodymium vanadate (3.34%) in place of part of the lead vanadate,  $3(\text{Pb, Pr})_3(\text{VO}_4)_2\text{PbCl}_2$ . The fact that, under these experimental conditions, quinquevalent praseodymium isomorphous with quinquevalent vanadium is incapable of existence, fails to support the arrangement of the rare earths in the periodic system proposed by Prandtl and Grimm (A., 1924, ii, 615).  
T. H. P.

**Preparation of Intermetallic Compounds by the Wet Method.** A. MAZZUCHELLI and A. VERCILLO (*Atti R. Accad. Lincei*, 1925, [vi], 1, 233—235; cf. A., 1924, ii, 119).—A 35% solution of antimony trichloride in dilute hydrochloric acid (1:1) is practically inert towards copper at the ordinary temperature, but at 100° deposits on it a thin, adherent, metallic film, which stops further action. If, however, the liquid contains a considerable amount of cuprous chloride, the action at 100° becomes continuous and leads to the formation of the compound,  $\text{Cu}_2\text{Sb}$ . Under similar conditions, treatment of tin with a mixture of cuprous and stannous chlorides yields an alloy with  $\text{Sn} : \text{Cu} = 1 : 6$ , possibly consisting of the compound  $\text{Cu}_3\text{Sn}$  covered with granules of copper; antimony trichloride and tin give the alloy  $\text{Sb}_2\text{Sn}$ ; arsenic trichloride and copper, the compound  $\text{As}_2\text{Cu}_3$ ; telluric chloride and copper, a compound having the composition  $\text{Te}_3\text{Cu}_2$ , but consisting probably of a mixture of  $\text{TeCu}$  or  $\text{TeCu}_2$  with tellurium; tellurium chloride and lead give, not the compound  $\text{PbTe}$ , but pure tellurium. Neither bismuth chloride and antimony nor antimony chloride and bismuth yield antimony-bismuth alloys. The results obtained are discussed in relation to the considerations advanced by Mylius and Fromm (A., 1894, ii, 235).  
T. H. P.

**Reactions in Liquid Hydrogen Sulphide.** G. N. QUAM (*J. Amer. Chem. Soc.*, 1925, 47, 103—108).—A simple method of preparing pure liquid hydrogen sulphide is described. The reactions of a large number of organic and inorganic substances in contact with liquid hydrogen sulphide over a long period of time (months) and over a wide temperature range (usually at the ordinary temperature) are described, the substances being tabulated as regards their solubility and/or reactivity. Many reactions took place very slowly. Oxidising salts all react and cause the separation of free sulphur. The existence of the hydrate,  $\text{H}_2\text{S} \cdot 6\text{H}_2\text{O}$  (Scheffer and Meijer, A., 1919, ii, 502), is confirmed. Dry sulphur dioxide reacts vigorously with liquid hydrogen sulphide; bismuth trichloride forms the compound  $\text{BiSCl}$ .  
L. J. H.

**Reducing Action of Sodium Hyposulphite in Alcoholic Solution.** L. EYMER (*Rev. gén. Mat. Col.*, 1925, 39, 96—97).—When cotton dyed with a red direct cotton dye or indigo is introduced together with 5 c.c. of water into a boiling mixture of 50 mg.

of dry sodium hyposulphite and 15 c.c. of alcohol, the resulting mixture continues to boil smoothly, hydrogen sulphide is evolved, and the cotton is completely decolorised. Under similar conditions, the alcohol being replaced by an equal volume of water, the resulting mixture commences to boil vigorously, sulphur dioxide is liberated, but no decolorisation of the dyed cotton occurs. The effect of the alcohol is evident only when the reducing mixture contains 70—95% of alcohol, but decolorisation occurs most easily in 82% alcohol, and is probably due to its solvent action on the products of decomposition. The addition of alcohol to an aqueous solution of sodium hyposulphite does not increase its reducing action on dyed cotton.

A. J. H.

**Preparation of Selenides from Hydrogen Selenide and Solutions of Metallic Salts.** L. MOSER and K. ATYNSKI (*Monatsh.*, 1925, 45, 235—250; cf. Fonzes-Diacon, A., 1900, ii, 345, 348, 402, 405, 546, 730; 1901, ii, 22, 60, 100).—Pure hydrogen selenide, prepared by the action of hydrochloric acid on magnesium selenide in an apparatus specially devised to prevent admixture with air, was continuously passed into an enclosed volume of water. Solutions of metallic salts were added drop by drop to the saturated solution, which was mechanically stirred. Under these conditions, the metallic selenides were always produced in the presence of excess of hydrogen selenide and no excess of metallic ions (which frequently act as reducing agents) were at any time in the solution. In this way, deposition of metal and formation of complexes and double salts which might veil the primary reaction were avoided. In the purification and analysis of the selenides so obtained, air was carefully excluded at every stage, the operations of filtration, washing, and dissolving being always carried out in an indifferent atmosphere. Analytical results showed that previously described selenides were often mixtures containing selenium to which the ascribed colour is due (the sodium and potassium selenides described by Berzelius as red are actually pure white). The following *selenides* are described: *ferrous*, FeSe, black, becoming brown by oxidation in air; *ferric selenide* could not be prepared in the pure state; *manganous*, MnSe, reddish-yellow (cf. Fonzes-Diacon, *loc. cit.*); *nickelous*, NiSe, black; unlike the sulphide, it shows no tendency to form a colloidal solution; *cobaltous*, CoSe, similar to that of nickel; *zinc*, ZnSe, lemon-yellow, decomposes on drying. Selenides of chromium, aluminium, and uranium cannot be prepared in the wet way; Berzelius' statement that a dark red aluminium selenide is formed from hydrogen selenide and a solution of an aluminium salt is inaccurate. *Molybdenum*, MoSe<sub>3</sub>, dark brown, dissolves in alkali sulphides and selenides with formation of double salts. *Tungsten*, WSe<sub>3</sub>, black; *thallium*, Tl<sub>2</sub>Se, bluish-black. Silver, Ag<sub>2</sub>Se, black, unstable, losing selenium on drying, soluble in alkali hydroxides, sulphides, and selenides; forming complex compounds. *Mercuric*, HgSe, black (double salt HgCl<sub>2</sub>·2HgSe); with solutions of mercurous salts, a mixture of mercuric selenide and selenium is precipitated. *Lead*, PbS, black, on account of its insolubility

and the speed of reaction of lead salts with hydrogen selenide, is preferred to the silver salt for both detection and determination of the gas. *Bismuth*,  $\text{Bi}_2\text{Se}_3$ ; *cuprous*,  $\text{Cu}_2\text{Se}$ , from a solution of a potassium cuprous salt, brown or black (cf. Fonzes-Diacon, *loc. cit.*); oxygen converts the selenide into  $\text{CuSeO}_3$ . *Cupric*,  $\text{CuSe}$ , black, becomes green by oxidation in air. *Cadmium*,  $\text{CdSe}$ , dark brown, is moderately stable (yellow double salt,  $3\text{CdSe}$ ,  $\text{CdI}_2$ ). *Arsenious*,  $\text{As}_2\text{Se}_3$ , dark reddish-brown, unstable, is soluble in alkali selenides, ammonium carbonate, and ammonium hydroxide, with formation of dark brown complex compounds. *Arsenic*,  $\text{As}_2\text{Se}_5$ , brownish-red, is similar to the trisulphide. *Antimonious*,  $\text{Sb}_2\text{Se}_3$ , dark brown, is soluble in alkali sulphides and selenides. Antimonic selenide could not be prepared. *Stannous*,  $\text{SnSe}$ , black, is fairly stable; *stannic*,  $\text{SnSe}_2$  is dark reddish-brown. *Aurous*,  $\text{Au}_2\text{Se}$ , black, is very unstable (complex potassium salt). *Auric*,  $\text{Au}_2\text{Se}_3$ , black. *Platinic*,  $\text{PtSe}_2$ , black, unstable, forms complex salts with alkali sulphides and selenides; *palladous*,  $\text{PdSe}$ , is dark brown. In general, the metal selenides correspond in composition with the sulphides, are much less stable, oxidise quickly in air, and cannot be dried without decomposition. The deeper colour of the selenides compared with the sulphides is attributed to the higher atomic weight of selenium.

A. C.

**Double Selenates of Thallous Selenate and the Selenates of Bivalent Metals.** L. C. LINDSLEY and L. M. DENNIS (*J. Amer. Chem. Soc.*, 1925, 47, 377—379).—Double selenates of the formula  $\text{Th}_2\text{SeO}_4 \cdot \text{M}''\text{SeO}_4 \cdot 6\text{H}_2\text{O}$  with copper, cobalt, nickel, magnesium, and manganese were prepared and analysed. They are isomorphous with the corresponding double sulphates, the acute angles being about  $40^\circ$  greater with a corresponding decrease in the obtuse angles.

L. J. H.

**Dithiomolybdates.** H. TER MEULEN (*Chem. Weekblad*, 1925, 22, 218—220).—Ammonium dithiomolybdate is readily obtained pure by the method of Krüss (A., 1884, 1268). When boiled with dilute hydrochloric acid, it yields molybdenum trisulphide:— $3(\text{NH}_4)_2\text{MoO}_2\text{S}_2 + 6\text{HCl} = 2\text{MoS}_3 + \text{MoO}_3 + 6\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$ ; the oxy-sulphide,  $\text{MoO}_2\text{S}$ , is obtained by the action of sodium sulphide on the oxychloride in absolute alcohol. If acetic acid is used in place of hydrochloric to decompose the dithiomolybdate, stable colloidal solutions of the trisulphide are obtained. The fusion of sodium carbonate and the trisulphide or tetrathiomolybdate also yields the dithio compound,  $\text{MoS}_3 + 2\text{Na}_2\text{CO}_3 = \text{Na}_2\text{MoO}_2\text{S}_2 + \text{Na}_2\text{S} + 2\text{CO}_2$ .

S. I. L.

**Silicododecatungstic Acid.** E. O. NORTH and G. D. BEAL.—(See ii, 607.)

**Potentiometric Study of the Reaction between Chlorine Water and Iodide Ion.** E. MÜLLER and D. JUNCK (*Z. Elektrochem.*, 1925, 31, 206—209).—The potentiometric titration of chlorine water with potassium iodide and *vice versa* cannot be carried out with great accuracy, since chlorine escapes during the titration. A series of such titrations has, however, served to throw light on

the course of the reaction between chlorine and iodide ion. In the titration of chlorine water with potassium iodide alone or in the presence of sulphuric acid, the curve shows two breaks which correspond with the reaction  $3\text{Cl}_2 + \text{I}' + 3\text{H}_2\text{O} = \text{IO}_3' + 6\text{HCl}$ , followed by  $\text{IO}_3' + 5\text{I}' + 6\text{HCl} = 3\text{I}_2 + 3\text{H}_2\text{O} + 6\text{Cl}'$ . In the presence of hydrochloric acid, the reaction proceeds in the three stages:  $3\text{Cl}_2 + \text{I}' + 3\text{H}_2\text{O} = \text{IO}_3' + 6\text{H}' + 6\text{Cl}'$ ;  $\text{IO}_3' + 2\text{I}' + 3\text{Cl}' + 6\text{H}' = 3\text{ICl} + 3\text{H}_2\text{O}$ ;  $3\text{ICl} + 3\text{I}' = 3\text{I}_2 + 3\text{Cl}'$ . In the titration of potassium iodide solution with chlorine water, alone or in the presence of sulphuric acid, two breaks are observed, the first corresponding with complete displacement of the iodine and the second with the reaction  $\text{I}_2 + 6\text{H}_2\text{O} + 5\text{Cl}_2 = 2\text{IO}_3' + 12\text{H}' + 10\text{Cl}'$ . In the presence of hydrochloric acid, the reactions are  $\text{I}_2 + \text{Cl}_2 = 2\text{ICl}$ ;  $2\text{ICl} + 4\text{Cl}_2 + 6\text{H}_2\text{O} = 2\text{HIO}_3 + 10\text{H}' + 10\text{Cl}'$ .  
N. H. H.

**Potentiometric Study of the Reduction of Iodate with Iodide.** E. MÜLLER and D. JUNCK (*Z. Elektrochem.*, 1925, **31**, 200—206).—An accurate potentiometric titration of the reduction of potassium iodate with potassium iodide in the presence of hydrochloric acid may be made provided that the acid concentration is not too high. With low concentrations of acid, the curves show one break corresponding with complete reduction. With intermediate concentrations, two breaks are observed, which correspond with the consecutive reactions (i)  $\text{IO}_3' + 2\text{I}' + 6\text{H}' + 3\text{Cl}' = 3\text{ICl} + 3\text{H}_2\text{O}$  and (ii)  $3\text{ICl} + 3\text{I}' = 3\text{I}_2 + 3\text{Cl}'$ . Titrations could therefore be made with 0.4 of the usual quantity of iodide, but since with higher concentrations of acid low results are obtained for both breaks, it is considered safer to work with low concentrations and titrate to the stage of complete reduction. These complications are avoided to a very large extent if sulphuric acid be used, since its range of permissible concentration is greater and the formation of iodine chloride is impossible. In the reverse titration of iodide with iodate, the presence of too much hydrochloric acid obscures the stage of complete reduction, but on further addition of iodate a good value is obtained for the completion of the reaction corresponding with (i) above. Here also the use of sulphuric acid is recommended, however.

In the titration of potassium periodate with potassium iodide in sulphuric acid and in low concentrations of hydrochloric acid, only one break, corresponding with complete reduction, is observed, and it is more marked in the first instance. With high concentrations of hydrochloric acid, there are two breaks, corresponding with the stages  $\text{IO}_4' + 3\text{I}' + 8\text{H}' + 4\text{Cl}' = 4\text{ICl} + 4\text{H}_2\text{O}$  and  $4\text{ICl} + 4\text{I}' = 4\text{I}_2 + 4\text{Cl}'$ . The reverse titration gives results analogous to those observed with the iodate.  
N. H. H.

**Reduction of Permanganic Acid by Arsenious Acid and Mechanism of the Oxidation of Manganous Salts to Permanganic Acid.** A. TRAVERS (*Bull. Soc. chim.*, 1925, [iv], **37**, 456—471).—Permanganic acid is reduced by arsenious oxide in presence of sulphuric or nitric acid to a manganic salt and manganese dioxide. In presence of hydrofluoric, phosphoric, or arsenic acid the

whole of the manganese may be converted into the corresponding manganic salt. Reduction to manganous salts occurs in presence of a considerable excess of arsenious oxide.

*Manganic fluoride, orthophosphate, metaphosphate, and ortho-arsenate* are described. Aqueous solutions of these salts are quite stable in presence of the corresponding acids. The fluoride is very slightly ionised in aqueous solution.

The oxidation of manganous salts to permanganates in presence of silver nitrate and ammonium persulphate has been investigated. On mixing cold concentrated solutions of silver nitrate and ammonium persulphate, a crystalline precipitate,  $3\text{Ag}_2\text{O}_3 \cdot \text{AgNO}_3$ , is obtained, which in acid solutions evolves ozone and oxidises manganous salts to permanganates. The oxidation may be effected by persulphate alone in presence of hydrofluoric, phosphoric, or arsenic acid, or of sulphuric or nitric acid to which a little hydrofluoric acid has been added. If the acidity of the oxidising medium is considerable, the process is reversed, the permanganic acid being reduced to manganous salt. Excess of an alkali fluoride arrests the oxidations at the stage of manganic salts, the double salts of the type  $\text{MnF}_3 \cdot 2\text{NaF}$  resisting all attempts at further oxidation.

Evidence is brought forward in favour of the view that silver peroxide or ammonium persulphate in presence of acids furnishes ozone, which is responsible for the oxidation. The subsequent reduction in strongly acid solutions is attributed to the action of hydrogen peroxide resulting from the decomposition of Caro's acid, which is formed in appreciable amounts in such solutions.

J. S. C.

**Influence of Neutral Salts on the Reaction between Ferric Chloride and Stannous Chloride.** W. F. TIMOFEEV, G. E. MUCHIN, and W. G. GUREVITSCH (*Z. physikal. Chem.*, 1925, **115**, 161—176).—Neutral salts accelerate the oxidation of stannous chloride by ferric chloride. The effects of dilute solutions of sodium, potassium, and ammonium ions of the same concentrations, and of barium ions of half these concentrations, are equal, the action here thus depending solely on the valency of the ions. The acceleration due to cadmium chloride is, however, much less. The effect of continued additions of sodium chloride is not proportional to the amounts added. The reaction velocity at first increases rapidly, but afterwards slowly approaches a limiting value, attained in saturated sodium chloride solution; at the same time, the reaction changes slowly from the third to the second order. The temperature coefficient of the reaction and its change on additions of sodium chloride has been ascertained.

L. F. G.

**Potassium Chlororuthenites.** R. CHARONNAT (*Compt. rend.*, 1925, **180**, 1271—1273; cf. Howe, A., 1902, ii, 86; 1904, ii, 490, 665; Miolatti, A., 1902, ii, 246; Gutbier, A., 1921, ii, 457; Aoyama, A., 1924, ii, 771; Krauss, A., 1924, ii, 196, 770, 772; Charonnat, A., 1924, i, 706).—The complex salts of ruthenium and potassium chlorides with water which could not be formulated on Werner's theory are not, in fact, anomalous. The brown salt,  $\text{K}_2\text{Ru}^{\text{III}}\text{Cl}_5 \cdot \text{H}_2\text{O}$ ,

and the red salt,  $K_2Ru(H_2O)Cl_5$ , are not isomerides, but differ in respect of ruthenium valency. The brown salts contain less water than is indicated by the formula; the alkali salts are not transformed by chlorine into hexachlororuthenates. The red salts are only formed from the brown ones by the prolonged action of reducing agents; they lose a molecule of water between  $140^\circ$  and  $180^\circ$ , and are easily converted into hexachlororuthenates by chlorine. The red salts are, in fact, aquochlororuthenites,  $[Ru^{III}(H_2O)Cl_5]X_2$ , and the brown salts are hydroxychlororuthenates,  $[Ru^{IV}(OH)Cl_5]X_2$ . The valency of the ruthenium in the red salt is settled by its preparation from potassium ruthenotrioxalate,  $[Ru^{III}(C_2O_4)_3]K_3$ . The brown but not the red salts liberate iodine from potassium iodide and hydrochloric acid.

R. A. M.

**Production of Active Hydrogen.** H. COPAUX, H. PERPEROT, and R. HOCART (*Bull. Soc. chim.*, 1925, [iv], 37, 141—153).—Several substances were tested as a means of measuring activation, tungsten trioxide proving the best. The extent of reduction suffered is measured by direct titration (Fontès and Thivolle, cf. A., 1923, ii, 264). Electrical activation is very small at atmospheric pressure. Activation by passage over a catalyst did not occur (cf. Mitchell and Marshall, T., 1923, 123, 2448).

L. J. H.

**Preparation of Hydroxylamine.** C. DE W. HURD and H. J. BROWNSTEIN (*J. Amer. Chem. Soc.*, 1925, 47, 67—69).—Hydroxylamine is formed in butyl alcohol solution from the hydrochloride and sodium butoxide; after filtration from sodium chloride, the hydroxylamine is crystallised by cooling in an ice-salt mixture. The yield is 50%. Methods of recovery of the remainder are suggested.

L. J. H.

**Preparation of Nitroxyl Chloride and Bromide and their Action on Grignard's Reagent.** N. ZUSKINE (*Bull. Soc. chim.*, 1925, [iv], 37, 187).—Nitroxyl chloride,  $NO_2Cl$ , may be prepared by the action of phosphorus oxychloride on nitric acid; nitroxyl bromide by passing nitrogen dioxide and bromine vapour over a catalyst of calcined bone at  $200$ — $250^\circ$ . With Grignard's reagent, the corresponding nitrogen compounds are not formed, but, e.g., diphenyl with some chlorinated (or brominated) benzene.

L. J. H.

**Large-scale Preparation of Sodium Amalgam in the Laboratory.** R. R. READ and C. LUCARINI (*Ind. Eng. Chem.*, 1925, 17, 480).—The amalgam is prepared by adding the mercury to the melted sodium under toluene. A steel mercury flask is used from which the top has been cut and two holes bored in it (for a thermometer and stirrer and for introduction of the mercury). The top is replaced after introduction of the sodium and toluene and before applying heat.

D. G. H.

**Magnetic Ferric Oxide.** H. ABRAHAM and R. PLANIOL (*Compt. rend.*, 1925, 180, 1328—1329).—Ferric oxide can be prepared in two interconvertible forms, magnetic and non-magnetic.



The ordinary oxide (colcothar) is red and non-magnetic. The other form is brownish-yellow and nearly as strongly ferromagnetic as magnetite. The red oxide is reduced at  $500^{\circ}$  by hydrogen or carbon monoxide to magnetite,  $\text{Fe}_3\text{O}_4$ . This burns in air to give the non-magnetic ferric oxide; slow oxidation by a current of air at  $200$ — $250^{\circ}$  gives the magnetic variety, which is stable at the ordinary temperature. The magnetic property is not lost at  $600^{\circ}$ , but at  $700^{\circ}$  transformation to the red, inactive form is rapid and complete. The two ferric oxides, magnetic and non-magnetic, may correspond with two series of ferric salts.

R. A. M.

**Rare Earths. XX. Preparation and Properties of Metallic Neodymium.** H. C. KREMERS (*Trans. Amer. Electrochem. Soc.*, 1925, 47, 221—227).—Reduction of neodymium chloride by means of sodium gave an impure metal powder. Electrolysis of the oxide in fused cryolite gave alloys containing much aluminium. A fused mixture of neodymium fluoride and potassium fluoride in proportions corresponding with the cryolite molecule was used as solvent for the oxide, but gave bad yields. Larger quantities of the metal containing 3% of iron were prepared by electrolysis of the fused chloride with small amounts of sodium chloride in an iron cell. The first product of electrolysis is the subchloride,  $\text{NdCl}_2$ , which is subsequently reduced to the metal. The metal,  $d^{15}$  7.05, is silver-white, tarnishes in air, and is attacked by hot water and dilute acids. Its kindling temperature is  $270^{\circ}$ , and the metal is not pyrophoric. It readily alloys with iron, aluminium, nickel, and copper. [Cf. *B.*, 1925, 407.]

C. S.

**Spectroscope Lighting Unit.** R. C. FREDERICK and E. R. WEBSTER (*Analyst*, 1925, 50, 234—235).—The apparatus is specially designed for the spectroscopical examination of blood, particularly with regard to suspected carbon monoxide poisoning. The cell containing the blood is held by a wire spring arrangement in front of a small pocket torch with dry battery, of the shape of a fountain pen of exaggerated diameter, and this is firmly secured in a retort stand. In order to provide a comparison spectrum, the whole apparatus is duplicated and clamped at the necessary angle.

D. G. H.

**Monochromatic Illuminator for Gas Flames.** H. B. GORDON (*J. Amer. Chem. Soc.*, 1925, 47, 1045—1046).—The metallic salt is placed in a porcelain trough with perforated sides surrounding the air holes of a Bunsen burner and is vaporised into the air supply of the burner by an electrically heated wire.

S. K. T.

**Electrical Heating Apparatus in the Laboratory.** A. H. W. ATEN (*Chem. Weekblad*, 1925, 22, 174—182).—The advantages of electrical heating, and the methods of constructing heating plates, water-baths, crucible furnaces, muffle furnaces, drying ovens, water ovens, stills, extraction apparatus, and electric welding apparatus are described. The methods of calculating the resistances

and currents required and the temperatures attainable are illustrated. A heating element for use in cutting wide glass tubing is described.  
S. I. L.

**Decomposition Apparatus.** E. REMY (*Chem.-Ztg.*, 1925, 49, 392).—Destruction of organic matter, by heating the substance in 20% hydrochloric acid and adding potassium chlorate in small portions until the reaction is complete, is carried out in a flask provided with a stoppered side tube and thermometer. The flask is fitted with a reflux condenser which carries a wide tube containing a mixture of 2 parts of soda-lime and 1 part of sodium thiosulphate which prevents the escape of chlorine.  
F. B.

**Method of Viscosimetry with Variable Velocity of Flow. Velocity Function of the Viscosity of Disperse Systems. III.** R. AUERBACH (*Kolloid-Z.*, 1925, 36 (*Zsigmondy-Festschr.*), 252—259).—A new form of viscosimeter is described for studying the relationship of viscosity to the hydrostatic pressure. The liquid flows from a graduated tube, 150 cm. long, through a capillary tube and tap into a wide open reservoir level with the lower readings of the graduated tube. Other taps above and below the capillary are provided for convenience in manipulation. The height of the liquid is read at frequent intervals. For details of construction and numerical treatment reference should be made to the original paper. The large number of readings rapidly obtained with a single passage through the capillary is advantageous for systems which undergo viscosity changes on mechanical treatment. The viscosity of a 1% gelatin solution agreed with Ostwald's equation for lower hydrostatic pressures, but approximated to Poiseuille's law for higher pressures.  
E. M. C.

**Distilling Flask for Corrosive Liquids.** L. SATTLER and B. R. MORTIMER (*Ind. Eng. Chem.*, 1925, 17, 495).—The upright side arm of a Claisen type distilling flask is modified to allow a short thermometer to hang from the stopper, whilst the stopper of the flask is hollow with 0.5-mm. tubing sealed to either end to allow of inert gas being slowly bubbled into the flask. The distilling side arm has an inner seal to prevent contamination.  
D. G. H.

**Modified Claisen Vacuum Distillation Apparatus.** R. A. PETERS (*Proc. Physiol. Soc.; J. Physiol.*, 1924, 59, xxvii).—The apparatus embodies two main points: (1) the bottom of the distilling column is so designed that flasks of different capacity can be fitted rapidly by rubber Gooch crucible cones; (2) a tap of large bore is placed in the delivery tube. By closing this tap before disconnecting the distilling flask the vacuum in the receiver can be maintained.  
CHEMICAL ABSTRACTS.

**Mercury Distillation Apparatus.** J. WETZEL (*Chem.-Ztg.*, 1925, 49, 373).—The mercury is boiled in a flask, condenses in the air-cooled pear-shaped neck, and runs down into an annular channel at the bottom of the neck, from which it flows into a receiver.

The apparatus is suitable for small quantities of metal and may be used equally well at normal or low pressures. S. K. T.

**Apparatus for Evaporating under Diminished Pressure Liquids that "Bump."** H. SCHMALFUSS and H. WERNER (*J. pr. Chem.*, 1925, [ii], **109**, 345—346).—A stout, wide tube is fitted on the outside with a conical cap carrying a bulb and another ground-on fitting to connect, by means of a cock, with the vacuum pump. The apparatus is heated by a closed oil or other suitable bath and the whole is mounted on a shaking machine, with flexible connexions to the gas etc. "Bumping" and spirting are prevented by the shaking and, as the cap fits on outside the tube, there is no contamination of the contents with grease or other sealing medium. The dry residuum is easily removed. W. A. S.

**Platinum-Resistance Thermometry at Low Temperatures.** M. S. VAN DUSEN (*J. Amer. Chem. Soc.*, 1925, **47**, 326—332).—The equation

$$t = (1/\alpha)\{(R/R_0) - 1\} + \delta\{t/100 - 1\}t/100 + \beta\{t/100 - 1\}t^3/100^3,$$

obtained by the addition of a single term to the Callendar equation, expresses accurately the resistance of platinum as a function of temperature on the thermodynamic scale throughout the range 0° to -190°;  $R$  is the resistance at  $t^\circ$ ,  $R_0$  the resistance when  $t=0$ , and  $\alpha$ ,  $\delta$ , and  $\beta$  are constants, dependent on the purity of the platinum and determined by a calibration at or near the b. p. of oxygen in addition to the usual points in melting ice, boiling water, and boiling sulphur. L. J. H.

**Flame Analysis.** O. C. DE C. ELLIS and H. ROBINSON (*J. Chem. Soc.*, 1925, **127**, 760—764).—An apparatus is described for photographing flames at any desired interval after initiation. The camera shutter consists of a large, slotted wheel which is revolved at any desired speed so that rapidly successive images of the flame are obtained on the same plate; the flame is simultaneously photographed in a revolving-film camera, this latter serving both as a chronograph and to record the speed of the flame, since the reflexions from an electrically vibrated tuning fork are recorded on the film at the same time. S. K. T.

**Laboratory Apparatus.** W. STEINKOPF [with W. OHSE and K. BUCHHEIM] (*J. pr. Chem.*, 1925, [ii], **109**, 347—351).—Cyanogen bromide is conveniently and safely prepared (cf. Scholl, A., 1896, i, 585) in a litre bottle fitted with a stopper carrying a stirrer, dropping-funnel, and thermometer. The reaction being finished, the stopper is replaced by another carrying a tube leading into another similar bottle, also stoppered and fitted with a calcium chloride tube. The leading tube is of T-shape, and is provided with a ramrod so that it can be cleared if it becomes plugged with solidified cyanogen bromide. The first bottle is then surrounded by water at 70—80°; the second is surrounded by ice. Only the vent (the calcium chloride tube) need be (loosely) connected with the draught. If anhydrous cyanogen bromide is required, tubes

containing calcium chloride and sodium wire, in that order, are inserted in the leading tube and are gently warmed.

To prevent the side tube of the still becoming plugged when substances that readily solidify are distilled under diminished pressure, the arm is surrounded by an electrically heated coil of resistance wire both above and below the cork, connexions through the latter being made with thick tinned copper wire.

Soxhlet extractions may be carried out at the b. p. of the solvent in the ordinary apparatus by surrounding it first with a sheet of thin asbestos board and then with a coil of resistance wire, electrically heated.  
W. A. S.

**Combustion Micro-bomb and Micro-calorimeter. II.**  
W. A. ROTH and R. LASSÉ (*Z. Elektrochem.*, 1924, **30**, 607—609).—Using the combustion bomb already described (A., 1924, ii, 748) with a more suitable thermometer, the error in the determination of heats of combustion is reduced to about 0.04%. In the case of benzoic acid, it is difficult to obtain complete combustion, but the results, when suitably weighted, give an accurate mean value.  
C. H. D. C.

**Identity of "Alumen" in Pliny's Natural History.** K. C. BAILEY (*Nature*, 1925, **115**, 764).

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### Mineralogical Chemistry.

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**Chemical Composition of the Earth.** H. S. WASHINGTON (*Amer. J. Sci.*, 1925, [v], 9, 351—378).—From a consideration of the composition of meteorites and rocks, the velocity of earthquake waves at different depths, and the density and compressibility of minerals and rocks, some conclusions are reached as to the distribution of matter within the earth. The following zones are deduced : central core, consisting of nickel-iron, Fe 90·67, Ni 8·50%, corresponding with meteoric iron (3400 km. thick); lithosporic shell consisting of patches of silicates in a sponge of metal, corresponding with pallasites (700 km.); ferrosporic shell, corresponding with meteoric stones (700 km.); peridotitic shell (1540 km.); basaltic shell (40 km.); and granitic shell or surface crust (20 km.). The volume, mass, and chemical composition are calculated for each of these zones, and the composition of the earth as a whole is deduced as : Fe 39·76 (31·82 as free metal, and 7·94 in silicates), O 27·71, Si 14·53, Mg 8·69, Ni (free) 3·16, Ca 2·52, Al 1·79, S 0·64, Na 0·39, Co 0·23, Cr 0·20, K 0·14, P 0·11, Mn 0·07, C 0·04, Ti 0·02, total 100·00. There is an excess of iron for combination with silicon and oxygen. This composition is compared with that of the sun and the average composition of the earth's crust (cf. this vol., ii, 63).  
L. J. S.

**Mica Group.** A. N. WINCHELL (*Amer. J. Sci.*, 1925, [v], 9, 309—327).—Isomorphism depends not on the valency but on the atomic volumes of the elements. Fluorine, chlorine, or hydroxyl may “proxy” for (rather than replace) oxygen; potassium does not proxy for hydrogen, nor titanium for silicon. The best available analyses of biotite are calculated to percentages of atoms (omitting O, H, F). The atomic percentages are Si, 31.8 to 38.5 (*i.e.* 5/16 to 6/16); Al, 12.7—25% (2/16—4/16),  $\text{Mg} + \text{Fe}'' + \text{Mn}$  16.5—36.8% (3/16—6/16), K (+Na+Ba+Ca) 12.5% (2/16). The series therefore ranges from  $\text{H}_4\text{K}_2\text{Mg}_6\text{Al}_2\text{Si}_6\text{O}_{24}$  to  $\text{H}_4\text{K}_2\text{Mg}_5\text{Al}_4\text{Si}_5\text{O}_{24}$ . Here titanium and ferric iron proxy for magnesium; if they proxy for aluminium the second term would be  $\text{H}_2\text{K}_2\text{Mg}_5\text{Al}_6\text{Si}_5\text{O}_{24}$ , but this does not agree quite so well with the analyses. The several analyses are plotted on a square diagram at the four corners of which are  $\text{H}_4\text{K}_2\text{Mg}_6\text{Al}_2\text{Si}_6\text{O}_{24}$  (phlogopite),  $\text{H}_4\text{K}_2\text{Mg}_5\text{Al}_4\text{Si}_5\text{O}_{24}$  (eastonite), and the corresponding iron compounds  $\text{H}_4\text{K}_2\text{Fe}_6\text{Al}_2\text{Si}_6\text{O}_{24}$  (annite), and  $\text{H}_4\text{K}_2\text{Fe}_5\text{Al}_4\text{Si}_5\text{O}_{24}$  (siderophyllite). The optical data ( $\alpha$ ,  $\gamma$ , and  $\gamma - \alpha$ ) plotted on the same diagram show appreciable increases in these values only for the members richer in iron. Variations in the optic axial angle are perhaps more closely connected with the relative amounts of hydroxyl and fluorine. L. J. S.

**Mica Group. II.** A. N. WINCHELL (*Amer. J. Sci.*, 1925, [v], 9, 415—430; cf. preceding abstract).—The “heptaphyllite” system, with seven atoms in the nucleus, *e.g.*,  $\text{KAl}_3\text{Si}_3$  or  $\text{KAl}_5\text{Si}_4$ , is represented by four end-members, muscovite  $\text{H}_4\text{K}_2\text{Al}_6\text{Si}_6\text{O}_{24}$ , polyolithionite  $\text{H}_4\text{K}_2\text{Li}_6\text{Si}_6\text{O}_{18}$ , phengite  $\text{H}_4\text{K}_2\text{Al}_4\text{Si}_8\text{O}_{25}$ , and protolithionite  $\text{H}_4\text{K}_2\text{Fe}''_3\text{Al}_4\text{Si}_5\text{O}_{22}$ , which are placed at the corners of a tetrahedron. The majority of the plotted analyses fall on or near two of the surfaces of the tetrahedron, and are representative of two three-component systems, muscovite–polyolithionite–protolithionite and muscovite–protolithionite–phengite, which are referred to respectively as the lepidolite and muscovite systems. There are no series of mixed crystals between the two main groups of micas—the octophyllite or biotite and the heptaphyllite or muscovite–lepidolite systems. In the former the optic axial plane is parallel to the plane of symmetry (010) with  $\rho < v$ , and in the latter it is perpendicular with  $\rho > v$ . L. J. S.

**Occurrence of Palladium and of Rhodium in British Guiana.** J. B. HARRISON (*Off. Gazette, Brit. Guiana*, May 3, 1924, No. 181).—The diamond-bearing gravels near Oewang, near the Kaieteur gorge, Potaro River, yield a black concentrate of ilmenite sand with specks of gold and a few minute grains (total weight 44 mg.) of a white metal. This is malleable but somewhat brittle, and is slowly dissolved by hot strong nitric acid or aqua regia, giving a rose-red solution. A small quantity of ammonium chloro iridate was separated, and the tests indicate the presence of palladium and rhodium in variable amounts in the different grains. One grain from this locality has been identified as platinum (Spencer, *Min. Mag.*, 1924, 20, 186, 217). L. J. S.

**Occurrence of Palladium Amalgam (Palladium Mercuride) in British Guiana.** J. B. HARRISON and C. L. C. BOURNE (*Off. Gazette, Brit. Guiana*, Feb. 27, 1925, No. 71).—A further small supply of the white metal as fragments and nuggets up to 12 g. has been found in the diamond-washings of the Kangaruma district, Potaro River. These have  $d$  13.33–15.82 and lose in weight when heated, with further losses on successive heatings up to about  $1400^{\circ}$ . The residual metal (34.8–45.6%) is porous with  $d$  10.0–11.0 (after hammering, 11.33–11.9), and consists of palladium with traces of rhodium, platinum, and gold. It was afterwards found that the loss is due to mercury (54.4–65.2%). A re-examination of the material previously described as palladium and rhodium (preceding abstract), also showed the presence of much mercury; and it is suggested that that described as “allopalladium” (Spencer, *Min. Mag.*, 1924, 20, 217) is also the same. The material is hard (scratching rolled nickel), crystalline, and denser than palladium or mercury. L. J. S.

**Radioactive Minerals as Geological Age Indicators.** H. V. ELLSWORTH (*Amer. J. Sci.*, 1925, [v], 9, 127–144).—Previous work on the determination of the age of minerals by the ratio of the lead to the total uranium and thorium contents is discussed and new data are recorded. A theory is proposed accounting for the variations in the composition of uraninites etc., according to which all minerals containing the oxide  $\text{UO}_2$  undergo self-oxidation at a rate depending on the rate of disintegration of the uranium and thorium. S. K. T.

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## Analytical Chemistry.

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**Portable Gas Analysis Apparatus.** H. D. MURRAY (*J. Chem. Soc.*, 1925, **127**, 769—770).—A gas burette is connected by means of a three-way tap to a sparking chamber provided with a mercury reservoir; this is similarly connected to a pipette having two in-leads, one, through which the gas is drawn, reaching to the bottom of the bulb. Suitable absorbents are drawn up into the pipette as required; the analyses are carried out in the usual way.

S. K. T.

**Burette for Micro Gas Analysis.** J. A. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1925, **47**, 109—112).—A simple form of apparatus is described for the micro-analysis of quantities of mixed gases up to 20 mm.<sup>3</sup>, with an absolute accuracy of about 0.1% on 10 mm.<sup>3</sup> A calibrated tube of 0.3 mm. bore is connected to a small adsorption bulb above, and also has a bulb below, whilst U-tubes at each end contain some confining liquid (mercury or water). An analysis cannot be vitiated on account of a gas bubble parting from the rest in the measuring tube as bubbles can always be collected again in one or other of the bulbs.

L. J. H.



**Fusion Mixture for Isopycnetric Analysis.** E. CLERICI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 329—332; cf. A., 1922, ii, 578).—Further mixtures of thallium salts have now been prepared which allow of the separation of minerals of all specific gravities between 1 and 5.4. For values below 5, solutions of thallium formate, either with or without the malonate, are preferable. Fused mixtures of thallium formate and fluoride have specific gravities up to 5.38 at 100° and up to 5.4 at 110°. T. H. P.

**Destruction of Organic Matter by Hydrogen Peroxide : Its Use in Toxicology.** G. MAGNIN (*J. Pharm. Chim.*, 1925, [viii], 1, 333—336).—In the detection and determination of inorganic poisons in viscera etc., the organic matter is destroyed by warming on the water-bath with a 30% solution of hydrogen peroxide, preferably in the presence of a little sodium hydroxide. The liquid is then acidified, filtered, and treated with sulphur dioxide, the excess of which is removed on the water-bath. C. P. S.

**Theory of certain Electrometric and Conductometric Titrations.** E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1925, 47, 332—337).—A mathematical analysis, from the point of view of the mass action law, of the location of the end points obtained in hydrogen electrode and conductivity titrations. In electrometric titration, if either the acid or the base is weak, inaccuracies in the end-point (0.3% in the most unfavourable case studied) arise. If the dissociation constant of one is less than  $10^{-11}$ , the other being strong and the total concentration normal, no inflexion will be obtained. In conductometric titration the limits (of dissociation constant) before the inflexion disappears are wider, but the error in the end-point is much greater. When both  $K_a$  and  $K_b = 10^{-6}$ , the "break" in the curve occurs about 2% before the true end-point. In general, the electrometric method gives results rather nearer the true end-point. L. J. H.

**Behaviour of Electrodes of Platinum and Platinum Alloys in Electrometric Analysis. I. Dissimilar Electrodes.** R. G. VAN NAME and F. FENWICK (*J. Amer. Chem. Soc.*, 1925, 47, 9—19).—Two dissimilar inert electrodes show an abrupt difference of potential at the end-point of an oxidimetric titration. This is primarily a time effect due to the different rates at which they approach equilibrium, magnified by the large increase in the sensitivity of equilibrium potentials to a given change in concentration near the end-point. The end-point thus indicated agrees within the equivalent of 0.5 c.c. of 0.1*N*-titrant with that obtained from the single-potential curve of either electrode. A freshly-ignited platinum electrode immersed in a solution of silver nitrate usually acquires the electromotive behaviour of silver, apparently owing to an invisible coating of silver. L. J. H.

**Behaviour of Electrodes of Platinum and Platinum Alloys in Electrometric Analysis. II. Polarised Electrodes.** R. G. VAN NAME and F. FENWICK (*J. Amer. Chem. Soc.*, 1925, 47, 19—29; cf. preceding abstract).—For electrometric analysis, two electrodes

polarised by a constant potential of 0.2—1 volt applied with 20,000 ohms resistance in series with the electrodes is recommended. The potential difference between the electrodes is slight during the titration, but becomes large abruptly at the end-point when the electrode reaction is nearly reversible before the end-point and largely irreversible after it, and is large at first, but vanishes abruptly at the end-point in the converse case. The difference in the end-point from that indicated by the break in the potential curve of a single electrode is usually negligible. The end-point break in titrations employing the potential of a single electrode may often be improved by polarising this with respect to an auxiliary electrode.  
L. J. H.

**Application of Three-electrode Valves in Electrometric Titrations.** W. D. TREADWELL and C. PAOLONI (*Helv. Chim. Acta*, 1925, 8, 89—96).—The apparatus of Goode (A., 1922, ii, 307) is modified so that a conductivity cell can be used for electrometric titrations instead of a hydrogen electrode. The conductivity cell is connected to a source of alternating current of about 11 volts and any changes in conductivity are made to affect the potential of the grid. The anode potential of the valve is 26.3 volts and the titration is followed by means of a millivoltmeter in the anode circuit. Titration curves are given for hydrochloric acid with brucine and barium hydroxide and with a mixture of sodium hydroxide and sodium carbonate.  
M. B. D.

**Electrometric Titration with the use of Quinhydrone.** H. NIKLAS and A. HOCK (*Z. angew. Chem.*, 1925, 38, 407—409).—The hydrogen of a platinum-hydrogen electrode may be replaced by quinhydrone added to the solution to be tested, the quinhydrone being decomposed into quinone and quinol, giving a definite hydrogen partial pressure. The value of  $p_H$  is  $2.04 + p/0.0577$ , where  $p$  is the measured potential in volts; the method is accurate between  $p_H$  2.05 and  $p_H$  8.0. Above this value, an error is introduced through the oxidation of quinol and its increased dissociation. Within these limits, the method is much more rapid than the standard one. [Cf. B., June 26th.]  
C. I.

**Spectrophotometric Determination of  $p_H$ .** F. VLÈS (*Compt. rend.*, 1925, 180, 584—586; cf. Brode, A., 1924, ii, 346).—The determination of  $p_H$  from the intensity of absorption at the absorption bands of an indicator, as hitherto described, involves a tedious empirical calibration against a series of standard buffer solutions for each new concentration of indicator used. From a consideration of the absorption constants of the two tautomeric forms supposed to be in equilibrium, and of the ionic dissociation of the indicator, it is shown that where the  $p_H$  value is not extremely small it should be a simple function of the absorption ratio, and independent of the concentration of indicator, so that the calibration should be unnecessary. This is found to be the case with "normal" indicators such as cresol-red and bromothymol-blue, where the results are always correct to the first decimal place for  $p_H$ . Crystal-

violet and methyl-red, on the other hand, are classed as "abnormal," there being a marked deviation from the simple relationship expected, which is attributed to the presence of a third component.  
G. M. B.

**Colorimetric Determination of Hydrogen-ion Concentration.** E. RICHARD (*J. Pharm. Chim.*, 1925, [viii], 1, 328—333).—Equal volumes of an appropriate one-colour indicator are added to the liquid under examination and to 0.01*N*-sodium hydroxide solution. After 2—3 mins., the colours are compared in a colorimeter, and the  $p_H$  is calculated from one of the formulæ:  $p_H = p_K + \log E/(e-E)$  or  $p_H = p_K - \log (e-E)/E$  (according as  $E/(e-E)$  is greater or less than unity), where  $E$  is the colorimeter reading for the sodium hydroxide solution,  $e$  that for the solution being examined, and  $p_K$  is a constant depending on the indicator used. Constants and ranges of seven indicators are tabulated. C. P. S.

**Potassium Ferritripyrocatecholoxide as an Indicator for Acidimetry and Alkalimetry.** K. BINDER (*Z. anal. Chem.*, 1925, 66, 1—13).—Potassium ferritripyrocatecholoxide dissolves in water to a red solution which remains unchanged with alkalis but turns violet with a small amount of acid owing to hydrolysis of the acid salt first formed, with the production of potassium aquoferridipyrrocatecholoxide, which is decomposed to a green compound with more acid and finally yields a ferric salt. Addition of alkali to this yellow solution produces the same colour changes in the reverse order. For use as an indicator, a 1.25% solution of the red salt in freshly boiled, distilled water is prepared and 10 drops of this are required for *N*-acids, 5 drops for 0.5*N*-acids, and 1 drop for 0.1*N*-acid; the neutral tint is reddish-violet. The indicator has the same range of usefulness as phenolphthalein, and is just as sensitive to carbon dioxide; the alkali used therefore must be freed from carbonates with barium hydroxide. For the determination of ammonia, an excess of standard acid is added to the solution, which is then titrated with alkali to a violet colour. The indicator is useful for titration of the weaker organic acids, but cannot be used with pyridine. As the compound oxidises readily, it must be stored away from the air and alkaline solutions must be titrated without delay. Directions are given for the preparation of the compound (cf. A., 1912, i, 184, 445).  
A. R. P.

**Salt Errors of Indicators in Solutions Poor in Electrolytes.** I. M. KOLTHOFF (*Rec. trav. chim.*, 1925, 44, 275—278).—Most indicators show a too acid reaction in solutions containing only small quantities of electrolytes. The apparent  $p_H$  as shown by buffer solutions and the actual  $p_H$  determined by means of the hydrogen electrode are tabulated for various solutions and indicators and the appropriate corrections given to an accuracy of 0.05 to 0.1 in the  $p_H$  value. The widest deviations are shown by phenol-red and bromophenol-blue, the smallest by cresol-red, bromocresol-purple and neutral-red. The indicators recommended for colorimetric determination of  $p_H$  in dilute solutions of electrolytes are  $\alpha$ -naphthol-

blue, cresol-red, neutral-red, bromothymol-blue, bromocresol-purple, methyl-red, and methyl-orange. S. I. L.

**Use of *p*-Nitrobenzoic Acid as an Acidimetric Standard.** W. M. THORNTON, jun., and D. GETZ (*Amer. J. Sci.*, 1925, [v], 9, 176—180).—*p*-Nitrobenzoic acid is an accurate primary acidimetric standard, its advantages being ease of purification, compactness, and high molecular weight. Before titration, the weighed acid is dissolved in a large excess of boiling alcohol to prevent subsequent precipitation; phenolphthalein is used as indicator. S. K. T.

**Determination of Chlorides by Calorimetric Titration. Titration of Mixtures of Cyanide and Halides.** P. M. DEAN and E. NEWCOMER (*J. Amer. Chem. Soc.*, 1925, 47, 64—67).—The slightly modified method of Dean and Watts (A., 1924, ii, 421) is applicable with fair accuracy to single salts, but with mixtures only complete precipitation is indicated. Thus organic halogen compounds reduced by sodium in liquid ammonia do not give solutions which may be determined in this way, as some cyanide is simultaneously formed. L. J. H.

**Test for Bromine.** R. LORENZ, E. GRAU, and E. BERGHEIMER (*Z. anorg. Chem.*, 1924, 136, 90—94).—A delicate reagent for the detection of bromine is made by dissolving fluorescein, twice crystallised from 80% alcohol, in cold 35% acetic acid and applying this solution to a loose filter-paper, which is then allowed to dry in the air and preserved away from light. The neutralised solution to be tested is placed in a round flask, so that it reaches to the bottom of the neck, and 5 c.c. of a strong solution of potassium permanganate and 0.02 c.c. of strong sulphuric acid are added. A piece of the test-paper is then affixed to the under side of the stopper, which is replaced in the flask and the whole set aside in the dark for 15 mins. A red coloration on the paper indicates the presence of bromine; the test will detect 0.01 mg. of potassium bromide in 50 c.c. of water or in a saturated solution of sodium chloride. A. R. P.

**Iodometric Methods based on the Formation of Cyanogen Iodide. IV.** R. LANG (*Z. anorg. Chem.*, 1925, 144, 75—84).—Since cyanogen bromide is not easily affected by reducing agents, bromides may be accurately determined by oxidation with iodate in acid solution in presence of cyanide, the excess of iodate being titrated with hydrazine in acid solution ( $\text{IO}_3^- + 2\text{Br}^- + 3\text{HCN} + 3\text{H}^+ = \text{ICN} + 2\text{BrCN} + 3\text{H}_2\text{O}$ ). The time required for oxidation may be diminished by addition of a small quantity of alkali chloride. The oxidation may also be effected with permanganate, excess of the latter being removed with nitrite (in sulphuric acid solution) or a ferrous salt (in phosphoric acid solution), the latter being preferred; potassium iodide is then added and the liberated iodine titrated with thiosulphate. Small quantities of chloride do not interfere. Several modifications suitable for the titration of bromides and iodides together are described. Periodate is not so suitable for the method as iodate, although it is satisfactory in presence of suitable amounts of hydrochloric acid and bromide for direct oxidation of iodides;

periodate may also be used in the determination of cyanide and thiocyanate together ( $\text{CNS}' + \text{IO}_4' = \text{ICN} + \text{SO}_4''$ ). S. I. L.

**Detection of Traces of Iodides.** F. B. WADE (*Ind. Eng. Chem.*, 1925, 17, 470).—The salt, sprinkled on a damp filter-paper impregnated with starch solution, is exposed to chlorine.

D. G. H.

**Determination of Small Amounts of Iodine as Iodide and Iodate.** N. A. LANGE and L. A. WARD (*J. Amer. Chem. Soc.*, 1925, 47, 1000—1003).—The alkaline sample, containing 0.01—0.10 mg. of iodine, is evaporated with hydrogen peroxide to oxidise nitrites, filtered, and the filtrate, rendered neutral to litmus, partly evaporated and divided into two parts. *o*-Tolidine in alcohol is added to each, one being previously saturated with hydrogen sulphide to reduce iodate to iodide and the excess removed. Hydrogen peroxide is then added to each solution and also to a series of ten standard potassium iodide solutions treated with *o*-tolidine solution as above. After 5 mins., the bluish-green colour which develops is matched with the standards. Comparison cannot be made after 10 mins. Interfering substances (*e.g.*, chlorides and bromides in concentrations exceeding 1500 parts per million, salts of heavy metals) may be eliminated by distilling the sample with steam in acid solution with ferric sulphate, the liberated iodine being absorbed in sodium hydroxide solution. The lower limit of the test is 6—7 parts per million.

S. K. T.

**Iodometric Titrations.** M. DIMITROV (*Z. anorg. Chem.*, 1924, 136, 189—192).—In order to economise potassium iodide the standardisation of thiosulphate solutions may be carried out satisfactorily as follows: a definite quantity of the solution is treated with a small crystal of potassium iodide and a slight excess over the stoichiometrical quantity of potassium iodate required to produce sufficient iodine to react with the thiosulphate; the solution is then titrated very slowly with a standard solution of hydrochloric acid, adding starch towards the end of the titration. By using this method, a titration requires only 0.05 g. instead of 2 g. of iodide.

A. R. P.

**Detection and Determination of Small Quantities of Fluorine.** R. J. MEYER and W. SCHULZ (*Z. angew. Chem.*, 1925, 38, 203—206).—The fluoride solution is concentrated, acidified with strong acetic acid, and treated with excess of 1% lanthanum acetate solution. Solid ammonium acetate is added in large excess and the whole is warmed. After a time, depending on the amount of fluorine present, a flocculent precipitate of lanthanum fluoride deposits, which becomes pulverulent when kept or heated. The amount of lanthanum acetate adsorbed by this precipitate is corrected for by heating it with ammonium acetate and acetic acid solutions, washing, and weighing before and after gentle heating, which converts the normal acetate into oxide without affecting the fluoride. Precipitation by calcium and thorium salts is shown to be

unsatisfactory for the determination of small quantities of fluorine.  
[Cf. *B.*, June 26th.] S. K. T.

**Determination of Nitrogen in Oil, Coke, and Proteins.** H. TER MEULEN (*Rec. trav. chim.*, 1925, **44**, 271—274).—The material is thoroughly mixed with seven times its weight of sodium carbonate and heated in a current of hydrogen saturated with water vapour at 100°. The whole of the nitrogen is converted into ammonia, which is determined in the usual way. Proteins give figures by this method generally slightly higher than those obtained by the Kjeldahl method, but pure organic substances give figures corresponding exactly with the theoretical. S. I. L.

**Determination of Nitrogen [in Explosives].** M. MARQUEYROL [with L. CHENEL, FRIEDERICH, D. FLORENTIN, KOEHLER, and P. LORLETTE] (*Mém. Poudres*, 1925, **21**, 326—379).—The Schloesing method with various modifications and the Lunge nitrometer method, as applied to the determination of nitrogen in nitrates and nitric esters, are discussed and compared in detail. The latter is preferred. C. I.

**Determination of Nitrous Vapours.** A. T. SCHLIESING (*Mém. Poudres*, 1924, **21**, 127—132).—Details are given for the use of special absorption vessels (cf. this vol., ii, 566). These vessels are of U-shape, the two vertical limbs being connected near the top by a horizontal tube. Sufficient absorbing liquid (about 30 c.c.) is used just to fill this connecting tube, through which the gas bubbles. The gas is drawn forward by means of a water-jacketed aspirator, each bubble being in contact with the absorbent for about 1.5 to 2 minutes. A known quantity of standard alkali is placed in the absorber and is titrated back at the end of the test. W. T. K. B.

**Reactions for Nitrates and Nitrites.** S. VÁGI (*Z. anal. Chem.*, 1925, **66**, 14—16).—In the presence of an equal volume of concentrated sulphuric acid, solutions of nitrates and nitrites give a yellow colour with 2% alcoholic benzidine, but nitrites only give a yellow colour with an acetic acid solution of benzidine. Chlorates and ferric chloride also give a yellow colour with alcoholic benzidine in the presence of sulphuric acid, but may be distinguished from nitrates and nitrites by the red colour produced with the same reagent in the presence of hydrochloric acid, which destroys the yellow colour due to nitrates and nitrites. A 1% aqueous solution of sodium 8-amino- $\alpha$ -naphthol-3 : 6-disulphonate or of sodium 1 : 8-dihydroxynaphthalene-3 : 6-disulphonate gives an orange-coloured solution and  $\alpha$ -naphthol-5-sulphonic acid a wine-red colour with nitrates in 50% sulphuric acid. Nitrites, chlorates, and ferric chloride give the same reactions in more dilute sulphuric acid. An acetic acid solution of sodium 8-amino- $\alpha$ -naphthol-3 : 6-disulphonate gives a citron-yellow colour with nitrites. A. R. P.

**Reactions of Nitrates and Nitrites.** S. VÁGI (*Z. anal. Chem.*, 1925, **66**, 101—104).—A 1% solution of the following reagents in 50% acetic acid gives characteristic colours with dilute nitrite

solutions (the figures in brackets denote minimum concentration of nitrite in mg. per litre for colour to be visible in 40 c.c. of the test solution): pyrogallol, reddish-brown, changing to yellow on keeping (0.1); pyrocatechol, reddish-brown (0.1), becoming green then colourless with ammonia; quinol, intense yellow (5.0); orcinol (0.33% solution), intense bright yellow (1.0); resorcinol (0.25% solution), bright yellow (1.0). A solution of 1 g. of  $\alpha$ -naphthol and 0.5 g. of sulphanilic acid in 100 c.c. of glacial acetic acid and 300 c.c. of water gives an orange-yellow solution with nitrites (0.1) becoming rose-red with ammonia. The colour with a corresponding  $\beta$ -naphthol solution is pale yellow, and with pyrocatechol rose-red (0.1). A solution of 1 g. of benzidine and 1 g. of sodium 8-amino- $\alpha$ -naphthol-3 : 6-disulphonate in 400 c.c. of 20% acetic acid gives a yellowish-brown solution with nitrites which becomes rose-red (0.1) in 1 hr. Nitrates give a green colour with a 1% solution of pyrocatechol in strong sulphuric acid and a violet-brown colour with a corresponding pyrogallol solution; nitrites give a similar reaction. A. R. P.

#### Determination of Phosphorus in the Presence of Vanadium.

G. W. GRAY and C. D. GARBUTT (*J. Iron and Steel Inst.*, May 1925; [Advance proof]).—The material is dissolved in a mixture of nitric and hydrochloric acids, the silica removed, the iron separated with ether, and the phosphorus precipitated as magnesium ammonium phosphate in the presence of citric acid; the precipitate is dissolved in nitric acid and the phosphorus determined as phosphomolybdate.

M. E. N.

**Detection of Silicic Acid.** R. LORENZ and E. BERGHEIMER (*Z. anorg. Chem.*, 1924, **136**, 95—96).—For the detection of silicic acid in distilled water or sodium chloride solutions, the solution is heated at 80° and treated with 1 c.c. of a solution of 8 g. of potassium molybdate in 100 c.c. of 1 : 1-nitric acid. The green colour of the potassium silicomolybdate solution so formed is compared with that of a standard prepared from a solution of sodium silicate.

A. R. P.

#### Rapid Determination of Carbon in Organic Compounds.

H. D. WILDE, jun., and H. L. LOCHTE (*J. Amer. Chem. Soc.*, 1925, **47**, 440—446).—The substance (80—200 mg.), preferably in compressed tablet form, is burned in a small calorimetric bomb in the presence of oxygen at 25 atm. pressure, and 0.5N-barium hydroxide solution, the carbonate being subsequently determined volumetrically. If complete combustion is not attained, the substance may be placed in powder form in a weighed gelatin capsule, allowance being made for the carbon dioxide produced by combustion of the latter. Liquids may also be analysed by using a gelatin capsule. Halogen compounds give appreciable amounts of oxyhalogen derivatives, which impair the accuracy of the results. This is circumvented by adding hydrazine hydrate and aluminium to the alkali from the bomb in an evacuated apparatus, distilling with hydrochloric acid and collecting the carbon dioxide evolved in standard alkali solution. Sulphur can be determined gravimetri-

cally in the solution from the bomb as sulphate. The results are as accurate as those obtained by Liebig's method. F. G. W.

**Micro Determination of Potassium in Blood Serum and Other Fluids.** F. LEBERMANN.—(See i, 714.)

**Substitute for Cobalt Glass.** J. MEYER (*Helv. Chim. Acta*, 1925, 8, 146—148).—Marked superiority is claimed for the use of a gelatin filter dyed with crystal-violet over that of blue glass in the flame test for potassium in presence of sodium. The preparation of the filter is described. M. J.

**Separation and Determination of the Alkali Metals, using Perchloric Acid. III. *n*-Butyl Alcohol and Ethyl Acetate as Mixed Solvents in the Separation and Determination of Potassium, Sodium, and Lithium.** G. F. SMITH and J. F. ROSS (*J. Amer. Chem. Soc.*, 1925, 47, 1020—1026).—A mixture of equal volumes of *n*-butyl alcohol and ethyl acetate is shown to be satisfactory for the separation of perchlorates of sodium and potassium, potassium and lithium, and sodium and lithium subsequent to the separation of potassium. In the first case, two separations are necessary (cf. A., 1923, ii, 182; this vol., ii, 436, 437). S. K. T.

**Determination of Calcium in Blood by Tisdall's Method.** E. P. CLARK and J. B. COLLIP.—(See i, 713.)

**Critical Studies on Methods of Analysis. XV. Magnesium.** L. A. CONGDON and G. VANDERHOOK (*Chem. News*, 1925, 130, 241—243, 258—261, 273—276).—The use of sodium salts as precipitants in the methods of determining magnesium as magnesium ammonium phosphate or arsenate gives more nearly correct results than the use of ammonium salts, probably owing to slight adsorption of part of the precipitant by the precipitate which counterbalances loss due to the slight solubility of the precipitate. Weighing the precipitate in each case after ignition to pyrophosphate is preferable to an indirect determination by alkalimetric or iodometric processes. [Cf. B., June 26th.] A. R. P.

**Determination of Magnesium in Presence of Aluminium.** F. L. HAHN (*Z. anorg. Chem.*, 1925, 144, 142—144; see Jander and others, *ibid.*, 142, 329).—The method of determining magnesium in presence of large quantities of aluminium by precipitating as magnesium ammonium phosphate in presence of tartaric acid, which holds aluminium in solution, whilst found to give exact results by some workers, has been found unsuitable by the author, and is not recommended. S. I. L.

**Reagent for Aluminium.** L. P. HAMMETT and C. T. SOTTERY (*J. Amer. Chem. Soc.*, 1925, 47, 142—143).—The supposed precipitate of aluminium hydroxide is dissolved in hydrochloric acid and ammonium acetate solution containing ammonium aurintricarboxylate. After lake formation (crimson for aluminium) has taken place, the solution is made alkaline with ammonia solution containing



ammonium carbonate. This removes interfering lakes formed from chromium and alkaline-earths. Ferric iron must first be removed.

L. J. H.

**Gravimetric Determination of Aluminium and its Separation from Manganese by the Use of "Infusible White Precipitate."** B. SOLAJA (*Chem.-Ztg.*, 1925, 49, 337—338).—The solution is neutralised with ammonia, ammonium chloride is added, and the mixture digested overnight with a quantity of "infusible white precipitate" ( $\text{ClHg}\cdot\text{NH}_2$ ) equal to ten times the amount of alumina present. The precipitate is collected, washed with cold water, and ignited to alumina. The process effects complete separation of aluminium from manganese in one operation and the precipitated aluminium hydroxide filters more readily than that produced by ammonia. [Cf. *B.*, June 26th.] A. R. P.

**Alkalimetric Determination of Aluminium Salts and Free Acids in the Presence of One Another.** T. SABALITSCHKA and G. REICHEL (*Arch. Pharm.*, 1925, 263, 193—196).—Excess of sulphuric acid in a solution of aluminium sulphate may be determined by titration with potassium hydroxide, using as indicator either the colouring matter of pæonies (red in acid, colourless in aluminium sulphate solution containing no excess of acid) or sodium alizarin-sulphonate. By the method of Stock (*A.*, 1900, ii, 247, 315)—titration with alkali in the presence of barium chloride, using phenolphthalein as indicator—the total amount of acid in the solution (*e.g.*, excess acid and acid equivalent to aluminium) may be found, the difference between total and excess acid showing the amount of aluminium present. Stock's method applies only to the sulphate and chloride, but, *e.g.*, the acetate is converted into the sulphate by treatment with excess of strong sulphuric acid. After evaporation to fuming, the residue is dissolved in water and diluted to a known volume. Part of the solution is then examined for excess acid by titration with alkali, using the pæony indicator, until colourless. Another part is treated with barium chloride and titrated with alkali, using phenolphthalein, to redness, then heated to boiling to remove the colour, and re-titrated to rose colour, the total titration giving the total acid. The pæony indicator is prepared by heating the red petals of *Paeonia peregrina*, Mill., var. *officinalis*, Retz, and *P. arborea*, Don., with 90% alcohol. Excess of this indicator gives a bad end-point. B. F.

**Potentiometric Standardisation of Potassium Permanganate Solution with Sodium Oxalate.** C. DEL FRESNO (*Z. Elektrochem.*, 1925, 31, 199—200).—Potassium permanganate may be standardised potentiometrically with sodium oxalate at 70°. The end-point is sharply marked and is the same as in the chemical titration. N. H. H.

**Separation of Iron, Chromium, Aluminium, and Phosphoric Acid from Zinc, Nickel, Cobalt, and Manganese, and Determination of the Last Four Elements.** K. K. JÄRVINEN (*Z. anal. Chem.*, 1925, 66, 81—100).—The ordinary methods of

separating iron, chromium, aluminium, and phosphoric acid from the members of the ammonium sulphide sub-group by means of ammonia, barium carbonate, or sodium acetate have to be repeated several times owing to adsorption of the monoxides by the sesquioxide precipitate. This may be overcome and a complete separation obtained in one operation, in the case of iron, or two, in other cases, by the following procedure. The chloride solution is neutralised with ammonium carbonate until a faint permanent precipitate forms and boiled with 2 g. of ammonium sulphate. The boiling solution is treated with 4 g. of sodium nitrite and cooled; the precipitate contains all the iron and phosphoric acid and most of the aluminium and chromium. After filtering and washing, the filtrate is boiled with a further 1 g. of sodium nitrite to remove any remaining sesquioxide. For the separation of zinc, cobalt, nickel, and manganese from the filtrate, successive precipitations with hydrogen sulphide under pressure in 0.035*N*-hydrochloric acid, 2% acetic acid and 2% ammonia are recommended. The precipitates in each case are converted into sulphate for weighing. The zinc sulphate should be tested colorimetrically by thiocyanate for the presence of traces of cobalt. [Cf. *B.*, June 26th.] A. R. P.

**Gravimetric Determination of Iron and a Rapid Method for Dissolving Ignited Iron Oxide.** N. A. TANANAEV (*Z. anorg. Chem.*, 1924, **136**, 184—188).—Ferric oxide obtained by the ignition of a precipitate of hydroxide produced by the addition of ammonia to a solution of ferric sulphate, chloride, or nitrate invariably retains traces of water even after heating for 1 hr. over a blast burner. Analyses of pure iron wire by this method gave results as much as 2% too high, but more nearly correct figures were obtained if the ignited oxide was moistened with nitric acid, dried, and again heated as before. Evaporation of a solution of ferric nitrate to dryness followed by calcination of the residue also gave correct results. Strongly ignited ferric oxide may be dissolved readily in 1:1-hydrochloric acid if a few drops of a solution of stannous chloride are added from time to time. A. R. P.

**Separation of Nickel and Copper from Iron.** E. G. R. ARDAGH and G. M. BROUGHALL (*Univ. Toronto, Sch. Eng. Res. Bull.*, 1925, **5**, 227—235).—Conditions are given for the complete separation of nickel and copper from ferric hydroxide by means of ammonia and ammonium sulphate or chloride. The method is applicable to ores containing these three metals. [Cf. *B.*, 1925, 381.] T. H. P.

**Detection and Determination of Nickel by Means of  $\alpha$ -Furildioxime.** B. A. SOULE (*J. Amer. Chem. Soc.*, 1925, **47**, 981—988).—Aqueous or alcoholic solutions of  $\alpha$ -furildioxime give a red precipitate,  $C_{22}H_{14}O_6N_4Ni$ , from slightly ammoniacal solutions of nickel salts and may be used in place of  $\alpha$ -dimethylglyoxime for the detection (1 in  $6 \times 10^6$ ) and determination of this metal. In quantitative work, the precipitate may be weighed directly, or ignited to nickelous oxide, or dissolved and the metal determined by electrolysis or by a cyanide titration. Ferrous iron must be

absent; ammonio-cobaltous ions must be oxidised with hydrogen peroxide. In presence of manganic salts, acetic acid and sodium acetate must be added (cf. Brunck, A., 1907, ii, 582, 989).

S. K. T.

**Carbon Error in the Quantitative Deposition of Nickel and Iron from Complex Oxalate Electrolytes.** P. K. FRÖLICH (*Analyst*, 1925, 50, 224—230).—No conditions were found under which nickel could be deposited from oxalate electrolytes without contamination by organic matter, but in the case of iron the metal is not contaminated at the beginning of the reaction, and contamination can be sufficiently retarded to allow of quantitative deposition by the addition of ammonium chloride. [Cf. B., June 26th.]  
D. G. H.

**Determination of Vanadium.** W. HARTMANN (*Z. anal. Chem.*, 1925, 66, 16—23).—The vanadium solution, whether obtained by dissolving the substance in acids or by an alkali fusion, is evaporated with sulphuric acid until fumes are evolved, hydrochloric acid is added, and the evaporation repeated to reduce the vanadic acid to vanadyl salt. After dilution and heating at 70°, the vanadium is determined by titration with permanganate which has been standardised against a pure vanadium compound or against a similar material to that analysed, but of known vanadium content. If oxalic acid or other similar substance is used as standard, the vanadium results are always a little too high, but may be corrected by multiplying by 0.9915. Details are given of the methods used in analysing ferrovanadium and commercial vanadium pentoxide. [Cf. B., 1925, 381.]  
A. R. P.

**Determination of Antimony.** V. AUGER (*Ann. Chim. analyt.*, 1925, 7, 100).—Of the methods for determining antimony proposed by Ecke (A., 1924, ii, 705), the first is worthless for both chemical and arithmetical reasons, and the second will fail in the presence of much copper. [Cf. B., 1925, 430.]  
D. G. H.

**Fluorescence as a Criterion of Purity in Organic Compounds.** E. BAYLE and R. FABRE (*J. Pharm. Chim.*, 1925, [viii], 1, 248—253).—The spectrophotometric curves defining the colour of the fluorescence of a substance (cf. A., 1924, ii, 583) are shown to be criteria of the purity of the latter. The curves exhibit peaks which gradually attain a stable maximum position as the impurities are removed.  
S. K. T.

**Rapid Determination of Phenols in Essential Oils, using Small Quantities of Material.** L. RETI (*Chem.-Ztg.*, 1925, 49, 306).—On shaking 0.5 or 1.0 c.c. of the oil with 3—5% sodium hydroxide solution in an absorption vessel ("phenolometer") constructed like Gerber's butyrometer, and centrifuging the mixture a good separation is obtained; the diminution in volume, corresponding with the amount of phenol present, can be read with great accuracy to 0.01 c.c. [Cf. B., 1925, 424.]  
A. C.

**Test for Pentoses.** P. THOMAS (*Bull. Soc. Chim. biol.*, 1925, 7, 102—112).—When an aqueous solution of a pentose, or of com-

plex derivatives containing a pentose, is poured carefully on to a 0.3% solution of  $\beta$ -naphthol in concentrated sulphuric acid, a deep blue (ultramarine) ring is formed; the colour is intensified on gentle shaking and diffuses into the acid, the original ring of colour becoming greenish-brown. The reaction appears to be characteristic of pentoses and does not occur with the other sugars, aldehydes, and ketones examined. The blue colour seems to be due to direct combination between the pentose and  $\beta$ -naphthol, and does not involve the intermediate formation of furfuraldehyde. The latter gives an intense orange-red colour with  $\beta$ -naphthol, above which a green ring forms, but no blue colour is produced.

C. T. G.

**Reducing Action of Dextrose on Copper Salts in Alkaline and Acid Solution.** P. FLEURY and P. TAVERNIER (*Bull. Soc. Chim. biol.*, 1925, 7, 331—335).—The reducing action of dextrose on copper salts is influenced in acid solution (Barfoed's copper acetate reagent) by the presence of many chlorides, mannitol, and the concentration of the copper, whilst in alkaline solution (Bertrand's reagent) all alkaline and alkaline-earth salts, as well as mannitol, have a retarding effect. [Cf. *B.*, 1925, 417.]

D. G. H.

**Interaction of Dextrose and Methylene-blue in an Alkaline Medium.** E. KNECHT and E. HIBBERT (*J. Soc. Dyers Col.*, 1925, 41, 94—95).—The possibility of over-reduction of methylene-blue in the reaction between this dye and dextrose in an alkaline medium is avoided, and the reaction is thereby made available for the determination of dextrose, by acidifying the product within a few seconds after the commencement of the reaction. A mixture containing sodium hydroxide, dextrose, and methylene-blue is boiled in an atmosphere of carbon dioxide, or preferably nitrogen, excess of hydrochloric acid is quickly added, and the excess of methylene-blue titrated in the usual way with titanous chloride and iron alum. Thiocarmine-*R* in the presence of rosinduline-*B* and sodium tartrate is quantitatively reduced by titanous chloride before the latter dye is affected. [Cf. *B.*, 1925, 348.]

A. J. H.

**Determination of Volatile Organic Acids.** A. BOHANES (*Chem. Listy*, 1925, 19, 121—123).—The time of distillation of volatile organic acids may be reduced by the addition of glycerol (50 c.c. to 100 c.c. of liquid to be distilled) with or without water. The temperature must not materially exceed 120°, and if necessary the operation is finished in a current of steam. [Cf. *B.*, June 26th.]

D. G. H.

**Determination of Formic Acid in Blood and Urine.** F. DE EDS.—(See i, 713.)

**Detection of Ethyl Phthalate in Ethyl Alcohol.** J. T. RALEIGH and S. U. MARIE (*J. Amer. Chem. Soc.*, 1925, 47, 589—590).—Detection of ethyl phthalate in ethyl alcohol by evaporating the sample to dryness with dilute sodium hydroxide solution, and

fusing the residue with resorcinol, is untrustworthy, as the aqueous extract of the fused mass still shows a fluorescence, although of a slightly different colour, in the absence of ethyl phthalate. A suggested alternative is to evaporate the sample to a small volume and pour the residue into a large volume of very dilute sodium hydroxide solution. The presence of ethyl phthalate is indicated by a turbidity, but the test is not conclusive. F. G. W.

**Chemical Nature of Fats. I. Iodine Super-value of Fatty Oils and Unsaturated Fatty Acids.** B. M. MARGOSCHES, L. FRIEDMANN, and W. TSCHÖRNER.—(See i, 629.)

**Determination of Formaldehyde.** E. SCHULEK (*Ber.*, 1925, 58, [B], 732—736).—The formaldehyde solution is added to an excess of standard potassium cyanide solution in the presence of magnesium sulphate, which accelerates the hydrolysis of the primarily-formed potassium derivative of glycollonitrile,  $2\text{CH}_2(\text{OK})\cdot\text{CN} + \text{MgSO}_4 + 6\text{H}_2\text{O} = 2\text{CH}_2(\text{OH})\cdot\text{CO}_2\text{K} + \text{Mg}(\text{OH})_2 + (\text{NH}_4)_2\text{SO}_4$ . After 1—2 mins. the precipitated magnesium hydroxide is dissolved by ammonium chloride, a little potassium iodide and not more than 2—3 drops of ammonia (10%) are added, and the excess of potassium cyanide is titrated rapidly with 0.05*N*-silver nitrate solution. The method is accurate in the presence of 10% of acetaldehyde, 50% of acetone, or 50% of ethyl alcohol.

For the determination of very small amounts of formaldehyde, the solution under investigation is added to a measured excess of standard potassium cyanide solution. After 2—3 mins. the mixture is acidified strongly with concentrated hydrochloric acid and treated with bromine water until permanently yellow; excess of bromine is removed by addition of phenol. Potassium iodide is added to the clear, colourless solution, and the liberated iodine is titrated after 30 mins. with sodium thiosulphate. The potassium cyanide solution must be standardised iodometrically. The process gives accurate results in the presence of 5% of acetaldehyde, 50% of acetone, ethyl alcohol, or methyl alcohol, or of 1% of dextrose or lactose. [Cf. *B.*, 1925, 423.] H. W.

**Analysis of Xanthate.** W. S. CALCOTT, F. L. ENGLISH, and F. B. DOWNING (*Eng. Min. J. Press.*, 1924, 118, 980—981).—The xanthate is precipitated as the copper salt from a slightly alkaline solution by means of copper sulphate-sodium tartrate reagent, the precipitate is collected and decomposed with nitric acid, the copper being determined volumetrically. Sulphides or thio-carbonates, but not thiosulphates, sulphites, carbonates, xanthyl disulphide, or ethyl xanthate cause high results. A. A. E.

**Qualitative Test for Weak [Organic] Bases.** R. ROBINSON (*J. Chem. Soc.*, 1925, 127, 768—769).—A saturated solution of ferric chloride in concentrated hydrochloric acid when added to a solution of a weak base in light petroleum produces three layers, the middle one of which contains the base. This behaviour is due to the formation of ferrichlorides. Carboxylic acids, acid chlorides, thiophen, safrole, diphenyl ether, and methyl and ethyl

alcohols do not give the reaction, the two last named being too soluble in water. Other applications of the reaction are described.  
S. K. T.

**Toxicological Detection of Hydrocyanic Acid by Chelle's Reaction.** G. MAGNIN (*J. Pharm. Chim.*, 1925, [viii], **1**, 336—339).—After keeping for periods up to 6 years, specimens of viscera suspected to contain hydrocyanic acid have been tested by the direct phosphoric acid method and by the method of Chelle. The former method gave negative results in all cases; the latter gave results identical with those originally obtained on the fresh specimens.  
C. P. S.

**Determination of Cyanamide.** L. A. PINCK (*Ind. Eng. Chem.*, 1925, **17**, 459—460).—The adverse effect of the presence of cyanamide derivatives on the determination of cyanamide by the usual methods may be overcome by extracting the crude material with water, precipitating the silver cyanamide in an aliquot portion of the extract by adding concentrated ammonia and ammoniacal silver nitrate solution, dissolving the precipitate in dilute nitric acid, and either titrating the silver cyanamide with thiocyanate or, if carbide is present, determining its nitrogen content. Re-dissolution and re-precipitation of the silver cyanamide is necessary if a very large proportion of dicyanodiamide is present.  
D. G. H.

**Determination of Picric Acid in the Presence of other Nitro-compounds.** L. DESVERGNES (*Ann. Chim. Analyt.*, 1925, **7**, 97—100).—To an alcoholic solution of the dry, powdered material is added a solution of potassium iodide and iodate, and the mixture titrated with sodium thiosulphate solution. Extraction with carbon tetrachloride may be used to separate the picric acid when mixed with 1-nitronaphthalene. [Cf. *B.*, 1925, 429.]  
D. G. H.

**[Determination of] Uric Acid in Blood.** W. G. LENNOX and M. F. O'CONNOR.—(See i, 711.)

**Silicododecatungstic Acid.** [Determination of Alkaloids.] E. O. NORTH and G. D. BEAL (*J. Amer. Pharm. Assoc.*, 1924, **13**, 889—898, 1001—1009).—When a solution containing sodium tungstate, sodium silicate, and hydrochloric acid is shaken with ethyl ether, and the ethereal solution evaporated, stable white crystals,  $4\text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$ , are obtained. The potassium and ammonium salts were prepared, as well as salts of organic bases, the alkaloidal salts being but slightly soluble. Alkaloids may be determined volumetrically by treating an extract, acidified with hydrochloric acid, with the silicotungstic acid solution until a drop of the supernatant liquid yields a green colour with a reddish- or brownish-orange coloured solution of malachite-green in hydrochloric acid.  
CHEMICAL ABSTRACTS.

**Potentiometric Determination of Alkaloids with a Hydrogen Electrode.** F. MÜLLER (*Z. Elektrochem.*, 1924, **30**, 587—600).—The results obtained by the electrometric titration of various

alkaloids are given, together with the corresponding  $p_H$  curves. In the case of atropine, by means of a back titration with sodium hydroxide free from carbonate after adding excess of hydrochloric acid, the break in the  $p_H$  curve corresponds with  $k_{B\cdot OH}=1\times 10^{-4}$  ( $16.5^\circ$ ). Cocaine gave  $k_{B\cdot OH}=2.5\times 10^{-6}$  ( $24^\circ$ ) and narcotine  $0.73\times 10^{-8}$  ( $24^\circ$ ). No values could be calculated for veratrine, narceine, and theobromine, the first-named being a mixture of several alkaloids, and the last two giving no sharp break in the curves. The titration of alkaloid salts with alkali hydroxide gives satisfactory results in the cases of pilocarpine and *isopilocarpine* hydrochlorides ( $k_{B\cdot OH}=1.07\times 10^{-7}$  and  $0.68\times 10^{-7}$  at  $18^\circ$ ) and of emetine and arecoline hydrobromides [ $k_{B\cdot OH}=0.81\times 10^{-6}$  ( $16^\circ$ ) and  $1.45\times 10^{-7}$  ( $17.5^\circ$ ), respectively]. With morphine hydrochloride, disturbing reduction reactions occur, which are partly eliminated by the use of a smooth platinum electrode, and with codeine phosphate, the breaks in the curve are not sharp enough for conclusions to be reached. The most suitable indicators for the different cases are indicated where possible from the potentiometric measurements.

C. H. D. C.

**Simple Determination of the Alkaloid-content of Nux Vomica and of Strychnos Preparations.** T. SABALITSCHKA and C. JUNGEMANN (*Pharm. Zentr.*, 1925, **66**, 145—150).—That the official method of determination is faulty has already been pointed out (cf. *e.g.*, Herzog, "Chemische und physikalische Prüfungsmethoden des Deutschen Arzneibuches," 1924). It is found that the convenient procedure adopted for the lupin alkaloids (A., 1924, ii, 635) is well adapted for this determination also, with the further improvement that the ether-chloroform extract is filtered (with precautions to avoid evaporation) before the aliquot part is pipetted off. [Cf. B., 1925, 297.]

W. A. S.

**Microchemical Reactions for Tyramine and Histamine.** L. VAN ITALLIE and A. J. STEENHAUER (*Pharm. Weekblad*, 1925, **62**, 429—433).—The appearances under the microscope of the picrates, chloroplatinates, iodoplatinates, double bismuth iodides, phosphotungstates, and silicotungstates are described. S. I. L.

**Identification of Vat Dyes on Cotton.** J. I. M. JONES and W. KILBY (*J. Soc. Dyers and Col.*, 1925, **41**, 127—136).—Tables are given showing the reactions with various appropriate reagents of patterns of cloth dyed with commercial vat dyes, which are listed under trade names, with the "Colour Index" numbers when available. [Cf. B., 1925, 437.]

W. A. S.

**Detection of Urobilin in Urine and Determination of Chlorides in Blood.** RODILLON.—(See i, 722.)

**Determination of Bile Acids.** E. HERZFELD and A. HAEMMERLI.—(See i, 722.)

## General, Physical, and Inorganic Chemistry.

**Spectrum of Hydrogen.** E. GEHRCKE and E. LAU (*Ann. Physik*, 1925, [iv], **76**, 673—679; cf. A., 1923, ii, 197, 802).—A long, silvered discharge tube with a fluorite window has been used for the study of the continuous and many-lined spectra of hydrogen. In agreement with Schumann, a continuous spectrum is found to extend from 3300 to 1950 Å. When electrolytic hydrogen is used, a large number of lines are superposed on the continuous ground. These are shown to be due to carbon monoxide as an impurity. It is concluded that under the experimental conditions pure hydrogen shows a continuous spectrum free from lines. This view is not in harmony with the results of other observers, but the lines found nearly always agree with those traced to carbon monoxide. The same conditions of excitation cause both the continuous and many-lined spectra to be strongly developed. When the Balmer series appears strongly, these spectra are weak. Slow electrons therefore favour the appearance of both spectra. Stark has obtained a spatial separation of the continuous and many-lined spectra, and Horton and Davies give the excitation potentials as 12.6 and 15.9 volts. The authors have measured the intensities of the continuous and many-lined spectra under different conditions, and the results indicate a difference of 6 volts between the excitation potentials.

The parallelism between the effects of slow electrons and condenser discharges recorded earlier is confirmed and extended. Two groups of lines symmetrically distributed about 5881.87 and 5832.40 Å. are added to those already found. R. A. M.

**Ultra-violet Spark-spectra of some Elements.** R. J. LANG (*Phil. Trans.*, 1924, **A**, **224**, 371—419).—The spectrograph used is a modified form of that of McLennan (A., 1920, ii, 650) of greatly increased efficiency. The instrument was calibrated over the range 2000—200 Å., in which range the spectra of the following elements have been photographed: carbon, calcium, titanium, vanadium, chromium, manganese, cobalt, arsenic, molybdenum, cadmium, tin, antimony, tellurium, cerium, platinum, gold, lead, bismuth, thorium, and uranium. The wave-lengths recorded are given in tabular form, together with the corresponding data of other observers. R. W. L.

**Spectra of Oxygen and Sulphur.** E. BUNGARTZ (*Ann. Physik*, 1925, [iv], **76**, 709—728).—According to Sommerfeld, odd multiplicity of spectral terms is to be expected in the oxygen-sulphur-selenium sub-group of the periodic table. Evidence is cited that the *p* and *d* terms of the "doublet" system of the oxygen spectrum are really triple terms. Experimental details are given whereby Wood's method of exciting the Balmer series of hydrogen (A., 1920, ii, 569) can be applied to oxygen. The series spectrum



is obtained in great purity against a perfectly even background. In the ultra-violet, however, the band spectrum is not entirely eliminated. The extension of the experiments to sulphur has been worked out with interesting results. The series spectrum of sulphur has been completed by the addition of two triplets belonging to the I and II diffuse series and located in the near infra-red. A large number of new lines have been measured extending from 6173.53 to 8694.296 Å., and four lines for oxygen are recorded in the same region. The sulphur lines are narrow and complicated in structure, but they have been provisionally classified into series. R. A. M.

**Spectra of the Metals of the Aluminium Sub-group.** K. R. RAO (*Proc. Physical Soc.*, 1925, 37, 259—264).—The light from an aluminium spark under water was passed through the vapour of thallium and of indium heated in a steel tube provided with quartz windows to temperatures up to 1500°. Tables and photographs of the spectra as far as 2000 Å. are given. None of the lines of the principal series appears as an absorption line, even at the highest temperature. In both cases, at high temperatures there is a channelled space spectrum consisting of asymmetrical bands degraded towards the red. There is very marked absorption of the members of  $1\pi_2 - m\delta'$ . E. B. L.

**Series Spectra of Two-valency-electron Atoms of Phosphorus (P IV), Sulphur (S V), and Chlorine (Cl VI).** I. S. BOWEN and R. A. MILLIKAN (*Physical Rev.*, 1925, [ii], 25, 591—599).—The regular and irregular  $X$ -ray doublet laws, already shown to be applicable throughout the whole field of optics so long as a series of atoms of like electronic structure but varying effective nuclear charge is concerned, have been used to predict the positions of lines in the spectra of two-electron atoms, although in this case the spectra consist of triplets and singlets instead of doublets as in the case of stripped atoms. For P IV, 23 lines have been identified, for S V 17, and for Cl VI 6; 12 term values of P IV and 8 of S V were determined, and all known term values for two-electron atoms of magnesium, aluminium, silicon, phosphorus, and sulphur are tabulated. It is shown that when the frequency of a given spectral line progresses linearly with the atomic number (*i.e.*, to follow the irregular doublet law) the line is produced by a jump between orbits of the same total quantum number; the screening constants differ. A. A. E.

**Series Spectra of Three-valency-electron Atoms of Phosphorus (P III), Sulphur (S IV), and Chlorine (Cl V).** R. A. MILLIKAN and I. S. BOWEN (*Physical Rev.*, 1925, [ii], 25, 600—605; cf. preceding abstract).—There have been identified 21 lines of P III, 20 lines of S IV, and 10 of Cl V; 10 term values of P III and 10 of S IV, including the  $\alpha$  level, have been determined. Screening constants for one-, two-, and three-valency-electron systems increase regularly with the number of valency electrons, and decrease with increase in the atomic number. A. A. E.

**Chlorine Spark Spectra.** L. BLOCH and E. BLOCH (*Compt. rend.*, 1925, **180**, 1740—1742).—The oscillatory discharge in an electrodeless tube is capable of exciting first and second order spark spectra. Sodium chloride is introduced into a tube which is then evacuated. The salt decomposes, furnishing sufficient chlorine to maintain the discharge. If the discharge is interrupted the experiment must be started afresh. The spectrum contains lines due to chlorine, air, and alkali metal. The air lines are easily recognised, and only the lines which persist when another alkali chloride is substituted for sodium chloride are due to the halogen. The lines of the arc spectrum Cl I are absent. The first order spark spectrum, Cl II, contains the triplets 4819—4810—4794 and 4253—4241—4233 and the complex triplets 5457—5444—5423 and 3861—3851—3845 Å. Many new lines similar to the above have been found (but not recorded in this paper) and ascribed to Cl II. A large number of additional lines are ascribed to the second order spark spectrum Cl III. The Cl III spectrum extends far into the ultra-violet and includes the lines 3991·625, 3720·4, 3658·5, 3624·3, 3622·7, 3613·9, 3602·2.

R. A. M.

**Allocation of Terms to Some Multiplets in the Iron Spectrum.** S. GOUDSMIT (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 572—583).—Terms have been allocated to the members of the multiplets discovered by Walters in the iron spectrum, using the rules of Sommerfeld and Landé.

S. B.

**Structure of Cobalt Spectrum.** M. A. CATALÁN (*Z. Physik*, 1925, **32**, 336—369).—A classification of 517 lines is given and discussed; the energy levels show great similarity to those of iron; the terms show remarkable regularity.

E. B. L.

**Wave-length and Width of the *K*-Absorption Limit of Zinc.** B. WALTER (*Z. Physik*, 1925, **32**, 409—414).—This wave-length for zinc lies between the  $L_{\beta}$  line of tungsten,  $1279\cdot17 \times 10^{-11}$  cm., and the  $L_{\gamma}$  line of tantalum,  $1281\cdot0 \times 10^{-11}$  cm. The value calculated from Kossel's theory is  $(1280 \pm 1\cdot0) \times 10^{-11}$  cm.

E. B. L.

**Spectrum of Germanium.** J. LUNT (*Month. Not. Roy. Astr. Soc.*, 1924, **85**, 38—46).—The spectrum of germanium has been re-examined in the visible region. The spark discharge between metallic electrodes and the vacuum discharge through germanium chloride were both used, and the lines have been classified according to their behaviour under various discharge conditions. Discrepancies up to 1·5 Å. were found between the wave-lengths of the spark and vacuum tube lines.

S. B.

**Large Line-displacements in the Spectra of Germanium and Chlorine under Different Conditions of Temperature.** J. LUNT (*Month. Not. Roy. Astr. Soc.*, 1924, **85**, 148—156; cf. preceding abstract).—Displacements of certain lines in the spectra of germanium and chlorine, of the order of 1 Å., are occasioned by alteration of discharge conditions. The displacements in chlorine

have been tabulated from a comparison of the wave-lengths of the lines excited in germanium chloride vapour in vacuum tubes under widely differing types of discharge. The displacements are attributed to changes in "temperature" with the various conditions imposed, and a parallel is drawn with displacements observed in stellar spectra. S. B.

**Quartet-system Multiplets in the Arc Spectrum of Yttrium.** W. F. MEGGERS and B. E. MOORE (*J. Washington Acad. Sci.*, 1925, **15**, 207—210).—Measurements of the magnetic resolutions of yttrium arc lines have revealed prominent quartet terms which have their analogues in the scandium arc spectrum (Meggers, this vol., ii, 77). The agreement between the observed interval ratios for the quartet terms  $F$ ,  $F'$ , and  $G_1$  and those calculated by Landé's interval rule (*Z. Physik*, 1923, **15**, 189), is good, but poor for the quartet  $D$  term. M. S. B.

**Regularity in the Fine Structure of Spectral Lines.** G. JOOS (*Physikal. Z.*, 1925, **26**, 380—382).—The spacings of the fine structure of the cadmium triplets,  $2p-2s$ , and of the bismuth line 4722 are multiples of 0.05. The introduction of a further quantum number,  $f$ , is necessary to explain fine structure (cf. Ruark, Mohler, and Chenault, A., 1924, ii, 797). J. S. C.

**Pole-effect of Barium and Neodymium Rays in the Visible Region of the Spectrum.** J. M. MOHR (*Compt. rend.*, 1925, **180**, 1397—1399).—With metal electrodes, the pole effect is greater at the positive than at the negative pole; when salts are used, the reverse is true. The displacement of spectral lines is of the same magnitude and sign at the negative pole, using carbon electrodes, as at the positive pole of metal electrodes. Barium and neodymium salts were placed in the crater of a carbon electrode and the light from the centre of the arc and the two poles was examined in one operation with an interference spectrograph. The barium lines show (a) displacements up to 0.003 Å. for the negative pole and negligibly small displacements for the positive pole, and (b) a few lines with larger displacements, e.g., for 6141.75: negative +0.008, positive +0.002; and for 5777.77: negative -0.005, positive 0.000. The connexion between pole-effect and the lines in a series does not appear. The displacements are equally small with neodymium. Calcium lines were observed owing to impurity, and earlier measurements of the displacement are confirmed. This fact supports the view that the pole effect is not due to the density of the vapours. R. A. M.

**New Lines between 3100 and 2200 Å. in the Arc Spectrum of Lanthanum at Normal Pressure.** S. PINA DE RUBIES (*Compt. rend.*, 1925, **180**, 1478—1480).—The wave-lengths and intensities of more than 200 lines in the arc spectrum of lanthanum between the limits indicated are recorded. J. S. C.

**X-Ray Spectra of Praseodymium, Neodymium, and Samarium.** E. GLEDITSCH and E. BOTOLFSSEN (*Compt. rend.*, 1925, **180**, 1653—1655).—The X-ray spectra of praseodymium,

neodymium, and samarium have been investigated by the method of Siegbahn, using a rotating crystal of rock salt. The following values, in Ångström units, have been found for the characteristic wavelengths of the different rays. Praseodymium:  $\alpha=2.4635$ ,  $\beta_1=2.2632$ ,  $\beta_2=2.2218$ ,  $\beta_3=2.1268$ ,  $\gamma_1=1.9794$ ,  $\gamma_2=1.8844$ ,  $\gamma_3=1.8255$ . Neodymium:  $\alpha=2.3725$ ,  $\beta_1=2.1707$ ,  $\beta_2=2.1303$ ,  $\beta_3=2.0282$ ,  $\gamma_1=1.8708$ ,  $\gamma_2=1.7937$ ,  $\gamma_3=1.7390$ . Samarium:  $\alpha=2.2059$ ,  $\beta_1=2.0014$ ,  $\beta_2=1.9610$ ,  $\beta_3=1.8708$ ,  $\gamma_1=1.7159$ ,  $\gamma_2=1.6475$ ,  $\gamma_3=1.5970$ .  
W. H.-R.

**Absorption of a Line of the Principal Series of Singly Ionised Atomic Mercury.** L. A. TURNER and K. T. COMPTON (*Physical Rev.*, 1925, [ii], 25, 613—617).—Carroll's conclusion that the line 1942 Å. is a member of the principal series and 2225 and 2848 Å. of the subordinate series of mercury is supported by the fact that only the first shows absorption when light from an electrodeless discharge in mercury vapour is passed through a region of a low-voltage arc in mercury vapour containing a high concentration of positive ions. Further, the lines appear respectively at 6.7, 12.3, and 10.7 volts.  
A. A. E.

**Spectrum of Mercury under Heavy Current Excitation.** M. FUKUDA (*Japan. J. Phys.*, 1924, 3, 139—153).—The effect on the spectrum from a mercury arc of increasing the current density up to 5.3 amp./cm.<sup>2</sup> has been examined in detail. The effect consists mainly in the broadening of certain lines and in the appearance of a large number of lines "forbidden" by the selection principle. Previously known series in the spectrum have been extended to higher members, and 40 forbidden lines newly arranged in series. The critical field intensities required for the excitation of the newly-observed forbidden lines have been estimated. In addition, a large number of new lines, both of the arc and the spark types, have been observed, which have not yet been arranged in series.

S. B.

**Absorption and Emission Spectra of the Geissler Discharge in Mercury Vapour and in Mixtures of Mercury and Hydrogen.** L. A. TURNER and K. T. COMPTON (*Physical Rev.*, 1925, [ii], 25, 606—612).—The positive column is a strong absorber for many lines of the sharp and diffuse subordinate series, the strength of the absorption decreasing in the order  $2p-2s$ ,  $2p-3s$ , and  $2p-3d$ ,  $2p-4d$ ,  $2p-5d$ . The fact that the absorption by atoms in the  $2p_1$  state is greatest, but of the same order of magnitude as that by atoms in the  $2p_2$  and  $2p_3$  states is difficult to reconcile with the short life of the  $2p_2$  state. The bright region of the striated positive column (produced by addition of hydrogen) showed greater absorption of the  $2p-2s$  lines than did the dark region. The negative glow emitted the arc spectrum and the spark line 2848 Å.; the continuous positive column emitted the arc spectrum, the striated column emitting also HgH bands.  
A. A. E.

**Vacuum Thermo-element.** W. J. H. MOLL and H. C. BURGER (*Z. Physik*, 1925, 32, 575—581).—A very neat and sensitive thermo-

couple for use in spectroscopy is described and a graph of the mercury spectrum, automatically registered, given. E. B. L.

**Radiating Atoms in Magnetic Fields.** P. ZEEMAN (*J. Franklin Inst.*, 1925, **199**, 585—596).—A lecture reviewing the historical and theoretical development of the Zeeman effect.

F. G. T.

**Intensities of Lines in Multiplets.** H. N. RUSSELL (*Nature*, 1925, **115**, 835—836).

**Anomalous Dispersion and Multiplet Lines in Spectra.** C. V. RAMAN and S. K. DATTA (*Nature*, 1925, **115**, 946).—Attention is directed to observations parallel with those of Dorgelo (*Diss.*, Utrecht, 1924).

A. A. E.

**K-Absorption Levels of the Light Atoms.** H. ROBINSON (*Nature*, 1925, **115**, 945—946).—Revised  $\nu/R$  values ( $K$  level) have been obtained as follows: calcium, 296.6; sulphur, 180.3; magnesium, 93.6; sodium, 76.6; oxygen, 36.7. Details of the work and improved apparatus will appear elsewhere.

A. A. E.

**Semi-optical Lines in the X-Ray Spectra.** E. BÄCKLIN, M. SIEGBAHN, and R. THORÆUS (*Phil. Mag.*, 1925, [vi], **49**, 1320).—Polemical against Dauvillier and de Broglie (cf. this vol., ii, 458).

R. A. M.

**Continuous X-Ray Spectrum and Planck's Radiation Law.** A. MARCH (*Ann. Physik*, 1924, [iv], **75**, 711—742).—Mathematical, with a discussion of experimental results. The continuous background is regarded as a heat radiation emitted by atoms of the anticathode which have been strongly heated by collision with electrons.

A. S. R.

**Coherence of Superposed X-Radiations.** C. G. BARKLA and G. I. MACKENZIE (*Nature*, 1925, **115**, 942).

**Broadening of Lines in Arc Spectra and the Stark Effect.** H. LOWERY (*Phil. Mag.*, 1925, [vi], **49**, 1176—1183).—Lines produced in arc spectra by heavy currents (40 amps.) are affected similarly as in the Stark effect, i.e., lines showing the Stark effect were broadened in the same sense (Kimura and Nakamura, A., 1924, ii, 799). Interrupted arc spectra (A., 1922, ii, 176, 410) of copper, silver, gold, nickel, and magnesium have been studied. The broadening of lines is similar to that observed in the heavy current arc spectra, and is such as would be expected from the observations on the Stark effect. Duffield (A., 1911, ii, 350) found certain broadening effects. He employed heavy currents and the arc had to be struck repeatedly. His results are therefore compatible with the present work.

R. A. M.

**Experimental Control of Electrically Broadened Spectral Lines.** M. C. JOHNSON (*Proc. Physical Soc.*, 1925, **37**, 249—258).—The line  $H_\alpha$  from a discharge in an ordinary type of Pflücker tube was selected for examination, viewed through a micrometer

eyepiece attached to a 20-plate echelon and a Hilger constant-deviation spectroscope. The effects of inductance, capacity, current-density, of rectified and unrectified currents, and of a magnetic field were studied. The width was also varied by supplying additional ions from a heated filament. It is concluded that the width of the line depends on the number of charges which surround the emitting particle. E. B. L.

**Relative Mobility of Initial Positive Ions in Gas Mixtures at Low Pressures.** H. B. WAHLIN (*Physical Rev.*, 1925, [ii], 25, 630—635).—The initial mobility of ions at low pressures appears to be determined chiefly by the mass of the ion rather than by its dimensions. Aged ions have lower mobilities and are probably clusters. A. A. E.

**Ionisation of Salt Vapours. II.** V. KONDRATÉEV (*Z. Physik*, 1925, 32, 535—541; cf. A., 1924, ii, 291).—The vapours of zinc chloride and of sodium iodide were bombarded with slow electrons from a Wehnelt cathode, the nature of the ions being ascertained by determining the magnetic field required to deflect them through a certain arc. The chief process in zinc chloride vapour is decomposition into  $\text{ZnCl}^+$  and  $\text{Cl}^-$ , which occurs at  $12 \pm 1$  volts. There are also indications of the occurrence in very small quantity among the positive ions of  $\text{ZnCl}_2^+$ ,  $\text{Zn}^+$ , and either  $\text{Zn}^{++}$  or  $\text{Cl}^+$ . Preliminary results indicate that ionisation of sodium iodide causes the formation of  $\text{Na}^+$ ,  $\text{I}^-$ , and  $\text{NaI}^+$ . E. B. L.

**Variation of the Energy absorbed by Ionisation in Air when Excited by X-Rays of varying Wave-length.** L. GREBE (*Physikal. Z.*, 1924, 25, 599—601).—Determinations have been made of the ratio of the energy of an X-ray beam, after having ionised a layer of air, to the intensity of ionisation produced over the range 0.397 to 0.166 Å. Relative values of the beam energy were obtained by observing the thermal effect produced in a lead target. The values so obtained are compared with the corresponding values derived from an equation due to Küstner (*Strahlentherapie*, 1924, 27, 1) in which the total absorption is expressed as a function of the frequency and of the scattering effect. The values agree at the lower frequencies but diverge considerably at the higher ones. Appended is a discussion of the difficulties inherent in technique of this type and of the validity of Küstner's equation. R. W. L.

**Critical Potentials Associated with Excitation of Alkali Spark Spectra.** F. L. MOHLER (*U.S. Bur. Standards, Sci. Paper* 505, 1925, 20, 167—191).—Critical potentials for the production of radiation are found for rubidium vapour at 16 and 21.6 volts, and less defined potentials at 18, 25.2, and 68 volts. The ionisation curve shows a marked increase at 16 volts. Spark lines are excited at potentials between 17 and 25 volts. The intensity of these lines depends on the current density. The current density required to produce spark lines at 25 volts is estimated as 0.01—0.02 amp./cm.<sup>2</sup> With caesium, spark lines are excited with small

currents at 21.5 volts, and with large currents near 14 volts. Noticeable enhancement of all spark lines occurs at higher voltages, and a new spectrum appears above 40 volts. Critical potentials were found for potassium vapour at 19 and 23 volts (*U.S. Bur. Standards, Sci. Paper* 425) and increase of ionisation occurred at the higher potential. A similar increase is now found at 19 volts, and spark lines are excited at this point with high currents, and near 28 volts with low currents. Sodium vapour gives spark lines near 35 and 44 volts with large and small currents, respectively. Lithium vapour shows a critical potential at 54 volts and a single spark line occurs with large current densities at  $2934.15 \text{ \AA}$ . (cf. A., 1924, ii, 365). Evidence is adduced for the view that the potentials Li 54, Na 35, K 19, Rb 16, and Cs 14 measure the work required to remove a single electron from the rare gas shell of the normal atom. Each of these values, except that of sodium, is equal within experimental error to the ionisation potential of the neighbouring rare gas ion. Direct comparison is impossible in the case of sodium, since the ionisation potential of neon is unknown. The critical potential for low-current spark excitation gives the work necessary to remove two electrons by a single collision. The critical potentials of potassium and rubidium at 23 and 21.6 volts, respectively, apparently measure the work required to remove a second electron from an ion, of which the valency electron is already removed. The relative intensities of the spectra of caesium excited in the above thermionic discharge with different exciting potentials, in the high-voltage disruptive discharge (cf. this vol., ii, 4), and in the induction ring discharge (Dunoyer, A., 1922, ii, 729), are tabulated, and the fact that the two spark spectra of caesium, which have widely different excitation potentials, appear in nearly the same relative intensity in the thermionic discharge at 80 volts and in the disruptive discharge, indicates that the effective discharge in the latter is about 80 volts.

F. G. T.

**Electron Emission of Metals.** I. A. BECKER (*Ann. Physik*, 1924, [iv], 75, 781—800).—A general theoretical discussion of the subject. Richardson's work,  $\delta$ -radiation, and the emission of electrons by the action of  $\alpha$ -particles are specially dealt with.

A. S. R.

**Behaviour of Hydrogen in the Discharge due to Alternating Electric Fields of High Frequency.** R. W. LUNT (*Phil. Mag.*, 1925, [vi], 49, 1238—1249).—The author's technique (this vol., ii, 579) for investigating the chemical effects in gases of alternating electric fields of the order of  $10^7$  cycles per sec. is applied to the study of the ionisation produced in hydrogen at the frequency  $1.5 \times 10^7$ . The phenomena occurring in an ozoniser or ionisation vessel are analysed so that the voltage gradient and the current carried by the ions in the gas can be determined. An equation is given showing a connexion between impressed electric force, conduction current in the ionised gas, and the known motions of ions and electrons in hydrogen. From this it is possible to arrive at the mean intensity of ionisation of hydrogen under any given electrical conditions. This quantity

and also the impressed electric force are shown graphically over the pressure range 10—50 cm. The concept of equivalent temperature—that temperature at which the same density of ionisation would be produced by thermal dissociation as that observed in the ionisation vessel under any given conditions—is introduced. A series of values of this quantity at a series of voltages is expressed graphically against varying hydrogen pressure. R. A. M.

**Electron Emission from Oxide-coated Filaments.** L. R. KOLLER (*Physical Rev.*, 1925, [ii], 25, 671—676).—Since the electron emission of platinum-iridium filaments coated with barium and strontium oxides is decreased by the presence of oxygen and increased by that of argon, hydrogen, carbon monoxide, and carbon dioxide, or by positive ion bombardment, the effect is probably due to a film of the metal. A. A. E.

**Absorption Coefficient for Slow Electrons in Gases.** R. B. BRODE (*Physical Rev.*, 1925, [ii], 25, 636—644).—The absorption coefficients for electron accelerating voltages of 2—360 for argon, helium, methane, nitrogen, and carbon monoxide exhibit maxima at 12, 4, 7.5, 18, and 18 volts, respectively; the curve for hydrogen shows no maximum, the coefficient increasing steadily down to 2 volts. A. A. E.

**Double Impacts by Electrons in Helium.** G. GLOCKLER (*Nature*, 1925, 115, 909—910).—Polemical against Dymond (this vol., ii, 253). A. A. E.

**Double Impacts by Electrons in Helium.** E. G. DYMOND (*Nature*, 1925, 115, 910).—Polemical against Glockler (preceding abstract). A. A. E.

**Constancy of Total Photo-current from Sodium with Temperature Change 20° to -190°.** R. C. BURT (*Phil. Mag.*, 1925, [vi], 49, 1168—1176).—An evacuated electric bulb of soda-glass is immersed in molten sodium nitrate and a potential of 100 volts is applied between the latter and the lighted filament. Sodium is driven through the walls; it evaporates and condenses at the top inside the bulb. In order to maintain the sodium surface clean, the lamp is attached to a mercury pump with two intermediate liquid air-traps. The sodium can be distilled back to the bottom of the bulb, so that light from the filament may be incident on the sodium surface. The photo-current is then measured at the ordinary temperature and at the temperature of liquid air. If the surface of sodium is clean, the total photo-current is practically constant over this range. If, however, the surface is faintly contaminated, the current may vary much more at a low temperature than at the ordinary temperature. On the other hand, a surface slightly more contaminated by some unknown vapour may be several times less sensitive at -190° than at 20°. Ives (A., 1924, ii, 444) found a temperature effect on photo-emission from sodium. The effects were reproduced by the author by allowing the sodium surface to be contaminated. R. A. M.



**Direction of Emission of Photo-electrons.** P. AUGER and F. PERRIN (*Compt. rend.*, 1925, **180**, 1742—1744).—The large dispersion of photo-electrons is explained on the basis of three assumptions, (a) that the process of emission occurs instantaneously, (b) that the electron leaves its orbit tangentially, its kinetic energy increasing suddenly by  $N\nu$ , and (c) that the probability of emission for a given electron depends on the intensity of the incident radiation, or more precisely, on the square of the amplitude of the field acting on the electron.  
R. A. M.

**Evaluation of the Magnetic Moment of Atoms.** N. SEMENOV (*Z. Physik*, 1924, **30**, 151—152).—A criticism of the argument adopted by Stern and Gerlach, whose values are shown to be in error, in some cases by as much as 100%.  
R. W. L.

**Paramagnetism of the Rare Earths.** B. CABRERA (*Anal. Fis. Quím.*, 1925, **23**, 151—157; cf. A., 1924, ii, 142; this vol., ii, 173).—Data are given for the magneton numbers of the rare-earth metals, obtained from measurements, using the sulphates. Except for samarium, the values obtained approximate to whole numbers. Magneton numbers plotted against atomic numbers give a curve showing two maxima (cf. Meyer, this vol., ii, 173). This type of curve is not to be expected from the Bohr distribution of electrons but might be in agreement with the modified distribution suggested by Stoner (this vol., ii, 85).  
G. W. R.

**Significance of Spectroscopic Magneton Numbers.** E. C. STONER (*Phil. Mag.*, 1925, [vi], **49**, 1289—1309).—A theoretical discussion of the Landé-Sommerfeld schemes of co-ordinating multiplet structures and Zeeman effect. Electron orbits and cores are characterised by magnetic moments which are integral multiples of the Bohr unit. The azimuthal quantum number determines the magnetic moment of an electron orbit. The maximum term multiplicity is greater by two than the core moment the maximum value of which is equal to the number of electrons it contains in uncompleted groups. Magnetic balancing in pairs of core electrons gives rise to lower multiplicities, all odd or all even for odd or even numbers of core electrons. The magnetic moments deduced spectroscopically agree with those found by Gerlach and Stern. The core values are simply related with the ionic moments deduced from susceptibility measurements. The question of angular moments and the assignment of  $j$  values are discussed (cf. Pauli, this vol., ii, 339).  
R. A. M.

**Mass-spectra of Chemical Elements. VI. Accelerated Anode Rays Continued.** F. W. ASTON (*Phil. Mag.*, 1925, [vi], **49**, 1191—1201).—Indium is simple with mass number 115. Strontium is almost entirely 88, 86 occurring to the extent of only 3—4%; the principal constituent is decidedly less than a whole number, and the discrepancy between the atomic weight from mass spectra and chemical work (87.65) is no longer serious. Barium has a principal isotope of 138 slightly less than a whole number; there is no isotope below 136 but a minute amount of 136 or 137 may exist;

the chemical atomic weight is low. Lanthanum is simple, 139; praseodymium, simple, 141. Neodymium contains 142, 144, 146 not differing widely in relative amounts, with possibly a little 145. Cerium is 140, a whole number; a little 142 also exists. Zirconium has 90, 92, 94 (96 doubtful), the relative intensities of which are 10 : 2 : 4 : (1); the masses of zirconium isotopes are nearly integral with those of bromine, *i.e.*, less than whole numbers by about 0.1 unit. Cadmium has six isotopes 114, 112, 110, 113, 111, 116 in order of decreasing intensity; the masses appear to be integral with iodine (126.9). Cadmium resembles tin in respect of mass spectra. Tellurium has three isotopes 126, 128, 130, intensities 1 : 2 : 2; the mean atomic weight should therefore be greater than 128. Bismuth is a simple element of mass number 209. Silicon shows the 28 line strongly with faint lines corresponding with 29 and 30, so that the accepted atomic weight is probably low. Iron has two isotopes 56 and 54, intensities 20 : 1. Lead is complex, but the results are deferred. The elements remaining to be analysed are surveyed. Niobium, molybdenum, rhodium, ruthenium, and palladium will be very difficult to examine, but tantalum, tungsten, osmium, iridium, platinum, hafnium, and the rare earths should be less difficult. Gold and thallium will be difficult because of the difficulty of eliminating mercury completely. Thorium and uranium are the least hopeful because of their high atomic weights.

A complete list of all the non-radioactive isotopes so far discovered is given, as this paper marks the last of the series. Further work will be directed towards a more exact comparison of the masses of known isotopes rather than to the determination of the masses of the isotopes of the elements not yet studied.

R. A. M.

**Isotopes of Mercury.** F. STUMPF (*Z. Physik*, 1924, **30**, 173—174).—A short theoretical criticism of Aston's theory of isotopes, with particular reference to the isotopes of mercury and their relation to gold.

R. W. L.

**Exact Determination of the Atomic Mass of the Lithium Isotope 6.** J. L. COSTA (*Compt. rend.*, 1925, **180**, 1661—1662).—By a modification of the method of Aston, the mass of the atom of the lithium isotope 6 has been compared with that of helium, 4.000. Two separate determinations gave the mass of the lithium atom 6, as 6.010 and 6.009, respectively, with a possible error of  $\pm 0.002$ .

W. H.-R.

**Use of Fused Borax in the Determination of the Atomic Weight of Boron.** H. V. A. BRISCOE, P. L. ROBINSON, and G. E. STEPHENSON (*J. Chem. Soc.*, 1925, **127**, 150—162).—Following a review of previous determinations of the atomic weight of boron by methods which involve the use of fused borax, and give values appreciably higher than those obtained by methods involving the use of boron halides, a series of experiments is described in detail, in which the atomic weight of boron is determined from values obtained for the ratio borax glass : silver chloride. The evidence so obtained is held to condemn as unsatisfactory all methods involving the use of fused borax.

R. W. L.

**Revision of the Atomic Weight of Aluminium. III. Analysis of Aluminium Chloride.** H. KREPELKA and N. NIKOLIĆ (*Chem. Listy*, 1925, **19**, 158—163; cf. A., 1924, ii, 763).—Pure aluminium chloride was obtained by the action of dry chlorine on an intimate mixture of carbon and alumina at a red heat. The mixture was prepared by precipitation of aluminium hydroxide from a solution of the chloride in which finely-divided carbon was suspended and subsequent ignition of the precipitate in dry nitrogen. The mean of five determinations of the ratio  $\text{AlCl}_3 : 3\text{Ag}$  and of two determinations of the ratio  $\text{AlCl}_3 : 3\text{AgCl}$  gave 26.971 as the atomic weight of aluminium, when 35.458 and 107.880 were taken as the atomic weights of chlorine and silver, respectively.

A. R. P.

**Copper Oxide and the Atomic Weight of Copper.** R. RUEB and K. BODE (*Ber.*, 1925, **58**, [B], 852—859).—The recent determination of the atomic weight of copper by the authors (A., 1924, ii, 761) has been rejected by the German Commission on Atomic Weights on the ground that no evidence is adduced to prove that the final copper oxide is a well-defined chemical individual free from occluded gases. It is shown that copper oxide does not become constant in weight when ignited at any temperature between  $750^\circ$  and  $1020^\circ$ , losing not only occluded gases, but also a part of the chemically combined oxygen. At  $750$ — $900^\circ$ , the oxide becomes sufficiently constant in weight in a current of oxygen, but its freedom from occluded gases cannot be guaranteed. The composition of copper oxide in contact with oxygen at the atmospheric pressure is constant at all temperatures below about  $800^\circ$ ; above this temperature, traces of a lower oxide are produced which appear to remain dissolved in the cupric oxide, since otherwise the evolution of oxygen at a constant temperature would proceed until conversion into the lower oxide was complete. Homogeneous cupric oxide can therefore be produced by heating the oxide in a current of air and subsequently oxygen at  $1000^\circ$  and finally for a protracted period at  $700^\circ$  in oxygen. Repetition of this procedure with the same specimen of oxide shows that the loss in weight is considerable only after the first and second ignitions. Subsequently, the loss diminishes rapidly and becomes constant at 0.0008% after the sixth ignition; this loss appears to be due to slight volatility of the copper oxide. It is therefore considered that the conditions used by the authors are such that the final product was well-defined cupric oxide and that the value  $\text{Cu}=63.546$  is trustworthy.

H. W.

**Atomic Weight of Bromine. Inseparability of the Isotopes by Fractional Crystallisation.** P. L. ROBINSON and H. V. A. BRISCOE (*J. Chem. Soc.*, 1925, **127**, 138—150).—Ammonium bromide was subjected to prolonged fractional crystallisation and the atomic weight of the bromine in the final head and tail fractions was determined by measurement of the ratio  $\text{Ag} : \text{AgBr}$ . The mean values of the atomic weight of bromine in these fractions were very approximately the same, showing that no concentration of one isotope in

the mixture had been effected. The mean value obtained was  $79.914 \pm 0.003$ . A complete description is given of the elaborate experimental technique adopted. R. W. L.

**Determination of the Radioactive Content of the Air by Streaming.** H. BONGARDS (*Physikal. Z.*, 1924, 25, 679—682).—Data are given indicating the variation of the conductivity of air. R. W. L.

**Decay Constant of Radium Emanation.** L. BASTINGS (*Proc. Camb. Phil. Soc.*, 1925, 22, 562—566).—The decay constant,  $\lambda$ , of radium emanation has been determined to be  $0.1808 \text{ day}^{-1}$ , or the period of half-life to be 3.833 days, with a probable error of 0.2%. The method employed was the comparison of two emanation tubes of equal activities with a radium standard, the time being noted during which the combined activity of the two tubes fell to the original value of either taken separately. This gives a direct estimate of the half-life (cf. Curie and Chamié, this vol., ii, 8). S. B.

**Behaviour of the  $\alpha$ -Particles from Radium-F in a Longitudinal Electric Field.** W. HAMMER and H. PYCHLAN (*Physikal. Z.*, 1924, 25, 585—587).—Measurements have been made of the variation of the range of the  $\alpha$ -particles when accelerated or retarded for a portion of their path by a field of the order of 40 kilovolts/cm. The results are found to agree very well with the formula proposed by Geiger (A., 1910, ii, 473). R. W. L.

**Long-range Particles Emitted by Polonium.** (MLLE.) I. CURIE and N. YAMADA (*Compt. rend.*, 1925, 180, 1487—1489; cf. this vol., ii, 255).—Previous work is continued, layers of compressed air, oxygen, and carbon dioxide being substituted for metallic screens. The number of long-range particles is roughly proportional to the quantity of polonium and independent of the metal on which the polonium is deposited. The particles are not all of one type and their number decreases rapidly between 4 and 14 cm. of equivalent path. With oxygen and carbon dioxide, the number of long-range particles is roughly 10 per  $10^7$   $\alpha$ -particles. In air, they are about three times as numerous and their maximum range is about 16 cm. The possible nature of the particles is discussed. J. S. C.

**Quantitative Optical Method for Differentiating between  $\alpha$ - and H-Particles.** E. KARA-MICHAILOVA (*Physikal. Z.*, 1924, 25, 595—596).—The method is based on the variation of relative brightness of fluorescence produced by the rays on a zinc sulphide screen when examined several mm. from the end of the path. This characteristic serves to differentiate the two types of radiation. R. W. L.

**Retrograde H-Particles from Disintegrating Atoms.** G. KIRSCH (*Physikal. Z.*, 1925, 26, 379—380).—The experiments of Rutherford and Chadwick (A., 1922, ii, 682) do not afford any conclusive proof of the existence of backward-moving H-particles. J. S. C.

**Direct Determination of Distribution of Intensity in the Natural  $\beta$ -Ray Spectrum of Radium-*B* and -*C*.** L. F. CURTISS (*Proc. Camb. Phil. Soc.*, 1925, **22**, 597—600).—A preliminary account of experiments on the intensity of the continuous background in the  $\beta$ -ray spectrum of radium-*B* and -*C*, designed to decide whether its appearance is due to secondary effects, or whether it originates within the disintegrating atoms. The spectrum was resolved magnetically, and the intensity of the rays of different velocities determined by direct measurement of their charge with a Compton electrometer. The results so far obtained indicate that bare sources have a weaker continuous spectrum than thin-walled emanation tubes. S. B.

**Magnetic Spectrum of High-velocity  $\beta$ -Particles from Radium-*B*+*C*.** J. D'ESPINE (*Compt. rend.*, 1925, **180**, 1403—1405; cf. A., 1913, ii, 270, 899; 1914, ii, 607; 1924, ii, 447; this vol., ii, 85).—The existence of swift  $\beta$ -particles from radium-*C* is confirmed. Two particles are found for which  $H\rho=9960$  and 10,700, respectively. A band of high-velocity particles has also been observed between the values  $H\rho=15,000$  and 27,000. Although feeble, this band has been measured with different magnetic fields, and it consists of several groups of particles which traverse thin screens of aluminium easily. A table is given showing several of the principal groups of  $\beta$ -particles from radium-*B* and -*C*. The values agree with those of Ellis and Skinner (A., 1924, ii, 85, 137). R. A. M.

**Absorption of  $\beta$ -Rays by Matter.** G. FOURNIER (*Compt. rend.*, 1925, **180**, 1490—1492; cf. this vol., ii, 176).—The coefficients of absorption of  $\beta$ -rays for elements of which the atomic numbers do not exceed 50 are represented in a satisfactory manner by the linear equation previously reported. Experiments with elements possessing higher atomic numbers show that the absorption is complicated by the production of a secondary radiation. On the assumption that the absorption coefficients of the primary radiation are calculable from the linear formula, the values of the absorption coefficients of the secondary radiation for platinum, gold, thallium, and lead are calculated. These latter coefficients are much smaller than the former and the secondary radiation is held to be electromagnetic in nature. J. S. C.

**Characteristic  $\gamma$ -Ray Spectra and their Photo-electric Effect.** J. THIBAUD (*J. Phys. Radium*, 1925, [vi], **6**, 82—98).—A résumé of previous papers (cf. A., 1924, ii, 515, 717; this vol., ii, 10, 85, 176, 257). F. G. T.

**Heating Effect of  $\gamma$ -Rays from Radium-*B* and Radium-*C*.** C. D. ELLIS and W. A. WOOSTER (*Proc. Camb. Phil. Soc.*, 1925, **22**, 595—596).—A method has been devised for the determination of the heating effect of  $\gamma$ -rays in presence of  $\alpha$ -rays by measuring the difference in rise of temperature of aluminium and lead blocks exposed to the rays. The  $\alpha$ -rays produce the same heating effect in each metal, being completely absorbed, whilst the  $\gamma$ -rays heat

the lead more than the aluminium, owing to the higher absorption coefficient of the former metal. The account is preliminary.

S. B.

**Method of Analysis by Absorption of Radioactive Radiations.** (MME.) J. S. LATTÈS (*Compt. rend.*, 1925, **180**, 1400—1402).—A general method of analysis is described applicable to all kinds of complex radiation. Details of technique are given and the analysis shows that with every group of primary  $\gamma$ -rays a definite group of secondary  $\beta$ -particles is found to correspond. This is held to justify certain theoretical calculations based on the intensity of the secondary radiation.

R. A. M.

**Disintegration of Atoms.** H. PETTERSSON and G. KIRSCH (*Physikal. Z.*, 1924, **25**, 588—595).—A general review of present data with a discussion of the interpretations of the Cambridge and other schools.

R. W. L.

**Structure of Barium.** H. COLLINS (*Chem. News*, 1925, **130**, 307—310).—From consideration of data based on the laws of relative volume and of heat of formation, the structure of the barium atom is deduced as  $\text{CaTi}_2$ .

A. R. P.

**Properties of Chemical Compounds and Atomic Structure.** K. FAJANS (*Physikal. Z.*, 1924, **25**, 596—597).—The properties of chemical compounds are discussed in terms of polar and non-polar compounds of the Bohr atom.

R. W. L.

**Application of the Correspondence Principle to the Theory of Line-intensities in Band Spectra.** R. H. FOWLER (*Phil. Mag.*, 1925, [vi], **49**, 1272—1288).—Theoretical. A general summary with considerable extensions.

R. A. M.

**Electrical Conductivity of an Element and its Place in the Periodic System.** Z. A. EPSTEIN (*Z. Physik*, 1925, **32**, 620—638).—The electrical conductivities of metals are compared at temperatures which are the same fraction of their boiling points (absolute). These values multiplied by the cube root of the atomic volume,  $\chi V^{1/3}$ , when plotted against atomic numbers, show a regular decrease in each group from the maxima of the first members of the group. The point of view adopted is that of the mean inter-atomic conductivity, defined as the number of electrons transferred in unit time from atom to atom under a potential difference of 1 volt per atomic distance. An empirical relationship is shown to exist between the values for  $\chi V^{1/3}$  and the distribution of electrons according to Bohr's theory.

E. B. L.

**Periodic Classification of the Elements and the Electrical Constitution of Atoms and of Valency.** G. ODDO (*Gazzetta*, 1925, **55**, 149—174).—Various modifications are made in the table of the elements previously published (A., 1921, ii, 102), and conclusions are reached concerning the regions and structural conditions governing the ability of an element to combine with another. A ready electronic interpretation of the notion of valency is also derived.

T. H. P.

**Electron and Light-quantum from the Experimental Point of View.** R. A. MILLIKAN (*Z. physikal. Chem.*, 1925, **116**, 65—80).—A translation of a Nobel Lecture, delivered at Stockholm on May 23rd, 1924. L. F. G.

**Spectroscopy and Bohr's Theory of Atomic Structure.** P. D. FOOTE (*J. Franklin Inst.*, 1924, **198**, 344—363; 517—540).—A concise account of recent developments of the Bohr theory. S. B.

**Distribution of Transition Probabilities in the Atoms of Alkali Metals.** H. BARTELS (*Z. Physik*, 1925, **32**, 415—438).—In the majority of cases the probability of transition from one energy state to another cannot be ascertained from measurements of the intensity of the lines, as these lie in the infra-red. They can be deduced mathematically from considerations based on the conception of a central electric field, and from them the mean life of the Bohr states can be calculated from the quantum numbers. The case for sodium is worked out and that of the other alkali metals will be similar. E. B. L.

**World-Geometrical Properties Indicated by Quantised World-lines of the Electron in the Hydrogen Atom.** E. REICHENBACHER (*Z. Physik*, 1925, **32**, 505—517).—From a consideration of the relativity geometry of the quantised electron orbits in the hydrogen atom, it is deduced that the electron is characterised by a fundamental "proper time,"  $h/m_0c^2$  ( $h$ =Planck's constant,  $m_0$ =mass of electron at rest,  $c$ =velocity of light); at the end of this time, or some multiple of it, the electron must return to its original condition or emit radiation. E. B. L.

**Quantum Theory of the Ideal Gas.** A. EINSTEIN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 18—25).—Mathematical (cf. *ibid.*, 1924, 261). From a consideration of the dimensions of the variables of a gaseous system, and of its behaviour under adiabatic compression, or in a conservative force field, the evaluation of the equation of state for an ideal gas is shown to reduce to the determination of a universal function of a single variable. F. G. T.

**Quantum Radiation.** A. LODGE (*Nature*, 1925, **115**, 838).

**Calculation of Atomic Radii from Magnetic Susceptibility.** B. CABRERA (*Anal. Fis. Quím.*, 1925, **23**, 172—180).—The mean radius of the electronic orbits of an atom may be calculated, using a well-known theorem of Larmor, from the magnetic susceptibility without making any assumptions as to the structure of the atom. If the Bohr structure of the atom be assumed, then the radii of the orbits of the superficial electrons may be deduced. The atomic radii of the elements of the helium group, thus calculated, are approximately half of those calculated from the kinetic theory, which was to be expected if the Bohr structure be assumed. The results obtained for sulphur, chlorine, argon, potassium, and calcium are in good agreement with those obtained by Grimm (*A.*, 1922, ii, 127) from the theory of crystalline lattices. G. W. R.

**Bands in the Secondary Spectrum of Hydrogen.** G. H. DIECKE (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, 27, 490—500).—Extensions of the Fulcher bands in the secondary hydrogen spectrum are described. Three groups of bands, one in the red, one in the green, and one in the blue region, have been found. The zero and positive branches have been identified, and the negative branch may also be present. S. B.

**Structure of the Second Positive Group in the Band Spectrum of Nitrogen.** P. LINDAU (*Z. Physik*, 1924, 30, 187—199).—By generalising an analysis of such bands advanced previously (A., 1924, ii, 711) to include an analysis due to Hulthén and Johansson (*Z. Physik*, 1924, 26, 308), a new series formula is developed which leads to the conclusion that the differences between the wave-numbers of any two corresponding lines of the bands 3536, 3805 and 3755, 4059 are identical. Complete tables are given showing that the lines of the above bands may be arranged according to the above-mentioned series formula. R. W. L.

**Emission Band Spectra of Aromatic Compounds. II. Their Origin.** J. K. MARSH (*Phil. Mag.*, 1925, [vi], 49, 1206—1216; cf. this vol., ii, 470).—Tesla luminescence spectra are capable of interpretation in terms of a theory which makes use of the conclusions of Baly (A., 1914, ii, 318; 1915, ii, 440, 499) and of Henri (A., 1922, ii, 331, 679). Tesla bands confirm the measurements of absorption and fluorescence bands, by which it has been proved that the frequency differences between successive bands are often equal to the absolute frequency of a band in the infra-red. The recurrence of overtones must be supplemented by an explanation of the appearance of more than one constant frequency difference in the spectra. The author considers in detail the results with benzene. The vapour absorption spectrum shows band intervals of 159 and 921.4 ( $1/\lambda$ ). The emission spectrum exhibits intervals of 159 and 987. Henri has shown that the absorption spectrum of benzene vapour can be expressed by four equations of the type:

$$\nu = A - B + na - (pb + p^2b') + \alpha(m^2 - q^2),$$

where  $A - B$  is the contribution made by the quantification of an electronic energy change,  $na - (pb + p^2b')$  results from the quantification of atomic vibrations and  $\alpha(m^2 - q^2)$  from quantified rotations,  $n$  and  $p$  are integers.

The author selects one of Henri's equations [the others have  $(A - B)$  varying from the one chosen]:  $\nu = 37494 + 921.4n - 159(p + 2p^2)$ , and rewrites it  $\nu = 37494 + 6n \times 159(1 - 0.0358) - 159.2p(1 + 0.01257p)$ . All the fluorescence bands fit the equation:  $\nu = 37494 - 6n \times 159(1 + 0.0358) - 159.2p(1 + 0.01257p)$ . Thus the benzene bands are overtones of 159. The infra-red spectrum of ethylene consists of overtones of a band at  $1/\lambda = 476$  (three times 159) and of a band at 3049 (three times the great benzene band at  $9.8\mu$  or 1020). Accepting 159 and 1020 as the basic benzene frequencies, then  $0.5(1020 \pm 6 \times 159) = 987$  or 33 and  $6 \times 159 - 33 = 921$ . Thus the main features of the benzene spectra depend on 1020 and 159. The smaller frequency is due to the C:C linking, and



the larger differs but slightly from ordinary vibration common to all compounds with CH groups. Since this band recurs in the aliphatic substituted benzenes and the ultra-violet interval is a fraction smaller than  $\frac{1}{3}$ , it is argued that the infra-red band is itself an overtone of a band in the far infra-red. It is shown that all the infra-red bands of benzene are integral multiples of  $128\cdot25$ . Meyer and Bronk have analysed the  $3\cdot25\mu$  band (A., 1924, ii, 804) and the sub-groups are  $42\cdot7$  and  $84\cdot9$  apart. This suggests that  $42\cdot7$ ,  $84\cdot9/2$ ,  $128\cdot25/3$  is a constant corresponding with rotation of CH groups. It is suggested that the blue Tesla luminescence is due to C:O groups, as is also the  $5\cdot8\mu$  band. R. A. M.

**Anomalies of Intensity in Band Spectra.** R. MECKE (*Physikal. Z.*, 1924, 25, 597—599).—Theoretical. The subject is discussed from the point of view of the correspondence principle. Special reference is made to the cyanogen bands. R. W. L.

**Intensities in Band Spectra.** G. H. DIEKE (*Nature*, 1925, 115, 875).—A summary is given of the application to the lines of a band of the rules of Burger and Dorgelo (*Z. Physik*, 1924, 23, 258). A. A. E.

**Structure and Distribution of Band Spectra.** H. DESLANDRES (*Compt. rend.*, 1925, 180, 1454—1460; cf. A., 1919, ii, 486; 1920, ii, 69).—The frequencies of the bands in the infra-red absorption spectra of oxygen, carbon monoxide, hydrogen cyanide, ammonia, water vapour, and methane are represented by the expression  $K=qd_1/rs$ , where  $q$  and  $r$  are whole numbers,  $s$  is the number of atoms in the molecule, and  $d_1$  the fundamental frequency  $1062\cdot5$ . J. S. C.

**Band Spectra of Crystals and Complex Gases.** H. KÄHLER (*Proc. Nat. Acad. Sci.*, 1925, 11, 266—269).—The complete spectrum of uranyl salt crystals contains a high-frequency absorption branch and a low-frequency emission branch, the full spectrum being capable of expression by means of an equation of the band spectral type. The similarity to the absorption spectra of complex gases is shown by reference to Henri's data for the ultra-violet absorption of benzene. E. B. L.

**Influence of Temperature on the Ultra-violet Absorption Bands of Oxygen. Short-wave Iodine Spectrum.** C. FÜCHTBAUER and E. HOLM (*Physikal. Z.*, 1925, 26, 345—349).—The absorption bands of oxygen have been examined, at temperatures from  $400^\circ$  to  $1050^\circ$ , in the region between the wave-lengths 2000 and  $2200\text{ \AA}$ . With increasing temperature, the bands become more intense, and extend towards the region of longer wave-length. This behaviour is attributed to the increase in oscillation energy of the atom, and is probably connected with the increase of specific heat of gases with rise of temperature. The sensitiveness to temperature does not appear to depend on impurities in the gas. The edges of the absorption bands at the ordinary temperature have also been measured up to  $1830\cdot6\text{ \AA}$ . Comparison of the initial frequencies

with the final frequencies at different temperatures indicates that electron emission causes a considerable loosening of the bands between two oxygen atoms, and this results, not only in a large reduction of the fundamental frequency in the final state, but also in a large increase of the moment of inertia.

The line spectrum of iodine, produced under conditions practically equivalent to a spark discharge, has been examined between 2016.5 and 1830.5 Å. M. S. B.

**Infra-red Absorption Spectra of Aldehydes and Ketones.** J. LECOMTE (*Compt. rend.*, 1925, **180**, 1481—1482).—The infra-red absorption spectra of aldehydes are not identical with those of the isomeric ketones and the position of the band characteristic of the carbonyl group is not the same for aromatic as for aliphatic compounds. The positions of the absorption bands in the infra-red region of 8 aliphatic and 2 aromatic aldehydes and of 9 aliphatic and 6 aromatic ketones are recorded. J. S. C.

**Absorption Spectra of Various Aldehydes and Ketones and Some of their Derived Compounds.** J. E. PURVIS (*J. Chem. Soc.*, 1925, **127**, 9—14).—A method previously described (T., 1912, **101**, 1810) has been adopted in this work. The following substances show no selective absorption in solution: formaldehyde in water, paraldehyde, trithioformaldehyde, trithioacetaldehyde,  $\beta$ -trithiobenzaldehyde, methylal, and acetal in alcohol.  $\alpha$ -Diphenylglyoxime shows a weak band at 2380 Å. Curves are given showing the relative absorptive powers of the following substances: benzylideneacetone, benzylideneacetoxime, benzylidenedeoxybenzoin, benzylideneacetophenone, and cinnamylidenecamphor. The results are construed to support a theory of the influence of aldehydic and ketonic groups on the colour of substances. R. W. L.

**Absorptive Power of Liquids and their Vapours for Infra-red Radiation of Wave-length less than  $3\mu$ .** T. DREISCH (*Z. Physik*, 1924, **30**, 200—216; cf. this vol., ii, 178).—Tables are given of the data obtained by the author and other workers for water, benzene, and chloroform over the range 0.85 to  $3\mu$ . R. W. L.

**Explosion of Acetylene and Nitrogen. IV. Spectra of Explosions of Gases containing Hydrogen, Carbon, Nitrogen, and Oxygen.** W. E. GARNER and S. W. SAUNDERS (*J. Chem. Soc.*, 1925, **127**, 77—82).—Complete details are given of the method adopted to determine the spectra emitted when mixtures of acetylene, nitrogen, and oxygen are exploded. The results from mixtures of oxygen and acetylene and from mixtures of oxygen, nitrogen, and acetylene are held to show that the cyanogen spectrum is due to both carbon and nitrogen. R. W. L.

**Atmospheric Ozone as Absorbing Material for Radiations.** C. FABRY (*J. Math. Physics*, 1925, **4**, 1—20).—The emission spectra of the sun and stars, as observed from the surface of the earth, cease abruptly at about 2900 Å. The uniformity of the wave-length

limit shows that it is determined by atmospheric absorption. Hartley first suggested that the absorbing agent is ozone. Using the photographic method for ultra-violet spectrophotometry, the author has determined the absorption coefficients of the atmosphere for different wave-lengths in the range 2922—3143 Å. To obtain such measurements, it is necessary to vary the thickness of the absorbing layer and this was achieved by making observations with the sun at varying heights above the horizon. A comparison of the results with the absorption coefficients of ozone confirmed the hypothesis that the limit of the solar spectrum is due to the absorption band of this gas. The greatest part of the atmospheric ozone probably lies in a very high and inaccessible region. As the absorption coefficient of ozone is small below 2200 Å., a reappearance of the solar spectrum at these wave-lengths would seem not impossible, but attempts to observe it with a system of spectrographs, designed to eliminate scattered light of longer wave-lengths, were unsuccessful. The absorption in this region may be due to ordinary oxygen. The absorption bands of ozone in the spectral region 3300 Å. can also be detected when the sun is very near the horizon. S. B.

**Equilibrium of the Calcium Chromosphere.** E. A. MILNE (*Month. Not. Roy. Astr. Soc.*, 1924, 85, 111—141).—A full solution is obtained of the problem of the equilibrium under radiation pressure of an atmosphere consisting of atoms supposed to possess only two stationary states—the normal and one excited state. This special case of the general problem of equilibrium corresponds fairly with an atmosphere absorbing spectral lines derived from the normal state of the atom, such as the principal series of Na, Ca,  $\text{Ca}^+$ , etc. The law of density deduced for an atmosphere fully supported by radiation pressure is that the density at any point is inversely proportional to the square of the height of the point above a certain fixed level. For an atmosphere only partly so supported, the law is quite different, and the density decreases exponentially with height.

The least departure from exact balance between radiation pressure and gravity at great heights should cause an overwhelming concentration of the atmosphere into the lowest levels. This is in agreement with the great variations observed in the height of the calcium chromosphere. It is concluded that the high level calcium chromosphere of the sun must be fully supported by radiation pressure. The investigation confirms the author's previous estimate of the life of an excited atom deduced from solar data. S. B.

**Polarisation of Sodium Resonance Radiation in Magnetic Fields.** A. ELLETT (*J. Opt. Soc. Amer.*, 1925, 10, 427—437).—The polarisation of *D*-line resonance radiation with various orientations of the impressed magnetic field has been determined under conditions which eliminate the depolarising action of high vapour pressure. The results are not in quantitative agreement with any current theory. It has also been shown that a magnetic field produces a rotation of the plane of polarisation in resonance radiation, and that this rotation is due to the Larmor precession of the excited

atoms. The value of  $\tau$  for the  $2p_1$  orbit of sodium, calculated from the rotation, is  $1.35 \times 10^{-8}$  sec. S. B.

**Polarisation of Resonance Radiation in Weak Magnetic Fields.** G. BREIT (*J. Opt. Soc. Amer.*, 1925, **10**, 439—452; cf. A., 1924, ii, 441).—A theoretical discussion of the recent experimental results on this subject (cf. preceding abstract). S. B.

**Extinction of Resonance Fluorescence of Mercury.** H. A. STUART (*Z. Physik*, 1925, **32**, 262—272).—Light from a quartz mercury-vapour lamp was concentrated on a bulb containing mercury vapour. The resonance light produced was focussed on a second bulb containing mercury vapour and the light emitted from this second bulb was photographed, and the decrease in its intensity measured when gases were present at various pressures. The results are regarded as indicating that the radius of the mercury atom in the excited state is about three times as great as that of the normal atom. Collision with molecules of oxygen, hydrogen, and carbon monoxide transform the energy of the excited mercury atom into heat; with carbon dioxide, only 20% of the collisions, and with helium only 0.03%, are of this type. E. B. L.

**Polarised Fluorescence and Phosphorescence of Solutions of Dyes.** IV. W. L. LEWSCHIN (*Z. Physik*, 1925, **32**, 307—326).—Fluorescent light excited by polarised light is itself partly polarised, the extent up to a limit depending on the viscosity of the solvent. Increase of concentration or of temperature decreases the polarisation. An explanation of these facts is sought by regarding the source of the radiation as a di-pole the axis of which is rotated during the life period of the excited state. The angle of rotation corresponding with the degree of polarisation is calculated from the theory of the Brownian movement. E. B. L.

**Fluorescence and Chemical Change.** D. N. CHAKRAVARTI and N. R. DHAR (*Z. anorg. Chem.*, 1925, **142**, 299—328).—Eosin and other fluorescing substances are oxidised by air or reduced by suitable substances (sucrose etc.), both reactions being highly catalysed by light and yielding products which do not fluoresce. Thus, in general, experiments on fluorescence cause destruction of the eosin, but the chemical change is not directly connected with the phenomenon of fluorescence as assumed by Perrin (cf. Weigert, A., 1922, ii, 681). L. J. H.

**Influence of Magnetic Fields on the Polarisation of Resonance Fluorescence.** W. HANLE (*Z. Physik*, 1924, **30**, 93—105).—An investigation of the effects of magnetic fields of the order of 1 to 100 gauss on the resonance fluorescence of mercury vapour indicates that not merely does the field tend to depolarise the resonance fluorescence excited by plane polarised light, but it also rotates the plane of polarisation; the results also lead to values for the life of an excited atom in good agreement with those of other workers. It is shown that the effect observed is other than the Faraday effect. The phenomena are discussed at length with reference to the quantum theory. R. W. L.

**Chemiluminescence and Heteropolar Combination.** A. PETRIKALN (*Z. Physik*, 1925, **32**, 569—574).—The decomposition of the iodide of Millon's base is shown to be an endothermic reaction; above 350°, the decomposition is accompanied by the emission of light, the spectrum exhibiting the bands of mercuric iodide and the mercury lines 4047, 4359, 5461 Å.; with a specially made spectrograph the line 2537 was obtained. It is concluded that the electron holding the mercury and nitrogen atoms together belongs to the 2s orbit.

E. B. L.

**Tesla-luminescence Spectra. V. Polynuclear Hydrocarbons.** W. H. McVICKER, J. K. MARSH, and A. W. STEWART (*J. Chem. Soc.*, 1925, **127**, 999—1006; cf. A., 1924, ii, 712; this vol., ii, 12).—The emission spectra of seventeen polynuclear substances are described and the following conclusions are reached: the attachment of a phenyl group directly to one point of the benzene ring decreases the intensity of emission, *i.e.*, it decreases the amplitude of vibrations; when methylene groups are inserted between the nuclei, the amplitude of vibration is less affected and there is an increase in the length of the spectrum, mainly towards the red end; the spectrum is faint when the nuclei are separate and becomes more intense as the rings are fused into a connected structure; there is a simultaneous shift of the spectrum towards the red and an increase in the number of bands; introduction of the phenyl nucleus and of alkyl radicals into fused ring compounds appears to shorten the spectrum; Tesla-luminescence does not appear to be related to the length of the conjugated chain.

F. G. S.

**Luminescence of Solid Nitrogen and the Auroral Spectrum.** L. VEGARD (*Nature*, 1925, **115**, 837—838; cf. McLennan, this vol., ii, 88).—Polemical, and a claim for priority in the observation of the three maxima of the band  $N_1$ .

A. A. E.

**Ultra-violet Radiations and Antirachitic Substances.** J. C. DRUMMOND and T. A. WEBSTER (*Nature*, 1925, **115**, 837).—Kugel-mass and McQuarrie's observation (*Science*, 1924, **60**, 274) of the production of ultra-violet light when antirachitic substances undergo autoxidation could not be confirmed. The photographic fogging obtained by these authors was probably due to the known phosphorescence of fused silica.

A. A. E.

**Kinetic Theory of Metallic Conduction.** E. L. DAVIES and G. H. LIVENS (*Proc. Camb. Phil. Soc.*, 1925, **22**, 555—561).—It is shown that the kinetic theory of metallic conduction leads to formulæ for conductivity coefficients which are consistent with experimental data.

S. B.

**Dielectric Constants of Liquid and Solid Hydrogen.** M. WOLFKE and H. K. ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 627—630).—The dielectric constant of liquid hydrogen at its boiling point under atmospheric pressure has the value  $1.225 \pm$

0-001. The constant increases with falling temperature to the neighbourhood of the melting point, where it reaches its highest value, after which it decreases in solid hydrogen on further decrease of temperature. S. B.

**Dielectric Constants of Liquid Hydrogen and Liquid Oxygen.** G. BREIT and H. K. ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 617—620).—The dielectric constants of liquefied hydrogen and oxygen have been determined by the high-frequency oscillation method. The value for liquid hydrogen at 20° Abs. is given as 1.21, and for liquid oxygen at 70° Abs. as 1.50. The measurements, although of a preliminary character, indicate that the temperature variation of the dielectric constant is satisfactorily given by the Clausius-Mosotti expression. S. B.

**Dielectric Constant of Liquid Helium.** M. WOLFKE and H. K. ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 621—626).—The dielectric constant of liquid helium has been determined at its b. p. under 765 mm. pressure. The high-frequency oscillation method was used. The value determined is  $1.048 \pm 0.001$ , the temperature being 4.2° Abs. S. B.

**Measurement of the Dielectric Constants of Liquids.** H. HARRIS (*J. Chem. Soc.*, 1925, **127**, 1049—1069).—The determination of dielectric constants of liquids by alternating current bridge methods is discussed. The method employed by Nernst (A., 1894, ii, 437) and by Turner (A., 1901, ii, 53) is criticised. In the present determinations, a Schering and Semm's bridge is employed, a valve generator replaces the Nernst interrupter, and two non-reactive 1000-ohm coils the liquid resistances used by Nernst for the ratio arms. Details of the experimental and of the standard condensers are given and the method of correction for the earth capacities of the bridge and leads, the parallel resistance, and of the fibre end pieces of the experimental condenser, is outlined. The true dielectric constants of the following carefully purified liquids have been accurately measured at  $25^\circ \pm 0.01^\circ$ : benzene  $2.2482 \pm 0.0003$  and  $2.2488 \pm 0.0005$ ; carbon tetrachloride  $2.219 \pm 0.002$ ; chloroform  $4.6417 \pm 0.001$ ; ethylene dichloride  $10.131 \pm 0.001$ ; *o*-nitrotoluene  $26.066 \pm 0.005$ ; nitrobenzene  $34.093 \pm 0.007$ . F. G. S.

**Dielectric Constants of Good Conductors.** R. FÜRTH (*Physikal. Z.*, 1924, **25**, 676—679).—The method employed is to determine the torque on an ellipsoid, containing the fluid conductor, when suspended in an alternating electrical field of frequency 50. From the value obtained for this torque, classical electromagnetic theory leads to values of the dielectric constant if the conductivity be known. The values obtained for aqueous sucrose solutions over the range of concentration 20—60% are in agreement with those obtained by Drude when using a frequency corresponding with a wave-length of 70 cm. Results are also given for aqueous solutions of sodium chloride over the concentration range 0.0—0.1%. The

values obtained are not independent of the field strength, but diminish as the field diminishes.

R. W. L.

**Calculation of Refractive Indices by the Logarithmic Rule of Mixtures.** K. LICHTENECKER (*Physikal. Z.*, 1925, **26**, 297—302).—In previous papers (*ibid.*, 1924, **25**, 169, 666) it has been shown that the resistance of alloys and the dielectric constants of non-conducting binary mixtures are linear functions of their volume composition. The same rule has now been found to govern accurately the refractive indices of binary mixtures of liquids, in the absence of volume changes on mixing. The refractive indices of carbon disulphide-methylal mixtures are cited as an example, and the rule also holds for pyridine-water mixtures, when allowance is made for the volume contraction. The deviations from the rule may be used for the indirect measurement of volume changes on mixing liquids.

S. B.

**Rotatory Dispersive Power of Organic Compounds. XIV. Simple Dispersion in 1-Methylcyclohexylidene-4-acetic Acid.** E. M. RICHARDS and T. M. LOWRY (*J. Chem. Soc.*, 1925, **127**, 238—240).—Data are given for the dispersion-ratios  $\alpha/\alpha_{5461}$  over the range 6708 to 4072 Å. It has been found that the values obtained can be calculated by neglecting all terms in Drude's equation but the first and by assuming an absorption maximum at 2364. Despite the evidence, which indicates that the acid has no such characteristic frequency, the authors think that the dispersion of the acid is as simple in essence as their abbreviated form of Drude's equation would indicate.

R. W. L.

**Dynamic Isomerism. XVII. Mutarotation of Aluminium Benzoylcamphor.** I. J. FAULKNER and T. M. LOWRY (*J. Chem. Soc.*, 1925, **127**, 1080—1085; cf. Burgess and Lowry, this vol., i, 46).—*Aluminium benzoylcamphor*,  $(C_{17}H_{19}O_2)_3Al$ , m. p. 227—228°, has been prepared by the method used for the preparation of beryllium benzoylcamphor (Burgess and Lowry, *loc. cit.*), and, like the beryllium compound, it shows mutarotation although containing no mobile hydrogen atom. The mutarotation is reversible and has been observed in benzene, ethylene bromide, acetone, and chloroform. In ethylene bromide, the change extends over about a week, and in acetone and in chloroform it takes place in a few minutes. The fact that the mutarotation in chloroform is in the opposite direction to that in the other solvents used suggests the formation of a compound with the chloroform of higher rotatory power. The velocity of mutarotation in benzene, unlike that of the beryllium compound in this solvent when pyridine is present as catalyst, does not obey the unimolecular law, but is approximately proportional to the cube of the concentration, although the termolecular coefficients vary appreciably during the change. The course of the reaction in ethylene bromide after the first half-hour also conforms roughly to the termolecular law. It is suggested that the result may perhaps be associated with the necessity for inverting the points of attachment of three chelate groups in order to reverse the optical activity of the aluminium.

F. G. S.

**Optical Rotation and Atomic Dimension. IV.** D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1925, **47**, 1281—1284; cf. A., 1924, i, 837).—The specific rotations of chloro-, bromo-, and iodo-tetra-acetylglucose and of chloro- and bromo-triacetylxylose have been redetermined. The new values show a much closer agreement between the ratio of the difference in specific rotation, Cl-F, Br-Cl, and I-Br, and the ratio of the differences of atomic diameter as recorded by Bragg. J. S. C.

**Optical Rotation and Atomic Dimension. V.** D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1925, **47**, 1285—1298; cf. preceding abstract).—Two classes of asymmetric compounds containing substituted halogen atoms are recognised: (a) compounds in which the halogens are directly attached to the asymmetric carbon atom, (b) compounds in which the halogens modify an asymmetric group attached to the asymmetric carbon atom. In the latter case, the molecular rotation differences are proportional to the differences in atomic diameter recorded by Bragg. The specific rotations of halogen derivatives of salicin and their penta-acetates have been measured and the methods of preparation and properties of  $\alpha$ -fluoro-, chloro-, and bromo-acetyltetra-acetylglucose are given. J. S. C.

**Thermochemical Investigations on the Constitution of Acids in Solution.** D. D. KARVE (*J. Indian Chem. Soc.*, 1925, **1**, 247—262).—Further data in support of the Hantzsch theory of pseudo acids and ionogenic condition (cf. A., 1918, ii, 4; 1923, ii, 475) are obtained by an investigation of the heats of solution of hydrogen halides, sulphuric, nitric, formic, acetic, and trichloroacetic acids in aqueous and non-aqueous solvents. In the dissolution of an acid, purely physical phenomena all result in the absorption of heat, and the positive heats of solution are therefore due to combination between the acids and the solvents to form solvates which are either true or pseudo-oxonium hydrates of types (1)  $R \cdot CO_2H, H_2O$  or (2)  $R \cdot CO_2H \dots OR_2$ . The heats of solution of the above-mentioned acids in a large number of organic solvents are determined and discussed in relation to the Hantzsch theory, the main conclusions being as follows: with sulphuric acid, solvate formation of true oxonium salts of the type  $H_2SO_4, HOR_2$  ( $R=H$  or alkyl) occurs with much evolution of heat, whilst the relatively small heat of solution in ethyl sulphate and nitrobenzene denotes a very small tendency towards salt formation; hydrogen halides form oxonium salts and etherates of which only the hydrogen chloride compound can be isolated (cf. Steele, McIntosh, and Archibald, *Z. physikal. Chem.*, 1909, **55**, 152); the heat of solution of nitric acid in alcohol or ether is a measure of the heat of formation of the pseudo salt, whilst the smaller heats of solution in water, where the true hydroxonium salt is present, denote that transformation from the pseudo acid to the true acid is endothermic; with formic acid, the heat of solution in water is too small to be measured and therefore the dissociation of the acid absorbs very nearly the same amount of heat as is evolved by salt formation, whilst in acetone, alcohol, or ether the heat of solution is the heat of formation of the pseudo salt; with acetic acid, in water



the heat of solution is negative in concentrated solution and positive in more dilute solutions where sufficient of the hydroxonium salt is formed to overbalance the heat absorbed by dissociation; the heat of solution of trichloroacetic acid in water is small and is negative in solvents which do not contain oxygen, whilst the heat of solution is greatest in acetone, which, therefore, forms a true salt,  $\text{CCl}_3 \cdot \text{CO}_2 \cdot \text{H} \dots \text{OCMe}_2$ . The numbers of molecules of solvents required to produce inactivation of the various acids towards ethyl diazoacetate are also determined. J. W. B.

**Magneto-chemical Researches on the Formation of Open Chains and Nuclear Groupings in Organic Compounds.** P. PASCAL (*Compt. rend.*, 1925, **180**, 1596—1597).—The magnetic susceptibilities of a series of compounds containing a group  $-\text{C}_{6-n}\text{N}_n$ , where  $n$  is 0, 1, 2, 3, or 4, have been measured. The group was the skeleton of a nuclear grouping or of an open or closed chain. Increase in the number of ethylenic linkings and the formation of closed chains, like polymerisation, cause a marked decrease in diamagnetism. These factors thus increase the resultant magnetic moment of the molecule and correspond with increasing dissymmetry of electronic structure. On the other hand, an increased diamagnetism is observed in the cases of nuclei with three symmetrical double bonds. This effect is also found in open-chain compounds containing tertiary carbon or nitrogen atoms. The value  $-55.5 \times 10^{-7}$  has been used for the magnetic susceptibility of combined nitrogen. Direct measurements give  $-59 \times 10^{-7}$  (Hector) and  $-50 \times 10^{-7}$  (Také Soné). The author's earlier work on the additivity of diamagnetism (A., 1909, ii, 487, 788, 859; 1910, ii, 100, 179, 483, 580) is confirmed and extended. R. A. M.

**Colour and Molecular Geometry. III. Graphical Presentation of the Theory.** J. MOIR (*J. Chem. Soc.*, 1925, **127**, 967—972).—A simplification of the general theory (A., 1924, ii, 641) is possible since it appears that in most cases the active part of the hapton (T., 1923, **123**, 2801) is the oxygen or nitrogen it contains. Since these atoms have the same atomic diameter and occur at both ends of the molecule when the auxochrome is  $-\text{OH}$  or  $-\text{NH}_2$ , the wave-length of the absorption band is given by the simplified formula  $\lambda = 51.4(c + 1.77)\sqrt{c + 0.65}$ , in which  $c$  is half the distance between the terminal oxygen or nitrogen atoms round which the electron moves. The equation is approximately linear over the range of the visible spectrum, rendering the calculation of colour easy. The calculated positions of the absorption bands of a number of monocyclic and dicyclic compounds considered are in good agreement with the experimental values. F. G. S.

**Constitution of Nitric Acid and the Nitronium Salts formed from it by Perchloric and Sulphuric Acids.** A. HANTZSCH [with L. WOLF] (*Ber.*, 1925, **58**, [B], 941—961).—The absorption curve of solutions of nitric acid in water may be calculated with great accuracy from those of ethereal solutions of nitric acid and aqueous solutions of alkali nitrates. It is therefore justifiable to

conclude that such solutions contain equilibrium mixtures of the pseudo acid,  $\text{O}_2\text{N}\cdot\text{OH}$  and true acid (present as the hydroxonium salt,  $(\text{NO}_3)[\text{H}\cdot\text{OH}_2]$ ). Homogeneous nitric acid closely resembles its esters but its absorption is noticeably more feeble than might be expected from the slight constitutive difference between pseudo acid and ester, so that the presence of a third type of molecule must be assumed (cf. von Halban, A., 1923, ii, 835; Schaefer, A., 1917, ii, 61, 186). In addition, the pronounced electrical conductivity of nearly homogeneous nitric acid indicates the presence of some form other than the pseudo acid. Indications of the nature of the feebly-absorbent electrolyte are found in the observation that solutions of nitric acid in absolute sulphuric acid contain a largely dissociated electrolyte which is very much more transparent than an equally concentrated ethereal or aqueous solution of nitric acid. The analogous behaviour of acetic acid dissolved in absolute sulphuric acid, whereby the acetylum cation is produced, suggests the production of a nitronium cation and therefore the possible presence of the two salts,  $[\text{NO}(\text{OH})_2][\text{SO}_4\text{H}]$  and  $[\text{N}(\text{OH})_2][\text{SO}_4\text{H}]_2$ . It is remarkable that a nitronium salt of pyrosulphuric acid,  $\text{HS}_2\text{O}_7[(\text{HO})_2\text{NO}]$  or  $\text{S}_2\text{O}_7[(\text{HO})_3\text{N}]$ , was isolated by Weber in 1871. The conception of a nitronium cation is strengthened further by the isolation from almost anhydrous nitric and perchloric acids of *nitronium diperchlorate*,  $[\text{ClO}_4]_2[(\text{HO})_3\text{N}]$ , m. p.  $130^\circ$  (decomp.) after softening at  $55^\circ$ , and *nitronium monopерchlorate*,  $\text{ClO}_4[(\text{HO})_2\text{NO}]$ , decomp. above  $130^\circ$ ; these are stable salts which can be crystallised from perchloric acid and nitric acid, respectively. It is therefore considered that, contrary to the views of Sapozhnikov (A., 1915, i, 393), "nitrating" acid does not contain nitrogen pentoxide, but nitronium hydrogen sulphate,  $[\text{N}(\text{OH})_3](\text{SO}_4\text{H})_2$ ; this conception is confirmed by the observation that the absorption spectrum of nitrogen pentoxide dissolved in sulphuric acid differs from that of "nitrating acid." In homogeneous nitric acid, it is thus reasonable to conclude that analogous wandering of the hydrogen atom occurs to a more limited extent with the production of the nitronium ion and hence of the salt-like electrolyte, nitronium nitrate,  $(\text{NO}_3)_2[(\text{HO})_3\text{N}]$ . Almost anhydrous nitric acid is to be regarded as a solution of conducting nitronium nitrate in non-conducting pseudo nitric acid. On certain assumptions, it is calculated that the equilibrium mixture for the 98.6% acid at  $0^\circ$  contains 80% of pseudo nitric acid and 20% of nitronium nitrate (contrary to previous observations, the 100% acid is too unstable to permit observations at  $0^\circ$ ).

Optical analysis shows that the nitronium nitrate is completely hydrolysed by the addition of one molecular proportion of water, since from this point the absorption curves can be additively constructed from those of the pseudo acid in ether and the true acid in water. The conversion of the pseudo acid into the true acid (or its hydroxonium salt) is practically complete after the addition of 8 mols. of water, whereas the dissociation at this point does not amount to 40%. The last traces of the pseudo acid have disappeared after addition of 50 mols. of water, and the solution then contains only hydroxonium salt which is not completely ionised, in

the sense of the classical dissociation theory, in  $N/100$ -solution. In the most dilute solutions, the sole absorbent material is the nitrate ion; orthonitric acid and nitrogen pentahydrate do not exist (the so-called diacetylorthonitric acid,  $N(OH)_3(OAc)_2$ , is a molecular compound of the pseudo acid,  $[(CH_3 \cdot CO_2H)_2HO \cdot NO_2]$ ).

The reactions between the three strongest oxyacids, perchloric, sulphuric, and nitric, give particularly strong evidence in favour of the chemical theory of acids according to which the strength (acidity) can only be measured chemically in accordance with Berzelius' principles by their tendency towards salt formation and not physically by their ability to furnish hydrogen ions. According to the dissociation theory, perchloric acid is the strongest acid, followed by nitric and then by sulphuric acids. Actually, homogeneous perchloric acid is incomparably stronger than nitric acid, and sulphuric acid, which is more feebly ionised in aqueous solution, is in the homogeneous condition stronger than nitric acid, since it causes the production of nitronium sulphate. In aqueous solution, the great differences towards salt formation of the three acids are almost annihilated, since water as a basic anhydride, particularly in excess, and hence in dilute solution, converts them almost completely into hydroxonium salts.

Absolute nitric acid, m. p.  $-42.3^\circ$ , appears to be stable at  $-40^\circ$ . The 99.5% acid is somewhat unstable at  $0^\circ$ , whereas the 98.4% acid can be preserved for a few days at a moderate temperature. The minimum value observed for the electrical conductivity of 99.5% acid is  $\chi = 89 \times 10^{-4}$  at  $0^\circ$ , whereas an almost absolute acid gave the value  $\chi = 94 \times 10^{-5}$  at  $-40^\circ$ . The liquid acid, of the composition  $HNO_3 \cdot H_2O$ , is not a uniform material. Veley and Manley's observation that solutions of nitric acid exhibit a minimum conductivity is not confirmed.

H. W.

**Induction of Alternate Polarities, especially in Relation to the Extent and Intensity of Transmission.** A. LAPWORTH (*Chem. and Ind.*, 1925, **44**, 397—398).—The author's views on induced alternate polarities are limited to cases of induction through one saturated carbon atom (T., 1922, **121**, 426; A., 1921, ii, 543); transmission through two saturated carbon atoms in immediate or delayed succession can be explained on different lines, and it is not necessary to assume that a true inductive effect passes from one end of the reacting system through its full length. Complications not yet discussed arise from the polar effects produced by groups of atoms, such as the ethylene and acetylene groups, these effects being manifested in reactions depending on the development of active negative polarity on carbon atoms, e.g., nuclear hydrogen-substitution in the aromatic series.

R. B.

**Electronic Conception of Valency and Heats of Combustion of Organic Compounds.** M. S. KHARASCH and B. SHER (*J. Physical Chem.*, 1925, **29**, 625—658).—It is assumed that the heat of combustion is due to a liberation of energy when the valency electrons are shifted from the orbits occupied in methane and similar substances to those occupied in carbon dioxide, the latter orbits being

further from the carbon atom. The heat of combustion is then proportional to the number of electrons so displaced and for saturated hydrocarbons is equal to  $26.05N$  kg.-cal. per mol, where  $N$  is the number of electrons in the molecule that have the same position round the carbon atoms as in methane. This formula also applies to unsaturated hydrocarbons having the same arrangement of electrons round the carbon atoms as have saturated compounds, *i.e.*, to benzenoid and conjugated hydrocarbons, but in ethylene derivatives one pair of electrons is displaced and there is an additional liberation of energy of 13 kg.-cal., the heat of combustion being, therefore,  $26.05N + 13$ . When carbon is united to atoms other than hydrogen the energy liberated by the electrons concerned is less than 26.05 kg.-cal. and the heats of combustion of various classes of compounds are as follows: primary alcohols, ethers, esters, amines, and nitro compounds,  $26.05N + 13$ ; secondary alcohols and ketones,  $26.05N + 6.5$ ; tertiary alcohols, phenols, acids, amides, anilides, and amino-acids,  $26.05N$ . The calculated and experimental values of the heats of combustion of 278 compounds are given; in only 37 cases is the difference more than 1% and in 152 it is less than 0.5%.

A. G.

### Contraction Constants and Affinity of Solid Compounds.

A. BALANDIN (*Z. physikal. Chem.*, 1925, **116**, 123—134).—The contraction constants of 76 solid compounds as calculated by the formula  $C = V/\Sigma V_0$  (cf. Schilov, A., 1922, ii, 350) are in close agreement, in most cases, with those calculated from a new formula  $C = R - U/U_0$ , where  $R$  and  $U_0$  are constants depending on the nature of the anion and  $U$  is the heat of formation. The significance of the latter formula with reference to the oscillations of the component atoms of the salts is discussed (cf. A., 1924, ii, 719).

L. F. G.

**Form of Ultramicros.** H. SIEDENTOPF (*Kolloid-Z.*, 1925, **36** [*Zsigmondy-Festschr.*], 1—14).—The scintillation phenomenon is described, and the possibility of increasing the sensitiveness of this effect for the detection of ultramicros is discussed. The necessary conditions for obtaining a sufficient uniform illumination between cover-glass and slide, using a narrow aperture, are indicated, but it is shown that such a method would give no information as to the actual magnitude of the observed particles. By the application of Nicholson's interferometric measurements of the diameters of fixed stars to ultramicroscopy, positive results could, however, be obtained. The apparatus, which can be used for measuring microscopic as well as ultramicroscopic lengths, is described in detail, and the mathematics of the simpler cases are discussed.

L. L. B.

**Effect of Allotropic Change on the Grain Growth in Thallium.** G. ASAHARA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, **2**, 273—276).—A series of X-ray photographs of thallium near its transformation point shows that a crystal when once formed does not disintegrate into smaller ones when undergoing allotropic change. The crystal lattice thus glides easily from one type to another without fracture of the crystal. In most metals, grain

growth is accelerated by annealing, but in thallium the crystals appear to attain their maximum size very readily on heating. Subsequent heating and cooling does not destroy the crystallites.

R. A. M.

**Crystal Structure of the High Temperature Form of Cristobalite [SiO<sub>2</sub>].** R. W. G. WYCKOFF (*Amer. J. Sci.*, 1925, [v], 9, 448—459).—X-Ray diffraction measurements lead to a length for the edge of the unit cube, at temperatures between 290° and 430°, of  $7.12 \pm 0.01$  Å. The unit cube contains 8 mols. of SiO<sub>2</sub>. The atomic arrangement is such that the silicon atoms have the same grouping as in crystalline silicon with oxygen atoms located midway between each pair of nearest silicon atoms. Each silicon atom is surrounded by four equally distant oxygen atoms. The closest distance between oxygen and silicon is 1.54 Å.

J. S. C.

**Crystal Structure of Lithium Potassium Sulphate.** A. J. BRADLEY (*Phil. Mag.*, 1925, [vi], 49, 1225—1237).—The salt is a simple hexagonal sulphate. The crystal lattice was measured by means of a powder photograph. The unit cell consists of a prism of base 5.13 Å. and height 8.60 Å. containing 2 mols. of lithium potassium sulphate. The crystal is made up of a system of sulphate ions in hexagonal close packing, alternating with metallic ions. The lithium ions and the sulphate ions are arranged similarly. The potassium ions form a simple hexagonal lattice. The sulphate ion is a tetrahedron of oxygen atoms surrounding a central sulphur atom, the distance S—O being 1.5—1.6 Å. Intensity measurements on the X-ray spectrometer were used to determine the parameters fixing the relative positions of all the different kinds of atoms with the exception of lithium atoms. The positions of the latter were determined by spatial considerations.

R. A. M.

**Electrical Measurements on Metals of Great Purity (Tungsten, Molybdenum, and Nickel).** W. GEISS and J. A. M. VAN LIEMPT (*Z. Metallk.*, 1925, 17, 194—197).—Large single crystals of tungsten and of molybdenum were made by growing minute crystals of the former in the vapour of tungsten hexachloride and of the latter in molybdenum pentachloride, respectively, and the resulting crystals were drawn into wire. The tungsten wire so produced had an electrical resistance at 0° of 0.0491 ohm per metre length of 1 mm. cross-section, and the molybdenum wire 0.0503 ohm; the temperature coefficients were  $481 \times 10^{-5}$  and  $473 \times 10^{-5}$ , respectively. After annealing until recrystallisation had set in, the resistance of the tungsten wire decreased to 0.0482 ohm. Pure nickel was deposited on a small bullet of the metal heated electrically at 150° in an evacuated tube filled with nickel carbonyl; the metal was deposited on the bullet in a series of concentric shells which were quite free from iron, although the carbonyl contained appreciable amounts. The temperature coefficient of resistance of this metal was  $667 \times 10^{-5}$ ; after annealing at 1000° to effect recrystallisation, this increased to  $706 \times 10^{-5}$ .

A. R. P.

**Electrical Conductivity of Rock Salt and Calcite at High Temperatures.** F. VON RAUTENFELD (*Physikal. Z.*, 1924, 25, 602—604).—The electrical conductivities of rock salt over the range 600—800° and of calcite over the range 200—600° have been determined for direct current (D.C.) fields and for alternating current (A.C.) fields of frequency 1000, the fields being of the order of 200 volts/cm. For rock salt the conductivity varies logarithmically with the temperature, the A.C. values being slightly higher than the D.C. values. The conductivities parallel and perpendicular to the major axis and perpendicular to the cleavage plane of calcite bear an approximately constant ratio to each other; they vary approximately logarithmically with the reciprocal of the temperature. A description is given of the experimental technique. R. W. L.

**New Alloy of Iron and Nickel of High Permeability.** E. M. DELORAINE (*J. Phys. Radium*, 1925, [vi], 6, 20—28).—Largely a résumé of the work of Arnold and Elmen (*J. Franklin Inst.*, 1923, 195, 621). The physical properties of “permalloy,” a nickel-iron alloy containing about 80% Ni, are described. The maximum permeability is obtained by heating the material at 900° for an hour, allowing it to cool slowly, reheating at 600°, and allowing it to cool more rapidly. Its magnetic properties are affected by heat treatment, by mechanical strain, and by the presence of impurities, of which carbon is chief. The initial permeability at the ordinary temperature of this alloy may be more than thirty times that of soft iron. Possible uses of the alloy are discussed. It is specially good for submarine telegraphy, transmitting four times more rapidly than an ordinary cable. A. S. R.

**Magnetic Ferric Oxide.** R. CHEVALLIER (*Compt. rend.*, 1925, 180, 1473—1475).—Conversion of a commercial oxide having a composition closely approximating to  $\text{Fe}_3\text{O}_4$  into ferric oxide results in a change in the permanent magnetic characteristics. Experiments in which the magnetic properties were determined after heating for a fixed time at various temperatures show that between 600° and 700° the magnetic properties of ferric oxide decrease very rapidly but do not entirely disappear, since at temperatures in the region of 900° the strongly magnetic oxide, magnetite, is produced. The decrease in magnetic properties is of a permanent character and the original activity is not restored after heating for some hours at a lower temperature. J. S. C.

**Artificial Magnetic Anisotropy of Nickel. Realisation of a State with a particularly Simple Cycle.** R. FORRER (*Compt. rend.*, 1925, 180, 1394—1397; cf. this vol., ii, 486).—The discontinuities in the magnetisation cycle of nickel have been simplified. When the wire ( $l=50$  mm.,  $d=1$  mm.) is wound tightly round a 5 mm. cylinder only the  $S_2$  break is found, when it is wound loosely only the  $S_1$  discontinuity appears in the cycle. When a finer stretched wire is wound round a smaller cylinder, the reversible sides of the cycle are straight and parallel, whilst the break is now

97% of the height of the cycle. The term "critical field" is applied to that field which sharply reverses the oriented magnetisation, and the expression "coercive field" to that tending to annul the magnetisation. Systematic work shows that mere flexion round smaller and smaller cylinders first straightens the reversible part of the cycle. The reversible part increases until the coercive field reaches an upper limit near 9g. The same treatment applied to the stretched nickel wire (with a high coercive field) causes the appearance of jumps, diminishes the inclination of the reversible part, and causes the coercive field to decrease to the same limiting value of 9g. Finally, a perfectly definite state is reached, in which the reversible part of the cycle has a minimum inclination and a well-defined value of 9g for the critical field.

R. A. M.

**Evaluation of the Grating Energy of Crystals.** W. WESSEL (*Z. Physik*, 1924, 30, 217—224).—Analysis after the classical fashion of the thermal equilibrium between the vapour of a salt and its ionised radicals shows that the grating energy of the salt can be determined from known data and partial pressures of the ions present. The chemical constants involved are calculated by the method of Born and Heisenberg (*A.*, 1924, ii, 434). Direct measurements of the partial pressures of ions are wanting; they are projected by the author.

R. W. L.

**Migratory Constituents in the Crystal Lattice.** G. F. HÜTTIG (*Fortschr. Chem., Phys., Phys.-Chem.*, 1924, 18, 5—32; from *Chem. Zentr.*, 1924, ii, 2225—2226).—From a consideration of the equilibria of heterogeneous systems, it is concluded that systems of two components can exist in which the molecules of one component can move freely through the rigid lattice of the other component. Such systems are divided into three classes according to the form of their decomposition curves at constant pressure or constant temperature. A theory is deduced for the osmotic pressure of the mobile component. The decomposition curves are described by the equation  $\log p_0/p = k/n$ , where  $p_0$  is the vapour pressure of the solvent,  $p$  the vapour pressure of the solution,  $n$  the molecular weight of the solvent, and  $k$  a constant. A number of systems, e.g., uranosouranic oxide—uranous oxide—oxygen, are mentioned and the corresponding values of  $k$  given. This constant has the same significance as the reciprocal of the Raoult constant  $i$  in liquid solutions.

G. W. R.

**Physical Interpretation of X-Ray Spectra of Fatty Acids.** L. DE BROGLIE and J.-J. TRILLAT (*Compt. rend.*, 1925, 180, 1485—1487).—Fatty acids consist of chains of  $\text{CH}_2$  groups cut by  $-\text{CO}_2\text{H}$  planes of considerable electronic density and by planes of feeble or zero density which separate the  $-\text{CH}_3$  groups of neighbouring molecules. The planes of feeble density may be considered as planes of strong density provided a phase difference  $\pi$  is introduced. Under these conditions, the distribution of intensities in the X-ray spectra of fatty acids is readily explained.

J. S. C.

**Physical Chemistry of Proteins. V. Molecular Weights of Proteins. I. Minimal Molecular Weights of certain Proteins.** E. J. COHN, J. L. HENDRY, and A. M. PRENTISS (*J. Biol. Chem.*, 1925, **63**, 721—766).—Figures are given for the minimal molecular weights of the following proteins: gelatin, zein, gliadin, glutenin, edestin, caseinogen, hæmoglobin, hæmocyanin (*Limulus* and *Octopus*), serum-albumin and globulin, fibrin, egg-albumin, and Bence-Jones protein. The values have been calculated from a simultaneous consideration of the minimal molecular weights derived from the content of an individual element (*e.g.*, iron in hæmoglobin) or from that of an individual amino-acid, and of the equivalent weights as represented by combination with acids and bases, together with osmotic pressure determinations. C. R. H.

**Electrical Properties of Neon, Hydrogen, and Nitrogen.** S. P. MCCALLUM and C. M. FOCKEN (*Phil. Mag.*, 1925, [vi], **49**, 1309—1320).—A short filament was supported at a fixed distance from an earthed silvered plate, A, and another plate B was arranged parallel to A so that its distance from the filament could be adjusted. When  $a$  is the fixed distance,  $x$  the variable distance, and  $V$  the negative potential of the filament, the upper plate B is maintained at a negative potential  $Vx/a$ , thus establishing a uniform field  $X=V/a$  between the plates. The negative current to the fixed plate A is plotted against voltage and for two different distances of  $x$ , using neon at 20 mm. pressure, the curves are superposable up to 45 volts, after which the currents obtained with the larger distance are greater than those with the smaller distance. The same is true for the positive current to the adjustable plate. The divergence indicates some process of ionisation in addition to ionisation by collision of electrons with the molecules of the gas. With hydrogen at 4 mm., no divergence was found under the experimental conditions ( $V=85$  volts,  $X/p=30.4$ ). At 1 mm. pressure, a divergence occurred at  $V=72$  ( $X/p=103$ ). With nitrogen, no divergence appeared at 1.2 mm., but at 0.15 mm. it occurred at 46 volts ( $X/p=438$ ).

The rate of increase of ionisation with increase in electric force ( $X=V/a$ ) is very much greater in neon than in the two diatomic gases. Pressure produces much larger changes in conductivity in the diatomic gases than in neon. The results are compatible with ionisation by collision. The additional ionisation cannot be attributed to radiation, and is probably due to positive ions.

R. A. M.

**Magnetic Properties of Atoms and Molecules.** B. H. WILSDON (*Phil. Mag.*, 1925, [vi], **49**, 1145—1164; cf. this vol., ii, 481).—Theoretical. In the earlier papers it was assumed that precessional or nutational movements of the orbits which form the chemical bond synchronise the frequencies of the naturally untuned orbits in a manner whereby the total moment of momentum in opposite directions of the bond is equalised. This postulate with the principle of spatial quantising enables the author to arrive



mathematically at quantitative conclusions concerning magnetic properties which fit the data reasonably well. R. A. M.

**Electrical Birefringence of Limonene.** R. DE MALLEMAN (*Compt. rend.*, 1925, **180**, 1483—1485).—The Kerr constant for limonene has been determined, employing the author's method of measuring electrical birefringence (*ibid.*, 1923, **176**, 380). The rotatory power remains constant within the limits of experimental error in the electrical fields employed. The birefringence is small and positive in sign. The value of the Kerr constant in absolute units,  $6.5 \times 10^{-8}$  ( $15^\circ$ ,  $0.546\mu$ ), is intermediate between the values of benzene and of toluene and about four times that of pinene. The significance of this number from the point of view of structural formulæ is discussed. J. S. C.

**Influence of Occluded Gas on the Electrical Resistance of a Wire.** T. SEXL (*Z. Physik*, 1925, **32**, 333—335).—The change in resistance depends on the quantity of gas occluded, not on its chemical nature, and is expressed by the formula  $R=R_0(1+\alpha k)$ , where  $k$  is the ratio of the volume of the wire containing gas to that of the wire itself.

Applying Lorentz's theory of electrical conductivity and assuming that the increase in resistance is solely caused by the collisions of the electrons with the molecules of the gas, an equation for the conductivity is obtained which is in satisfactory agreement with experiment. E. B. L.

**Radio Technique in Metallurgy.** J. CZOCHRALSKI (*Z. anorg. Chem.*, 1925, **144**, 263—266).—It would be expected that if a needle rested on a particle of silicon in an aluminium-silicon alloy this combination would act as a radio detector. This, however, is not the case, the silicon having lost its activity in this direction, and it is suggested that detector action may be due to an impurity in ordinary silicon. Such a test for detector action may be useful in the examination of some alloys. A. G.

**New Property of Diamagnetic Gases at Low Pressures.** A. GLASER (*Sitzungsber. Akad. München*, 1924, 79—85).—The variation in the diamagnetic susceptibility of hydrogen, nitrogen, and carbon dioxide, at pressures below atmospheric, has been studied at  $15^\circ$  by a comparative method. The curves obtained, relating susceptibility with the pressure of the gas, are not simply linear, as required by the classical theory, but deviate from the straight line at pressures below 630 mm., 400 mm., and 360 mm. for hydrogen, nitrogen, and carbon dioxide, respectively, the values of susceptibility approaching three times the expected values at low pressures. This effect is regarded as due to the orientation of the molecules in the line of the magnetic field when the pressure is low enough to reduce the interference by collision of other molecules. The susceptibility is  $-0.000327 \times 10^{-6}$  and  $-0.000178 \times 10^{-6}$  unit for nitrogen and hydrogen, respectively, at 760 mm. and  $15^\circ$ . G. M. B.

**Polarisation of Light scattered by Organic Vapours.** A. S. GANESAN (*Phil. Mag.*, 1925, [vi], **49**, 1216—1222).—Imperfect polarisation of light scattered by gases and vapours (observed in a direction perpendicular to the incident beam) depends on the nature of the scattering substance. In argon and mercury vapour, the light is almost perfectly polarised; in hydrogen, the imperfection  $\rho$  (weak component/strong component) is 3.8%; in carbon dioxide, it is 11%. It is not, however, generally true that the imperfection of polarisation increases with the number of atoms in the molecule, because for ethyl ether and pentane (15 and 17 atoms, respectively) it is 3% and for triatomic carbon disulphide it is 16.7%. Accordingly, the author has studied series of related compounds: paraffins, some monohydric alcohols, chlorine substitution products of methane, benzene and its homologues, ketones, and some formic and acetic esters. In the paraffins the molecules increase in length from pentane to octane, but anisotropy of shape is not associated with increased depolarisation (optical anisotropy). A double bond increases depolarisation, *e.g.*, amylene shows a greater value for  $\rho$  than the normal value for the paraffin series. In *iso*-compounds  $\rho$  is less than the normal value. Benzene, toluene, and xylene have  $\rho=6.5\%$ . Methyl esters show greater values of  $\rho$  than ethyl esters. The symmetrical carbon tetrachloride has a smaller value of  $\rho$  than has chloroform. R. A. M.

**Metallic Reflexions. I and II.** I. EBELING (*Z. Physik*, 1925, **32**, 489—501).—The sharply-marked minimum in the reflective power of silver at 3160 Å. becomes less pronounced with increasing temperature and is displaced towards the red. The spectrum reflected from massive copper, the absorption spectrum of precipitated copper, and the suspension of colloidal copper in ruby glass, investigated by means of a photo-electric cell, show indications of a band structure; one of the reflexion minima, between 5800 and 3850, becomes slightly more accentuated at low temperatures. Some relations between the optical properties of metals in the solid, colloidal, and gaseous states are pointed out. E. B. L.

**Specific Heat of Incandescent Tungsten.** L. J. BOCK-STAHLER (*Physical Rev.*, 1925, [ii], **25**, 677—685).—Measurements of thermionic current changes lead to a value of 0.045 for the specific heat of tungsten between 2375° and 2475° Abs. A. A. E.

**Specific Heat of Superheated Ammonia Vapour.** N. S. OSBORNE, H. F. STIMSON, T. S. SLIGH, and C. S. CRAGOE (*U.S. Bur. Standards, Sci. Paper* 501, 1925, **20**, 65—110).—The specific heat at constant pressure of superheated ammonia vapour has been determined at temperatures from  $-15^{\circ}$  to  $+150^{\circ}$ , and pressures from 0.5 to 20 atm. The method adopted was to measure the rise in temperature produced by a measured electric power added as heat to a steady stream of vapour flowing through a vacuum-jacketed instrument. Elaborate precautions were taken and numerous corrections made for which the original must be consulted. The results may be expressed accurately by the empirical equation

$C_p = 1.1255 + 0.00238\theta + 76.8/\theta + 5.45p^{10^8}/\theta^4 + p(6.5 + 3.8p)10^{27}/\theta^{12} + 2.37p^6 10^{42}/\theta^{20}$ , where  $C_p$  is expressed in joules per g. per  $1^\circ$ ,  $p$  in metres of mercury at  $0^\circ$  and standard gravity, and  $\theta$  in degrees absolute. The values of  $C_p$  thus calculated agree with the experimental values within 0.3% in all cases. A few determinations of the Joule-Thomson coefficient have also been made. W. H.-R.

**Heat of Formation of Nitrogen Trichloride.** W. A. NOYES and W. F. TULEY (*J. Amer. Chem. Soc.*, 1925, **47**, 1336—1341).—The following are recorded: heat of solution of 1 mole of gaseous chlorine in carbon tetrachloride, 4539 cal.; heat of solution of 1 mole of gaseous hydrogen chloride in carbon tetrachloride, 3680 cal.; heat of interaction of 1 mole of nitrogen trichloride in solution with 3 moles of gaseous hydrogen chloride giving 3 moles of gaseous chlorine and solid ammonium chloride, 41,800 cal.; heat of formation of nitrogen trichloride in solution in carbon tetrachloride from gaseous nitrogen and gaseous chlorine, —54,700 cal. J. S. C.

**Heat of Formation of Acetalcohol.** T. P. G. SHAW (*J. Soc. Chem. Ind.*, 1925, **44**, 195—196T).—The heat of formation of acetalcohol [ $\beta$ -hydroxybutaldehyde] has been found to be 17,222 cal. (within 1—2%) by means of an adiabatic copper calorimeter, which is described. The chief source of error lies in the analysis of the mixture of acetaldehyde and aldol. R. B.

**Velocity of Sound in Liquids and its Relation to the Heat of Vaporisation.** T. V. IONESCU (*J. Phys. Radium*, 1924, [vi], **5**, 377—383).—The velocity of sound in a number of liquids was measured by a method which involved the manipulation of small quantities of liquid. Except for toluene the measured velocities agreed fairly well with Newton's formula, where  $V = \sqrt{E/\rho}$ . Comparison of the experimental values with those obtained from the formulæ  $V = \sqrt{L}$  (Boydan) and  $V = \sqrt{L/\alpha T}$  (Lewis) in which  $L$  represents the heat of vaporisation,  $\alpha$  the coefficient of dilatation, and  $T$  the absolute temperature, indicates that Boydan's formula leads to low values and Lewis' to high values. R. W. L.

**Freezing Points of Hydrofluoric Acid.** J. D. C. ANTHONY and L. J. HUDLESTON (*J. Chem. Soc.*, 1925, **127**, 1122—1128).—The freezing points of hydrofluoric acid have been determined for 0.025—4.140*N*-solutions, and the activities calculated. The freezing-point depression is found to be an almost linear function of the molarity. This is in accordance with the general theory (Davies and Hudleston, A., 1924, ii, 167), the increase of molecular conductivity in concentrated solutions (Deussen, A., 1905, ii, 311) not affecting the apparent molecular weight,  $2\text{HF} = \text{H}^+ + \text{HF}_2^-$ . Assuming that no appreciable quantity of double molecules,  $\text{H}_2\text{F}_2$ , exists in solution and applying the law of mass action to the ionic equilibria of  $\text{HF}_2^-$  and  $\text{HF}$  (Davies and Hudleston, *loc. cit.*), the total molarity of ions and molecules in solution is found and the freezing point calculated for a series of concentrations. It is found that

there is no appreciable difference between the calculated and the observed values of the freezing point up to 0.5*N*-solution.

F. G. S.

**Relation between the Temperature and Velocity of Transformation of Metastable Non-variant Systems.** N. I. STEPANOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, 2, 500—502).—Cases are considered in which the velocity of a transformation diminishes when the temperature is raised, use being made of the following equation for the absolute velocity of the transformation of metastable non-variant systems :

$$V = Ka^T(T_0 - T)^n,$$

where  $T_0$  is the absolute temperature of the equilibrated system,  $T$  the temperature at which the transformation occurs,  $n$  a positive number,  $a$  a number greater than 1, and  $K$  a positive coefficient depending on the units in which  $V$  is measured. The significance of each term in this equation is discussed and also the different types possible for the curves representing the velocity. The considerations advanced are in agreement with the results of Cohen's work on the mutual transformations of grey and white tin.

T. H. P.

**Transformation Temperature of Thallium.** G. ASAHARA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, 2, 253—276).—The value of the transformation temperature of thallium is  $232.5 \pm < 0.5^\circ$  when very pure electrolytic thallium is investigated by thermal analysis. This value is preferred to the rather lower value  $231.3^\circ$  recently obtained by X-ray analysis (this vol., ii, 483). The experimental curves (heating) showed a small second maximum, which has been traced to the physical conditions under which the work was carried out. It is not chemical in origin. Certain modifications in technique are detailed, and a summary of the existing data on the transformation point is added.

R. A. M.

**Extension of Trouton's Law to the Fusion of Metals.** A. JOUNIAUX (*Bull. Soc. chim.*, 1925, [iv], 37, 513—518).—Trouton's law is extended to the fusion of metals, and existing data are used to calculate the constant  $K = ML/T$  for a number of metals, where  $T$  is m. p. Abs.,  $L$  latent heat of fusion, and  $M$  molecular weight. On the assumption that metals are monatomic, the value of  $K$  generally diminishes with rise of melting point, but may be expressed by the empirical relation  $\log K = 0.8058/T - 0.28506 \log T + 1.20096$ . The values of  $K$  thus calculated agree well with the experimental values of  $ML/T$ , except for the alkali metals. The calculated values suggest diatomic molecules for these metals in contradiction to accepted views.

W. H.-R.

**Chemical Constant of Chlorine.** R. R. S. COX (*Proc. Camb. Phil. Soc.*, 1925, 22, 491—492).—Recent experimental data are used to correct the value of the chemical constant of chlorine given in a previous paper (*ibid.*, 1923, 21, 541). The new value of the constant, deduced from the dissociation of chlorine, is 0.64. There is still an unexplained discrepancy with the theoretical value of 0.9. S. B.

**Density of Bromoform. Application to the Testing of Aluminium.** P. PASCAL (*Bull. Soc. chim.*, 1925, [iv], **37**, 502—503).—The density of pure bromoform is determined as 2.9315, 2.8827, 2.8779, 2.7934, 2.7364, 2.6823, at 0°, 17.5°, 19°, 50°, 70°, and 90°, respectively. The density of aluminium lies within these values, and specimens may be tested by immersion in bromoform, the latter being gradually heated and stirred, and the temperature noted at which the specimen sinks. The specimen should be protected by a thin film of collodion, albumin, or 50% aqueous glycerol.  
W. H.-R.

**Density of Rock Salt and Calcite.** O. K. DEFOE and A. H. COMPTON (*Physical Rev.*, 1925, [ii], **25**, 618—620).—Rock salt has  $d\ 2.1632 \pm 0.0004$  g./c.c., and calcite has  $d\ 2.7102 \pm 0.0004$  g./c.c. at 20°. A. A. E.

**Isotopy of Lead.** (MLLE.) B. PERRETTE (*Compt. rend.*, 1925, **180**, 1589—1591).—The densities and the wave-lengths of certain arc lines of ordinary lead and of a uranium-lead from a Congo pitchblende have been compared and the following results obtained: Ordinary lead  $d^0\ 11.336_3 \pm 0.0004$ , atomic weight 207.20, atomic volume 18.2776; uranium-lead  $11.278_4 \pm 0.0004$ , 206.14, 18.2774, respectively. The constancy of atomic volume for isotopic elements is thus confirmed. The atomic weights are those obtained by Brennen (this vol., ii, 174). For the spectroscopic work, a vacuum arc was used in conjunction with a Fabry-Perot interferometer. Great precautions were taken to ensure an identical experimental arrangement for both isotopes. All the lines measured gave slightly higher values for uranium-lead than for ordinary lead. The results all refer to arc lines emitted by the neutral lead atom: wave-length 4058, difference in wave-length found  $0.0076 \pm 0.0008$ ; 3740,  $0.0070 \pm 0.0008$ ; 3684,  $0.0073 \pm 0.0008$ ; 3640,  $0.0072 \pm 0.0010$ ; 3573,  $0.0068 \pm 0.0010$ . No significance is attached to the apparent decrease in the difference.  
R. A. M.

**Relation between the Critical Temperature and the Expansion of Liquids.** N. DE KOLOSSOWSKY (*J. Phys. Radium*, 1925, [vi], **6**, 99—104).—The relation between the critical temperature and the expansion of a liquid for a given reduced temperature is expressed by the formula  $k_m(BT_c - 273) = 1$ , where  $k_m$  is the expansion modulus of the liquid at the reduced temperature, and  $B$  a numerical constant dependent on that temperature. For the reduced temperature  $T = 0.6T_c$ , the value of  $B$  is 2. It is shown that the expression in that case applies satisfactorily to a number of substances with critical temperatures between 127° and 1072° Abs. For the above reduced temperature van der Waals' formula  $\alpha_m T_c = \text{constant}$ , where  $\alpha_m$  is the coefficient of expansion of the liquid at the reduced temperature, has the form  $\alpha_m T_c = 0.75$ .  
F. G. T.

**Surface of State of cycloHexane.** N. N. NAGORNOV and L. A. ROTINJANC (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 371—404).—The results are given of physical measurements of

carefully purified *cyclohexane*, b. p.  $80.75^{\circ}/760$  mm., m. p.  $6.54^{\circ}$ ,  $d$  0.79063 at  $7^{\circ}$ , 0.78221 at  $16.12^{\circ}$ , 0.77384 at  $25.08^{\circ}$ , 0.75942 at  $40.21^{\circ}$ , 0.74416 at  $50.95^{\circ}$ , and 0.72215 at  $78.05^{\circ}$ . The value of the specific volume at  $t^{\circ}$  is given by  $1.26482/\{1-0.0011599(t-7)-0.000008356(t-7)^2\}$ . At  $25^{\circ}$ , the value of  $pv$  diminishes from 1 when  $p=760$  mm. to 0.9855 when  $p=50,000$  mm. to 55,000 mm. and then gradually increases to 1.0736 when  $p=200,000$  mm. The value  $554.02^{\circ}$  Abs. is found for the critical temperature ( $T_c$ ) and 30,835 mm. for the critical pressure ( $p_c$ ). For a number of temperatures ranging from  $275.95^{\circ}$  to  $-4.51^{\circ}$ , calculations have been made of the values of the constant  $f$  of van der Waals' equation,  $\log(p_c/p)=f(T_c-T)/T$ . Comparison of these numbers with those for *n*-hexane and benzene show that  $f$  has not the same value for all substances. Moreover, in each case, as the temperature falls the value of  $f$  at first diminishes to a minimum when  $\log(p_c/p)$  is about 0.7 and then increases. The paper contains a number of curves and tables of results, and reference is made particularly to the work of Young and Fortey (T., 1899, **75**, 873), Ramsay and Young (T., 1885, **47**, 82; A., 1887, 763), and Young and Thomas (T., 1895, **67**, 107).

T. H. P.

**Van der Waals' Equation of State.** J. J. VAN LAAR (*Z. physikal. Chem.*, 1925, **116**, 119—122).—Polemical, with reference to Berger's work (A., 1924, ii, 654; this vol., ii, 376). L. F. G.

**Apparatus for the Rapid Measurement of Surface Tension at the Interface of Two Liquids. Influence of Temperature.** P. L. DU NOÛY (*Compt. rend.*, 1925, **180**, 1579—1580).—The force necessary to drag a ring of thin platinum wire from the interface of two liquids is measured directly in dynes. An accuracy of 0.05 dyne can be attained in measuring the static interfacial tension between two liquids or solutions. The surface tension at a liquid/air interface decreases with rise in temperature; the interfacial tension increases with increasing temperature.

R. A. M.

**Surface Tension of Solutions of the Sodium Salts of  $\alpha$ - and  $\beta$ -Diphenylsuccinic Acids and of Fumaric and Maleic Acids.** I. RIBAS (*Anal. Fis. Quím.*, 1925, **23**, 148—150).—The surface tensions of solutions of the sodium salts corresponding with 5% solutions of the free acids were measured by the drop method. The values obtained, relative to water as unity, were  $\alpha$ -diphenylsuccinic acid 0.87,  $\beta$ -diphenylsuccinic acid 0.97, fumaric acid 0.99, maleic acid 0.96.

G. W. R.

**Capillary Rise of Water in Tubes of Various Metals.** E. K. CARVER and F. HOVORKA (*J. Amer. Chem. Soc.*, 1925, **47**, 1325—1328).—A convenient method for the accurate determination of surface tension is described. Water and benzene rise to the same height in tubes of glass as in tubes of various metals. These observations cannot be reconciled with those of Bigelow and Hunter (A., 1911, ii, 471), who found that these two liquids rose to greater heights in capillary tubes of metal than in tubes of glass. J. S. C.

**Influence of Pressure on Velocity of Diffusion of Metals in Mercury.** E. COHEN and H. R. BRUINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 555—564).—The velocity of diffusion of cadmium in mercury at 20° and 1500 atm. pressure has been determined. The increase of pressure from 1 atm. to this high value depresses the velocity of diffusion by about 5%. S. B.

**Potentiometric Measurement of Velocities of Diffusion of Metals in Mercury.** E. COHEN and H. R. BRUINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 535—554).—A potentiometric method has been described for the determination of the coefficient of diffusion of metals in mercury, which, within certain limits, can be applied at any desired temperature and pressure. This method has been used to determine the coefficient of diffusion of cadmium in mercury at 20° and 1 atm. pressure. S. B.

**Calculation of the  $P$ - $x$  Curves of Binary Liquid Mixtures.** L. FRANK (*Ber.*, 1925, **58**, [B], 962—964; cf. this vol., ii, 188).—Relationships are deduced from the partial pressure formulæ and the Duhem equation which permit the calculation of the total and partial pressure curves of liquid mixtures particularly when they are not greatly deflected. The composition of the gaseous phase can also be calculated. H. W.

**Molecular Compounds of Phenols. III. Behaviour of Binary Systems with Hydrogenated Phenols.** G. WEISSENBERGER and F. SCHUSTER (*Monatsh.*, 1924, **45**, 413—424; cf. Weissenberger and Piatti, this vol., i, 538, 539).—Determinations have been made at 20° of the vapour pressure (by a streaming method), of the viscosity, and of the surface tension (by the capillary rise method) of mixtures in eight successive proportions of each of the following pairs of substances: *cyclohexanol*–benzene, *cyclohexanol*–acetone, *cyclohexanol*–ethyl acetate, *cyclohexanol*–methyl alcohol, *cyclohexanol*–chloroform, 2-methyl*cyclohexanol*–benzene, 3-methyl*cyclohexanol*–benzene, and 4-methyl*cyclohexanol*–benzene. In each of these systems the observed vapour pressures are higher than those calculated from the molecular concentration by the Raoult–van't Hoff relation. The hydrogenation of the benzene nucleus has therefore completely suppressed the residual affinity made evident by similar experiments with phenols. The vapour pressure deviation reaches a maximum for mixtures which are in most cases equimolecular. These results are confirmed by the viscosity data, the viscosities of the mixtures being in all cases less than those calculated by the simple mixture law indicating a diminution of the intermolecular attraction. The surface tension values, again, are in all cases much smaller than the calculated values. The following surface tension values at 20° are recorded: *cyclohexanol* 34·5, 2-methyl*cyclohexanol* 31·3, 3-methyl*cyclohexanol* 29·6, 4-methyl*cyclohexanol* 30·5, methyl alcohol 22·7, acetone 22·8, ethyl acetate 23·3, benzene 28·8, chloroform 26·5 dynes/cm.

G. M. B.

**Molecular Compounds of Phenols. IV. Binary Systems with Phenol and its Ethers.** G. WEISSENBARGER, F. SCHUSTER, and K. SCHULER (*Monatsh.*, 1924, **45**, 425—435).—Determinations have been made of the vapour pressures at 15° of a series of mixtures of phenol with methyl alcohol, ethyl alcohol, acetone, and ethyl ether, respectively. The values observed are in all cases lower than those calculated from the mixture rule, and the divergence is a maximum in the system phenol-acetone for a concentration which corresponds with the compound  $2\text{Ph}\cdot\text{OH}, \text{Me}_2\text{CO}$  found by Schmidlin and Lang (A., 1910, i, 836) by thermal analysis of these mixtures. From similar maximum deviations, the existence is inferred of analogous compounds formed by phenol and the three cresols with alcohols, ketones, and ethers of the form  $2\text{Ar}\cdot\text{OH}, \text{M}$ , where M is a molecule of the second constituent. Corresponding measurements for mixtures of phenol with benzene, toluene, chloroform, carbon tetrachloride, and carbon disulphide show vapour pressures which are higher than the calculated. For the systems anisole and acetone, ethyl ether, carbon tetrachloride, and carbon disulphide, respectively, the vapour pressure values are again higher than those calculated. The methylation of the hydroxyl group of phenol thus completely suppresses compound formation with these substances, a result which lends support to the opinion of Pfeiffer and others that compound formation occurs in such cases by co-ordination with the hydrogen atom of the hydroxyl group. In the single system anisole-chloroform, however, the evidence points to formation of the compound  $2\text{Ph}\cdot\text{OMe}, \text{CHCl}_3$ . The oxygen atom is probably involved in this case.

Measurements of surface tension and viscosity at 15° are recorded for each of the above systems of phenol or anisole with volatile substances. The only clear indication obtained from the surface tension figures is a sharp maximum in the phenol-methyl alcohol system corresponding with the compound formation indicated by the vapour pressure measurements. The remaining surface tension data and the viscosity values lead to no precise conclusions.

G. M. B.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XLV. Binary Systems of Benzhydrol with Phenols and Amines.** R. KREMANN and H. DRAZIL (*Monatsh.*, 1924, **45**, 345—354; cf. A., 1919, ii, 457).—Fusion curves have been constructed for the binary systems given by benzhydrol with phenol,  $\alpha$ -naphthol,  $\beta$ -naphthol, quinol, resorcinol, pyrogallol, *o*-, *m*-, and *p*-nitrophenols, 2:4-dinitrophenol, picric acid,  $\alpha$ - and  $\beta$ -naphthylamine, *o*- and *p*-phenylenediamine, respectively. In the system benzhydrol and phenol a single compound is formed of the composition 1 mol. benzhydrol : 2 mols. phenol, m. p. 47.3°, no confirmation being obtained of the equimolecular compound (cf. Schmidlin and Lang, *Ber.*, 1912, **45**, 899). With  $\beta$ -naphthol, benzhydrol forms a compound (2 mols.  $\beta$ -naphthol : 3 mols. benzhydrol), m. p. 62°, and with picric acid a compound (2 mols. picric acid : 1 mol. benzhydrol), m. p. 131°. With the



remaining substances in the above list benzhydrol forms no compound, but yields in each case a simple eutectic. G. M. B.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XLVI. Binary Systems of Azobenzene with Phenols.** R. KREMANN, K. ZECHNER, and G. WEBER (*Monatsh.*, 1924, **45**, 305—310).—Fusion curves for the binary systems of azobenzene with various phenols show no compound formation. The eutectic temperatures and percentages of azobenzene in the eutectic mixtures with various phenols are as follow: *p*-nitrophenol 49°, 90%,  $\beta$ -naphthol 51°, 82%, quinol 55°, 1%, resorcinol 57·2°, 80%, *o*-nitrophenol 29°, 40%, *m*-nitrophenol 58°, 76%,  $\alpha$ -naphthol 48°, 66·5%, pyrocatechol 60°, 87·5%, pyrogallol 65°, 100%, 2:4-dinitrophenol, 54°, 72%, and picric acid, 56°, 67·5% of azobenzene respectively. G. M. B.

**Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XLVII. Binary Systems of Acids or Esters with Phenols.** R. KREMANN, E. ZECHNER, and H. DRAZIL (*Monatsh.*, 1924, **45**, 355—378; cf. preceding abstract).—Fusion curves have been constructed for the binary systems formed by succinic and cinnamic acids respectively with each of the following: phenol,  $\alpha$ -naphthol,  $\beta$ -naphthol, resorcinol, quinol, pyrocatechol, pyrogallol, *m*-nitrophenol, *p*-nitrophenol, 2:4-dinitrophenol, and picric acid, and for the system cinnamic acid and *o*-nitrophenol. No compound is formed between succinic acid and any of the phenols named, a simple eutectic being found in each case. Cinnamic acid, on the other hand, forms an equimolecular compound with picric acid, m. p. 106·5°, which is largely dissociated in the liquid phase at its melting point, whilst the melting-point curves of cinnamic acid with *m*-nitrophenol and 2:4-dinitrophenol show a practically horizontal portion between two eutectics in each case (at 77·5° and 29—36% of cinnamic acid with *m*-nitrophenol and at 91° and 30—41% of cinnamic acid with 2:4-dinitrophenol), indicating easily dissociated compounds which are probably, by analogy, equimolecular in composition. Cinnamic acid forms no other compounds, but gives a simple eutectic in each of the other systems examined. From these results, it is inferred that compound formation is due to the double bond rather than to the carboxyl group of cinnamic acid and to the nitro groups rather than to the hydroxyl group of the nitrophenols.

Complete fusion curves have been constructed for the binary systems of methyl oxalate with phenol,  $\alpha$ -naphthol,  $\beta$ -naphthol, pyrocatechol, quinol, resorcinol, pyrogallol, *o*-, *m*-, and *p*-nitrophenols, 2:4-dinitrophenol, picric acid, and *p*-toluidine, respectively. Methyl oxalate forms a compound with phenol, m. p. 47·5°, of the composition 4 mols. phenol to 1 mol. ester, and with quinol a compound, m. p. 94°, of the composition 1 mol. quinol to 4 mols. ester. Compound formation was not indicated in any other case, simple eutectics being found. Fusion curves have also been constructed for the binary systems ethyl oxalate with resorcinol,  $\beta$ -naphthol, and quinol over the ranges 0—62%, 0—75%, and 0—97% of ester,

respectively. There was no indication of compound formation, although Baeyer and Villiger have described an equimolecular compound of ethyl oxalate with quinol. G. M. B.

**Study of the Ternary Mixture: Water-Ethyl Alcohol-*n*-Butyl Alcohol.** F. DROUILLON (*J. Chim. phys.*, 1925, **22**, 149—168).—The system was studied by the synthetic method. Mixtures rich in water are totally miscible at ordinary temperatures, but separate into two layers on warming; on increasing the temperature still further, another critical solution temperature is reached. Mixtures poor in water form two layers at the ordinary temperature, but they are totally miscible at higher temperatures. The critical solution temperature for water-*n*-butyl alcohol is 129.5°, and the solution contains 28% of the alcohol. The results are tabulated and given in the form of curves. The position of conjugate points on the diagram was determined by analysis of the two liquid layers in equilibrium. Details of the method employed are given.

W. T.

**Compound AuCu in Gold Alloys.** L. STERNER-RAINER (*Z. Metallk.*, 1925, **17**, 162—165).—The compound AuCu separates in long, light-yellow needles from slowly cooled alloys of copper and gold containing 56.5% to 93.0% Au, and from copper-silver-gold alloys the composition of which falls within the region bounded by lines joining the silver corner of the ternary diagram to the points on the copper-gold side corresponding with alloys of the above composition. Rapid cooling of the alloy through the range 500° to 20° suppresses the separation of the compound, reduces the hardness and tensile strength of the alloy, and increases the ductility. [Cf. *B.*, July 24th.] A. R. P.

**Equilibrium Diagram of the Copper-Zinc System.** D. IITSUKA (*Mem. Coll. Sci. Kyoto*, 1925, **8**, 179—212).—A reinvestigation of the equilibria in the copper-zinc system has confirmed for the most part the results of earlier workers. Minor differences were, however, observed, especially in the positions of the boundary lines between the different constituents. In general, these were found to lie more towards the copper side than had previously been stated. The peritectic at 695° in alloys containing 20—30% Cu has only one saturation point, and that in alloys containing 0—12% Cu lies at 425°, which is much higher than previously found. The transformation in the  $\beta$  phase at 450—475° takes place in two stages, the maximum temperature of 475° occurring with 53% Cu. The  $\delta$  solid solution decomposes below 550° into eutectoidal  $\epsilon + \gamma$  and between 560° and 590° there is a small field of  $\delta + \gamma$  in alloys containing 26—30% Cu. Zinc begins to volatilise from the surface layers of brass at about 470°. [Cf. *B.*, July 24th.] A. R. P.

**Magnetisation of Ferro-Nickel [Alloys] (Thermomagnetic Properties).** M. PESCHARD (*Compt. rend.*, 1925, **180**, 1475—1478).—Alloys containing more than 34.4% of nickel ( $\text{Fe}_2\text{Ni}$ ) are reversible in the sense that their magnetic properties disappear and reappear at the Curie point, whilst alloys containing less than this

amount of nickel are irreversible. If sufficiently cooled the latter acquire a strong magnetisation which is connected with the change of the iron from the  $\gamma$  to the  $\beta$  modification. Under certain conditions, alloys in the " $\beta$ " state exhibit reversibility. The various cases possible are discussed and the experimental results expressed diagrammatically.

J. S. C.

**Solubilities in Water of Rubidium and Cæsium Chloroplatinates.** E. H. ARCHIBALD and L. T. HALLETT (*J. Amer. Chem. Soc.*, 1925, **47**, 1314—1318).—The solubility has been determined between  $0^\circ$  and  $100^\circ$  at  $10^\circ$  intervals. The solubilities in g./100 g. of water at  $0^\circ$  and  $100^\circ$  are respectively: rubidium salt 0.0137 and 0.334, cæsium salt 0.0047 and 0.0915.

J. S. C.

**Equilibrium in the System Zinc Sulphate-Water.** E. COHEN and A. L. T. MOESVELD (*Z. physikal. Chem.*, 1925, **115**, 433—439).—Further experiments have been undertaken which show that the earlier work of one of the authors (Cohen, *ibid.*, 1900, **34**, 179) was partly in error. The existence of the metastable monoclinic heptahydrate between  $7^\circ$  and  $35^\circ$  (Bury, this vol., ii, 119) is confirmed.

N. H. H.

**Solubility Curves of Zinc Sulphate.** E. COHEN and C. W. G. HETTERSCHIJ (*Z. physikal. Chem.*, 1925, **115**, 440—443).—A redetermination of the solubility curves of  $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (rhombic) has been made since the method of analysis used by one of the authors in previous work (Cohen, *ibid.*, 1900, **34**, 179) was subsequently shown to give results 0.4% too high. The transition point now found is  $37.9^\circ$ .

N. H. H.

**Solubility of Calcium Fluoride in Acetic Acid.** L. DUPARC, P. WENGER, and G. GRAZ (*Helv. Chim. Acta*, 1925, **8**, 280—284).—Calcium fluoride (fluorite) is not, as hitherto supposed, insoluble in dilute acetic acid. Acetic acid (0.5*N*) dissolves at  $40^\circ$  0.153 g., at  $60^\circ$  0.178 g., at  $80^\circ$  0.206 g., at  $100^\circ$  0.229 g. per litre. The corresponding figures for *N*-acid are 0.175, 0.203, 0.237, 0.264, and for 2*N*-acid 0.192, 0.229, 0.267, 0.300.

W. A. S.

**Solubility of Magnesium Hydroxide. I. Existence of different Modifications of Magnesium Hydroxide.** J. K. GJALDBÆK (*Z. anorg. Chem.*, 1925, **144**, 145—168).—The differences in the recorded values of the solubility of magnesium hydroxide in water are ascribed chiefly to the existence of two forms of the hydroxide, a labile and a stable form. Errors may also have arisen on account of the readiness with which the dissolved hydroxide attacks glass with the formation of magnesium silicate. Determinations, by the *E.M.F.* method, of the hydrogen-ion activity of solutions of magnesium chloride, saturated with the hydroxide by the addition of suitable quantities of sodium hydroxide, were made in paraffined vessels and showed that values of  $p\alpha_{\text{H}}$  (the negative logarithm of the hydrogen-ion activity) fell to a constant value, corresponding with the stable form of the hydroxide. This was also observed when the hydroxide was replaced by magnesium

oxide or metal and the final  $p\alpha_H$  values were in close agreement; the same values were obtained without an initial fall when the hydroxide was converted into the stable form before use. The initial hydrogen-ion activities, corresponding with the labile form of hydroxide, were less concordant. A. G.

**Solubility of Magnesium Hydroxide. II. Solubility Products and Dissociation Constants of the Magnesium Hydroxides.** J. K. GJALDBÆK (*Z. anorg. Chem.*, 1925, **144**, 269—288).—The hydroxyl-ion activities of saturated solutions of magnesium hydroxide in aqueous magnesium chloride were calculated from the hydrogen-ion activities, determined as already described (cf. preceding abstract). The magnesium-ion concentration was equal to the known concentration of the chloride plus that of the hydroxide and carbonate, determined by electrometric titration with acid; the activity coefficient of the latter ion was calculated from Bjerrum's formula,  $-\log f = nk\sqrt[3]{C_{ion}}$ , in which  $f$  is the activity coefficient,  $n$  the valency of the ions, and  $C_{ion}$  the ionic concentration. The solubility products at 18° of the stable and labile forms of the hydroxide were thus calculated to be  $10^{-10.93}$  and  $10^{-9.2}$ , respectively; the second dissociation constant was found to be approximately  $10^{-21}$  and, when allowance was made for incomplete dissociation, the calculated solubilities at 18° of the two forms were  $1.61 \times 10^{-4}$  and  $7.0 \times 10^{-4}$ , respectively; nearly all previously recorded values lie between these two figures. The molar heat of solution of the stable form is -2200 calories and that of the labile form approximately zero. A. G.

**Influence of the Variation of the Coefficient of Viscosity with Temperature on the Specific Heat of Solutions.** N. DE KOLOSSOWSKY (*Bull. Soc. chim.*, 1925, [iv], **37**, 605—608).—The specific heats of dilute aqueous solutions of organic substances such as carbamide, acetamide, dextrose, formic, oxalic, and citric acids are given accurately by  $(18\mu + 2n + 3)/(18\mu + M)$ , where  $M$  is the molecular weight of the substance,  $n$  the number of atoms in its molecule, and  $\mu$  the number of molecules of water per molecule of solute. For some substances, such as the saturated alcohols, there is a considerable deviation from the values calculated from this formula, but the deviation is given by the additional term  $350d(\eta_0 - \eta)/dT$ , where  $\eta_0$  and  $\eta$  are the coefficients of viscosity of the solvent and the solute respectively. The observed deviation agrees with the value calculated from this expression in the case of ethyl and propyl alcohols, acetic acid, and sucrose, but in the case of methyl alcohol there is a further discrepancy. G. M. B.

**Salt-formation between Creatine and Sodium Hydroxide.** A. HAHN and H. FASOLD (*Z. Biol.*, 1925, **82**, 473—484).—A saturated aqueous solution of creatine at 10° contains 10.9 g. of creatine per litre; at 12°, the amount lies between 14.4 and 14.9 g. The amount dissolved in sodium hydroxide increases from 12.72 g. per litre in 0.2*N*-solution to 23.20 g. in *N*-solution.  $K_a$  for creatine is  $5.2 \times 10^{-15}$ . Since  $K_b$  is  $5 \times 10^{-12}$  (A., 1921, i, 515), creatine is about

a thousand times stronger as a base than it is as an acid. The hydrolysis of the sodium salt of creatine increases with dilution, being almost complete in 0.05*N*- to 0.025*N*-solution. The velocity of the conversion of creatine into creatinine by sodium hydroxide increases slowly with the concentration of the alkali. O. O.

**Salt Solutions.** P. MONDAIN-MONVAL (*Ann. Chim.*, 1925, [x], 3, 72—190).—The formula,  $502LdT/T^2 + idc/c = 0$  is shown to represent the solubility of sodium and ammonium nitrates, the factor  $i$  being given by the relation  $dp/p = i \cdot dc/c$ , where  $p$  is the vapour pressure. Heats of solution are recorded (at 0° and about 18°) for potassium, sodium, and ammonium nitrates, potassium and ammonium chlorides, and potassium sulphate. The calculated and observed values of  $L$  agree except in the case of the last-named salt. Similar data are recorded for certain mixed salt solutions with a common ion. The general rule that the ratio of  $L$  above and below a transition point is equal to the ratio of the gradients of the respective solubility curves is confirmed for ammonium nitrate. For two curves meeting at a eutectic the relation:  $(dc_2/dT)/(dc_1/dT) = c_2L_2/c_1L_1$ , is verified for the above six salts; the suffixes 1 and 2 refer to the two curves. The same rule holds for solutions containing mixtures of salts with a common ion provided the left-hand side is multiplied by  $i_2/i_1$ . The relation  $d \log L/dc = -d \log i/dT$  is confirmed experimentally.

S. K. T.

**Ammoniation of Ions in Aqueous Solutions.** J. LOŠAN (*Rec. trav. chim.*, 1925, 44, 459—465).—Cryoscopic measurements of aqueous ammoniacal solutions of the chlorides of lithium, sodium, potassium, magnesium, and ammonium have been made in order to determine to what degree the metal ions are capable of binding ammonia molecules. Lithium and, still more, magnesium ions show this effect to a marked degree. In the other cases an increased depression of freezing point is observed, but this is attributed to the masking of the ammoniation effect by the hydration of ions and molecules by the solvent with a consequent decrease in its activity. This is demonstrated by comparison with analogous experiments in which ammonia is replaced by dextrose, which does not combine with the ions: here a still greater increase of depression is observed (potassium excepted). The ammoniation effect is taken as proportional to the differences between corresponding depressions in the two sets of experiments. This gives decreasing ammoniation in the order lithium, sodium, ammonium, potassium. The effect thus decreases with increase in ionic volume.

N. H. H.

**Displacement of Acids by Diffusion.** E. DEMOUSSY (*Compt. rend.*, 1925, 180, 1498—1500; cf. A., 1924, ii, 147).—Previous work is extended to include various mixtures of alkali and alkaline-earth chlorides with organic acids. The alkaline-earth chlorides yield numbers for the displacement of hydrochloric acid which are sensibly identical. The displacement is much smaller in the case of the alkali chlorides. Displacement of hydrochloric acid also varies with the degree of ionisation of the organic acid, and under comparable

conditions the order of the acids starting with the least efficient is : acetic, citric, formic, oxalic. Replacement of the chloride ion by the less mobile sulphate ion results in a reduced displacement. Analogous results were obtained with mixed solutions of potassium chloride and barium hydroxide. J. S. C.

**Absorption of Hydrogen Chloride in Concentrated Sulphuric Acid.** V. ČUPR (*Rec. trav. chim.*, 1925, **44**, 476—479).

—The absorption of hydrogen chloride in sulphuric acid over a range of concentration of 76.43 to 100.00%  $\text{H}_2\text{SO}_4$  has been measured at 25° and atmospheric pressure. The absorption shows a minimum at about 89%  $\text{H}_2\text{SO}_4$ , i.e., at a higher concentration than that corresponding with the hydrate  $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  which contains 84.48%  $\text{H}_2\text{SO}_4$ . N. H. H.

**Adsorption from Viscous Media by Charcoal.** G. WEISSENBACHER and H. WALDMANN (*Monatsh.*, 1924, **45**, 393—412).—The adsorption of iodine by five different varieties of charcoal from solution in glycerol, cyclohexanol, and *n*-butyl phthalate ( $d^{18}$  1.49, viscosity 13.5 times that of water) is found to reach a true equilibrium which obeys the Freundlich adsorption equation. The time required to reach equilibrium at 18° is 1.5 hrs. for glycerol, 1 hr. for cyclohexanol, and 3 hrs. for butyl phthalate solutions. Figures are recorded showing the variation of the adsorption from equivalent solutions of iodine as the composition of the solvent is varied by diluting the glycerol with water, the cyclohexanol and the butyl phthalate with benzene, whereby the viscosity of the liquids is much reduced. The amounts adsorbed at equilibrium are found to vary inversely as the viscosity of the medium for each set of mixtures, the values agreeing with an equation  $x/m = \beta/\eta^{1/\gamma}$ , where  $x$  is the amount adsorbed,  $m$  the weight of adsorbent,  $\eta$  the viscosity of the medium, and  $\beta$  and  $\gamma$  are constants peculiar to the substances involved, the values obtained for  $\beta$  and  $1/\gamma$  being : glycerol 5.19 and 0.447, cyclohexanol 1.11 and 0.515, butyl phthalate 1.060 and 0.0453. This effect is explained by the correlation of high viscosity with a high degree of polymerisation in the liquid and at the same time with a ready adsorption of the complex liquid molecules, which by competing with the iodine for the surface of the carbon lower the apparent adsorption. The addition of the less viscous liquid causes dissociation of the complexes, less adsorption of the liquid, and therefore more adsorption of iodine. By means of Freundlich's formula, the final concentration and amount adsorbed for a series of initial concentrations are calculated and found to agree with the values observed experimentally.

The results are found to be of the same type for the different varieties of charcoal used. G. M. B.

**"Activated" Graphite as a Sorbent of Oxygen.** D. H. BANGHAM and J. STAFFORD (*J. Chem. Soc.*, 1925, **127**, 1085—1094).—Graphite which has absorbed large quantities of hydrogen shows greatly increased activity as a sorbent of oxygen. A study of the kinetics of the sorption of oxygen showed that it took place at

constant pressure according to the equation  $s=kt^b$ , where  $s$  is the quantity of oxygen sorbed at time  $t$  after its introduction to the graphite,  $k$  and  $b$  being constants. The experiments were performed with graphite surrounding a platinum electrode in a small glass bulb, connected to the gas measuring system. By heating the graphite in a vacuum to  $350^\circ$ , and submitting it to the electric discharge in hydrogen, large quantities of the gas were taken up, and the graphite was then found to be very active towards oxygen. The activity towards carbon dioxide was scarcely changed. The equations for the sorption of oxygen all involved a common power of  $t$ , viz.,  $t^{0.190}$ . Experiment showed that the "induced" activity of the graphite towards oxygen was directly proportional to the hydrogen introduced electrically, and was independent of the amount of graphite used. Objections are raised to the view that hydrogen is maintained in an active state by the graphite and is removed by combination with oxygen, and a mechanism of the phenomenon based on the crystal structure of graphite is discussed. L. L. B.

**Adsorption by Activated Sugar Charcoal. II. Adsorbability of Hydrogen and Hydroxyl Ions.** E. J. MILLER (*J. Amer. Chem. Soc.*, 1925, **47**, 1270—1280).—The view that hydrogen and hydroxyl ions are equally adsorbed by charcoal is based on erroneous evidence, the hydroxyl ion being last instead of first in the series which expresses the adsorbability of anions by pure charcoal. Experiments have been carried out using pure, ash- and nitrogen-free charcoal (A., 1924, ii, 664). The adsorption of hydrochloric acid from its aqueous solutions is increased in presence of sodium chloride. Addition of sodium and potassium chlorides to solutions of the corresponding hydroxides results in an increase in the concentration of the alkali; this is attributed to hydrolytic adsorption, hydrochloric acid being adsorbed and an equivalent amount of alkali liberated. The strong inorganic bases are "negatively" adsorbed, i.e., the charcoal adsorbs water, leaving the alkali concentrated in a smaller volume. Adsorption from solutions of salts is either exclusively hydrolytic or partly hydrolytic and partly molecular. Certain theoretical points are discussed. J. S. C.

**Negative Adsorption and Oxidising Action of Suspended Charcoal.** T. ÖRYNG (*Kolloid-Z.*, 1925, **36**, 287—288; cf. A., 1913, 761).—Polemical, against Feigl (A., 1922, ii, 51). E. M. C.

**Adsorption of Vapours by Silica Gel by a Dynamic Method.** W. A. PATRICK and L. H. OPDYCKE (*J. Physical Chem.*, 1925, **29**, 601—609).—The adsorption of water, ethyl alcohol, carbon tetrachloride, and benzene vapour on silica gel containing 3.57% of water at  $30^\circ$  has been investigated by a dynamic method. The vapours were admixed with dry air in definite proportions and passed over the gel until equilibrium was attained. A hysteresis effect was observed with water vapour. The remaining liquids gave results which agreed with the authors' theory of capillary condensation. The time taken for water vapour to reach equilibrium was very long.

Since water undergoes an increase in viscosity with reduced pressure it must be highly viscous in the capillary pores of the silica gel.

M. B. D.

**Adsorption of Water Vapour and some other Vapours by the Surface of Glass.** D'HUART (*Compt. rend.*, 1925, 180, 1594—1596).—The weight of water adsorbed by the internal surface of the apparatus described varies little with temperature between 14° and 24°; it is proportional to the surface area and to the vapour pressure. This direct variation with vapour pressure holds between 5 mm. and the saturation point, but even in the highest vacua obtainable in the presence of phosphorus pentoxide a certain amount of water (0.009 mg./dm.<sup>2</sup>) adheres to the glass after several hours. With vapours other than water the adsorption is much feebler and often cannot be measured, as in the cases of ethyl alcohol, chloroform, benzene, and toluene. The apparatus described may be used for the rapid determination of the humidity of gases or of hydrogen in organic compounds, and for the determination of the vapour densities of very volatile liquids. The results in the vapour-density measurements are more accurate than those obtained by the method of Victor Meyer.

R. A. M.

**Sorption of Nitrous Oxide and Sulphur Dioxide by Glass.** D. H. BANGHAM and F. P. BURT (*J. Physical Chem.*, 1925, 29, 540—550; cf. this vol., ii, 284).—The sorption of nitrous oxide and sulphur dioxide by glass has the same time characteristics as were previously found with carbon dioxide. It was found impossible to remove completely the sulphur dioxide from the glass wool.

M. B. D.

**S-Shaped Adsorption Curve.** K. W. FLÖROV (*Kolloid-Z.*, 1925, 36, 215—217).—For reactions yielding a new solid phase of higher solubility product than that of the adsorbent, the initial portion of the adsorption curve is convex to the concentration axis (Pavlov, A., 1924, ii, 594). The complete adsorption curve, however, should be S-shaped. To prove this, the system barium sulphate-potassium chromate has been investigated, with barium sulphate as adsorbent. Three series of measurements, using the reactants in different proportions, gave three curves, all convex in their initial portions. The curve for 0.5 g. of barium sulphate to 100 c.c. of solution has a well-defined maximum. From the results, it is obvious that the reaction is complex, and for strong solutions, the equation  $2\text{BaSO}_4 + \text{K}_2\text{CrO}_4 = \text{BaSO}_4 \cdot \text{BaCrO}_4 + \text{K}_2\text{SO}_4$  is suggested.

L. L. B.

**S-Shaped Adsorption Curves and their Calculation.** Wo. OSTWALD and H. SCHULZE (*Kolloid-Z.*, 1925, 36, 289—300).—The adsorption of acetic acid by charcoal from mixtures of acetic acid and water was positive in all cases studied, with a maximum for 15% of acetic acid. Acetic acid was negatively adsorbed from mixtures with ten organic solvents, the effect being most marked for mixtures with ethylene bromide. The adsorption curve throughout the whole range of mixtures of dry acetic acid and ethylene bromide is S-shaped. Up to 15.8% of acetic acid, the



adsorption is positive, and above this point negative. The S-shaped curve is not fitted satisfactorily by any of the equations put forward by Ostwald and de Izaguirre (A., 1922, ii, 480; 1923, ii, 128), but the two separate portions of the curve fitted are accurately reproduced by the simplest of their equations. It is assumed that acetic acid and ethylene bromide form a compound containing 15.8% of acetic acid and that this compound alone is adsorbed, the component in excess behaving only as a solvent. There is some evidence of a eutectic point and of minima in the surface tension and viscosity curves in the neighbourhood of this composition. It is suggested that the point of zero adsorption from binary mixtures may be used to detect compound formation. E. M. C.

**Basic Exchange with Salts of Organic Nitrogen Compounds.** E. UNGERER (*Kolloid-Z.*, 1925, 36, 228—235).—The adsorption of salts of organic bases by calcium-permutite has been investigated, and the mechanism of the reaction has been found to depend upon base exchange, which follows the well-known adsorption isotherm. The salts used included the hydrochlorides of guanidine, betaine, methylamine, and aniline, tetramethylammonium iodide, arginine nitrate, and the alkaloids quinine, cinchonine, and strychnine, the alkaloids being dissolved in 94% alcohol to eliminate side-reactions on account of hydrolysis. Natural clay shows a similar behaviour towards the alkaloids. L. L. B.

**Evaporation of Water from Clean and Contaminated Surfaces.** N. K. ADAM (*J. Physical Chem.*, 1925, 29, 610—611).—The deductions of Hedestrand (this vol., ii, 102) on the influence of colloidal films on the rate of evaporation of water vapour from water surfaces are inconclusive, since the experiments only measure the rate of escape of water vapour as controlled by the air film existing on the water surface. The results only show that the rate of evaporation in the presence of a colloidal film did not diminish by more than 0.2%. M. B. D.

**Metallic Lustre. II.** W. D. BANCROFT and R. P. ALLEN (*J. Physical Chem.*, 1925, 29, 564—586).—When light of sufficient intensity seems to come from a single surface and there are suitable variations of intensity in space or time, metallic lustre is obtained. Substances such as solid dyes, potassium permanganate, etc. which show selective surface reflexion are so opaque for the rays thus reflected that the light comes practically from a single surface. M. B. D.

**Unimolecular Films on Water. Oriented Adsorption of Derivatives of Benzene.** W. D. HARKINS and E. H. GRAFTON (*J. Amer. Chem. Soc.*, 1925, 47, 1329—1335).—The areas occupied by the molecules of various hydroxyl derivatives of benzene have been derived from measurements of the surface tensions of aqueous solutions of these substances. The orientation of the molecules on the surface of water is discussed and the various molecular magnitudes are compared with the dimensions obtained for molecules of benzene, naphthalene, and anthracene in the crystalline form. The

molecules of phenol are oriented with the hydroxyl group in the liquid and the phenyl group on edge above it. In the case of quinol both hydroxyl groups are within the liquid whilst the phenylene group remains on the surface. J. S. C.

**Effect of Vapours of Some Organic Liquids on the Surface Tension of Water.** V. KOŘÁN (*Rec. trav. chim.*, 1925, **44**, 466—475).—The changes in the surface tension of water dropping into the saturated vapours of carbon tetrachloride, light petroleum, toluene, benzene, chloroform, triethylamine, and ethyl ether have been measured and the temperature influences in each case exactly determined. It is found that the surface activity of these vapours is parallel to the interfacial activity of the corresponding organic liquids on water. The results are discussed with reference to the views of Harkins. N. H. H.

**Surface Tension of Gelatin Solutions.** J. H. S. JOHNSTON and G. H. PEARD (*Biochem. J.*, 1925, **19**, 281—289).—There is no quantitative relationship between the surface tension of a colloidal solution and the potential difference between the particles and the medium. The surface tension of gelatin solutions is at a maximum at the isoelectric point  $p_H$  4.7 and again at  $p_H$  2.8—3.0, after which it decreases steadily. The minima are at  $p_H$  3.8—4.0 on the acid side and in the neighbourhood of  $p_H$  9 on the alkaline side. Increase of temperature or addition of electrolytes causes a lowering of surface tension of gelatin solutions. The surface tension of gelatin solutions is little affected by time after equilibrium is attained; this occurs in a few hours at 25°, except in the case of isoelectric gelatin. For such gelatin solutions the surface tension rises to the value for water as flocculation proceeds. S. S. Z.

**Sign of the Electrical Layer Furthest away from the Surface of a Solution in Contact with Air or Metal.** R. D. KLEEMAN and C. R. PITTS (*J. Physical Chem.*, 1925, **29**, 508—516).—Small bubbles of air rising up a tube containing a solution of a salt, acid, or alkali produce a fall of potential in the liquid in the tube. The fall of potential is attributed to the peeling off of charges from the electrical double layers associated with the surfaces of the bubbles. A tangential motion given to the liquid near one of the electrodes would tend to peel off the outermost layer of electricity and set up a difference in potential between the electrodes. No simple relations are disclosed. M. B. D.

**Influence of Colloidal Solutions on the Electrocapillarity of Mercury.** K. ŠANDERA (*Rec. trav. chim.*, 1925, **44**, 480—487).—The influence of various colloids, notably gelatin, glycogen, gum arabic, ferrous hydroxide, starch, arsenious sulphide, mastic, silica, aluminium hydroxide, and fatty acids, on the electrocapillarity of mercury has been investigated by the dropping mercury electrode method of Kučera (*Ann. Physik*, 1903, **11**, 529, 698). The minimum concentration which will affect the electrocapillarity appreciably varies considerably with different colloids. Thus for gelatin it is

0.001%; glycogen, 0.01%; gum arabic, 0.05%; ferrous hydroxide, 0.1%; starch, 0.03%; arsenious sulphide, 0.5%. The effect of change of concentration is demonstrated by the behaviour of gelatin in 0.0862*N*- and 0.137*N*-sulphuric acid. Here the first additions of colloid cause the greatest lowering of interfacial tension and similar results are given with colloidal silica in sodium chloride, but here the maximum of the capillarity curve is raised. The so-called anomalous adsorption was never observed. The influence of the electric charge of the colloids is expressed by the rule that, in general, positive colloids shift the maximum to the more negatively polarising potential and *vice versa*. The displacement of the maximum is influenced by the nature of the electrolyte. This may be due to a change of the electric charge of the colloids by the ions present. With colloidal silica, the order of mixing the solution affects the displacement. Experiments are described which show that the most effective degree of dispersion is intermediate between that of a suspension and molecular dispersion. The influence of positive and negative colloids as contrasted with positive and negative ions is explained by the assumption that the colloid particles have an apparent charge due to the selective adsorption of positive or negative ions which will then surround them by a double layer (of potential  $\zeta$ ). Thus "positive" particles adsorb with preference negative ions. From this it is deduced that the shift of the potentials corresponding with the maxima of the capillarity curves serves as a measure of the adsorption potential ( $\zeta$ ) surrounding the charged particles.

N. H. H.

**General Structure of Matter in the Colloidal State. I. Form and Chemical Composition of Disperse Particles in Suspensoids and Precipitates.** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36**, 237—240).—A résumé of the author's views. L. L. B.

**Alteration in the Fibre X-Ray Spectrogram of Cellulose on Swelling in Concentrated Aqueous Solutions.** J. R. KATZ and H. MARK (*Z. physikal. Chem.*, 1925, **115**, 385—404).—The swelling of cellulose (ramie) in concentrated solutions of acids, bases, and salts, which is much greater than in pure water (cf. A., 1924, ii, 652), has been studied by means of X-ray spectrograms. Swelling in solutions of zinc chloride, calcium thiocyanate, potassium iodide, and potassium iodide with mercuric iodide produced no change in the cellulose lattice. With the two latter solutions, however, the cellulose spectrogram disappeared if the preparations were not washed, but returned on washing. Swelling in nitric and sulphuric acids could not be studied fully owing to the ready solubility of the cellulose. In sufficiently strong solutions of sodium, potassium, and lithium hydroxides, the cellulose diagram gives place to that of a new substance the crystallites of which lie parallel to the fibres. After washing the preparations, both diagrams are observed. Ammoniacal copper oxide solution gives similar results. Concentrated solutions of this and of the alkalis cause an enlargement of the cellulose lattice up to 4%.

N. H. H.

**Cholesterol and its Esters. II.** E. KEESER (*Biochem. Z.*, 1925, **157**, 166—171).—The sols of cholesterol and of its esters confer their stabilising power on the colloid by which they are adsorbed. The nature of the cation in the salts derived from cholesteryl esters (*e.g.*, sodium or potassium salt of cholesteryl sulphuric acid) has a marked influence on the stabilising power of the latter. Methyl, ethyl, propyl, and butyl alcohols all raise the electrical conductivity of the sols of cholesterol and its esters, but as the concentration of the alcohol increases this rise becomes progressively less; in high concentrations of alcohol the conductivity and the dissociation are diminished. The stability of these sols is increased by the addition of alcohol. Addition of carbamide or glycine increases the stability of an arsenic trisulphide or a sulphur sol.

H. D. K.

**Silicate Solutions and Some Silicious Gels.** J. G. VAIL (*J. Soc. Chem. Ind.*, 1925, **44**, 214—219T).—A discussion and correlation of the properties and the uses of silicious gels and sols. The theory that colloidal silica particles always tend to coalesce into larger aggregates and finally to gel, and that whether sols or gels they adsorb positively charged ions on their surface, receives considerable support from observed facts.

L. A. C.

**Formation of Colloidal Manganese Dioxide in the Reduction of Permanganate by Arsenious Acid. Influence of its Adsorptive Power on the Extent of the Reaction.** M. GELOSO (*Bull. Soc. chim.*, 1925, [iv], **37**, 641—656).—The titration of potassium permanganate with sodium arsenite in 0.1*N*-solutions to a green colour gives consistent results within a certain range of concentration of sulphuric acid, the manganese being reduced to a state of oxidation corresponding with  $\text{Mn}_3\text{O}_5$ . In neutral solution or with insufficient acid, a brown turbidity or a yellow coloration is obtained, whilst an excess of acid gives a pink solution, the corresponding states of oxidation of the manganese ranging continuously from  $\text{MnO}_2$  through  $\text{Mn}_6\text{O}_{11}$  and  $\text{Mn}_3\text{O}_5$  to  $\text{Mn}_2\text{O}_3$ . The end-point is similar with certain concentrations of nitric acid but never in presence of tartaric or phosphoric acids. The degree of oxidation of the manganese at the end-point is affected considerably by  $\text{Ag}^+$  ions, less by  $\text{AsO}_4^-$  ions, whilst in presence of  $\text{Mn}^{++}$  ions the reduction proceeds quantitatively to  $\text{MnO}_2$ . The variation in composition of the reduction product with various conditions proves that the formulæ  $\text{Mn}_3\text{O}_5$  and  $\text{Mn}_6\text{O}_{11}$  do not represent definite compounds, the green liquid being a colloidal solution of  $\text{MnO}_2$  with other substances adsorbed. This sol has a wide absorption band extending to 4900 Å., and it polarises the light it scatters. A similar sol is obtainable by adding sulphuric acid to a solution containing permanganate and arsenite and diluting the product. The state of oxidation of the manganese in this solution is found to correspond with  $\text{MnO}_2$ , and the same is true of the black solid which it deposits on keeping. The latter contains arsenic but not as a definite compound. The composition of the colloid obtained in titration is probably

$n\text{MnO}_2\text{MnO}$ , where  $n$  is larger than 2, and the influence of some of the added salts is explained on this assumption. G. M. B.

**Is the Solution of Cellulose in Ammoniacal Copper Oxide a Peptisation?** E. BAUR (*Kolloid-Z.*, 1925, **36**, 257—259).—It is shown from the data of Hess and others (A., 1924, i, 143—148) that the distribution of copper between cellulose and a solution of cellulose in Schweitzer's reagent may be represented by an adsorption equation. E. M. C.

**Composition of Solutions of Cellulose in Ammoniacal Copper Oxide.** K. HESS and E. MESSMER (*Kolloid-Z.*, 1925, **36**, 260—264).—Baur's conclusion (see preceding abstract) that the combination of cellulose with "cuprammonium" is an adsorption process is controverted. No other metal behaves exactly like copper. The reaction is independent of the dispersion of the cellulose over wide ranges. Similar complexes are formed by other carbohydrates, of suitable constitution, which give true solutions. It is shown that an equation based on the mass-action law is more satisfactory for purposes of interpolation than is the one based on the hypothesis of adsorption. E. M. C.

**Plasticity of Cellulose in "Cuprammonium Hydroxide."** E. K. CARVER and H. FOLTS (*J. Amer. Chem. Soc.*, 1925, **47**, 1430—1434).—An improved form of Bingham and Green's plastometer (*Proc. Am. Soc. Test. Mat.*, 1909, **19**, ii, 640) is described. With this measurements have been made of the plasticity of 0.5—2% solutions of standard cellulose (cf. Gray and Cory, *Ind. Eng. Chem.*, 1924, **16**, 853, 1130), in "cuprammonium hydroxide" solution containing 1.5% of copper and 20.5% of ammonia, by weight, to which 2% of sucrose was added to reduce oxidation. The results obtained confirm those of Joyner (T., 1922, **121**, 1511, 2395). F. G. W.

**Cause of Conductivity of Casein Solutions.** M. FISCHENICH and M. PÓLÁNYI (*Kolloid-Z.*, 1925, **36**, 275—281; cf. A., 1920, i, 684; Plattner, A., 1923, i, 963).—The diffusion through a membrane of conducting substances from a neutral solution of casein is due neither to bacterial decomposition nor to membrane hydrolysis. On dialysis in collodion membranes the conductivity may fall to one-half without any precipitation of casein. Variations in the conductivity of the outer solutions after dialysis are ascribed to differences in permeability to impurities in the casein. The conductivity is reduced by 20% on dialysis through parchment and the outer liquid contains organic substances which are not casein. Since the addition of gelatin has substantially the same effect on the conductivity of neutral casein solutions when in solution at 25° and as a jelly at 0°, it is concluded that casein ions play no part in the conductivity of neutral casein solutions. E. M. C.

**Protein and Potassium Ions.** W. E. RINGER (*Z. physiol. Chem.*, 1925, **144**, 85—96).—Electrometric determinations have shown that nucleoprotein prepared from horse-serum combines,

in neutral solution, with potassium ions to a small extent. Euglobulin in potassium chloride solution depresses the activity of the chloride ions but not of the potassium ions; in alkaline solution, it depresses the activity of the potassium ions very slightly. Reduced and oxygenated hæmoglobin in neutral and acid solution exerts no influence on the potassium or chloride ions. It is concluded that, at neutral reaction, water-soluble proteins do not form complex ions, whereas water-insoluble proteins may combine with a small quantity of cations or a larger amount of anions. C. R. H.

**Relationship between Ostwald's Viscosity Equation and Poiseuille's Law.** K. MATTHÄUS (*Kolloid-Z.*, 1925, **36**, 281—282).—An expression for the viscosity in the turbulent state is derived from Ostwald's equation for colloidal solutions, which do not obey Poiseuille's law. E. M. C.

**Influence of Rate of Shear on the Measurement of the Viscosity of Disperse Systems. IV.** W. OSTWALD (*Kolloid-Z.*, 1925, **36**, 248—250).—The work of a number of investigators in this direction is reviewed. The simple logarithmic relation  $Vt^1 = kP^n$ , formerly applied by de Waele (*J. Oil and Colour Chem. Assoc.*, 1923, **6**, 33) and by Farrow and Lowe (*J. Textile Inst.*, 1923, **14**, 414) to capillary viscosimeter measurements with vaseline and starch paste, has been found by the author and his colleagues to hold for 25 sols when using capillary viscosimeters of varied types, and also when using the Hess or Couette apparatus. L. L. B.

**Viscosity and Elasticity of Soap Solutions.** H. FREUNDLICH and H. J. KORES (*Kolloid-Z.*, 1925, **36**, 241—243).—Viscosity measurements with the Couette apparatus show that solutions of sodium oleate and dilute solutions of sodium stearate possess no elasticity at the ordinary temperature. On the other hand, a marked elastic effect is shown by a solution of a mixture of the two soaps, in which both are present in about the same concentration as in the measurements with the pure soaps. L. L. B.

**Influence of Alcohol on the Viscosity of Blood-serum.** K. HAYASHI (*Kolloid-Z.*, 1925, **36**, 227).—A repetition of Fürth and Blüh's measurements of the viscosity of blood-serum containing alcohol (*ibid.*, 1924, **34**, 129). Three series of experiments are recorded, using an Ostwald viscosimeter in a water-bath at 20°, and in each case the viscosity rose practically linearly with the alcohol content. The minimum recorded by Fürth and Blüh was not confirmed. L. L. B.

**Emulsions.** W. SEIFRIZ (*J. Physical Chem.*, 1925, **29**, 587—600).—Emulsions of various paraffin hydrocarbons in water with casein as an emulsifying agent are of the oil-in-water type up to  $d$  0.828 and of the water-in-oil type above 0.860. The intermediate range gives rise to only very unstable emulsions which may be of either type. These results cannot be explained on the oriented molecular wedge hypothesis. The following electrolytes stabilise the oil-in-water emulsions: sodium hydroxide > barium hydroxide >

thorium nitrate > aluminium sulphate > barium chloride > sodium chloride. With the exception of the last two electrolytes, certain of the water-in-oil emulsions can be reversed by them. This effect cannot be ascribed to a lowering of the interfacial surface tension.

M. B. D.

### Effect of Added Substances on the Stability of Dispersoids.

II. P. P. VON WEIMARN and S. UTZINO (*Kolloid-Z.*, 1925, **36**, 265—274).—The stability of dispersoid sulphur solutions, prepared by grinding sulphur with dextrose, generally increases with the addition of increasing amounts of salts up to a concentration of the order of 0.01 millimol. per litre and decreases for higher concentrations. For chlorides the concentration needed to give maximum stability decreases with the valency of the cation, and the relative increase in stability at the maximum increases with the valency. No increase in stability was found with potassium nitrate. A second region of maximum stability in more concentrated solutions is shown by certain sulphur compounds. This second maximum stability is well marked with potassium thiocyanate (at 10 millimols. per litre) and is also found with calcium thiocyanate and potassium sulphate, but not with sulphuric acid. Attention is directed to a general analogy between the behaviour of sulphur and cellulose.

E. M. C.

**Colloid Chemistry of the Vitamin Problem.** F.-V. VON HAHN (*Kolloid-Z.*, 1925, **36**, 271—274).—Some 50 foodstuffs of widely different types showed a close agreement between the surface activities of the aqueous extracts or juices and the contents of water-soluble vitamins. With onions, bananas, milk, and egg yolk the surface activities were too high, but much lower values were obtained after ultrafiltration; the majority of the extracts underwent no change on ultrafiltration. The percentage reductions of the surface tension of water for extracts grouped according to their vitamin contents were: nil 0—1.4, low 1.8—9.2, medium 10—17, high 15—26. Marked reductions in surface activity resulted from heating or drying apples and potatoes. In a separation by Funk's method, the fractions rich in vitamin reduced the surface tension by about 25%, whilst the vitamin-free fractions reduced it by 2—4%. It is suggested that the characteristic action of foodstuffs containing vitamins is to be ascribed to an increase in the permeability of the walls of the intestine to colloids and substances of high molecular weight owing to the high surface activity of substances in the vitaminoid state.

E. M. C.

**Stability of Colloidal Solutions. III. Coagulation of Copper Ferrocyanide Sol.** K. C. SEN (*J. Physical Chem.*, 1925, **29**, 516—539; cf. A., 1924, ii, 830).—A solution of a negatively charged copper ferrocyanide sol prepared from potassium ferrocyanide and copper chloride and subsequent dialysis was found to be normal so far as the Schultze-Hardy law is concerned. When a univalent electrolyte was used for coagulating the sol, the anion was found to exert a considerable effect. Thus, nine times the number

of equivalents of salt were required for coagulation when potassium ferrocyanide was substituted for potassium bromide. The effect of the anion is not so marked with bi- and ter-valent cations. The effect of dilution is to stabilise the sol towards uni- and bi-valent coagulating ions and to make it more sensitive to ter- and quadri-valent ions. The behaviour of potassium chloride was anomalous in that dilution apparently had no effect. This behaviour was found to be due to the presence of a considerable amount of potassium ferrocyanide. Sucrose is without effect when potassium chloride is used as a coagulant, but makes the sol unstable towards barium chloride. Ethyl and propyl alcohols sensitise it towards all coagulating ions. The sol becomes more stable to all electrolytes on keeping, which is probably due to the release of some free ferrocyanide ion by the slow hydrolysis of the colloid, and this stabilises the remaining sol. Potassium ferrocyanide increases the stability of the sol towards potassium chloride and barium chloride to a maximum after which the stability decreases. The antagonistic effect between pairs of salts is due to the stabilising effect of the ions which carry a charge opposite in sign to that of the precipitating ion.

M. B. D.

**Stability of Colloidal Solutions. II. Stability of Colloidal Solutions of Chromium Hydroxide and Copper Ferrocyanide in Presence of Stabilising Ions and Coagulation of the Colloids by Mixtures of Electrolytes.** K. C. SEN and M. R. MEHROTRA (*Z. anorg. Chem.*, 1925, **142**, 345—366).—The stability of chromium hydroxide sols towards potassium sulphate or oxalate is increased by successive additions of hydrochloric acid up to a maximum and is then reduced by further quantities. Mixtures of the two salts, on the other hand, have additive coagulating powers. Similar results are obtained with copper ferrocyanide, with ferrocyanide or alkali as stabiliser and potassium or barium chloride as coagulant. The theory is fully discussed and the conception of antagonistic effects between cations is rejected for the majority of such cases. The ion bearing the same charge as the colloid exerts the preponderating influence. Stabilisation by dilution, or by one of a mixture of electrolytes, and the phenomenon of acclimatisation are related and explicable on the same theory.

L. J. H.

**Influence of Wave-length on the Coagulation of a Colloidal Solution by X-Rays.** A. DOGNON (*Compt. rend. Soc. Biol.*, 1924, **91**, 197—199; from *Chem. Zentr.*, 1925, ii, 1447—1448).—The coagulation of a mastic sol, sensitised by sodium chloride, is promoted by exposure to Röntgen rays, the longer waves appearing to effect the coagulation somewhat faster than shorter waves. The energy absorbed by the solution was the same in both cases.

R. B.

**Velocity of Coagulation of Antimony Trisulphide.** C. K. JABŁCZYŃSKI and A. PRZEZDZIECKA-JEDRZEJOWSKA (*Bull. Soc. chim.*, 1925, [iv], **37**, 608—612; cf. this vol., ii, 35).—By the optical method previously described it has been found that the velocity of



coagulation of antimony trisulphide sols, in the presence of small amounts of potassium chloride, is in accordance with Smoluchowski's equation. The stability of the sol is much diminished when the free hydrogen sulphide has been removed by means of a stream of hydrogen.

G. M. B.

**Velocity of Coagulation of Colloidal Mixtures.** C. K. JABŁCZYŃSKI and H. LORENTZ-ZIENKOWSKA (*Bull. Soc. chim.*, 1925, [iv], 37, 612—615; cf. preceding abstract).—Since the coagulation of mixed sols containing arsenious and antimonious sulphides in various proportions is found to proceed according to the same law found to hold for sols of these two substances separately, the process of coagulation must be a purely physical one. Any selective chemical action would have produced a deviation from the observed relation.

G. M. B.

**Theory of Peptisation and Protective Effect of Colloids and Non-electrolytes.** K. C. SEN (*Kolloid-Z.*, 1925, 36, 193—202).—The peptisation of hydroxides with acids shows that an adsorption of the acid always precedes colloid formation. In the peptisation of metallic salt solutions and the formation of basic salts, the hydrogen ion is probably the actual peptising agent, the action of the metal ion being of less importance. A consideration of Langmuir's adsorption theory shows that in general an adsorption should occur wherever there is a possibility of chemical action. Experiments are described in support of this theory. The view that only ions and charged colloids can act as peptising agents is emphasised. Neutral molecules and proteins effect the stabilisation of a sol by an adsorption and covering of the colloid particles, such stabilisation being only effective in the presence of electrolytes. Protected colloids in general owe their stability to the Helmholtz double layer, and the protective action of such different substances as glycerol, sucrose, egg-albumin, etc. is probably the same. The behaviour of non-electrolytes and proteins varies slightly, in that the adsorption complex of the former can be easily destroyed, whilst the protein forms a solid surface coating.

The conclusions drawn by Loeb from his work on the protective action of gelatin for collodion particles (cf. A., 1923, ii, 301) are criticised, and the theory of Liesegang's rings is discussed.

L. L. B.

**Nature of Swelling in Substances giving a Debye-Scherrer Diagram.** J. R. KATZ and H. MARK (*Proc. K. Akad. Wetensch. Amsterdam*, 1924, 27, 520—528).—The changes taking place in certain colloids during imbibition have been studied by the X-ray method. Whereas cellulose, fibroin, and chitin show no change in the lattice during swelling, this is not always the case. With inulin the lattice volume increases by 8—11% when the total volume of the colloid increases by 11½%. Soluble starch probably exhibits similar behaviour. It would therefore seem that imbibition may be either an intermicellar or an intermolecular process according to the nature of the substance. The lattice will only change with the latter type of imbibition.

S. B.

**Cause of the Characteristic Extensibility of Caoutchouc. Alteration of X-Ray Spectrum of Caoutchouc on Extension.**

J. R. KATZ (*Kolloid-Z.*, 1925, **36**, 300—307).—Unstretched *Hevea* caoutchouc gives an amorphous X-ray spectrogram. Stretched caoutchouc gives in addition a line spectrogram, corresponding with an assemblage of "crystals" arranged with their axes in the direction of the stretching. The relative intensity of the line photogram increases with the stretching and finally the whole of the caoutchouc appears to be in the "crystalline" form. The interferences are confined to a small diffraction angle. The size of the lattice is about 8 Å. in the direction of stretching. The elementary cell is probably smaller in one or more directions than the caoutchouc molecule and possibly corresponds with simple units, such as tri-isoprene. Caoutchouc consists of a crystalline and an amorphous substance, but, since the crystalline interference lines occur only with more than 100% stretching, the early stages in the extensibility must be ascribed to some cause other than the formation of "crystalline" material.

E. M. C.

**Effect of Drying on Permanently Deformed Gels.** E. HATSCHKE (*Kolloid-Z.*, 1925, **36**, 202—206; cf. *ibid.*, 1924, **35**, 67).—Gels in the form of quadratic prisms, made by pouring the sol into paraffined paper moulds and cooling, were subjected to bending or twisting forces, so that they received a permanent deformation. In the case of both bent and twisted prisms, the deformation increased considerably on drying, *e.g.*, in one case the torsion before drying was 62°, and after drying 433°. The question is discussed as to whether the change on drying is a consequence of the preceding deformation, or the characteristic form of the gel. Special moulds for giving an initial bend or twist to gels were prepared, and with these, no increase of deformation occurred on drying. The conclusion is reached that deformation causes some radical change to take place in the gelatin.

L. L. B.

**Periodic Stratification of Magnesium Hydroxide.** K. PORR (*Kolloid-Z.*, 1925, **36**, 208—215).—In order to investigate more thoroughly the nature of Liesegang's layers, the ring-system formed by the interaction of magnesium chloride and ammonia has been qualitatively and quantitatively studied. Which of the two reagents is contained in the gelatin has no essential influence on the banding; in both cases a "clearing" ring appears, and the rings disappear on diffusion of ammonium chloride into the gel. When ammonia diffuses into gelatin containing magnesium chloride, it is found that with decreasing magnesium chloride concentration, the rings increase in number and thickness, whilst the space between them decreases; with decreasing ammonia concentration, the rings decrease in number and thickness, whilst the space between them increases; with decreasing ammonium chloride concentration, the rings increase in number and thickness, whilst the space between them decreases; with decreasing gelatin concentration, both the rings and the space between them increase in thickness, whilst their number remains the same; with falling temperature, both the rings

and the space between them increase in thickness. The rhythmic precipitation occurs in coarsely dispersed colloid and molecular media, such as clay, 0.6% agar, silicic acid, fine sand, and glass beads in water.

L. L. B.

**Electro-ultrafiltration of Gelatin and Glue.** H. BECHHOLD and A. ROSENBERG (*Biochem. Z.*, 1925, **157**, 85—97).—A new method for the purification of colloids by a combination of ultrafiltration and electrodialysis is described in detail. In a relatively short time colloids may be freed almost completely both from electrolytes and dialysable decomposition products. A method of double ultrafiltration combined with electrodialysis, by which liquid is ultrafiltered at both the cathode and the anode of the electrodialyser, permits of the complete removal of salts from gelatin and from glue. By this means a globulin has been separated from glue.

H. D. K.

**Cataphoresis of Metal Sols in Organic Dispersion Media.** F. EVERS (*Kolloid-Z.*, 1925, **36**, 206—207).—Phenomena similar to those observed by Hatschek and Thorne (this vol., ii, 197) with nickel sols in benzene, in presence of caoutchouc, were also observed by the author and Harries (*Ber.*, 1923, **56**, 1048) in the case of platinum sols stabilised by caoutchouc. Cataphoresis showed that both positively and negatively charged particles were present in the sol. From the fact that the disperse platinum always separates at the electrode with perhydrocaoutchouc, it is inferred that the platinum in the solution is aggregated with the caoutchouc.

L. L. B.

**Theory of Membrane Equilibria.** E. HÜCKEL (*Kolloid-Z.*, 1925, **36**, 319—320).—A correction (cf. this vol., ii, 528).

E. M. C.

**Direct Measurement of Mean Free Path of Uncharged Silver Atoms in Nitrogen.** F. BIELZ (*Z. Physik*, 1925, **32**, 81—102).—Silver was heated in a silica tube to a temperature of 1100° and its vapour allowed to pass through an orifice and impinge on glass plates. The thickness of the deposit was measured by an optical method after converting the metal into the iodide. The product of the mean free path in cm. and the pressure of the nitrogen in mm. of mercury was approximately constant = 0.0098. The radius of the silver atom was found to be  $1.0 \times 10^{-8}$  cm., an inexplicably small value.

E. B. L.

**Dissociation of Chlorine.** H. VON WARTENBERG and D. WEIGEL (*Z. anorg. Chem.*, 1925, **142**, 337—344).—In part polemical against Trautz and Geissler (this vol., ii, 294). The dissociation of chlorine at 1205°, determined by Meyer's method, agrees, within the limits of error, with the values of Henglein (A., 1922, ii, 823) and of Wohl (A., 1924, ii, 600).

L. J. H.

**Dissociation of Auric Chloride.** M. PETIT (*Bull. Soc. chim.*, 1925, [iv], **37**, 615—623; cf. Rose, T., 1895, **67**, 881).—The total pressures produced when auric chloride is heated to temperatures

from  $100^{\circ}$  to  $251^{\circ}$  have been measured by a static method and the results compared with those of Rose and of Meyer (*Diss.*, Paris, 1912). The dissociation of the trichloride is practically irreversible, but the pressure observations are satisfactory if taken at progressively rising temperatures. An estimate of the vapour pressure of the trichloride is obtained from separate experiments in which the weight of auric chloride volatilised in a known volume is determined. By subtraction of these values of vapour pressure from the total pressures observed the dissociation pressures of auric chloride are obtained. By means of Clapeyron's equation the heat of formation of the trichloride from aurous chloride and chlorine is found at various temperatures: it rises from 16.8 to a maximum of 20.6 between  $181^{\circ}$  and  $202^{\circ}$  and then falls to 15.6 large calories between  $229^{\circ}$  and  $251^{\circ}$ . The temperature at which the dissociation pressure = 760 mm. is calculated to be  $249^{\circ}$ .  
G. M. B.

**Deduction of the Type of a Two-component System by Means of the Addition of a Third Component.** F. A. FREETH (*J. Physical Chem.*, 1925, **29**, 497—507).—The principle of Schreinemakers, that any two solid substances will always yield a characteristic solubility diagram, which is the same in type for every possible liquid used as solvent, provided that the liquid in question does not form compounds with either of them, can be used to differentiate between types of binary systems about which thermal analysis cannot give final evidence. It is suggested that an isothermal of the system water-potassium nitrate-sodium nitrate at about  $140^{\circ}$  would decide the correct interpretation of the results of Madgin and Briscoe (T., 1923, **123**, 1608, 2914) and those of Hissink (A., 1900, ii, 339). It is improbable that ammonium nitrate and ammonium sulphate form mixed crystals (cf. Perman and Howells, T., 1923, **123**, 2130). An isothermal at  $170^{\circ}$  with water as a third component would provide the necessary evidence as to the correctness of the assumption. The case of *d*-camphor oxime-*l*-camphor oxime is also discussed.  
M. B. D.

**Properties of Physical Systems in the Neighbourhood of the Critical State.** L. GAY and N. PERRAKIS (*J. Chim. phys.*, 1925, **22**, 169—185).—The authors discuss the critical state for two phases in a system of any degree of complexity. Application of the phase rule shows that if  $n$  is the number of degrees of freedom of the system, and if  $(n-1)$  independent variables are fixed, then any two properties of the two phases considered can be represented as a function of the  $n$ th variable by a single curve. When one of the phases disappears the properties are represented by a surface. The authors show that by suitable numerical representation it is always possible to define this equilibrium curve. When variations imposed on a physical system cause it to pass through the critical state, a decrease in the number of phases is not indicated unless the properties studied concern one of these two phases. The authors investigate the modes of numerical representation so that the critical curve around the critical point

is fairly straight and of appreciable length. The conditions for this desideratum are given. W. T.

**System Chloride-Sulphate-Sodium-Water.** A. J. PELLING (*J. S. Afr. Chem. Inst.*, 1925, 8, 3—6).—The 94.5° isotherm, and extra data for the 0° isotherm of this system are given, and the invariant solution at 94.5° is determined. B. F.

**Free Energy and Heat Content of Tellurium Dioxide and of Amorphous and Metallic Tellurium. Reduction Potential of Tellurium.** R. SCHUMANN (*J. Amer. Chem. Soc.*, 1925, 47, 356—362).—Cells of the type  $\text{Te}(s) + \text{TeO}_2(s) | \text{HClO}_4(0.10-0.74N) | \text{H}_2$  (1 atm.) have an *E.M.F.* of  $-0.5286$  at 25° and  $-0.5213$  at 45°. The free energy of formation of tellurium dioxide is  $-64,320$  cal. and its heat of formation is  $77,700$  cal. at 25°. The amorphous and metallic forms of tellurium have identical electrometric properties. The amount of tellurium dissolved is proportional to the activity of the hydrogen ion in solution so it must be present as a univalent positive ion, perhaps  $\text{Te}(\text{OH})_3^+$  or  $\text{TeO}(\text{OH})^+$ . The molal reduction potential of tellurium corresponding with  $\text{Te}(s) + 2\text{H}_2\text{O} = \text{TeO}(\text{OH}) + 3\text{H}^+ + 4\ominus$  is  $-0.5590$  volt. L. J. H.

**Law of Volatility.** C. MATIGNON (*Bull. Soc. chim.*, 1925 [iv], 37, 503—513; cf. Matignon, A., 1908, ii, 465).—The superiority of carbon as a reducing agent, compared with silicon, is attributed to the volatility of carbon monoxide and dioxide. If the reduction of a metallic oxide is written in the form  $\text{MO} + \text{C} = \text{CO} + \text{M} - Q$  cal., the free energy of the reduction process is given by the relation  $A = 8T(\log T + 2.05) - Q$ , and reduction will occur as soon as the temperature is sufficiently high to give a positive value to  $A$ . In cases in which both initial and final systems contain volatile substances, the same considerations apply, each volatile molecule in the initial system being counterbalanced by a gaseous molecule in the final system, and the volatility being measured by the difference in the number of gaseous molecules in the initial and final systems. W. H.-R.

**Reactivity in the Solid State between Acidic and Basic Metal Oxides.** F. DE CARLI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 533—537; cf. A., 1924, ii, 758).—Heating curves were determined for equimolecular mixtures of basic and acidic oxides. For the mixture  $\text{MoO}_3$ -BaO reaction began at 290°, the temperature rising to 1200° in 25 sec., and a white friable mass resulting. The thermal effects in the following cases were much weaker and occurred at the temperatures indicated.  $\text{MoO}_3$ -CaO 650°;  $\text{MoO}_3$ -PbO 650°;  $\text{MoO}_3$ -SnO 400°;  $\text{MoO}_3$ -CdO about 500°;  $\text{MoO}_3$ -NiO about 495°;  $\text{MoO}_3$ -CoO 410°;  $\text{MoO}_3$ -ZnO 270°, and a weaker effect at 720°;  $\text{MoO}_3$ -MgO no reaction.  $\text{WO}_3$ -BaO 190°;  $\text{WO}_3$ -CaO 245°;  $\text{WO}_3$ -PbO 210°;  $\text{WO}_3$ -SnO 265°;  $\text{WO}_3$ -CdO 250°;  $\text{WO}_3$ -NiO 260°;  $\text{WO}_3$ -CoO 255°;  $\text{V}_2\text{O}_5$ -BaO 270°;  $\text{V}_2\text{O}_5$ -CaO 630°;  $\text{V}_2\text{O}_5$ -PbO about 560°;  $\text{V}_2\text{O}_5$ -CdO 480°;  $\text{V}_2\text{O}_5$ -SnO 250°;  $\text{V}_2\text{O}_5$ -ZnO 260°;  $\text{V}_2\text{O}_5$ -MgO 455°;  $\text{Cr}_2\text{O}_3$ -BaO 220°;  $\text{Cr}_2\text{O}_3$ -

CaO about 550°. Tin dioxide, bismuth trioxide, lead dioxide, and alumina react only with barium oxide. F. G. T.

**Behaviour of Clays, Bauxites, etc. on Heating. III.** H. S. HOULDSWORTH and J. W. COBB (*Trans. Ceram. Soc.*, 1923—1924, **23**, 279—292).—The shrinkage of clays is not a continuous process but takes place in a number of stages, each stage being completed at a definite temperature. The shrinkages of considerable magnitude occur at almost the same temperatures with the different clays, *i.e.*, 530°, 880°, 950°, and 1030—1060°. Changes in density and in refractive index of kaolinite also occur at these temperatures. The temperatures of appreciable dehydration of kaolin and fireclays (420—450°) and other minerals were determined on heating slowly. These temperatures were raised considerably (80° or more) when reached rapidly. The shrinkage of kaolin at 530° is associated with its dehydration. Kaolin and fireclays show a distinct heat absorption at 500—530° and a heat evolution at 950°. Pure alumina, prepared by calcining the nitrate, gives an exothermic reaction at 1060° and red bauxite at 1000°. Thermal changes are shown by many of the other substances examined. Except in the case of cyanite and biotite, all the endothermic reactions occur at the same temperatures as those at which a loss in weight begins when the materials are heated under similar conditions. None of the indications of exothermic and endothermic reactions with clays can be attributed to the presence of small quantities of impurities. The change responsible for the exothermic effect at 950° with clays could be completed on continued heating at 900°, and that causing the evolution of heat at 1060° with alumina could be completed by a similar heating at 950°. No evolution of heat at 950° was detected when mixtures of alumina and silica of composition  $\text{Al}_2\text{O}_3 + 2\text{SiO}_2$  were heated, or when mixtures of the composition  $\text{Al}_2\text{O}_3, \text{SiO}_2 + \text{SiO}_2$ , prepared from sillimanite, cyanite, andalusite, or allophane, and silica, were heated. The changes observed on heating clays may be due both to changes in the chemical constitution of the molecules of the clay and to a rearrangement of those groups of molecules which form the unit of crystal structure of the clay. [Cf. *B.*, 1925, 500.] H. S. H.

**Measurement of Very High Electrolyte Resistances by Kohlrausch's Method.** H. ULICH (*Z. physikal. Chem.*, 1925 **115**, 377—384).—An improved form of the Kohlrausch apparatus is described, in which a thermionic valve is used as a source of alternating current. The arrangement permits of the measurement of resistances of the order  $10^5$  ohms as easily and accurately as those of 100 to 1000 ohms. N. H. H.

**Trustworthiness of the Quinhydrone Electrode for the Measurement of Hydrogen-ion Concentration in Various Solutions.** I. M. KOLTHOFF (*Z. physiol. Chem.*, 1925, **144**, 259—271).—Comparison of the results of  $p_{\text{H}}$  determinations of a large number of solutions by means of the quinhydrone and hydrogen

electrodes indicates that, in protein-free solutions, the former gives excellent results if the liquid is well buffered and has  $p_H < 9$ . In weakly buffered solutions the limiting  $p_H$  is displaced towards the acid side. In all cases, good results are obtained at  $18^\circ$  with  $p_H < 8$ . In acid and in weakly buffered solutions, good results are obtained by application of Biilmann's equation. Error due to the presence of proteins is dependent on the kind and concentration of the protein and on the  $p_H$ ; the more alkaline the solution, the greater the disturbance and the less constant the results. In agreement with Lester (*J. Agric. Sci.*, 1924, **14**, 634), the author finds that the electrode can be used for the determination of the  $p_H$  of milk, cream, and whey. The  $p_H$  of saliva can be obtained providing it is not distinctly alkaline; the error for blood-serum at  $p_H > 6$  is large but for diluted blood-serum it is much smaller.

P. W. C.

**Solvation of Ions and the Electrode Potential.** J. HEYROVSKÝ (*Rec. trav. chim.*, 1925, **44**, 447—450).—Some consequences of the author's solvation formula for electrode potential (cf. this vol., ii, 544) are worked out. It is shown that for a concentration cell with electrodes of a univalent metal in  $N$ - and  $3N$ -aqueous solutions of its binary salt the *E.M.F.* should be 10—12 millivolts greater than that calculated from the Nernst formula. In this and similar deductions it is assumed that the ions do not form complex anions which would lower their "activity" considerably. From the formula the abnormal "activity" should increase proportionally with the molecular weight of the solvent. N. H. H.

**Abnormal Ionic Activities in Concentrated Alkoxide Solutions.** Z. KONTNÍKOVÁ and M. SHIKATA (*Rec. trav. chim.*, 1925, **44**, 451—458).—In order to test the deductions of Heyrovský from his formula for electrode potential (see preceding abstract) the authors have measured the *E.M.F.* of concentration cells having sodium or potassium amalgam electrodes in solutions of the corresponding alkoxides in ethyl and in *isoamyl* alcohols. With dilute solutions the cells give values corresponding with the Nernst logarithmic formula, but with concentrations greater than about  $1.8N$  with ethyl alcohol and  $0.8N$  with *isoamyl* alcohol they show abnormal ionic activity (greater in the latter case) in agreement with Heyrovský's formula. Concentrated sodium *isoamyl*-oxide solutions exhibit a peculiar slow decrease of activity.

N. H. H.

**Conditions Affecting the Reproducibility and Constancy of Weston Standard Cells.** W. C. VOSBURGH (*J. Amer. Chem. Soc.*, 1925, **47**, 1255—1267).—The presence of small amounts of acid in the electrolytes does not appreciably affect the *E.M.F.* and tends to make the cells more reproducible and less liable to vary. All mercuric salts must be completely removed from the mercurous sulphate, which should not be exposed to air after purification. Abnormalities result from the presence of basic mercurous sulphate.

J. S. C.

**Thermodynamic Potential Difference at the Boundary of Two Liquid Phases.** S. WOSNESSENSKY (*Z. physikal. Chem.*, 1925, **115**, 405—423).—Measurements have been made with cells of the types *N*-calomel electrode|aqueous solution *A*|non-aqueous solution|aqueous solution *B*|*N*-calomel electrode, and *N*-calomel electrode|aqueous solution|non-aqueous solution|*N*-calomel electrode. Solutions of the following electrolytes at different concentrations were used: potassium chloride, lithium chloride, picric acid, potassium thiocyanate, ammonium thiocyanate, potassium iodide, salicylic acid, calcium chloride, nitric acid, hydrochloric acid, acetic acid, succinic acid, sodium sulphate, phosphoric acid, citric acid, sulphuric acid. The non-aqueous solvent was usually *isoamyl* alcohol, but in a few cases this was replaced by phenol. The values for the *E.M.F.* can be calculated from the distribution formula  $C_1/C_2^n=k$ . When  $n=1$  the *E.M.F.* should become zero. The experimental results support this assumption. N. H. H.

**Formation of Mixed Electrodes at Phase Boundaries.** K. HOROVITZ (*Z. physikal. Chem.*, 1925, **115**, 424—432).—The results obtained by the author and his co-workers for the boundary potential between glass and aqueous solutions are given in brief and a reply is made to the criticism of Gross and Halpern (this vol., ii, 405). N. H. H.

**Polarisation Capacity and Electrical Double Layers.** A. L. CLARK (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 275—292).—Experiments have been carried out to determine whether the Helmholtz double layer actually exists and to ascertain the cause of the variations in capacity of polarised surfaces when charged to varying potential differences. Cells were made by immersing a large electrode of mercury, platinum, platinum-black, gold, tungsten, lead, or carbon in an electrolyte solution and then inserting a small electrode of the same substance. Capacities were determined by the direct and oscillation period methods, the values determined by the latter method being usually much smaller than those determined directly. Neither the concentration of the electrolyte (except in very dilute solutions, when the capacity appears to increase) nor the distance between the electrodes over a range extending down to 0.01 mm. has much effect. The capacity is practically unchanged when potassium hydroxide is substituted for sulphuric acid as dissolved electrolyte. The results are discussed and are shown to afford support for the reality of the Helmholtz double layer. J. S. C.

**Recent Studies on Reversible Oxidation-Reduction in Organic Systems.** M. CLARK (*Chem. Reviews*, 1925, **2**, 127—178).

**Dropping Mercury Cathode.** I. J. HEYROVSKÝ (*Rec. trav. chim.*, 1925, **44**, 488—495).—An introduction to and review of experimental work by the author and his collaborators (cf.



following abstracts). The process at the dropping mercury cathode may consist (1) in the deposition of cations or (2) in the reduction of any substance capable of being chemically reduced. In (1), the dropping mercury cathode "deposition potential" series differs from the reversible "electrolytic potential" series owing to differences in the affinities of the metals for mercury, but in (2), the "reduction potential" series of reducible ions must run strictly parallel to the series of "reduction electrode-potentials" as measured under similar conditions by a platinum electrode, since the electrode material does not enter into consideration. The characteristics of the polarisation curves are turning points indicating sudden increases in current due to decomposition of the electrolyte. Theory shows that these turning points are not sharp, but that the current-voltage curve is exponential; for comparison the critical point is taken as that at which the tangent to the curve has an angle of  $45^\circ$  to the axes. If the concentration of a reducible substance is less than  $10^{-4}$  g.-equiv./litre, the polarisation curve after rising becomes horizontal again and the current remains constant until the potential of a new reduction is reached. This "wave" type of curve, due to the exhaustion of reducible matter surrounding a drop, is characteristic of a concentration of about  $10^{-4}$ , becomes less with increasing dilution, and vanishes at about  $10^{-6}$  g.-equiv./litre. In the presence of nitrobenzene the polarisation curve exhibits a maximum owing to adsorption phenomena (cf. Shikata, this vol., ii, 304). Strongly oxidising anions have little effect on processes at the dropping cathode, owing to their repulsion from the cathode, but less stable anions, such as zincates, plumbites, and certain metal cyanides, are decomposed at a certain potential into their components and the metallic ion is immediately deposited on the cathode. Owing to periodic change of surface during drop formation, the galvanometer usually oscillates and the form of the oscillation is characteristic of the process, a large oscillation corresponding with a reduction process or evolution of hydrogen, whilst a small oscillation accompanies amalgam formation. The deposition potential of a particular metal becomes more negative as the solution is diluted, a tenfold dilution causing a change of about 57, 26, and 18 millivolts for uni-, bi-, and ter-valent cations, respectively, and marked deviations from these numbers indicate the presence of complex ions or other complicating factors.

W. H.-R.

**Dropping Mercury Cathode. II. The Polarograph.** J. HEYROVSKÝ and M. SHIKATA (*Rec. trav. chim.*, 1925, **44**, 496—498).—A description of an instrument for recording photographically the polarisation curves from a dropping mercury cathode. The potential across the cell is gradually increased by the motion of a wheel contact along a resistance wire mounted on a rotating drum. A second rotating drum carries a photographic film on which the curve is traced by light from a mirror-galvanometer.

W. H.-R.

**Dropping Mercury Cathode. III. Theory of Overpotential.** J. HEYROVSKÝ (*Rec. trav. chim.*, 1925, **44**, 499—502).—Hydrogen over-potential is connected with the catalytic influence of different metals upon the combination of hydrogen atoms into molecules. If the combination proceeds according to the scheme (1)  $2\text{H} \rightarrow \text{H}_2$ , theory shows that when the hydrogen-ion concentration changes from  $c_1$  to  $c_2$ , the deposition bend in the current-voltage curve should be displaced by  $\pi - \pi' = (RT/F) \log c/c'$ , by 58 millivolts for a tenfold dilution, which is exactly one-half the actual displacement in the case of the mercury dropping cathode. This discrepancy can be accounted for if it is assumed that some of the hydrogen ions deposited unite with electrons at the cathode to form negative ions, and that the hydrogen molecules are produced, by the union of positive and negative ions at the mercury surface according to the scheme (2)  $\text{H}^+ + \text{H}' \rightarrow \text{H}_2$ , for which  $\pi - \pi' = 2(RT/F) \log c_1/c_2$ . This theory applies only to metals with high over-potentials for which the velocity of reaction (2) is greater than that of reaction (1). W. H.-R.

**Dropping Mercury Cathode. IV. Changes in Overvoltage with the Concentration of Hydrogen Ions.** P. HERASYMENKO (*Rec. trav. chim.*, 1925, **44**, 503—513).—Using the dropping mercury cathode the hydrogen deposition potential has been determined at 16—18° in solutions of hydrochloric, sulphuric, acetic, propionic, boric, and carbonic acids, and in solutions of hydrogen sulphide, and buffer solutions of acetic and propionic acids, the hydrogen-ion concentration being calculated from the dissociation constants. There is close agreement between the observed results and those calculated by means of the formula

$$\pi_1 - \pi_2 = 2(RT/F) \log c_1/c_2,$$

where  $\pi_1$  and  $\pi_2$  are the potentials for concentrations of hydrogen ions  $c_1$  and  $c_2$  (cf. Heyrovský, preceding abstract). In order to maintain an approximately equal conductance, the acids used were diluted by a 0.1N-potassium chloride solution. The dropping mercury cathode can therefore be used as an indicator for hydrogen ions, the value of the deposition potential of hydrogen changing regularly with the concentration of hydrogen ions. In this way the dissociation constants of hydrogen sulphide, boric acid, and carbonic acid in the presence of potassium chloride have been determined. The work of Glasstone (this vol., ii, 43, 133) is criticised, and the change in overvoltage produced by the addition of sodium sulphate to sulphuric acid solutions is regarded as due to the change in concentration of hydrogen ions owing to the formation of the acid sulphate complex. W. H.-R.

**Dropping Mercury Cathode. V. Deposition of Arsenic, Antimony, and Bismuth.** V. BAYERLE (*Rec. trav. chim.*, 1925, **44**, 514—519).—The cathodic deposition of arsenic at the dropping mercury cathode is complex in both acid and alkaline solutions, and does not show reversible shifts on the polarisation curves. From acid solutions the deposition of antimony and bismuth proceeds reversibly, the normal deposition potentials (relative to

the calomel electrode) being  $-0.038$  and  $0.0$  volt, respectively. In alkaline solution the deposition of bismuth resembles metallic deposition from zincates or plumbates, in accordance with the distinctly metallic nature of bismuth, and in contrast with the more complicated results for arsenic and antimony. The solubility products of antimony and bismuth hydroxides are determined as :  $[\text{Sb}^{+++}][\text{OH}'^3]=4 \times 10^{-42}$ , and  $[\text{Bi}^{+++}][\text{OH}'^3]=4.3 \times 10^{-31}$ .

W. H.-R.

**Dropping Mercury Cathode. VI. Electro-deposition of Manganese and the Complexity of Manganous Ions in Ammoniacal Solutions.** J. BŘEZINA (*Rec. trav. chim.*, 1925, **44**, 520—527).—From neutral or acid solutions of manganous chloride, the electro-deposition of manganese at the dropping cathode proceeds reversibly, the deposition potential from a molar solution being  $-1.326$  volts relative to the normal calomel electrode. The polarisation curves permit the detection of manganous salts in solution down to  $10^{-6}$  g.-mol./litre. The deposition potential becomes more negative in the presence of ammonia owing to the formation of complex cations; this fact is also indicated by cryoscopic measurements.

W. H.-R.

**Dropping Mercury Cathode. VII. Nickel and Cobalt.** N. V. EMELIANOVA (*Rec. trav. chim.*, 1925, **44**, 528—548).—Nickel is not deposited reversibly at the dropping mercury cathode. The turning points on the polarisation curves are abnormally displaced by dilution, and the primary process consists in the reduction of nickel from the bivalent to the univalent state. In neutral or acid solutions this is followed by the deposition of metallic nickel; the deposition potential is much affected by the presence of other salts and of hydrogen ions, and is rendered more negative by the addition of ammonia owing to the formation of complex ions, although very small quantities of ammonia render it more positive. In excess of potassium cyanide nickel salts do not deposit metallic nickel but are only reduced to the univalent nickel complex cyanide. Neutral or acid solutions of pink cobalt chloride deposit cobalt at a potential  $0.200$  volt more negative than nickel, but abnormal dilution effects are again observed. A solution of the blue chloride in concentrated calcium chloride solution deposits cobalt at a more positive potential than the pink solution, indicating that the blue ions are the more active and are dehydrated. Ammonia renders the deposition potential more negative. From complex cyanides cobalt is not deposited but reduction to the bivalent complex takes place. In meteoric iron, copper, nickel, and cobalt may be detected and roughly determined by observing the deposition potentials at the dropping cathode from solutions of known concentration in hydrochloric acid.

W. H.-R.

**Dropping Mercury Cathode. VIII. Electrolysis of Some Complex Cyanides.** E. B. SANIGAR (*Rec. trav. chim.*, 1925, **44**, 549—579).—Iron is not deposited on the dropping mercury cathode from solutions of potassium ferrocyanide at potentials of  $0$  to

—2 volts relative to the calomel electrode. This indicates that even in the most dilute solutions of ferrocyanides the concentration of ferrous ions is less than  $10^{-40}$  g.-equiv./litre.

Silver is deposited on the dropping cathode from solutions of potassium argenticyanide at a potential of —0.235 volt relative to the calomel electrode. This potential is independent of the concentration of the solution, since the complex  $\text{Ag}(\text{CN})_2^-$  ionises first to  $\text{AgCN} + \text{CN}'$ , and only a very small fraction of the molecular  $\text{AgCN}$  dissociates into  $\text{Ag}^+$  and  $\text{CN}'$  ions, so that the concentration of silver ions is always constant. The corresponding normal deposition potential is +0.485 volt. With increasing voltage the deposition increases rapidly to a maximum intensity which is followed by a sharp fall, after which silver is still deposited until a potential of —1.9 volts is reached, at which potassium begins to be deposited. Similar maxima are met with in the case of auricyanide solutions, and are caused by the adsorption of  $\text{AgCN}'$  complexes on the surface of the mercury. This absorption becomes less as the potential of the cathodes becomes more negative and finally desorption occurs owing to the electrostatic repulsion. The polarisation curve develops a maximum or a distinct displacement according to the relative magnitudes of the adsorption and desorption processes.

W. H.-R.

**Dropping Mercury Cathode. IX. Tin.** J. SMRZ S. J. (*Rec. trav. chim.*, 1925, **44**, 580—590).—Tin is deposited reversibly on the dropping cathode from freshly prepared acidic solutions of stannous chloride, the normal deposition potential being —0.285 volt relative to the calomel electrode. The presence of tin can be detected down to  $10^{-6}$  mole/litre, but on keeping dilute solutions hydrolysis occurs and the wave in the polarisation curve disappears. From freshly-prepared alkali stannite solutions tin is deposited reversibly; a  $4 \times 10^{-4}M$  stannite solution deposits tin at —1.10 and —1.05 volts from  $N$  and  $0.1N$ -sodium hydroxide solutions, respectively. On keeping, these solutions are unstable owing to the formation of colloidal stannous hydroxide and to partial auto-oxidation of stannite to stannate. In normal sodium hydroxide solution, the solubility product  $[\text{Sn}^{++}][\text{OH}']^2 = \text{about } 10^{-28}$ ; the acidic solubility product of stannous hydroxide,  $[\text{SnO}_2\text{H}'][\text{H}'] = 6 \times 10^{-18}$ ; the constant for the formation of the complex anion  $K_A = [\text{Sn}(\text{OH})'_3]/[\text{Sn}^{++}][\text{OH}]^3 = 4 \times 10^{24}$ . Of the hydroxides of lead, zinc, and tin, lead hydroxide is the strongest and stannous hydroxide the weakest, the acidic order being the reverse. W. H.-R.

**Dropping Mercury Cathode. X. Some Organic Bases.** W. PODROUŽEK (*Rec. trav. chim.*, 1925, **44**, 590—599).—The polarisation curves for solutions of tetramethyl- and tetraethyl-ammonium iodides in the presence of lithium chloride indicate that the organic radicals are deposited reversibly on the dropping cathode, the deposition character being that of an amalgam formation. The normal deposition potentials relative to the calomel electrode are —1.880 and —1.936 volts for the tetramethyl and tetraethyl radicals, respectively. In solutions containing lithium

chloride, quinine is reduced at the dropping cathode, the potential depending on the concentration of hydrogen ions. The polarisation curves show a maximum owing to adsorption (cf. Sanigar, this vol., ii, 676), this effect being detected down to a concentration of  $10^{-6}$  mol. of quinine per litre.

W. H.-R.

**Dropping Mercury Cathode. XI. Influence of Anions.**

B. A. GOSMAN (*Rec. trav. chim.*, 1925, **44**, 600—607).—In solutions of potassium nitrate or chlorate, a sufficiently negative polarisation causes reduction of the anion to take place at the dropping mercury cathode. The mechanism of the process is obscure and the potentials vary greatly with the acidity. In neutral solutions, nitrates do not interfere with the deposition of metals when the *P.D.* is less than  $-1.45$  volts, whilst, if present in small quantities only, neither nitrates nor chlorates interfere with the cathodic deposition of even the most positive metals. Sulphates are quite without effect on cathodic deposition.

The polarisation curves for saturated solutions of lead sulphate show that increased solubility takes place in the presence of sulphuric acid owing to the formation of complex anions.

W. H.-R.

**Electrokinetic Phenomenon. Electrocapillarity of Fused Tellurium Dioxide.**

A. ŠIMEK and (MISS) H. KADLCOVA (*Rec. trav. chim.*, 1925, **44**, 608—628).—Drops of fused tellurium dioxide on a platinum surface heated by a direct current at  $800$ — $950^{\circ}$ , move from the negative to the positive pole. The movement is accompanied by a deformation of the drops, the curvature of the side facing the negative pole being less than that of the other side. Under given conditions, the velocity increases as the drops become larger, but does so less rapidly than the weight of the drops. The velocity of movement and the force by which the drops are driven are both roughly proportional to the current intensity up to a certain limit. Numerous other substances, including selenium dioxide, were examined, but in the pure state did not show the above phenomenon. If tellurium dioxide is added to drops of fused sodium sulphate, chloride, tungstate, or pyrophosphate, the previously flattened drops become much more spherical and, under the influence of a direct current, move more rapidly than pure tellurium dioxide, a velocity of  $16$  cm./sec. being sometimes attained. The direction of motion depends on the concentration of tellurium dioxide and may be reversed as the latter gradually evaporates. The phenomenon is due to changes of interfacial tension caused by potential differences.

W. H.-R.

**Electrolysis of Molten Alloys. VI. Copper Alloys (Cu-Zn, Cu-Sn, Cu-Ag, Cu-Al).** R. KREMANN and R. GRUBER-REHENBURG (*Monatsh.*, 1924, **45**, 311—322; cf. this vol., ii, 132).—The interference of zinc oxide in the case of a brass, and of gas bubbles in the case of copper-silver alloys made observations with these alloys impossible. When a copper-tin alloy containing 58% of copper was placed in a fireclay capillary (diameter about  $1.5$  mm.)

and an electric current passed at  $950^{\circ}$  for 1.5 to 4 hrs. the change of concentration could scarcely be detected with a current density of 2 amp./mm.<sup>2</sup>, and was not very marked at 6.9 amp./mm.<sup>2</sup>, when the more conducting metal, copper, moved towards the anode, the highest difference of concentration between anode and cathode material being 3%. This observation is exceptional, as the better conducting metal usually moves to the cathode. A copper-aluminium alloy treated in the same way at  $1050^{\circ}$  for 2–4 hrs. showed a continuously increasing concentration of copper at the cathode as the current density was raised to 13.2 amp./mm.<sup>2</sup>, the excess of copper reaching the value 4%. The electrodes were formed by air cooling the ends of the tubes and so keeping some alloy solid.

G. M. B.

#### Electrolysis of Molten Alloys. VII. Silver-Lead Alloys.

R. KREMANN and O. BENDA (*Monatsh.*, 1924, **45**, 339–343).—Electrolysis of a silver-lead alloy containing 50% of lead at  $1000^{\circ}$ , with iron electrodes, for 4 hrs. showed a migration of silver to the cathode and of lead to the anode which increased in extent up to a current density of 13.2 amp./mm.<sup>2</sup> without showing sign of attaining a maximum. Differences of composition of 4–5% were observed and the results were not affected when the length of the capillary was increased from 20 to 30 cm. The effects observed here and with the copper-aluminium alloys (cf. preceding abstract) are small compared with those obtained in the electrolysis of alloys of low melting point at similar current densities, the difference being attributed to the greater relative effect of diffusion of the metals at these higher temperatures.

G. M. B.

#### Electrolysis of Molten Alloys. VIII. Tin-Zinc Alloys.

R. KREMANN and O. BAUKOVAC (*Monatsh.*, 1925, **45**, 379–383).—The passage of an electric current for 4 hrs. at  $400^{\circ}$  through a tin-zinc alloy between iron electrodes caused movement of the more highly conducting metal, zinc, towards the cathode. The difference in concentration produced increased to 11.7% of tin when the current density was raised to 12.3 amp./mm.<sup>2</sup> and would reach a maximum at about 25–30 amp./mm.<sup>2</sup> Observations on alloys of varying composition showed the effect to be greatest for an alloy containing 50 atoms % of tin.

G. M. B.

#### Electrolysis of Molten Alloys. IX. Tin-Aluminium Alloys.

R. KREMANN and J. DELLACHER (*Monatsh.*, 1924, **45**, 385–391).—Electrolysis of a tin-aluminium alloy containing 58.5 atomic-% of tin, for 4 hrs. at  $800^{\circ}$  causes an increase of concentration of tin at the anode and of aluminium at the cathode, the largest difference of concentration of tin produced being 8% for a current density of 12.3 amp./mm.<sup>2</sup> The effect appears to reach a maximum near this point. Variation of the initial composition of the alloy shows that the effect is greatest with 50 atomic-% of tin. The results at a chosen current density (8.3 amp./mm.<sup>2</sup>) are practically the same at  $800^{\circ}$ ,  $1200^{\circ}$ ,  $1400^{\circ}$ , and  $1600^{\circ}$ , so that the differences with alloys of high and low melting point depend more on the character of the individual metals than on the temperature.

G. M. B.

**Action of Gelatin on Electrolytic Cadmium.** E. MILLIAU (*Bull. Soc. chim. Belg.*, 1925, **34**, 143).—Attention is directed to the fact that addition of gelatin or other colloids to electrolytes consisting of solutions of metallic salts of weak acids, such as acetic acid, does not result in the formation of smooth metallic deposits; such deposits are obtained only from solutions of salts of strong acids, such as sulphates, fluosilicates, or fluoborates. A. R. P.

**Periodic Electrochemical Phenomena.** E. S. HEDGES and J. E. MYERS (*J. Chem. Soc.*, 1925, **127**, 1013—1026).—Some periodic reactions previously described by the authors (*A.*, 1924, ii, 325, 542) have now been examined electrochemically, using an apparatus in which the electrical and chemical effects of the reactions could be registered simultaneously. In the case of activated metallic couples dissolving in hydrochloric acid or ammonium chloride, the potential difference between the couple and the solution, and between the two components of the couple, undergoes periodic fluctuations which synchronise with the periodic evolution of gas. A potential difference exists between the activated and inactive forms of a metal. Some new reactions, involving the periodic deposition of metals, are described. The change consists in an alternate formation and dissolution of a metallic film which is accompanied by a corresponding oscillation of the electro potential. When magnesium dissolves in dilute hydrochloric acid containing ferrous sulphate in solution, hydrogen is evolved continuously, but in other cases—*e.g.*, when magnesium dissolves in 2% ammonium chloride solution with addition of small quantities of cobalt chloride, ferrous sulphate, nickel chloride, or copper sulphate—the rate of evolution of hydrogen is periodic. Examples are given of “auto-periodic” reactions, in which the dissolving metal is also the activating agent. Copper, when activated by cold rolling, and dissolved in a mixture of nitric and hydrochloric acids, furnishes very regular waves representing both the potential and the pressure of the evolved gas. The best results are obtained with an acid made by mixing 25 c.c. of nitric acid (*d* 1.42), 10 c.c. of hydrochloric acid (*d* 1.16), and 70 c.c. of water. L. L. B.

**Behaviour of Silver Iodide in the Photo-voltaic Cell.** T. S. PRICE (*J. Physical Chem.*, 1925, **29**, 557—563).—Polemical against Garrison, *A.*, 1924, ii, 401. The increased negative potential due to the photo-effect cannot be explained by increased solubility of silver iodide in light. A possible explanation is that colloidal silver formed on the decomposition of silver iodide has a higher solution pressure than massive silver. M. B. D.

**Technique for Measuring the Hydrogen-ion Concentration of Distilled Water and Unbuffered Solutions not in Equilibrium with the Carbon Dioxide of the Air.** L. E. DAWSON (*J. Physical Chem.*, 1925, **29**, 551—556).—The  $p_H$  value of distilled water, using bromothymol-blue and bromocresol-purple as indicators, has been found to be 7.0. The water was prepared by distilling two-thirds of its volume of distilled water in a “pyrex”

glass flask and using the residual third. Great care must be taken to exclude carbon dioxide when the water is being withdrawn from the container or a more acid value will be obtained.

M. B. D.

**Theory of the Velocity of Chemical Reactions.** J. N. BRÖNSTED (*Z. physikal. Chem.*, 1925, **115**, 337—364).—A more precise treatment of the author's theory of reaction velocity in solution (A., 1922, ii, 699) is presented. The objection of Bjerrum (A., 1924, ii, 240) to the deduction of the formula depends partly on misunderstanding and partly, as does his "concentration hypothesis," on views relative to reaction velocity and equilibrium which are not generally acceptable. The theory of Christiansen (this vol., ii, 47) is also discussed. It appears possible to develop the author's theory in such a way that the reaction constant can be resolved into two factors one of which depends on the reaction and the other on the solvent.

N. H. H.

**Effect of Diffusion on Time Rate of Chemical Change.** S. SANO (*Japan. J. Phys.*, 1924, **3**, 133—137).—A theoretical discussion of the effect of diffusion on the rate of chemical change.

S. B.

**Time Rates of Vaporisation and Chemical Changes on Surface of Contact of Two Fluids.** S. SANO (*Japan. J. Phys.*, 1924, **3**, 117—131).—On the basis of several thermodynamical assumptions, the author obtains expressions for the rates of vaporisation and the chemical reactions on the surface of separation of two fluids.

S. B.

**Rate of Oxidation of Nitric Oxide. I. Method of Measuring the Velocity of a Rapid Gaseous Reaction.** M. LATSHAW and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1925, **47**, 1201—1207).—An apparatus suitable for the study of the kinetics of rapid gas reactions is described in which the pressure changes (as indicated in the present instance by a 1-bromonaphthalene manometer) are recorded on a photographic film mounted on the drum of a kymograph.

J. S. C.

**Rate of Oxidation of Nitric Oxide. II. Velocity of the Reaction between Nitric Oxide and Oxygen at 0° and 30°.** R. L. HASCHE and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1925, **47**, 1207—1215).—Using the apparatus and experimental procedure described in the preceding abstract, the experimental numbers obtained in a study of the oxidation of nitric oxide by oxygen at 30° are in good agreement with the assumption of a reaction of the third order. The acceleration in the velocity coefficients at 0° is ascribed to the formation of nitrogen trioxide and also to the imperfect state of nitrogen tetroxide at temperatures so close to its b. p. Increase of the surface:volume ratio by the introduction of glass wool into the reaction vessel caused a marked acceleration in the third-order velocity expression in the latter half of the reaction at 30°, the effect being less pronounced at 0°.



No evidence of autocatalysis was found. The negative temperature coefficient of the reaction is due to intermediate compound formation.

J. S. C.

**Initial Rate of Decomposition of Nitrogen Pentoxide.**

E. C. WHITE and R. C. TOLMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 1240—1255).—A colorimetric method of analysis for nitrogen dioxide has been developed, capable of measuring partial pressures as low as 0.3 mm. with an accuracy of about 5%. The (unimolecular) thermal decomposition is found to be unimolecular also in its initial stages. The results of the investigation supply no confirmation of the hypothesis that the reaction is autocatalytic. The reaction mixture was formed by mixing freshly-prepared nitrogen pentoxide with oxygen and ozone, the latter serving to re-oxidise the decomposition products until exhausted. The observed rates of reaction are in good agreement with those obtained by Daniels and Johnston (*A.*, 1921, ii, 249).

J. S. C.

**Explosion of Ammonia with Carbon Monoxide and Oxygen.**

J. W. BEESON and J. R. PARTINGTON (*J. Chem. Soc.*, 1925, **127**, 1146—1150).—Two volumes of carbon monoxide mixed with one volume of oxygen were exploded with varying quantities of ammonia, at a temperature of 85° and pressure of 380 mm. so that no steam condensed. All mixtures which could be ignited showed approximately the same decomposition of ammonia, viz., 95.3%. With some mixtures containing more than 45% of ammonia, the first spark did not cause explosion, a period of induction being observed, after which the propagation of the flame from the spark to the walls of the bulb was so slow that it could be followed visually. No ignition occurred in mixtures in which the ratio  $\text{NH}_3/(2\text{CO} + \text{O}_2)$  exceeded 0.924.

W. H.-R.

**Gaseous Explosions. I. Initial Temperature and Rate of Rise of Pressure.**

G. G. BROWN, E. H. LESLIE, and J. V. HUNN (*Ind. Eng. Chem.*, 1925, **17**, 397—402).—The rate of rise of pressure in a gaseous explosion is dependent not only on the rate of the chemical reaction but also on the initial temperature. This can be shown from theoretical considerations which also demand a critical initial temperature. Experiments in a constant volume bulb show that in mixtures containing an excess of fuel this critical initial temperature is 75°, since the maximum rate of rise of pressure is obtained from gases preheated to that temperature. M. B. D.

**Effect of Nitrogen and Carbon Dioxide Dilutions on Explosion Limits of Acetone and Methyl Alcohol and their Mixtures.**

H. CROUCH and E. K. CARVER (*Ind. Eng. Chem.*, 1925, **17**, 641—642).—The explosion limits of acetone and methyl alcohol in air are 2.5 and 6.1%, respectively; for the lower limit and 10.4% for the upper limit for acetone. No explosion takes place if the air contains less than 11% of oxygen. The lower limit is scarcely changed by varying the oxygen content of the air down to about 13%. This effect is not observed when carbon dioxide acts as a diluent in place of nitrogen owing to its higher heat capacity.

The law of mixtures of Le Chatelier, which states that a mixture of any two limit mixtures (both upper or both lower) will itself be a limit mixture, was found to hold for the mixtures studied.

M. B. D.

**Ignition of Carbon Disulphide Vapour and its Phosphorescent Flame.** H. B. DIXON (*Rec. trav. chim.*, 1925, **14**, 305—322).—An apparatus designed to measure the "lag" prior to the ignition of mixtures of carbon disulphide vapour with hydrogen, carbon dioxide, methane, and other gases both in air and oxygen is described, in order to obtain information concerning the effects due to the gradual heating of the mingling gas by the pre-flame combination and to contact with the wall of the silica tube during this period, which were not considered in earlier work (cf. Dixon and Coward, T., 1909, **95**, 514), and the observed lag and corresponding ignition temperatures for a large number of various mixtures both in air and oxygen are recorded. Carbon disulphide maintains the ignition point at a low temperature approximating to its own. When the lag exceeded 2 or 3 sec. the gases often failed to unite, but normal behaviour was restored by prolonged sweeping out of the cylinder with air or oxygen, and the cause of non-ignition is shown not to lie in the formation of a deposit of carbon monosulphide on the active surface of the silica (cf. Dixon and Russell, T., 1899, **75**, 603). Ethylene and acetylene possess a strongly inhibitive effect on the ignition of carbon disulphide mixtures, 1% of ethylene raising the ignition temperature of a mixture of carbon disulphide and hydrogen from 215° to 410°. Mixtures of carbon disulphide and methane are used to investigate the phenomena of phosphorescent flame which is observed when the temperature of the furnace reaches 180—190°, the flame always starting some way above the jet. The products of this phosphorescent combustion are mainly carbon monosulphide (collected as a brownish-red film) and sulphur dioxide, a large quantity of carbon disulphide escaping unburnt; practically no carbon is combusted, and the absence of steam in the products shows that the methane passes through the flame unburnt. The brown deposit is formed only when phosphorescence is visible and can itself become luminous and start the phosphorescent flame. A trace of gaseous "poison" (ethylene, acetylene, coal gas, or nitrogen peroxide) introduced into the mixture of gases before they mingle inhibits both phosphorescence and the formation of the deposit, but the toxic gas has no action if introduced into the phosphorescent flame itself. Assuming the main reaction of incipient combustion to be  $\text{CS}_2 + \text{O}_2 = \text{CS} + \text{SO}_2$ , an explanation of this action of the poison by its condensation on the surface of the active carbon monosulphide molecule is elaborated.

J. W. B.

**Influence of a Magnetic Field on certain Chemical Reactions.** M. A. PARKER and H. P. ARMES (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 203—207).—Investigations on the influence of magnetic fields on the rate of certain chemical reactions have shown conclusively that the reduction of ferric chloride in hydrochloric

acid solution by metallic iron or aluminium and the reduction of permanganate in acid solution by metallic iron are hastened in the field, there being a definite relationship between the extent of reduction and the strength of the field. The phenomena observed during the reduction of ferric chloride in hydrochloric acid solution by magnesium are attributed to the formation of a magnetic deposit on the metal. The effect of stirring the solutions during reduction diminishes the difference in the extent of reduction in a given time in and out of the field.

J. S. C.

### Hydrogen Peroxide as an Oxidising Agent in Acid Solution.

**II.—I. Oxalic Acid. II. Formic Acid.** W. H. HATCHER and G. W. HOLDEN (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 231—246; cf. *ibid.*, 1923, [iii], **17**, III, 119).—I. The oxidation of oxalic acid to carbon dioxide and water in presence of hydrogen peroxide proceeds according to the conditions for a unimolecular reaction, the velocity being considerably increased in the presence of nitric or of hydrochloric acid. Evidence is put forward in favour of the view that hydrogen peroxide forms a complex, which is not a per-acid, with the non-ionised molecules of oxalic acid, which complex later breaks down into water and carbon dioxide.

II. The oxidation of formic acid proceeds along similar lines, the effect of addition of nitric acid being, however, to stabilise the peroxide, the reaction velocity being thereby lessened. Hydrochloric acid rapidly causes decomposition of hydrogen peroxide and scarcely any oxidation is effected. The complex formed is probably performic acid.

J. S. C.

**Accelerating Action of Carbohydrates on the Oxidation of Acetoacetic Acid.** Z. ERNST and J. FORSTER (*Magyar Orvosi Archivum*, 1924, **25**, 363—367).—Mannitol, glycerol, mono- and tri-butylin have the same accelerating action on the oxidation of acetoacetic acid by hydrogen peroxide as observed by Shaffer with dextrose. On the contrary, mono- and di-hydric alcohols, di- and poly-saccharides and organic acids do not produce an acceleration.

CHEMICAL ABSTRACTS.

**Velocity of Saponification of Ionic Esters.** J. N. BRÖNSTED and A. DELBANCO (*Z. anorg. Chem.*, 1925, **144**, 248—256).—The first stage in the hydrolysis of the ester of a dibasic acid is a reaction between hydroxyl ion and undissociated ester, but the second stage takes place between two ions, hydroxyl ion and the ester ion,  $R(OEt)O'$ , and its velocity may therefore be expected to show a positive, exponential salt effect. This has been verified for the hydrolysis of the potassium derivative of nitrourethane (A., 1896, i, 207) by sodium hydroxide; the nitrocarbamate ion at first formed decomposes very rapidly with liberation of nitrous oxide and the reaction is thus readily followed:  $-NO_2:N\cdot CO_2Et + OH' \rightarrow -NO_2:N\cdot CO_2- + EtOH$ ;  $-NO_2:N\cdot CO_2- \rightarrow N_2O + CO_3''$ . This reaction is equally accelerated by the addition of potassium chloride, sulphate, or cobalticyanide, salts having the same cation but anions of different valencies, but tetrammineplatinum chloride and luteo-cobaltic chloride, salts with cations of higher valencies, have much

greater effects; this was to be expected because the reacting ions are negative (cf. A., 1922, ii, 481, 699). A. G.

**Kinetic Study of the Reduction of Mercuric Bromide by Sodium Formate.** F. BOURION and J. PICARD (*Compt. rend.*, 1925, **180**, 1599—1602; cf. A., 1924, ii, 613).—The reaction between mercuric chloride and sodium formate in excess has been studied by the Ostwald isolation method. The reaction is definitely bimolecular, although the equation suggests that it is termolecular. The discrepancy is explained by the formation of a complex salt  $\text{HgBr}_2 \cdot \text{H} \cdot \text{CO}_2\text{Na}$ , which reacts with a molecule of sodium formate. The effective reaction would then be bimolecular. At  $40^\circ$  the rate of reduction of mercuric bromide by sodium formate is about half the rate observed for mercuric chloride. R. A. M.

**Kinetics of Swelling and Shrinking of Gels.** I. S. LIEPATOFF (*Kolloid-Z.*, 1925, **36**, 222—226).—The velocity of swelling when the process takes place in the pure state, satisfies the formula  $K = 1/t \cdot \log_e m/(m-Q)$ , where  $m$  is the swelling-maximum,  $Q$  the degree of swelling at the time  $t$ . If the swelling is accompanied by any secondary process, the equation  $\gamma K = 1/t \cdot \log_e m/(m-Q\gamma)$  holds better, where  $\gamma$  is the velocity coefficient of the secondary process. Experiments to test the validity of these equations were undertaken with glue and gum tragacanth in pure water, 0.025*N*-potassium hydroxide, hydrochloric acid, potassium dichromate, and potassium ferricyanide, and the second equation was found to embrace all cases of gel swelling. The shrinking of the gel in ethyl alcohol of various strengths, in methyl alcohol, and in formaldehyde, shows that the velocity of shrinking may be expressed by the equation  $K = \{1/(a-E)t\} \log_e (a-Z)E/(E-Z)a$ , where  $a$  is the initial water-content of the gel,  $E$  the water given up in time  $t_\infty$ , and  $Z$  the water given up in time  $t$ . In many cases the equation  $\gamma K = \{1/(a-E)t\} \log_e (a-\gamma Z)E/(E-\gamma Z)a$  is more satisfactory. L. L. B.

**Velocity of Decomposition of Solids. I. Dissociation of Magnesium Carbonate.** M. CENTNERSZWER and B. BRUŽS (*Z. physikal. Chem.*, 1925, **115**, 365—376; cf. this vol., ii, 206).—The velocity of the dissociation of natural and of artificial magnesium carbonate has been studied by means of an apparatus which measures the volume of carbon dioxide evolved in a given time. The velocity does not depend on the surface of the solid phase or on the rate of diffusion of the carbon dioxide, but corresponds with a reaction of the first order. The dissociation proceeds in three stages as follows: (i)  $2\text{MgCO}_3 = \text{MgO} \cdot \text{MgCO}_3 + \text{CO}_2$ ; (ii)  $2(\text{MgO} \cdot \text{MgCO}_3) = 3\text{MgO} \cdot \text{MgCO}_3 + \text{CO}_2$ ; (iii)  $3\text{MgO} \cdot \text{MgCO}_3 = 4\text{MgO} + \text{CO}_2$ . The temperature quotients for  $10^\circ$  are: stage (i) (experiments on magnesite), about 3; stages (ii) and (iii) (experiments on artificial magnesium carbonate), 4.3 and 3.2 respectively. N. H. H.

**Action of Ammonium Chloride Vapour on Metals and the Conformity of Ammonium Salts with Hydroxonium Salts as Acids.** K. A. HOFMANN, F. HARTMANN, and K. NAGEL (*Ber.*, 1925, **58**, [B], 808—817).—Comparison of the action of dry hydrogen

chloride with that of ammonium chloride vapour on metals at 250–350° by measurement of the volume of hydrogen evolved under similar conditions shows the latter to be one hundred times more active than the former with respect to copper, about forty times as active in the cases of nickel and silver, and at least five times as active in the case of iron. The action cannot therefore be due to the primary dissociation of ammonium chloride into hydrogen chloride and ammonia; this is confirmed by the absence of appreciable quantities of nitrogen from the gaseous products of the change and by the observation that the activity increases with increasing concentration of ammonium chloride vapour and hence with increase in concentration of undissociated ammonium chloride molecules. Since the metalamine chloride is a primary product of the change the latter consists in a substitution process in which the metal displaces hydrogen from the ammonium complex. The ability of the metal to form a chloride and an ammine complex and of the metallic surface to facilitate the displacement of hydrogen by solution followed by emission as the hydrogen molecule appear to be the essential factors underlying the change, thus accounting for the observation that, whereas the reactivity of the metals towards gaseous hydrogen chloride at 200° follows the order  $\text{Fe} > \text{Ni} > \text{Cu} > \text{Ag} > \text{Hg}$ , which accords with the heats of formation of the chlorides from metal and hydrogen chloride, the sequence towards ammonium chloride vapour is  $\text{Fe} > \text{Cu} > \text{Ni} > \text{Ag} > \text{Hg}$  or  $\text{As}$ . Ammonium chloride, and probably all ammonium salts, behave therefore as acids since they permit the replacement of hydrogen by metal. It is therefore directly comparable with aqueous hydrochloric acid which, according to Hantzsch (this vol., ii, 359), contains the hydroxonium salt  $[\text{OH}_3]\text{Cl}$ . Since the hydroxonium complex is less stable than the ammonium group, ammonium chloride requires a higher temperature than hydrogen chloride for the development of an appreciable activity towards metals. Thus, at 200°, copper is quantitatively converted into cuprous chloride with evolution of hydrogen by aqueous hydrochloric acid, whereas the corresponding change with ammonium chloride solution does not take place below about 250°.

H. W.

#### **Influence of Impurities in Zinc on its Solubility in Acids.**

R. VONDRÁČEK and J. IZÁK-KRIŽKO (*Rec. trav. chim.*, 1925, **44**, 376–389).—The velocity of the dissolution of pure zinc and its alloys in 0.5*N*-sulphuric acid has been studied by casting the metal into a cylinder 2 cm. in diameter one face of which, ground (and sometimes polished), was alone left free to attack by the acid, the remainder of the cylinder being protected, and measuring the volume of hydrogen evolved per sq. cm. per unit time during the period of dissolution. With pure zinc ( $\text{Fe}$  0.002,  $\text{Pb}$  0.038,  $\text{Cd}$  0.002,  $\text{Cu}$  0.003%,  $\text{Sb}$  traces) the solution velocity increases for the first hour, remains constant for 6 hrs., and again increases slightly about the eighth hour. When the surface is polished 2 hrs. elapse before the normal intensity is reached; thus the “induction period” is dependent on the mechanical treatment of the surface. Mercury

and aluminium have a decided lowering influence on the velocity of dissolution, the former completely inhibiting the evolution of gas after 2.6 c.c./cm.<sup>2</sup> have been evolved. Lead is practically indifferent, whilst cadmium, arsenic, tin, antimony, iron, and copper (after a certain passivity of the alloy has been observed at the beginning of the solution process) increase the solution velocity in the order given, the reaction velocities compared with that of pure zinc as unity being 1.15, 1.75, 2.80, 6.4, 11.5, and 12.2, respectively, for alloys containing 1% of the metal when solution to a depth of 0.2 mm. has occurred. For alloys of zinc with tin and cadmium, the maximum solution velocity is not markedly influenced by increasing the content of these metals from 0.5 to 1.0%, whereas, in the case of iron, the increase is almost directly proportional (within the limits 0.01 to 1.23%) to the amount of the metal present. The contradictory results of previous investigators are discussed in the light of the above results. J. W. B.

**Influence of Thermal and Mechanical Treatment on the Rate of Dissolution of Aluminium in Hydrochloric Acid.** X. WACHÉ and G. CHAUDRON (*Compt. rend.*, 1925, **180**, 1495—1497).—The rate of dissolution of aluminium in hydrochloric acid is decreased by hammering or heating the metal to a high temperature for some time. Generally speaking, the more rapidly the fused metal is cooled the greater will be the rate of dissolution in acid. Pure aluminium is much less readily attacked than the commercial specimens containing small amounts of silicon and iron. The rate of dissolution appears to be independent of grain size. J. S. C.

**Water-line Corrosion of Iron and Steel, with special reference to the Action of the so-called "Inhibitors" of Corrosion.** U. R. EVANS (*J. Soc. Chem. Ind.*, 1925, **44**, 163—169t).—Two distinct types of corrosion are discussed under the expression "water-line attack." On areas above the water-line which become wetted through splashing or variations in water-level, the conditions are favourable for rapid corrosion. If the rust forms as a uniform blanket over the whole of the wetted surface and continues to adhere, the subsequent rate of corrosion will be determined by the rate at which dissolved oxygen can pass through the blanket to the metallic surface, although the softened layer contains sufficient graphite or uncorroded iron to render it a conductor. Cast iron undergoes softening, but the changes in structure may escape notice until it is tested with a knife. In many fresh- and salt-waters the zone just below the water-line is remarkably free from corrosion owing to the formation of a protective, adherent oxide-film. In such waters, the area rather lower down suffers corrosion in consequence of electric currents flowing between these unaërated areas as anode and the aërated portions at the water-line as cathode. If "inhibitive chemicals," such as sodium carbonate or potassium carbonate, which tend to reduce total corrosion through the formation of a protective film, are added to waters containing chlorides, the corrosion may be localised at the water-line, because close adhesion of the protective film is most

likely to fail at that point. In such cases, although the total corrosion, indicated by loss of weight, may be reduced, the metal may be perforated more rapidly than in the absence of the inhibitor. Potassium chromate appears to be a safer inhibitor than sodium carbonate, but actual experiment is advisable before either of them is added to a corrosive water, in order to ensure that corrosion is absolutely prevented and not simply localised, with consequent greater damage.

R. B.

**Corrosion of Iron [Erosion].** W. R. WHITNEY (*Ind. Eng. Chem.*, 1925, **17**, 385—388).—When a water jet impinges on an iron surface, erosion takes place only when the water contains dissolved oxygen. Erosion of metals is probably due to the removal of the products of corrosion and not so much to disintegration by the formation of vacuum pockets by the rapidly moving propeller etc.

M. B. D.

**Corrosion of Iron in Absence of Oxygen.** J. W. SHIPLEY, I. R. McHAFFIE, and N. D. CLARE (*Ind. Eng. Chem.*, 1925, **17**, 381—385).—When iron is introduced into buffer solutions free from oxygen it evolves gaseous hydrogen from solutions more acid than  $p_H$  9.4, which is the hydrogen-ion concentration of a saturated solution of ferrous hydroxide. In the presence of oxygen, ferric hydroxide is formed and between  $p_H$  9.4 and 7.0 the rate at which the dissolved oxygen diffuses to the metal surface controls the reaction. Ferric hydroxide is soluble in solutions more acid than  $p_H$  7.0 in which the hydrogen-ion concentration again controls the rate of corrosion and the reactions concerned are independent of the oxygen supply. No change in the potentiometer readings could be discovered when hydrogen or nitrogen was bubbled over one electrode as was found by Bancroft (A., 1924, ii, 686).

M. B. D.

**Oxygen Distribution as a Factor in the Corrosion of Metals.** U. R. EVANS (*Ind. Eng. Chem.*, 1925, **17**, 363—372).—Qualitative experiments on the water-line corrosion of iron and zinc show that the results can be explained by the theory of differential aëration. The appearance of the corroded specimen can be divided into four zones: the dry top portion; the portion above the water-line which is wetted by creeping of the cathodically produced alkali upwards over the surface; the portion below the water surface which is aërated and cathodic and develops an oxide film showing interference colours; the lower portion, which is not reached by oxygen and is therefore anodic. The junction between the third and fourth zones is covered by a mantle of the metallic hydroxide, which is deposited by the metal salt from the anodic portion coming into contact with the sodium hydroxide from the cathodic portion. The oxide film becomes thick enough to give interference colours owing to the combined effect of dissolved oxygen and cathodic treatment, which renders it only partly protective and it is thus able to increase its thickness. If a disc of metal is whirled in an aërated liquid, it corrodes evenly all over its surface and the corrosion product is

far more adherent than when the metal is subjected to differential oxidation. In the case of iron under these conditions, the relatively soluble ferrous hydroxide is probably oxidised to ferric hydroxide before it is out of the reach of adhesional forces. M. B. D.

**Acid Corrosion of Metals. Effect of Oxygen and Velocity.** W. G. WHITMAN and R. P. RUSSELL (*Ind. Eng. Chem.*, 1925, **17**, 348—354).—A survey has been made of the effect of dissolved oxygen on the corrosion of mild steel, chromium steel, aluminium, lead, copper, nickel, monel metal, and tin in various acids from 20° to 50°. With metals, such as iron, which evolve hydrogen as gas in the presence of acids, the effect of dissolved oxygen is more important in the weaker acids where hydrogen evolution is slow. The effect of dissolved oxygen is not important with oxidising acids. Oxygen decreases the corrosion rate in the case of aluminium and chromium steel in strong nitric and sulphuric acids owing to the formation of a film of aluminium oxide and a passivity effect, respectively. Copper and nickel, which do not evolve hydrogen from acids, are quite resistant to non-oxidising acids in the absence of oxygen but may be rapidly attacked when oxygen is present. In some cases the corrosion of a metal in the presence of oxygen is from 100 to 200 times the rate that held when it was absent. The effect of the velocity of stirring of test pieces of copper in aerated sulphuric, hydrochloric, and acetic acids was found to increase the corrosion in the cases where the dissolved oxygen had a large effect when the metal was at rest. This is due to the fact that the velocity decreases the thickness of the stationary film of liquid on the metal surface through which the oxygen has to diffuse. The effect of velocity of stirring of steel in 80—100% sulphuric acid is also given. M. B. D.

**Oxidation of Copper-Nickel Alloys at High Temperature.** N. B. PILLING and R. E. BEDWORTH (*Ind. Eng. Chem.*, 1925, **17**, 372—376).—Both nickel and copper oxidise at temperatures of about 1000° so that the square of the amount of oxidation is proportional to the time of exposure. Copper oxidises about thirty times as fast as nickel. Copper-nickel alloys oxidise in a similar manner to their constituent metals except those containing from 30 to 80% of nickel in which the rate of oxidation increases much more rapidly with temperature. The rate of oxidation can be followed by measuring the increase in the electrical resistance of a standard wire test piece as well as by the increase in weight. M. B. D.

**Catalytic Effects in the Oxalate-Permanganate Reaction.** G. N. RIDLEY (*Chem. News*, 1925, **130**, 305—306).—Data obtained for the velocity of the reaction between oxalic acid and potassium permanganate at varying temperatures appear to indicate that the reaction is catalysed, not only by manganous ions, but also by undissociated manganous sulphate. The velocity of the reaction at 25° is considerably increased by passing a small current through the solution, probably owing to increase in the rate of movement of the cations induced by the current. A. R. P.



**Promoter Action in Homogeneous Catalysis. II. Mechanism of the Promotion of Copper Salts in the Catalytic Decomposition of Hydrogen Peroxide by Ferric Salts.** A. C. ROBERTSON (*J. Amer. Chem. Soc.*, 1925, **47**, 1299—1314; cf. A., 1924, ii, 29).—Cupric acid is present in cases where the catalytic decomposition of hydrogen peroxide by ferric salts is promoted by copper and the formation of this acid is catalysed by the presence of minimal amounts of ferric salt. As the concentration of iron is reduced, the region of maximum promotion approaches the value  $2\text{Fe}:\text{3Cu}$ . The reaction  $2\text{FeO}_3 + 3\text{CuO} \rightarrow \text{Fe}_2\text{O}_3 + 3\text{CuO}_2$  is a possible mechanism of the promotion. "Promotion" is defined and the conditions under which promotion occurs are discussed. J. S. C.

**Negative Catalysis of Oxidation Reactions.** N. R. DHAR (*Z. anorg. Chem.*, 1925, **144**, 289—303).—The oxidation of phosphorus, chloroform, sulphites, stannous salts, and various organic reducing agents by atmospheric oxygen is hindered or retarded by the presence of easily oxidised compounds such as sodium arsenite, quinol, glycerol, and sugars. The decomposition of nitrous acid into nitric acid and nitric oxide and of phosphorous and hypophosphorous acids into phosphine and phosphoric acid is also retarded by addition of a mild reducing agent. The mechanism of these and other negatively catalysed reactions may be best explained by assuming that molecular complexes are formed between the original substance and the catalyst and that these are more slowly oxidised than either compound separately. This view is supported by the investigations of other workers. A. R. P.

**Synthetic Catalysts.** G. CUSMANO (*Gazzetta*, 1925, **55**, 218—224; cf. A., 1919, ii, 61).—Further investigations have been made on compounds acting as catalysts to the reaction  $\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$ . The life of such catalysts depends on their resistance to chlorination by either the chlorine or, more commonly, the sulphuryl chloride, and the nature of the carbon skeleton is of importance mainly in relation to this resistance. Ethylenic and alicyclic linkings, by uniting with chlorine, lead to the destruction of the catalyst. Phenyl benzyl ketone rapidly loses its catalytic activity owing to halogenation of the methylene group, whereas dibenzoyl, like other  $\alpha$ -diketones, such as camphoquinone, diketocineole, and isatin, is almost inert, although highly resistant to chlorination. On the other hand,  $\beta$ - and  $\gamma$ -diketones, like benzoylacetone and acetylacetone, favour the synthesis, but ultimately undergo chlorination.

That some relationship is established between the contiguous carbonyl groups of the  $\alpha$ -diketones at the expense of those affinity residues which, in monoketones or in diketones with the carbonyl groups further apart, effect the catalytic action, is shown by the fact that oximes of ketones and both mono- and di-oximes of  $\alpha$ -diketones catalyse the synthesis of sulphuryl chloride. Similar properties are exhibited by the nitrones and furazans, particularly by the furazan of diketocineole.

The experimental data are to be published later. T. H. P.

**Decomposition of Nitrous Acid by Light and by Catalysts.**

K. B. MUKERJI and N. R. DHAR (*Z. Elektrochem.*, 1925, **31**, 255—258; cf. Rây and others, *T.*, 1917, **111**, 413).—The reaction  $3\text{HNO}_2 \rightleftharpoons \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$  is of the first order and has a sub-normal temperature coefficient, the value of which increases with rise of temperature. The velocity coefficient in both light and the dark increases slowly with increase of concentration of the nitrous acid. The velocity coefficients are considerably greater (from 200 to 400%) when the reaction is carried out in open vessels than when closed vessels are employed. This is attributed to a displacement of equilibrium owing to the removal of nitric oxide under the former conditions. The velocity of the reaction is markedly accelerated by light, and to a greater extent when closed vessels are used. The following substances act as positive catalysts for the reaction: ferric nitrate, cobalt nitrate, nickel nitrate, chromium chloride, copper sulphate, nitric acid, potassium chlorate, potassium nitrate, sulphuric acid, ferric hydroxide sol, molybdcic and titanlic acids, bromocamphor, thiocarbamide, dinitrophenol, carbamide, phthalic anhydride, citric, tartaric, and formic acids, potassium oxalate, potassium formate, boric acid, and tartar emetic. The following act as negative catalysts: sucrose, dextrose, glycerol, alcohol, hydrogen peroxide, ethyl ether, quinol, phenol, brucine, strychnine, narcotine, and quinine sulphate. Manganese nitrate and barium sulphate are without effect. The results indicate that reducing agents retard reactions involving auto-oxidation and reduction processes.

F. G. T.

**Catalytic Combination of Ethylene and Hydrogen in the Presence of Metallic Copper. III. Carbon Monoxide as a Catalyst Poison.**

R. N. PEASE and L. STEWART (*J. Amer. Chem. Soc.*, 1925, **47**, 1235—1240).—A continuation of the investigations on the poisoning of catalysts (*A.*, 1923, ii, 862). Quantitative measurements of the influence of carbon monoxide on the activity of a copper catalyst towards a mixture of ethylene and hydrogen at 0° show that the catalyst is very sensitive to the poison, less than 0.05 c.c. of carbon monoxide being sufficient to reduce the catalytic efficiency of 100 g. of copper by 90%. It is shown that the metallic surface owes 90% of its efficiency as a catalyst to less than 1% of the regions which are active in adsorption. Adsorption measurements, even at pressures as low as 1 mm., furnish no trustworthy index of catalytic activity for hydrogenation catalysts. Carbon monoxide is a "temporary" poison, pumping out at 250° being sufficient to restore the activity of the catalyst.

J. S. C.

**Thermal Decomposition of Ammonia upon Various Surfaces.**

C. N. HINSHELWOOD and R. E. BURK (*J. Chem. Soc.*, 1925, **127**, 1105—1117).—The thermal decomposition of ammonia has been investigated in silica vessels, and on the surfaces of heated platinum and tungsten wires. In all cases equilibrium corresponds with almost complete decomposition of the ammonia, whilst up to the highest temperature reached, 1050° in a silica vessel, no sign of a homogeneous reaction was observed, the decomposition being

entirely a surface reaction. The reaction on a silica surface is of the first order with respect to ammonia, and strongly retarded by hydrogen, the retarding influence,  $C$ , being expressed by a relation of the type,  $-d[\text{NH}_3]/dt = k[\text{NH}_3]\{1 - C[\text{H}_2]\}$ . The results for silica surfaces, in general, agree with those of Bodenstein and Kranendieck (A., 1912, ii, 1155), but the nature of the particular silica surface exerts a remarkable effect on the temperature coefficient of the reaction, the retarding effect of the products, and the effect of temperature on the retarding effect. In contradiction to the work of Bodenstein (*loc. cit.*) the authors find that in suitable silica vessels, (1) added hydrogen may have just as large a retarding effect as hydrogen formed *in situ* by the reaction, (2) the temperature coefficient may be very high, and (3) the retarding influence of the products may be constant over a range of  $200^\circ$ .

The reaction on a heated platinum wire is of the first order as regards ammonia, and is retarded by hydrogen, but differently from the retardation in the case of silica, the equation being  $-d[\text{NH}_3]/dt = k[\text{NH}_3]^n/[\text{H}_2]$ , where  $n$  is approximately equal to 1. Nitrogen has practically no effect on this reaction, which corresponds with a heat of activation of 140,000 cal. The reaction on a heated tungsten wire is of zero order with respect to ammonia, and is uninfluenced by the products of reaction. It is much more rapid than with platinum, but the temperature coefficient is smaller and corresponds with a heat of activation of 38,700 cal. W. H.-R.

**Catalysis by the Action of Subdivided Metals. III. Heat of Adsorption of Hydrogen on Nickel.** B. FORESTI (*Gazzetta*, 1925, 55, 185—201).—The author's results (A., 1923, ii, 747; 1924, ii, 320) are discussed in relation to those of Beebe and Taylor (A., 1924, ii, 159), and further results are given showing the relation between the temperature of evacuation of the finely-divided nickel and the heat of adsorption, as well as the effect on the latter of reheating the metal. These results render it highly probable that the surface of the nickel or other metal in similar condition is composed of adsorbent centres of varying force, and that the catalytic activity is determined by such centres as are able to adsorb gases and retain them firmly. T. H. P.

**Induced Oxidation and its Mechanism Explained on the Basis of the Formation of Ions during Chemical Reactions.** A. N. DEY and N. R. DHAR (*Z. anorg. Chem.*, 1925, 144, 307—312).—Sulphur, sucrose, dextrose, ethyl alcohol, starch, potassium oxalate, sodium tartrate, sodium arsenite, and similar mild reducing agents are oxidised at the ordinary temperature by passing air through their solutions in which finely-divided copper, cuprous chloride, cuprous oxide, zinc, or yellow phosphorus is suspended. Finely-divided copper dissolves in cold solutions of sodium arsenite, sodium phosphite, sodium citrate, potassium tartrate, citric acid, tartaric acid, and sucrose only in the presence of oxygen, but it dissolves in cold ammonium nitrite solution also in the absence of oxygen,

probably owing to the direct action of the nitrous acid set free by hydrolysis. The oxidising action of the phosphorus, copper, zinc, and other reducing agents in the above cases is probably due to the formation, by the oxidising action of the air, of ions which can oxidise molecular oxygen and the activated oxygen molecule then attacks the sulphur, alcohol, etc.

A. R. P.

**Platinum Oxide as a Catalyst in the Reduction of Organic Compounds. VII. Effects of Numerous Substances on the Platinum Catalysis of the Reduction of Benzaldehyde.**

W. H. CAROTHERS and R. ADAMS (*J. Amer. Chem. Soc.*, 1925, **47**, 1047—1063; cf. A., 1924, i, 968).—The effect of various substances on the catalytic reduction of benzaldehyde in 95% alcohol by hydrogen in presence of platinum oxide has been studied. A catalyst which has lost its activity by contact with aldehyde (cf. A., 1923, ii, 310) is not reactivated by the addition of ferrous chloride, but if the mixture containing the exhausted catalyst is shaken with air, either before or after the addition of the ferrous chloride, a permanent partial restoration of the catalytic activity is achieved. Ferrous and ferric hydroxides increase the rate of reduction at first, thereafter retarding it, apparently by covering the catalyst with a gelatinous film, as the addition of hydrochloric acid, which by itself has a depressing effect, completely restores the activity. Metallic iron, ferric oxide, chloride, and acetate, ferrous chloride and sulphate, all promote the catalysis. Ferric nitrate in small amount (0.1—1.0 millimol.) causes the reduction to cease before all the aldehyde is reduced, whilst a larger proportion (10 millimols.) carries the reduction further, with production of toluene. It is concluded that the promoter effect is due to iron ions. Manganese, nickel, cobalt, vanadic acid, chromic chloride, uranyl acetate, and alkalis are promoters. Palladium is a promoter, but may be acting as an independent catalyst. Sodium chromate and zinc acetate in small amount (0.1 millimol.) are promoters, but larger proportions (1.0 millimol.) almost completely suppress the reduction. Copper chloride is a promoter, the acetate a depressant. Titania, molybdenum, silver, tungsten, osmium, iridium, aluminium, and gold, as well as mineral acids, are without effect on the catalysis. Mercury and lead act as catalyst poisons, but a considerable proportion of either is necessary to suppress the reduction completely. Of sodium salts, the chloride and bromide increase the induction period, but are otherwise inert. The iodide acts as a weak depressant, probably through the liberation of iodine. The nitrate is a weak depressant, whilst the nitrite, inert in small amounts, completely inhibits the reduction when 1.0 millimol. is present. The sulphate and chlorate are inert, the cyanide is a poison. Using a catalyst which has been promoted with ferrous chloride, hydrochloric acid decreases the rate of reduction, but causes the latter to go beyond the alcohol stage. Sodium nitrate causes some acetal formation, whilst the nitrite is again a powerful depressant. The first reduction product is in all cases the primary alcohol, any formation of hydrocarbon always taking place subsequently, and

more slowly. The results are discussed in relation to those of F. G. W. Faillebin (A., 1923, i, 92).

**Hydrogen Electrode.** H. T. BEANS and L. P. HAMMETT (*J. Amer. Chem. Soc.*, 1925, **47**, 1215—1226).—An attempt has been made to classify some of the conditions which give rise to variable potentials of hydrogen electrodes with platinum catalysts and to show how these variabilities may be eliminated. The formation of platinum-black necessitates the presence of some impurity, since pure chloroplatinic acid gives only bright electro-deposits. Bright metallic deposits of platinum prepared electrolytically are catalytically active for the hydrogen-hydrogen ion reaction, and their life although much shorter than that of platinum-black, is sufficient to allow of their use as hydrogen electrodes. Consideration of the various methods for obtaining active surface shows that it is not so much the extent of the surface as the quality that determines activity, and freshly-prepared surfaces are most active. The rate of attainment of equilibrium depends on removal of oxygen, which is in turn determined by cell-design, nature of the surface, and hydrogen-ion concentration of the aqueous medium. Hydrogen electrode measurements are possible in unbuffered solutions in the neutral range provided the electrodes are perfectly clean. J. S. C.

**Tervalent Copper.** M. VRTIŠ (*Rec. trav. chim.*, 1925, **44**, 425—434).—The compound of trivalent copper obtained by the anodic or persulphate oxidation of copper sulphate in alkaline solution in the presence of tellurates has been investigated. The rôle of the latter is that of a peptising and stabilising agent only, the production of trivalent copper being determined only by the alkalinity of the solution. Periodates act similarly to tellurates. This is confirmed by potentiometric measurements which show that the concentration of the  $\text{Cu}^{+++}$  ions is unaffected by changes in the concentration of the tellurate ions. From these and other observations it is inferred that the formula most nearly expressing the composition of the trivalent copper compound (in potassium hydroxide solution) is  $\text{K}[\text{Cu}(\text{OH}_4)]$ . N. H. H.

**Electrolytic Deposition of Tungsten.** J. A. M. VAN LIEMPT (*Z. Elektrochem.*, 1925, **31**, 249—254).—Tungsten powder (99.3% pure) may be obtained, up to 80% of the theoretical yield, by electrolysis at 950° molten sodium tungstate at a current density of 15 amp./cm.<sup>2</sup>, in a quartz crucible between tungsten electrodes. The tungsten results from the reduction of the molten tungstate by the nascent sodium liberated at the cathode:  $6\text{Na} + 5\text{Na}_2\text{WO}_4 = \text{W} + 4\text{Na}_4\text{WO}_5$ . Pure tungsten is obtained so long as the mass remains neutral or weakly alkaline. If it becomes too strongly alkaline the tungsten redissolves. In acid fusions, reduction of  $\text{W}_2\text{O}_7^{2-}$  ions by the sodium occurs with the formation of "tungsten bronzes" of the type  $\text{M}_2(\text{WO}_3)_n$  (cf. Brunner, *Diss.*, Zürich, 1903). The electrical resistance of these "bronzes" decreases rapidly with rise of temperature owing to the gradual liberation of tungsten. The anode reaction is  $\text{WO}_4^{2-} + \text{Na}_2\text{WO}_4 = \text{Na}_2\text{W}_2\text{O}_7 + 0.5\text{O}_2$ . When

unattackable electrodes are used in a cell without a diaphragm, the products of these electrode reactions react, making the mass alkaline:  $4\text{Na}_4\text{WO}_5 + 3\text{Na}_2\text{W}_2\text{O}_7 = 10\text{Na}_2\text{WO}_4 + \text{Na}_2\text{O}$ . Electrolysis may be made continuous under these conditions by gradually adding tungstic oxide. In the presence of  $\text{WO}_4^{--}$ , a tungsten anode is oxidised, the oxide dissolving to keep the fused mass neutral. Tungsten may be deposited in an adhesive, polishable layer on copper, nickel, or cobalt by using these metals as cathodes in the electrolysis of fused acid tungstates at  $1000^\circ$ . Lithium acid tungstates give the best results. Repeated layers of tungsten may be thus deposited if the surface layers of "tungsten bronzes" are removed between each electrolysis. The tungsten is formed by the decomposition of "tungsten bronzes" primarily deposited. Crystal growth of a monocrystalline tungsten filament may be obtained by electrolysis at low current densities in neutral or acid melts (cf. A., 1924, ii, 558).

F. G. T.

**Reduction of Uranyl Salts by Means of a Dropping Mercury Cathode.** P. HERASYMENKO (*Chem. Listy*, 1925, **19**, 172—179).—Uranyl salts are reduced at a dropping mercury cathode first to derivatives of quinquivalent uranium. Further reduction ensues only when the polarisation becomes very considerable. The polarisation curves of the reduction show a very marked maximum when the metal is all in the quinquivalent form, but this maximum disappears in the presence of certain electrolytes such as potassium or lithium chlorides, probably owing to adsorption of the reduced products at the surface of the electrode.

A. R. P.

**Instability of Phthalate Solutions towards the Hydrogen Electrode.** C. Z. DRAVES and H. V. TARTAR (*J. Amer. Chem. Soc.*, 1925, **47**, 1226—1230; cf. Merrill, A., 1922, i, 326; Oakes and Salisbury, A., 1922, ii, 468; Clark, *ibid.*; Wood and Murdick, A., 1922, i, 735).—Measurements with the cell  $\text{Hg}|\text{Hg}_2\text{Cl}_2, \text{KCl}(1.0N)|\text{KCl}(1.0N)|\text{phthalate solution}|\text{H}_2$  show that the instability of phthalate solutions towards the hydrogen electrode is dependent on the relative amount of platinum-black on the latter. Complete reduction of potassium hydrogen phthalate to the corresponding hexahydro derivative has been accomplished in aqueous solution using heavily platinised gauze as electrode.

J. S. C.

**Photochemical Decomposition of Nitrosyl Chloride.** E. J. BOWEN and J. F. SHARP (*J. Chem. Soc.*, 1925, **127**, 1026—1028).—The photochemical decomposition of nitrosyl chloride has been studied in an all-glass apparatus using light of spectral range approximately 4400—5200 Å. Approximately two quanta are absorbed for each molecule decomposed. The heat of reaction is  $\text{NOCl} + 45,000 \text{ cal.} \rightarrow \text{NO} + \text{Cl}$ , from which the maximum wavelength capable of causing the decomposition is calculated as 6270 Å., which corresponds almost exactly with the point at which the absorption of nitrosyl chloride begins, but the absorption in red light is too weak to enable the decomposition to be studied. Since the quantum of blue light is greater than the minimum quantum

necessary for decomposition, it is probable that the decomposition is a true unimolecular process,  $\text{NOCl} + h\nu \rightarrow \text{NO} + \text{Cl}$ , followed by spontaneous reactions re-forming nitrosyl chloride, possibly through the intermediate compound  $\text{NOCl}_2$ . The rate of reaction does not therefore follow the unimolecular equation, in contradiction to the assumption of Kiss (A., 1923, ii, 598), whose further conclusions are criticised.

W. H.-R.

**Mercury Helide.** J. J. MANLEY (*Nature*, 1925, **115**, 947; cf. this vol., ii, 57, 314).—A correction; the simplest formula assignable to mercury helide is  $\text{HgHe}_{10}$ .

A. A. E.

**Action of Natural Waters on Copper.** H. HENSTOCK (*J. Soc. Chem. Ind.*, 1925, **44**, 219—220t).—Boiling water containing 0.0024 part per 100,000 of sodium chloride, or equivalent quantities of magnesium chloride or potassium chloride, attacks copper with the formation of soluble copper compounds, but copper is not attacked by solutions of calcium chloride, magnesium sulphate, sodium sulphate, calcium sulphate, magnesium hydrogen carbonate, or calcium hydrogen carbonate of approximately equivalent dilution, nor by sodium or magnesium chloride solution if equal quantities of calcium hydrogen carbonate or calcium hydroxide are also present. No action on copper could be detected with water containing solely organic matter in solution. In certain cases where natural soft waters have been found to attack copper apparatus, the cause has always been attributable to the presence of traces of sodium or magnesium chloride, and can be prevented by the addition of small quantities of lime.

L. A. C.

**Mechanism of the Formation of Malachite from Basic Cupric Carbonate.** J. R. I. HEPBURN (*J. Chem. Soc.*, 1925, **127**, 1007—1013).—When equivalent solutions of cupric sulphate and sodium carbonate are mixed at the ordinary temperature, the precipitated basic cupric carbonate (over a range of concentration from 0.005*N* to 3*N*) consists of a hydrogel of highly hydrated material of low refractive index and opaque in polarised light. If immediately washed free from adhering reagents and suspended in pure water, this initial precipitate is stable, but normal crystals of malachite are gradually formed if the precipitate is suspended in a solution of carbon dioxide. If left in contact with the precipitating reagents, the change to malachite is accelerated by increasing concentration, and in this case the product consists entirely of malachite sphæro-crystals. When malachite is formed at 100° from the blue solutions prepared by dissolving the basic carbonate in a saturated solution of sodium hydrogen carbonate, the product (in the absence of foreign nuclei) consists of a surface film of sphæro-crystals of size about 6 $\mu$ ; the film is disrupted into individual sphæro-crystals on boiling. In both cases the presence of gelatin retards but does not prevent the formation of malachite.

W. H.-R.

**Mixed Basic Silver-Copper Salts.** G. MALQUORI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 392—396).—Investigation of the

system cupric hydroxide, silver nitrate, water at  $20^{\circ}$  indicates the existence of only one basic salt,  $3\text{Cu}(\text{OH})_2 \cdot 2\text{AgNO}_3 \cdot 3\text{H}_2\text{O}$ , which is decomposed by water but is stable in presence of silver nitrate solutions having concentrations not less than 0.78%. T. H. P.

**Solubility of Silver in Water.** I. H. KŘEPELKA and F. TOUL (*Chem. Listy*, 1925, **19**, 182—184).—After contact with pure silver foil for 24 days, carefully redistilled water contained 0.035 mg. of silver per litre; in 14 days 0.021 mg., and in 7 days 0.012 mg. were dissolved. Previous heating of the silver in an atmosphere of pure hydrogen appreciably reduced its solubility in water. As the experiments were conducted in vessels of Bohemian glass, it is possible that the alkali derived from the vessels had an influence on the solubility. A. R. P.

**Hydrates of Calcium Carbonate.** J. HUME (*J. Chem. Soc.*, 1925, **127**, 1036—1039).—A solution of sucrose (25 g.) in water (100 c.c.) was shaken with lime and filtered, the filtrate being treated with carbon dioxide at  $0^{\circ}$ , and then exposed at  $0^{\circ}$  to the action of atmospheric carbon dioxide. After 2 or 3 days crystals of calcium carbonate hexahydrate were deposited,  $d^{15}$  1.789. In contact with water at or above  $0^{\circ}$ , the hexahydrate slowly changes into anhydrous calcium carbonate, but in the above sugar-lime mixture the hexahydrate is stable below  $10.4^{\circ}$  and the anhydrous salt above  $17^{\circ}$ ; between  $10.4$  and  $17^{\circ}$  the stable phase is a pentahydrate,  $d^{15}$  1.834, which changes into the anhydrous form in contact with water. Between  $10.4^{\circ}$  and  $25^{\circ}$  the hexahydrate is first precipitated from the above sugar-lime mixtures, and then slowly changes into the form stable at the particular temperature. No evidence of lower hydrates has been obtained. W. H.-R.

**Direct Formation of Mercuric Oxybromides.** H. PÉLABON (*Compt. rend.*, 1925, **180**, 1500—1501).—Employing a method analogous to that previously reported (this vol., ii, 222), the existence of the oxybromides,  $\text{HgO} \cdot \text{HgBr}_2$  and  $4\text{HgO} \cdot \text{HgBr}_2$ , has been demonstrated, and evidence obtained for the existence of a third of which the exact composition is uncertain. J. S. C.

**Constitution of Boric Acid and Some of its Derivatives.** P. H. HERMANS (*Z. anorg. Chem.*, 1925, **142**, 399—300).—In explanation of previous work (this vol., i, 500) it is stated that acids formed from co-ordinated boron compounds,  $[(\text{HO})_2\text{BO}]\text{H}$  and its derivatives are strong, but derivatives of boron trihydroxide,  $\text{B}(\text{OH})_3$ , are neutral. Equilibrium exists between the two forms where an oxygen atom neutralises two of the co-ordination valencies. L. J. H.

**New Type of Alkali Borate: Pentaborates.** V. AUGER (*Compt. rend.*, 1925, **180**, 1602—1604).—Alkali borates are known of the following types:  $\text{MBO}_2$ ,  $\text{M}_2\text{B}_4\text{O}_7$ ,  $\text{M}_2\text{B}_{10}\text{O}_{16}$ ,  $\text{Li}_2\text{B}_8\text{O}_{13}$  (Le Chatelier, A., 1897, ii, 448), and probably  $\text{Na}_2\text{B}_8\text{O}_{13}$  and  $\text{Na}_2\text{B}_6\text{O}_{10}$  (A., 1915, ii, 449). Fractional crystallisation of potassium tetraborate in the presence of a large excess of boron trioxide yields boric



acid, decaborate, and tetraborate between the temperature limits  $-3^{\circ}$  and  $+80^{\circ}$ . Solutions in which the ratio B/K is 2.5/1 yield at  $115-120^{\circ}$  microcrystalline prisms having the composition  $K_2HB_5O_9 \cdot 2H_2O$ . If a concentrated solution of potassium tetraborate is heated in a sealed tube at  $115-120^{\circ}$  and seeded with the pentaborate this substance is very readily formed.

The sodium salt is formed by simple heating of borax and water to  $115^{\circ}$  in a sealed tube. R. A. M.

**X-Ray Investigation of the Crystalline Nature of China Clays etc.** G. SHEARER (*Trans. Ceram. Soc.*, 1923—1924, **23**, 314—317).—The X-ray spectra of powdered (1) china clay, (2) equimolecular mixtures of china clay and alumina, (3) mixtures of china clay (1 mol.) and alumina (2 mols.) and (4) alumina, after being heated at  $1200^{\circ}$  and  $1700^{\circ}$ , were obtained, together with that of natural sillimanite. Sillimanite is the principal constituent of china clay after heating at  $1200^{\circ}$  or  $1700^{\circ}$ . The mixture (2) consisted of free sillimanite and free alumina, as did the mixture (3) after heating at  $1200^{\circ}$ . A new crystalline constituent had been produced in (3) on heating at  $1700^{\circ}$ . The crystals present in the clay were neither very large nor very small. H. S. H.

**Dehydration of Kaolinite.** J. V. SAMOILOFF (*Trans. Ceram. Soc.*, 1923—1924, **23**, 338—339).—From a study of the thermal phenomena observed on heating various minerals it is concluded that on dehydration kaolinite is decomposed into  $Al_2SiO_5$  and silica. The characteristic exothermic reaction about  $900^{\circ}$  is due to the molecular rearrangements of  $Al_2SiO_5$ , the same exothermic reaction being observed with allophane. H. S. H.

**Action of Heat on Kaolinite and Other Clays.** I. J. W. MELLOR and A. SCOTT (*Trans. Ceram. Soc.*, 1923—1924, **23**, 322—329).—The dehydration of kaolinite does not take place at a fixed temperature and is completed above  $500^{\circ}$ . Kaolinite when heated at about  $500^{\circ}$  decomposes into silica, alumina, and water. The critical point about  $900^{\circ}$  is connected with a transformation in the form of the alumina set free about  $500^{\circ}$ . Sillimanite of the same composition as the natural mineral can develop below  $1200^{\circ}$ , and probably forms above that temperature solid solutions with  $3Al_2O_3 \cdot 2SiO_2$ . A new compound, which may be  $3Al_2O_3 \cdot 2SiO_2$ , is formed when kaolinite is heated at  $1700^{\circ}$ . H. S. H.

**Reaction of Siloxen with Halogen Compounds.** H. KAUTSKY and H. THIELE (*Z. anorg. Chem.*, 1925, **144**, 197—217; cf. A., 1924, ii, 852).—The  $\text{:SiH}$  groups in siloxen,  $Si_6H_6O_3$ , react with halogen acids, alkyl and aryl halides, and halogenoacetic acids according to the equation  $\text{:SiH} + \text{RX} = \text{:SiX} + \text{RH}$ , where X is chlorine, bromine, or iodine. When gaseous hydrogen bromide is used monobromosiloxen is formed quantitatively, proving the presence of 6 silicon atoms in the molecule of siloxen. In the presence of water, ammonia, or amines, the halogen compounds first formed are decomposed:  $\text{:SiX} + H_2O = \text{SiOH} + \text{HX}$ ,  $\text{:SiX} + 2R \cdot NH_2 = \text{:SiNHR} + R \cdot NH_3X$ . The reaction with organic halogen compounds does not

take place between the pure substances in the dark, but may be made sensitive to long wave-lengths by the presence of substances which absorb these, such as oxysiloxen or suitable dyes; the reaction products, oxy-, halogen-, or amino-siloxens, being absorbent, act as auto-sensitisers. The reaction may also be induced in the dark by other reactions, such as the oxidation of a trace of the siloxen with oxygen or the production of the siloxen *in situ* from calcium silicide and hydrochloric acid. The system siloxen-oxygen can act as a powerful oxidising agent, chloroform or carbon tetrachloride being oxidised in the dark to carbonyl chloride. A. G.

**Action of Some Gases on Silicates.** H. VON WARTENBERG (*Z. anorg. Chem.*, 1925, **142**, 335—336).—Metals cannot be kept in a reducing atmosphere at 1200° or 1300° in vessels of silica or porcelain without the production of appreciable quantities of silicon. The presence of ferrous oxide in porcelain also leads to reactions such as the absorption of chlorine, which has been observed at 1000°. Owing to slow penetration of the walls by the gas the action may continue over a very considerable time. L. J. H.

**Treatment of Malacon. Separation of Celtium [Hafnium] from Zirconium.** (MLLE.) M. MARQUIS, P. URBAIN, and G. URBAIN (*Compt. rend.*, 1925, **180**, 1377—1380; cf. A., 1922, ii, 463; 1923, ii, 80).—Malacon is a zirconium silicate from Madagascar, containing small amounts of celtium, thorium, rare earths (mainly yttrium group), iron, titanium, niobium, uranium, and traces of tantalum. It can be decomposed by sulphuric acid or potassium hydrogen sulphate. The strong aqueous solution of sulphates is treated with potassium sulphate in excess, when the double sulphates of zirconium and celtium are precipitated. The double sulphate of zirconium and potassium is distinctly less soluble than the celtium analogue. The fractionation must be carried out in strongly acid solutions or else hydrolysis occurs. Complex oxalates, tartrates, and carbonates can be prepared, but separation is best effected through the double carbonates. If a mixture of zirconium and celtium salts is repeatedly treated with saturated sodium carbonate solution the first liquors are rich in zirconium and poor in celtium. The zirconium complexes are more stable than those of celtium and celtia is a stronger base than zirconia. Alkali precipitates zirconium before celtium from mixtures of simple salts, but in complex salts the reverse is true. The method of separation which follows from the above results is described.

The authors regard photographic quantitative analysis by X-ray spectra (Coster and Hevesy) as untrustworthy. R. A. M.

**Quadrivalent Lead.** J. ŠTĚRBA-BOEHM and M. AUERSPERGROVÁ (*Rec. trav. chim.*, 1925, **44**, 390—399).—An unsuccessful attempt has been made to prepare lead disulphide ( $\text{PbS}_2$ ) by the action of hydrogen sulphide on lead dioxide. The action of gaseous hydrogen sulphide in an atmosphere of carbon dioxide results in a product containing some combined and some free sulphur. The total sulphur found at the ordinary temperature was 4.16% (ratio

of combined to free = 1 : 1.61) and with increasing temperature rose to a maximum of 20.87% (ratio of combined to free = 1 : 1) at about 100°. With higher temperatures, the total sulphur and the proportion of free sulphur showed a decrease owing to evaporation of the latter. It is probable that the following reactions occur: (i)  $\text{PbO}_2 + \text{H}_2\text{S} = \text{PbO} + \text{S} + \text{H}_2\text{O}$ ; (ii)  $\text{PbO}_2 + 2\text{H}_2\text{S} = \text{PbS} + \text{S} + 2\text{H}_2\text{O}$ ; and that at 100° (ii) is predominant. By the action of liquid hydrogen sulphide at the ordinary pressure reaction (i) appears to prevail. An aqueous solution of potassium sulphide reacts very slowly with lead peroxide forming, probably, lead sulphide. In all cases the action is incomplete. Gaseous hydrogen sulphide gives lead sulphide only with a methyl-alcoholic solution of lead tetrachloride. Improved methods for the determination of lead and sulphur are described.

N. H. H.

**Chromates of the Metals of the Cerium Group.** F. ZAMBONINI and G. CAROBBI (*Rend. Accad. Sci. Fis. Napoli*, 1925, [iii], **31**, 17—24).—The anhydrous chromates of lanthanum, praseodymium, and neodymium were obtained by heating intimate mixtures of the chlorides of these metals with potassium chromate to temperatures above 600°. A similar attempt to prepare anhydrous cerium chromate at 1000° resulted in the formation of a mixture of chromium sesquioxide and cerium dioxide. In addition to the octahydrates of the above salts prepared by Britton (A., 1924, ii, 763), the following new hydrates were prepared by precipitation methods from cold solutions.  $\text{La}_2(\text{CrO}_4)_3 \cdot \text{H}_2\text{O}$ ,  $\text{Nd}_2(\text{CrO}_4)_3 \cdot 10\text{H}_2\text{O}$ ,  $\text{Pr}_2(\text{CrO}_4)_3 \cdot 10\text{H}_2\text{O}$ ,  $\text{Sm}_2(\text{CrO}_4)_3 \cdot 9\text{H}_2\text{O}$ .

F. G. T.

**Solid Hydrides of Arsenic and Antimony.** G. DRUCE (*Chem. Listy*, 1925, **19**, 156—157).—With aqueous sodium hydroxide trihydrogen arsenide yields sodium arsenide, which is immediately hydrolysed with the formation of solid dihydrogen diarsenide and the evolution of hydrogen. In a similar way, trihydrogen antimonide yields sodium antimonide, which with hydrochloric acid gives the solid dihydrogen diantimonide and hydrogen. The solid antimonide is also obtained when a solution of sodium hydroxide is electrolysed with an antimony cathode.

A. R. P.

**Solid Antimony Hydride.** E. J. WEEKS and J. G. F. DRUCE (*J. Chem. Soc.*, 1925, **127**, 1069—1072).—Stibine was passed over solid sodium hydroxide, which became coated with a grey deposit. When the latter was treated with water, hydrogen was evolved, and the grey residue, after washing with dilute hydrochloric acid and drying in a vacuum desiccator, consisted of amorphous antimony dihydride,  $\text{Sb}_2\text{H}_2$ . The reactions involved may be expressed by (1)  $\text{SbH}_3 + 3\text{NaOH} \rightarrow \text{SbNa}_3 + 3\text{H}_2\text{O}$ , and (2)  $2\text{SbNa}_3 + 6\text{H}_2\text{O} \rightarrow \text{Sb}_2\text{H}_2 + 6\text{NaOH} + 2\text{H}_2$ . The same compound may also be obtained by the electrolysis of sodium hydroxide at an antimony cathode. Antimony dihydride is slightly decomposed when heated in hydrogen at a dull red heat, and completely decomposed at a higher temperature.

W. H.-R.

**Amphoteric Hydroxides. II. Tantalum Acid and Alkali Tantalates.** G. JANDER and H. SCHULZ (*Z. anorg. Chem.*, 1925, **144**, 225—247; cf. A., 1923, ii, 772).—Preparations of tantalum acid made by the addition of nitric acid to aqueous sodium tantalate at 0° and 100° both showed hysteresis loops in the moisture content–vapour pressure curves. Alkali tantalates were prepared by fusing the hydroxides with tantalum pentoxide and crystallising from water; tantalum acid is precipitated from the aqueous solutions by acids, including carbonic acid, but the precipitate is soluble in excess of strong acid. Different proportions of potassium hydroxide and tantalum pentoxide always lead to the same crystalline tantalate; from highly concentrated solutions crystals of different form were obtained but these were readily converted into the first form and probably differed only in water of crystallisation. By the addition of sodium hydroxide to aqueous potassium tantalate two sodium salts, also differing only in water of crystallisation, were obtained and a lithium tantalate was similarly prepared. Analysis showed that each of these salts contained alkali metal and tantalum in the atomic proportion 7 : 5, and not 4 : 3 as has been found previously; the data agree with the formulæ  $7K_2O, 5Ta_2O_5, 24H_2O$ ;  $7Na_2O, 5Ta_2O_5, 22H_2O$ ;  $7Na_2O, 5Ta_2O_5, 40H_2O$ , and  $7Li_2O, 5Ta_2O_5, 40H_2O$ .

The acid is probably a complex acid in which the oxygen atoms of orthotantalum acid have been replaced by  $TaO_4$  groups:  $H_7[Ta(TaO_4)_4]$ . The molecular weight of the potassium salt, as determined by comparing the diffusion coefficient with that of sodium hexamolybdate periodate, is 1750 compared with the calculated value of 1450 and is thus of the right order of magnitude; conductivity data indicate that the acid is at least hexabasic.

A. G.

**Preparation and Properties of Disulphur Difluoride.** M. CENTNERSZWER and C. STRENK (*Ber.*, 1925, **58**, [B], 914—918; cf. A., 1924, ii, 167).—The approximate physical constants of disulphur difluoride, obtained by heating silver fluoride with sulphur, are m. p.  $-105.5^\circ$ , b. p.  $-99^\circ$ ,  $d^{100}$  1.5, mol. wt. 93.2. The gas yields a yellow or white deposit when introduced into a dry, vacuum flask, but decomposition ceases after 12—24 hrs. and the “purified” gas then gives no deposit when brought into a second flask and does not attack mercury (contrast *loc. cit.*). Disulphur difluoride does not appear to be completely stable towards heat. Its production from sulphur and silver fluoride is probably accompanied by that of other fluorides of sulphur, some of which are relatively difficultly volatile.

H. W.

**Formation and Decomposition of Polythionates.** F. FOERSTER (*Z. anorg. Chem.*, 1925, **144**, 337—340).—Although the intermediate formation of sulphylic acid in the reaction between sulphur dioxide and hydrogen sulphide in aqueous solution cannot be detected, the author considers that the assumption is justified by analogy with the reaction between sulphur dioxide and selenium dioxide. That thiosulphuric and sulphuric acids are the primary

products of the hydrolysis of trithionic acid may be shown by maintaining a mixture of potassium trithionate and potassium acetate at 50° for some days; in the absence of potassium acetate, the sulphuric acid formed in the reaction decomposes the thio-sulphuric acid with the formation of sulphur dioxide and sulphur owing to the sensitiveness of thiosulphuric acid to hydrogen ions (cf. Riesenfeld, this vol., ii, 229; Foerster, *ibid.*, 148; and Foerster and Hornig, A., 1923, ii, 23).

A. R. P.

**Influence of Hydrogen Ions on the Mechanism of the Reduction of Ferric Salts by Sodium Thiosulphate.** J. HOLLUTA and A. MARTINI (*Z. anorg. Chem.*, 1925, **144**, 321—326).—The mechanism of the reduction of ferric salts by sodium thiosulphate may be expressed as follows: (1)  $\text{Fe}^{+++} + 2\text{HS}_2\text{O}_3' \rightleftharpoons [\text{Fe}(\text{S}_2\text{O}_3)_2]' + 2\text{H}^+$ ; (2)  $[\text{Fe}(\text{S}_2\text{O}_3)_2]' + \text{Fe}^{+++} = 2\text{Fe}^{++} + \text{S}_4\text{O}_6''$ ; (3)  $\text{H}^+ + \text{S}_4\text{O}_6'' = \text{HS}_4\text{O}_6'$ . The reaction is retarded by the addition of acids in a similar way to the action of neutral salts; with excess of hydrogen ion reaction (1) goes from right to left, whereas a small amount of acid (0.05 mol. per litre) increases the concentration of the ferric ions by repressing hydrolysis and consequently accelerates reaction (2). As the acidity of the solution increases, a side reaction of the fourth order commences to take place thus, (4)  $2\text{Fe}^{+++} + 2\text{HS}_2\text{O}_3' = 2\text{Fe}^{++} + \text{HS}_4\text{O}_6' + \text{H}^+$ , and when the acidity exceeds 0.5N this becomes the sole reaction that takes place. With very high acidity, the thiosulphate slowly decomposes into sulphite and sulphur and the velocity constant of (4) rapidly falls.

A. R. P.

**System Chromium-Hydrogen.** G. F. HÜTTIG and F. BRODKORB (*Z. anorg. Chem.*, 1925, **144**, 341—348).—Chromium, electrolytically deposited at -50° from concentrated solutions of chromic acid containing a little chromic sulphate, may contain up to about 0.45% H, which appears to be present in the form of a super-saturated solid solution. At the ordinary temperature, the hydrogen pressure of this chromium is less than 1.0 mm., but at 58° a sudden evolution of hydrogen takes place, although a temperature of 350° is required in order to remove the whole of the gas. No reproducible relations between temperature, pressure, and hydrogen concentration could be established. X-Ray examination showed that hydrogen increases very slightly the lattice parameter of chromium. Electrolytic chromium free from gas has  $d_4^{25}$   $7.138 \pm 0.003$  and  $d_4^{50}$   $7.156 \pm 0.001$ , hence its atomic volume is 7.286 at 25° and 7.268 at -50° and its coefficient of expansion between -50° and +25° is  $1.2 \times 10^{-5} \pm 0.3 \times 10^{-5}$ .

A. R. P.

**Composition of Rust.** R. STUMPER (*Bull. Soc. chim. Belg.*, 1925, **34**, 150—158).—Analyses of many samples of iron rust show that this material has a very variable composition but always contains ferrous oxide and a greatly preponderating amount of ferric oxide; representing its composition as  $x\text{FeO}, y\text{Fe}_2\text{O}_3, z\text{H}_2\text{O}$ ,  $x=1$ ,  $y=2$  to 20, and  $z=2$  to 30. On allowing iron to rust in water the percentage of ferrous oxide to total oxides falls hyperbolically with the time; thus after 1 day the rust contains

43.3% FeO, after 5 days 22.7% FeO, and after 15 days 9.5% FeO. Extrapolation of this curve to zero time indicates that the oxide first formed during the rusting of iron is ferrous oxide and this becomes further oxidised to ferric oxide at a rate that decreases rapidly at first with the time, then more slowly, finally approaching an equilibrium.

A. R. P.

### **Precipitation of Ferric Salts with Ammonium Sulphide.**

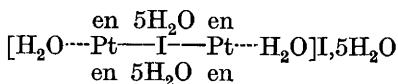
H. KŘEPELKA and W. PODROUŽEK (*Rec. trav. chim.*, 1925, **44**, 416—424).—The composition of the precipitate obtained by the interaction of colourless ammonium sulphide solution and ferric salt solutions (in an atmosphere free from oxygen) is investigated. The composition of the precipitate depends on the hydrogen-ion concentration, and therefore on the iron salt employed, the concentrations of the solutions, and the velocity of addition. Concentrated ferric salt solutions and very dilute solutions of ammonium sulphide give a mixture of ferrous sulphide and free sulphur, the reaction occurring in acid medium and the ferric ion attaining an oxidation potential sufficiently high to oxidise the sulphide ion of the ammonium sulphide. If the ferric salt be precipitated with a concentrated solution of ammonium sulphide (ordinary analytical conditions), the hydrogen-ion concentration falls below the necessary minimum before the reaction is complete, and the precipitate consists of a mixture of ferrous and ferric sulphides and free sulphur. The free sulphur cannot be abstracted in stoichiometric amount because of the presence of water (probably of hydration) which cannot be removed by washing the precipitate with alcohol. Very concentrated solutions of ammonium sulphide and dilute ferric salt solutions (and therefore the slow addition of the ferric salt solution to the ammonium sulphide) yield only ferric sulphide. If all the ferric salt is not separated from the solution the ferric sulphide is unstable and undergoes the spontaneous reaction:  $\text{Fe}_2\text{S}_3 = \text{FeS} + \text{FeS}_2$  (cf. Mecklenburg and Rodt, A., 1918, ii, 167), and the ferrous sulphide then reacts with the surplus of ferric ions:  $2\text{FeS} + 2\text{Fe}_2(\text{SO}_4)_3 = 6\text{FeSO}_4 + 2\text{S}$  (cf. Budnikov and Krause, A., 1922, ii, 782).

J. W. B.

**Potassium Chlororuthenates and the Co-ordination Number of Ruthenium.** S. H. C. BRIGGS (*J. Chem. Soc.*, 1925, **127**, 1042—1048).—In contradiction to the co-ordination theory, apparently isomeric forms of the compound  $\text{K}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$ , were reported by Howe (A., 1902, ii, 86) and by Miolati and Tagiuri (A., 1901, ii, 246), and this discrepancy is examined. According to the conditions, the addition of potassium chloride to a cold acidified solution of ruthenium trichloride results in the formation of one or both of the two compounds  $\text{K}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$  and  $2\text{K}_2\text{RuCl}_5 \cdot 3\text{H}_2\text{O}$ , both of which belong to Miolati's series, and give yellow solutions unaffected by chlorine or bromine vapour. The only salt of Howe's series has composition  $2\text{K}_2\text{RuCl}_5 \cdot 3\text{H}_2\text{O}$ , and is prepared either by the action of alcohol and hydrochloric acid on Miolati's salt or on a mixture of ruthenium trichloride and potassium chloride. In either case, the mixture is boiled, the alcohol distilled off, and the

solution kept for 1 week before being evaporated to crystallisation. Howe's salt gives an intensely black coloration with chlorine or bromine, the colour becoming yellow after prolonged action, and Miolati's salt can then be isolated from the yellow solution. A hot acidified solution of Howe's salt is oxidised on exposure to air, yielding a compound,  $K_2RuCl_5 \cdot K_2RuCl_5OH$ . These compounds require a higher co-ordination number than 6, and 8 is the most probable value. W. H.-R.

**Intermediate Compound of High Molecular Weight in the Decomposition of  $[Pt\ en_2]I_2$  by Acids.** A. SCHLEICHER and W. SCHMITZ (*Z. anorg. Chem.*, 1925, **142**, 367—372; cf. A., 1923, i, 1120).—By the treatment of  $[Pt\ en_2]I_2$  with dilute sulphuric acid a compound is obtained to which the structural formula



is assigned. Simultaneously precipitated iodine leads to decomposition to platinum iodide and the formation of ethylenediamine sulphate, a reaction brought about immediately by strong acids. The propylenediamine compound behaves similarly. L. J. H.

**Preparation of Dust-free Liquids by Distillation.** J. D. GARRARD (*Trans. Roy. Soc. Canada*, 1924, [iii], **18**, III, 126—127).—An investigation of the conditions under which dust-free water may be obtained by distillation in a vacuum without ebullition shows that, provided "bumping" be avoided, neither the temperature of distillation nor the temperature difference between the two bulbs employed as distillation vessel and receiver has any appreciable effect on the number of motes in the distillate, and the distillation bulb may safely be taken to complete dryness. "Steaming-out" is the most satisfactory method of cleaning prior to filling. Determinations of the scattering of light in water prepared in various types of glass show that whereas the use of soft soda, Pyrex, or Jena ware yields sensibly identical values, water obtained in lead-glass apparatus has a scattering power 20—40% higher. The dust-free water is invariably contaminated with particles on shaking even after agitation, rinsing back, and redistilling as often as twenty times. J. S. C.

**Purification and M. P. of Potassium and Sodium Cyanides.** GRANDADAM (*Compt. rend.*, 1925, **180**, 1598—1599; cf. this vol., 419).—Neutralisation of hydrocyanic acid by alcoholic potassium hydroxide results in a product which is only 99% pure. A better product is obtained by purifying the commercial product (95%) in an absolutely anhydrous medium. Fractional vacuum distillation was unsatisfactory (Bucher, *J. Ind. Eng. Chem.*, 1917, **9**, 233). In opposition to Bronn, the alkali cyanides are appreciably soluble in liquid ammonia at  $-33.5^\circ$  (roughly 4%). The usual impurities (carbonate, cyanate, hydroxide) are much less soluble. Recrystallisation from anhydrous ammonia gave products 99.9% pure by

determination with silver. The only two ordinary metals in the presence of which this degree of purity could be maintained were silver and gold. No reaction occurred in the absence of oxygen and moisture. The gold-silver couple possesses feeble thermo-electric properties, but this difficulty was overcome by the aid of a very sensitive galvanometer. The m. p. found were, sodium cyanide  $563.7 \pm 0.3^\circ$ ; potassium cyanide  $634.5 \pm 1^\circ$ . R. A. M.

**Formation of Aluminium Borides.** H. FUNK (*Z. anorg. Chem.*, 1925, **142**, 269—279).—Mixtures of aluminium turnings, magnesium powder, sulphur, and boron trioxide were heated in a crucible lined with aluminium oxide to which a small proportion of pipe-clay was added as binding material. From the regulus crystals of aluminium borides could be obtained. On melting these the liquid formed two layers, the upper layer yielding mainly crystals of the formula  $AlB_2$ . Crystals of composition closely approximating to  $AlB_{12}$  were also obtained. High temperature and excess of boron favour the formation of the latter, low temperature and excess of aluminium the former. L. J. H.

**Preparation and Properties of Carbides.** E. FRIEDERICH and L. SITTIG (*Z. anorg. Chem.*, 1925, **144**, 169—189).—Carbides of titanium, zirconium, vanadium, tantalum, and niobium were prepared pure by heating the oxides with the calculated weights of carbon at temperatures of  $1100^\circ$  to  $1900^\circ$ ; impure *scandium carbide* was obtained by fusing the oxide-carbon mixture at  $3000^\circ$  and probably has the formula  $Sc_4C_3$ . Carbides of molybdenum, tungsten, and silicon were prepared from the metals. Melting points were determined by measuring the energy radiated at the m. p. (cf. this vol., ii, 419) or with an optical pyrometer; those of niobium and tantalum carbides,  $4000$ — $4100^\circ$ , are the highest recorded for chemical compounds. All the above carbides, except that of silicon, are good conductors of electricity. A. G.

**Separation of Zirconium from its Ores as Phosphate.** J. H. DE BOER [with A. E. VAN ARKEL] (*Z. anorg. Chem.*, 1925, **144**, 190—196).—For the separation of zirconium, the ore is fused with potassium hydrogen sulphate, the fused mass extracted with water, and the metals precipitated as hydroxides and redissolved in concentrated hydrochloric acid. From the strongly acid solution zirconium is precipitated as the phosphate,  $Zr(HPO_4)_2$ , and is thereby separated from all other metals except hafnium. The phosphate is readily washed by decantation with hydrochloric acid and water and may then be dissolved in hydrofluoric acid and the zirconium reprecipitated as hydroxide. Similarly, hafnium may be isolated, and zirconium and hafnium may probably be separated by utilising the different solubilities of the complex acids formed when the phosphates are dissolved in hydrofluoric acid. A. G.

**Generation of Hydrogen Sulphide.** A. HENWOOD, R. M. GAREY, W. GOLDBERG, and E. FIELD (*J. Franklin Inst.*, 1925, **199**, 685—686).—A copious supply of pure hydrogen sulphide may be obtained by gently heating a mixture of sulphur and paraffin wax.



Removal of the spent charge is facilitated by the previous admixture of ignited asbestos. F. G. T.

**Production of Ozone by Silent Discharge at Low Pressures.** E. WARBURG and W. RUMP (*Z. Physik*, 1925, **32**, 245—251).—Siemens tubes were used in which the passages for the gas varied from 1 to 3.5 mm. in width. The oxygen contained 3.5% of nitrogen, and the potential varied from 5000 to 9000 volts. As the pressure was reduced the current across the tube increased, but the yield of ozone diminished, at first slowly, then more rapidly, and for pressures below 200 mm. it was proportional to the pressure. With air the yield of ozone is greater than the value corresponding with the partial pressure of the oxygen. E. B. L.

**Theory of Chemical Action in Siemens Ozone Tubes.** E. WARBURG (*Z. Physik*, 1925, **32**, 252—261).—The problem is treated as one of ionisation by collision, and it is assumed that negative ions are all electrons and that positive ions are oxygen molecules. Calculation shows that 6 to 9% of the electron impacts and very few of the collisions of the positive ions produce ozone. As the number of impacts is inversely proportional to the free path it is directly proportional to the pressure, thus accounting for the reduced yield when the pressure is reduced (cf. preceding abstract). The theory does not account satisfactorily for the effect of width of the layer of gas nor for the inefficiency of high-frequency alternating current. E. B. L.

[Ultra-balance.] W. H. F. KUHLMANN (*Ber.*, 1925, **58**, [B], 961).—A comment on the communication of Holtz and Kuhlmann (this vol., ii, 319). H. W.

**Calcspars Lenses for Intense Polarised Light.** W. SCHÜTZ (*Z. Physik*, 1925, **32**, 502—504).—When passed through a calcspars lens cut parallel to the optic axis, the ordinary ray forms an image nearer to the lens than that of the extraordinary ray. The former can be blocked out and the latter used as a source of polarised light. Still more effective is a combination of two lenses which may be made to act either as a parallel plate or as a diverging lens for one ray while converging the other. As the ratio of the refractive indices of the two rays varies but slightly with the wave-length, the one system can be used throughout the spectrum. E. B. L.

**Photographic Plates for Detection of Mass Rays.** F. W. ASTON (*Proc. Camb. Phil. Soc.*, 1925, **22**, 548—554).—In early work on positive-ray spectra, "landscape" plates, Schumann plates made by the original method, and "half-tone" plates were successively used. Very slight changes in the gelatin employed in the emulsion affect the sensitivity of plates to mass-rays. Emulsions containing much gelatin are very insensitive to the mass-rays of the heavier elements, and in studying these it was finally found necessary to "schumannise" the "half-tone" plates by dissolving away the gelatin in sulphuric acid. The details of this somewhat difficult procedure

are given. The sensitivity of the plates so prepared is very variable and cannot be completely controlled, but at their best they are very sensitive. S. B.

**Constant-level Water Baths.** H. J. WING (*Ind. Eng. Chem.*, 1925, **17**, 630).—An easily constructed modification of Brooks' apparatus (cf. A., 1924, ii, 669) may be made by using a Gooch crucible filtering tube, a small wide bottle, etc., as the main part, and four suitable glass tubes. The amount of water entering must not be greater than can be carried off by the fall tube, which should empty as far below the water surface as possible, and not be large enough to allow the back passage of air. The overflow tube must be longer than that which carries off the excess water from the bath.

D. G. H.

**Micro-furnace for High Magnifications.** H. S. ROBERTS and T. STADNICHENKO (*J. Opt. Soc. Amer.*, 1925, **10**, 605—608).—To permit the use of a 16-mm. objective, a microscope stage furnace was constructed, the heating element of which was a doubled strip of nichrome ribbon. The charge was inserted into the fold of the heater between two strips of silica glass. Oxidation was prevented by the circulation of helium through the furnace. A current of 40 amp. through the heater produced a temperature of 800°.

F. G. T.

**Vacuum Door.** R. F. MEHL and D. P. SMITH (*Ind. Eng. Chem.*, 1925, **17**, 598).—An inner steel tube and a surrounding glass tube stand in mercury. The outer tube is prolonged at the top into a bulb connected to the vacuum system and containing the plugged end of the steel tube together with the section just below, bored with small holes. Evacuation raises the mercury level in both tubes to barometric height, which is just below the bulb, and a slow stream of the gas to be admitted to the system is bubbled up the steel tube. Mercury and gas are discharged into the bulb, and the mercury level quickly adjusts itself to the new pressure.

D. G. H.

**Laboratory Pump.** D. H. CAMERON (*Ind. Eng. Chem.*, 1925, **17**, 585).—The circulating liquid flows by gravity to the beaker containing the inlet valve of the pump which is operated by suction from a water vacuum pump. The pump consists of a vertical glass cylinder with a check valve at the bottom (cf. A., 1923, ii, 65) and connected at the top with the vacuum system, and also by means of an inverted U-tube and vertical tubing, to a flexible rubber tube carrying the short-stemmed inlet funnel. This is provided with a cork float and is clamped so that it swings in the beaker with the altering liquid level. When air is no longer free to pass through the inlet valve, liquid is drawn in until suction is broken by the level in the beaker falling below the upper edge of the funnel; air is then again admitted, the check valve opens, and the liquid is discharged from the pump by gravity.

D. G. H.

**Use of Long Mercury Manometers.** E. SWAN (*J. Amer. Chem. Soc.*, 1925, **47**, 1341—1342).—A method is given for the construction of a mercury manometer.

J. S. C.

**Improved Fischer Vacuum Fractionator.** L. SATTLER (*Ind. Eng. Chem.*, 1925, **17**, 583).—The chief modifications consist in two traps to prevent the distillate from being carried into the vacuum pump, and a reservoir in which the distillate collects during the changing of the receiver, whilst strain is removed from the apparatus by introduction of a coil between two stopcocks. D. G. H.

**Microturbidimeter.** O. E. CONKLIN (*J. Opt. Soc. Amer.*, 1925, **10**, 573—580).—Rapid measurements of the comparative turbidities of small amounts of liquids may be made with a microscope cell consisting of a plano-convex lens placed convex side downwards on a piece of plate glass. The sample fills the space between these, its thickness increasing outwardly from the point of contact. The cell is placed over an electric lamp having a straight filament, so that the filament crosses the point of contact. For a constant current consumption of the lamp, the length of filament visible through the cell is inversely proportional to the square root of the turbidity of the liquid. A piece of flashed opal glass in which a concave lens has been ground just cutting through the opal coating is used as a turbidity standard. A lever device is described for measuring the length of the visible filament in the absence of a stage micrometer. For photographic emulsions the turbidity is proportional to the concentration of the silver halide. The relative and specific turbidities of a number of fluids are compared, measurements being reproducible to within 2%. F. G. T.

**Automatic Devices for Extracting Alkaloidal Solutions.** S. PALKIN, A. G. MURRAY, and H. R. WATKINS (*Ind. Eng. Chem.*, 1925, **17**, 612—614).—Aqueous solutions may be extracted with an immiscible solvent by connecting the solvent boiling flask with the side arm of the tubular extractor which contains the solution to be extracted. In the case of heavy solvents a long wide tube open at each end is employed, whilst for light solvents a long funnel tube provided at the bottom with small holes is placed through the two layers of liquid, projecting well above them. Substances more difficult of extraction demand rather more complicated apparatus in which the solvent enters the liquid wholly or partly in the form of vapour. D. G. H.

**Modified Soxhlet Extraction Apparatus.** B. KÖHLER (*Collegium*, 1925, 187—188).—The apparatus consists of a small squat flask fitted with a wide tube and ground glass connexion. The tube is bent at right angles and passes into the upper portion of the Soxhlet receptacle which contains the material to be extracted, and is fitted with condenser and ground glass connexion. From the bottom of the receptacle, a siphon tube leads back to the flask. The end of the siphon tube can be attached to a filter-pump after extracting the material and the extracted material can be recovered quantitatively. D. W.

**Discovery and Properties of Hafnium.** G. HEVESY (*Chem. Reviews*, 1925, **2**, 1—41).

## Mineralogical Chemistry.

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**Structure of Iron-Nickel Meteorites.** R. VOGEL (*Z. anorg. Chem.*, 1925, **142**, 193—228).—There is a break in the composition curve of mixed crystals of iron and nickel at 1455°, corresponding with the  $\delta$ — $\gamma$  inversion. At the transition point the  $\delta$ -mixed crystals contain 6%, and the  $\gamma$ -mixed crystals 30% Ni. The structure of the meteoric material does not differ essentially from that of synthetic alloys. Kamazite and taenite are respectively the  $\delta$ - and  $\gamma$ -mixed crystals, with their nickel content variable as a result of supersaturation. The former is deposited primarily from the fused mass, the latter mainly secondarily as a result of the phase change at the transition point. Plessite consists of supercooled, supersaturated crystals, either from the fused mass as a whole or, more usually, from the mass remaining after the separation of the kamazite. All these structures are unstable at the ordinary temperature and are converted, by suitable annealing, into homogeneous  $\gamma$ -mixed crystals, the rate of conversion depending on the nickel content as well as on the temperature, being faster for the alloys poorer in nickel. Impurities also greatly affect the rate of conversion. Etching figures are discussed in relation to structure, and a system of classification of the meteoric alloys is offered. L. J. H.

**Lead Sulphobismuthite of Volcanic Origin.** F. ZAMBONINI, O. DE FIORE, and G. CAROBBI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1925, [iii], **31**, 24—29).—A crystalline mineral, for which the name cannizzarite is proposed, has formed since 1921 in the lower parts of fumaroles on Vulcano (Isole Eolie, Lipari Islands), where the emission of acid volcanic gases is greatest and access of air is prevented. The temperature of the region is 550—615°. The crystallographic constants were not determined accurately, but the mineral appears to be of rhombic habit, and isogonal with bismuthinite and antimonite in the 001 zone.  $d^{10}$  6.54. The analysis corresponds with the formula  $\text{PbS}_2\text{Bi}_2\text{S}_3$ . It is probably formed by the action at high temperatures of hydrogen sulphide on the chlorides of bismuth and lead. F. G. T.

**Properties and Occurrence of Zeolites.** O. WEIGEL (*Sitzungsber. Ges. Beförder. ges. Naturwiss. Marburg*, 1924, 73—101; from *Chem. Zentr.*, 1924, ii, 2239).—In the formation of zeolites, the solvent remains within the interstices of a comparatively rigid silicate lattice without participating in its structure. The atoms of the silicate lattice lose energy, necessary for overcoming the internal pressure of the solvent, which serves for the formation of the lattice. The lattice on account of its rigidity remains unaffected under different conditions, whereby the energy of internal pressure becomes free, so that saturation by adsorption of other substances is possible. The readiness with which base exchange can take place is explained by the weakening of the linkings in the silicate lattice. The re-

lationship between temperature, vapour pressure, and the content of adsorbed molecules may be expressed by a modification of van der Waals' equation:  $n = n/b - R(T - T_s)v^2/(v - nb)\sqrt{aa'}$ , where  $n$  is the number of molecules adsorbed by each silicate molecule,  $T_s$  is the temperature corresponding with the actual saturation pressure of the liquid phase of the adsorbed substance in the region of the adsorbing crystal, and  $R$ ,  $T$ ,  $v$ ,  $a$ , and  $b$  have their usual significance. Experimental data gave good agreement with results calculated from the equation.

G. W. R.

**Combination of Water in the Zeolites.** V. ROTHMUND (*Rec. trav. chim.*, 1925, **44**, 329—339).—A theoretical paper in which various views concerning the manner in which water is combined in the zeolites are critically examined and discussed. Examination of the vapour-pressure curves to determine whether definite hydrates exist has led to opposite conclusions in the hands of different investigators, some (Damour, Friedal, Tammann, Rinne) obtaining a continuous curve, others (Beutell and Blaschke) obtaining a "step" curve denoting the existence of definite hydrates. In the zeolites Böhm has shown that the loss and readsorption of water is not reversible, a "hysteresis" lag being observed over certain temperature ranges. Theories of absorption and solid solution are discussed and in this connexion it is noted that the dehydrated zeolites can reabsorb, in place of water, alcohol, bromine, iodine, etc. or ammonia, hydrogen, nitrogen, methane, and other gases (ammonia being most strongly absorbed), the quantity absorbed being of the same order of magnitude as in the case of charcoal and governed by the usual formula,  $v = \alpha p^{1/n}$ . In spite of their crystalline nature the zeolites closely resemble colloidal substances such as silica gel and permutite, and the author suggests that the processes of absorption of water by all "swelling" substances such as starch, albumin, etc. are similar phenomena.

J. W. B.

**Analysis of Alvite.** S. BEDR-CHAN (*Z. anorg. Chem.*, 1925, **144**, 304—306).—A sample of pure alvite had the following composition: 25.65%  $\text{SiO}_2$ , 0.63%  $\text{TiO}_2 + \text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ , 2.08%  $\text{CaO}$ , 1.11%  $\text{MgO}$ , 2.05%  $\text{ThO}_2$ , 0.71%  $\text{Ce}_2\text{O}_3$  etc., 7.57%  $\text{Fe}_2\text{O}_3$ , 41.92%  $\text{ZrO}_2$ , 4.66%  $\text{HfO}_2$ , 4.55%  $\text{BeO} + \text{Al}_2\text{O}_3$ , 6.30%  $\text{H}_2\text{O}$ , total 97.23%. The hafnia was determined by X-ray analysis and the other constituents by the usual methods.

A. R. P.

### Analytical Chemistry.

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**Apparatus for Accurate Analysis of Small Quantities of Gas.** D. S. CHAMBERLIN and D. M. NEWITT (*Ind. Eng. Chem.*, 1925, **17**, 621).—An improved form of the Bone and Wheeler gas analysis apparatus (A., 1908, ii, 221) is described, with which samples of from 1 to 5 c.c. of gas can be analysed with an accuracy of 0.01%.  
M. B. D.

**Automatic Burette and Flask for Standard Alkali Solutions.**

H. R. McMILLIN (*Ind. Eng. Chem.*, 1925, **17**, 592).—The burette is connected by a 3-way tap to a "pyrex" glass flask containing the standard solution. The flask is provided with a "suberite" ring, and evaporation from it is checked by means of potassium hydroxide solution, which together with a calcium chloride tube also excludes carbon dioxide. The apparatus is free from attachment and can readily be shaken.

D. G. H.

**Quantitative Spectral Analysis.** W. GERLACH (*Z. anorg.*

*Chem.*, 1925, **142**, 383—398).—Contrary to statements in the literature, the "ultimate" rays (last observed lines of an impurity as it is continuously removed) are the strongest under the conditions of exposure. Quantitative measurements of the amount of impurity remaining are possible by comparison of the intensity of these lines with that of neighbouring lines of the main substance, but standard exposures of specimens of known composition with the same principal substance are essential.

L. J. H.

**Graphic Comparison of Potential Scales and Electrode Potentials.** L. J. BIRCHER (*Ind. Eng. Chem.*, 1925, **17**, 622).—

The graphic representation of typical potential scales as vertical lines and the single potentials of typical half-cells as horizontal lines, with numbers indicating the potential values of the latter on the three standard scales, provides a sufficient number of typical junctions to enable others to be placed.

D. G. H.

**Electrometric Titration.** J. C. BRÜNNICH (*Ind. Eng. Chem.*, 1925, **17**, 631—632).—Electrometric titrations can be made without the use of hydrogen gas or a calomel cell by combining a pure graphite electrode with a platinum spiral electrode through a millivoltmeter. The potential given by this arrangement is approximately zero in neutral solutions, +0.18 volt in 0.01*N*-acid, and -0.13 volt in 0.01*N*-alkali.

M. B. D.

**Rapid Electroanalysis. Separations by Graded Potentials.**

A. LASSIEUR (*Ann. Chim.*, 1925, [x], **3**, 235—324).—A simple apparatus is described for rapid electroanalysis which permits of the use of graduated potentials. The experimental conditions are worked out for the determination of copper, bismuth, antimony, lead, and tin, and certain mixtures of these (cf. A., 1924, ii, 15, 568; this vol., ii, 159). Electrodes coated with antimony can retain lead when the concentration of the latter in the electrolyte is 2 g. per litre. Stannic chloride is reduced during the deposition of tin when the potential difference is 320 millivolts or more; antimony catalyses the reaction. The complex formed by adding hydrofluoric acid to an antimonious solution which has been oxidised by potassium chlorate is partly reduced on the passage of the current. This does not occur when potassium dichromate is used as the oxidising agent. [Cf. B., July 24th.]

S. K. T.

**Calomel Electrodes.** C. J. SCHOLLENBERGER (*Ind. Eng. Chem.*, 1925, **17**, 649).—A satisfactory calomel electrode may be

made from a separating funnel by removing the stopcock, fusing on a length of glass tubing, inserting an inner tube projecting into the body of the funnel, and out through the stem. In this is placed the potassium chloride and the tube is jointed to the stem and plugged with a ground-in rod. This stopper is lightly pressed upon when the cork is inserted in the funnel. Calomel and mercury are placed in the funnel and contact with the mercury is established by means of a bent tube in the cork. [Cf. *B.*, July 24th.] D. G. H.

**Calomel Half Cells for Industrial Hydrogen-ion Measurements.** H. C. PARKER and C. A. DANNER (Ind. Eng. Chem., 1925, 17, 637—639).—Four easily controlled types of cells are described, the first for laboratory use with a ground glass joint sealed with mercury, the second a flow type with porous cup, the third a combined hydrogen electrode and calomel half cell, and the fourth a rugged industrial half cell entirely surrounded with bakelite casing. [Cf. *B.*, July 24th.] D. G. H.

**Salt Error of Cresol-red.** W. D. RAMAGE and R. C. MILLER (*J. Amer. Chem. Soc.*, 1925, 47, 1230—1235).—The salt error of cresol-red in solutions containing 5 to 35 parts per 1000 of sea-salts has been determined from a comparison of the Sørensen values of samples of sea-water of known salinity as determined by electrometric and colorimetric methods using this indicator. The correction to be applied to the colorimetric determinations over the range of salinity indicated varies from  $-0.11$  to  $-0.27$  Sørensen unit.

J. S. C.

**Detection and Determination of Chloride, Bromide, and Thiocyanate in the Presence of Cyanide.** E. SCHULEK (*Z. anal. Chem.*, 1925, 66, 169).—The priority of Polstorff and Meyer's formaldehyde method (*A.*, 1912, ii, 988) is acknowledged, but priority is claimed for the boric acid method previously described (this vol., ii, 432).

A. R. P.

**Determination of Iodide.** E. SCHULEK (*Z. anal. Chem.*, 1925, 66, 161—169).—The methods of Winkler (*A.*, 1916, ii, 109) and of Bugarszky and Horváth (*A.*, 1909, ii, 932) for the determination of iodide in the presence of chloride and bromide have been modified so that the whole operation can be conducted at the ordinary temperature. When much iodide is present together with bromide, the very faintly acid solution is treated with chlorine water until bromine begins to be displaced, and the liberated bromine is removed by addition of a 5% solution of phenol. The iodate formed is determined iodometrically after addition of potassium iodide and phosphoric acid. If only a small amount of iodide is present bromine water or alkali hypobromite may be used for the oxidation. The presence of magnesium or calcium salts interferes with the reaction. [Cf. *B.*, 1925, 543.]

A. R. P.

**Action of Some Oxidising Agents on Sulphate and its [Volumetric] Determination with Iodate.** W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1925, 47, 1319—1325; cf. *J. Ind. Eng. Chem.*, 1922, 14, 1162).—Previous work is continued. The amounts of



bromate and dichromate are less than those required for the complete conversion of sulphite into sulphate. This is probably due to the formation of some dithionic acid which resists further oxidation. Iodate completely oxidises to sulphate, and this fact permits of the accurate determination of sulphites by this oxidant. Solutions of potassium iodate maintain their concentration over indefinite periods of time. An electrometric method of end-point determination may be used for the determination of sulphites in coloured solutions. J. S. C.

**Nessler's Reagent Without Potassium Iodide.** L. W. WINKLER (*Z. Unters. Nahr. Genussm.*, 1925, **49**, 163—165).—The modified reagent is prepared by dissolving mercuric iodide in a solution containing potassium bromide and sodium hydroxide, preferably made with tap-water of medium hardness. With natural waters, the reagent may cause some precipitation. To prevent this, use is made of a second solution containing sodium potassium tartrate and sodium hydroxide in which mercuric iodide is dissolved. A. G. P.

**Iodometric Methods Depending on the Formation and Determination of Cyanogen Iodide. III.** R. LANG (*Z. anorg. Chem.*, 1925, **142**, 280—298; cf. below).—The method is extended to the determination of hydrazine and hydroxylamine (separately or together), selenium, hydrogen peroxide, cyanides, thiocyanates, and ferrocyanides. The last three may be determined in the presence of each other. L. J. H.

**Determination of Oxides of Nitrogen (except Nitrous Oxide) in Small Concentration in the Products of Combustion of Coal Gas and in Air.** A. G. FRANCIS and A. T. PARSONS (*Analyst*, 1925, **50**, 262—272).—The absorption of oxides of nitrogen in large volumes of air and products of combustion by solutions of sodium hydroxide and hydrogen peroxide (Allison, Parker, and Jones, *U.S. Bur. Mines, Tech. Paper* 249) leads to formation of nitrite. Oxidation is complete when the gases are shaken in a closed bottle with acidified hydrogen peroxide for 3 hrs. Proportions of less than 1 in  $10^6$  are determined by passing a measured volume of gases through tubes immersed in liquid air, and treating the condensate with the same hydrogen peroxide mixture. The normal proportion of nitric oxide in the air was found to be 1—2 in  $10^8$ , falling to 0.3 after heavy rain, and rising to 15—16 during fog. S. I. L.

**Iodometric Methods Depending on the Formation and Determination of Cyanogen Iodide. II.** R. LANG (*Z. anorg. Chem.*, 1925, **142**, 229—256).—Previous work (A., 1922, ii, 782) is extended by the use of iodine monochloride and hypiodous acid as oxidising agents, the iodine liberated being determined by titration with potassium iodate in acid solution in the presence of a cyanide. Antimony, arsenic, copper, and iron, or mixtures of the last three together, may be titrated in this way. The modifications necessary in the presence of other heavy metals, both for these reactions and

in the direct determination of iodide, are described, but the details are too numerous for abstraction.

L. J. H.

**Theory of the Titration of Boric Acid.** M. ČIKRTOVÁ and K. ŠANDERA (*Chem. Listy*, 1925, **19**, 179—182).—Boric acid may be titrated accurately with sodium hydroxide in the presence of a saturated solution of certain inorganic salts, such as calcium or lithium chloride, which are strong dehydrating agents, as is also glycerol, which is commonly added to the solution in order to increase the strength of the acid. This action appears therefore to be due to the dehydration of boric acid and not to the formation of complexes.

A. R. P.

**Determination of Boric Acid in Presence of Aluminium, Iron, or Chromium Salts.** H. FUNK and H. WINTER (*Z. anorg. Chem.*, 1925, **142**, 257—268).—The removal of aluminium, chromium, or iron is necessary before boric acid can be determined by the method of Rosenblatt and Gooch (*A.*, 1887, ii, 299), but precipitation with alkali carries down some boron which cannot be removed. A successful separation is obtained if iron be precipitated as phosphate from slightly acid solution, and chromium is precipitated as hydroxide by the addition of iodide and iodate. Both methods are satisfactory for aluminium.

L. J. H.

**Apparatus for Determining Carbon Dioxide.** W. W. REED (*Chem. and Ind.*, 1925, **44**, 422).—In place of washing out the carbon dioxide by aspirating air through the apparatus, the gas is withdrawn by suction from the bottom of the flask, the calcium chloride tube being sealed to another tube, the height of which above the liquid is adjustable.

R. B.

**Determination of Dissolved Carbon Dioxide.** R. LEGENDRE (*Compt. rend.*, 1925, **180**, 1527—1529).—A critical account of various methods of determination of dissolved carbon dioxide (cf. Winkler, *A.*, 1904, ii, 215; 1912, ii, 1210; Haas, *A.*, 1917, i, 433; Osterhout and Haas, *A.*, 1918, ii, 24; Hall, *A.*, 1923, ii, 507; Shipley and McHaffie, *A.*, 1923, ii, 649; Lehmann and Reuss, *A.*, 1923, ii, 697; Spoehr and McGee, *A.*, 1924, ii, 275). In comparing the dissolved carbon dioxide content of different liquids it is of value to find the amount of alkali necessary to lower the hydrogen-ion concentration to a fixed level. The method of comparison chosen is that of passing air through the different samples of water maintained at a definite hydrogen-ion concentration and determining the amount of carbon dioxide carried over. This method is of use in analysing biological fluids and waters, and in investigating the respiratory exchange of aquatic animals.

L. F. H.

**Separate Determination of Potassium and Sodium in Urine.** O. VON DEHN.—(See i, 855.)

**Quantitative Variations of Homogeneous Mixtures of Two Salts and a New Indirect Method of Quantitative Analysis.** G. COMELLA (*Annali Chim. Appl.*, 1925, **15**, 123—136).—A method is described for calculating from the titre of a solution containing

two salts, such as sodium and potassium chlorides, the proportions of the two in the mixture. *N*-Solutions of sodium and potassium chlorides contain respectively 58.46 g. and 74.56 g. of the salt per litre, and replacement of 0.1 c.c. of *N*-sodium chloride by 0.1 c.c. of *N*-potassium chloride decreases the amount of sodium chloride present by 0.005846 g., increases that of potassium chloride by 0.007456 g., and increases the sum of the two by 0.00161 g.; these quantities may be regarded as the common differences of three arithmetic progressions. Thus, if 63.29 g. of the mixed chlorides per litre are found to give a *N*-solution, the corresponding terms in these progressions will be in position 3001, since  $(63.29 - 58.46) / 0.00161 + 1 = 3001$ . The amount of sodium chloride in 63.29 g. of the mixture is hence  $58.46 - (3000 \times 0.005846) = 40.922$  g., and that of the potassium chloride,  $3000 \times 0.007456 = 22.368$  g. T. H. P.

**Nephelometric Determination of Calcium and Magnesium.** L. KRISS.—(See i, 852.)

**Determination of Small Quantities of Magnesium as Magnesium Ammonium Phosphate in Presence of Much Aluminium.** G. JANDER, E. WENDEHORST, and B. WEBER (*Z. anorg. Chem.*, 1925, **142**, 329—334).—Contrary to Hahn (this vol., ii, 69), magnesium may be accurately determined as magnesium ammonium phosphate in presence of large quantities of aluminium (held in solution by tartaric acid), but the precipitate requires several days to form. L. J. H.

**Quadrivalent Lead.** [Determination of Lead and Sulphur.] J. ŠTÉRBA-BOEHM and M. AUERSPERGROVÁ.—(See ii, 699.)

**Simultaneous Electrolytic Determination of Copper and Lead.** H. BILTZ (*Ber.*, 1925, **58**, [B], 913—914).—Difficulties arise in the simultaneous anodic deposition of lead dioxide and cathodic separation of copper from solutions of the metals in nitric acid owing to the solvent action of nitrous acid on the dioxide. They may be overcome by electrolysis initially in moderately concentrated acid solution to which carbamide is added previously to dilution for completion of electrolysis; the process is continued until the copper has been deposited completely. H. W.

**Qualitative Tests for Copper, Iron, and Cobalt.** M. L. NICHOLS and S. R. COOPER (*J. Amer. Chem. Soc.*, 1925, **47**, 1268—1270).—Aqueous solutions of copper, iron, and cobalt salts give respectively brown, green, and orange-red precipitates (or colorations if in very dilute solution) with aqueous solutions of dinitrosoresorcinol. In neutral solution the reagent is capable of detecting 0.0040 mg. of copper, 0.0035 mg. of iron, and 0.0033 mg. of cobalt in 1 c.c. of solution. In dilute acid solution, the sensitiveness of the tests for cobalt and iron is increased by addition of sodium acetate. When testing for cobalt in presence of an excess of nickel, the concentration of the latter should be first reduced by treatment with dimethylglyoxime. J. S. C.

**Titration of Mercury with Potassium Cyanide and Jellinek's Titration of Weakly Dissociated Salts.** E. RUPP [with W. WEGNER and P. MAIHS] (*Z. anorg. Chem.*, 1925, **144**, 313—318).—The statements of Jellinek and Krebs (A., 1923, ii, 871) and of Jellinek and Kühn (A., 1924, ii, 695) that titration of mercuric chloride with potassium cyanide using phenolphthalein as indicator gives results that are 3% too low is shown to be erroneous provided that the cyanide used is pure, *i.e.*, that its cyanogen contents calculated from the argentometric and acidimetric titrations are nearly identical. The low results obtained by Jellinek are ascribed to the presence of free alkali in the cyanide, but correct results may be obtained with this impure cyanide if the mercuric chloride solution is added to an excess of the cyanide solution and the excess then titrated with hydrochloric acid and methyl-orange, or if the cyanide is first rendered neutral to methyl-orange with dilute sulphuric acid. Mercuric chloride may also be determined accurately by addition of dilute hydrocyanic acid to the neutral solution until the liquid has a slight odour, followed by titration of the liberated hydrochloric acid with standard alkali and methyl-orange. The titration of lead nitrate with trisodium arsenite (Jellinek and Kühn, *loc. cit.*) and of ferric chloride with thiosulphate (Jellinek and Vinogradov, A., 1924, ii, 703) both give variable results depending on the concentrations of the reacting substances.  
A. R. P.

**Potentiometric Determination of Cerium.** O. TOMIČEK (*Rec. trav. chim.*, 1925, **44**, 410—415).—A simple potentiometric method for the determination of tervalent cerium consists in the oxidation of the cerous sulphate or chloride in a very concentrated solution of potassium carbonate, in an oxygen-free atmosphere, by titration with potassium ferricyanide solution. About three-quarters of the amount of 0.05 or 0.1N-ferricyanide solution necessary for the reaction,  $2K_3Fe(CN)_6 + K_2CO_3, Ce_2(CO_3)_3 = 2K_4Fe(CN)_6 + 2Ce(CO_3)_2$ , is added to the cerium solution, carbon dioxide passed in until all air is expelled, and potassium carbonate added with continual stirring until the mixture contains 35% of carbonate. The titration is then completed in the manner described by Kolthoff and Tomiček (*ibid.*, 1924, **43**, 775). The sensitivity of the titration is unaltered by the presence of ferric iron, thorium or other cerite earths, and since ferrous iron is more easily oxidised than the tervalent cerium the method permits the simultaneous determination of both metals. The results are accurate to  $\pm 0.2\%$ .  
J. W. B.

**Volumetric Determination of Cerium.** J. ŠTĚRBA-BOEHM and V. MATULA (*Rec. trav. chim.*, 1925, **44**, 400—409).—To obtain satisfactory results for the determination of cerium in the presence of thorium and other rare earths the experimental conditions fully described in the original must be followed exactly. The earths, in the form of sulphates or chlorides, are dissolved in cold water, and a solution of potassium persulphate is added, followed by sodium hydroxide until the hydroxides just begin to be precipitated, then one drop of phenolphthalein, and again sodium hydroxide in excess. Sufficient base must be present to neutralise the sulphuric acid

formed by the reaction,  $\text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} = \text{K}_2\text{SO}_4 + \text{H}_2\text{SO}_4 + \text{O}$ , a slight excess not being objectionable. The solution is boiled for 25 min., cooled, and potassium iodide and hydrochloric acid are added. With gentle mixing, the precipitated hydroxides dissolve, and the liberated iodine is titrated with *N*/40-thiosulphate solution. This yields an approximate result ( $\pm 2\%$  of the actual cerium content), and exact results may now be obtained by using 1.5–2 g. of potassium persulphate (and the appropriate quantity of sodium hydroxide) for each gram of cerium present and regulating the period of ebullition according to the cerium content. When the cerium content is greater than 25% the sample should first be diluted with a small quantity of rare earth sulphates free from cerium. The results are accurate to  $\pm 0.16\%$  and the method is applied to the analysis of several cerium ores. Iron may be determined iodometrically in the presence of cerium if the oxidation be carried out by means of chlorine water in dilute hydrochloric acid solution. [Cf. *B.*, July 24th.] J. W. B.

**Analytical Chemistry of Indium.** J. HEYROVSKÝ (*Chem. Listy*, 1925, **19**, 168–172).—Indium may be deposited from acid or alkaline solutions on a dropping mercury cathode. The reaction is reversible and requires a cathodic potential of  $-0.503$  volt for the deposition of the metal from a molar solution. The method will detect indium in a solution containing as little as 0.01 mg. of metal in 25 c.c. Indium salts yield with excess of potassium or sodium hydroxide solutions of true salts of an acid derived from indium sesquioxide, but the salts are progressively hydrolysed on keeping until the solution contains less than  $0.25 \times 10^{-4}$  g.-equivalent of indium in true solution in *N*-sodium hydroxide. The ionic decomposition product of an alkaline solution of a freshly-prepared specimen of indium hydroxide is  $10^{-33}$  and of an acid solution of an aged specimen  $0.25 \times 10^{-18}$ . A. R. P.

**Separation of Gallium from Aluminium and Iron.** R. FRICKE (*Z. anorg. Chem.*, 1925, **144**, 267–268).—Gallium is not conveniently separated from large amounts of iron or aluminium by precipitating the latter with excess of ammonium hydroxide, but the method may be used when the gallium is nearly pure. A. G.

**Colorimetric Determination of Small Amounts of Iron.** W. B. WALKER (*Analyst*, 1925, **50**, 279–283).—In the thiocyanate method, the use of nitric acid containing nitrous acid is recommended to ensure rapid oxidation of all ferrous compounds, nitrous acid being then oxidised by hydrogen peroxide before addition of thiocyanate. Since phosphates interfere, the ferrocyanide method is to be preferred; nitrous acid should be removed by boiling before addition of the ferrocyanide. S. I. L.

**Electrometric Titration in the Determination of Ferrous and Ferric Iron in Magnetites.** H. R. ADAM (*J. S. Afr. Chem. Inst.*, 1925, **8**, 7–10).—The direct determination of ferric iron is carried out by running a slight excess of standard stannous chloride

solution into the almost boiling ferric iron solution, and titrating back with dichromate or iodine. If dichromate is used, the end-point is determined electrometrically, and the back titration may be continued to determine the total iron, there being two sharp rises of potential, the first when the excess of stannous chloride has been oxidised, and the second when the iron is completely oxidised. Back titration with iodine is simpler, but in this case the electrometric method has no advantage over the use of starch as indicator. The total iron may also be determined in the solution used for the ferrous iron, for after the determination of the latter with dichromate, titration with stannous chloride may be carried out as above. Titanium in solution does not affect the reduction of iron by stannous chloride. B. F.

**Colorimetric Determination of Molybdenum.** E. WENDEHORST (*Z. anorg. Chem.*, 1925, **144**, 319—320).—Hydrogen sulphide is passed into the ammoniacal molybdate solution, which is then acidified and the precipitate collected and roasted to oxide. This is dissolved in ammonia, the solution evaporated to dryness, and the residue dissolved in a known volume of water. An aliquot part of the solution is treated with a quantity of 5% glycerol solution saturated with hydrogen sulphide; 0.2*N*-sulphuric acid is then added drop by drop until the yellow colour reaches its maximum intensity. The colour is compared in a colorimeter with that of a standard solution of molybdenum trioxide treated in a similar manner. A. R. P.

**Separation of Molybdenum from Vanadium as Sulphide.** A. E. STOPPEL, C. F. SIDENER, and P. H. M.-P. BRINTON (*Chem. News*, 1925, **130**, 353—355).—Precipitation of molybdenum as sulphide in a sulphuric acid solution containing vanadium gives good results if the cold solution is saturated with hydrogen sulphide and then heated under pressure. The precipitate contains a few tenths of a mg. of vanadium, but a similar quantity of molybdenum fails to precipitate, so that there is a compensation of errors. If an ammoniacal solution of molybdic and vanadic acids is saturated with hydrogen sulphide and then treated with 2—3 g. of tartaric acid and hydrochloric acid until acid, all the molybdenum is precipitated as sulphide, retaining, however, 1—1.5 mg. of vanadium, which may be removed by reprecipitation. A. R. P.

**Determination and Separation of Rarer Metals from other Metals. V. Separation of Zirconium and Hafnium from Titanium, Cerium, and Thorium.** L. MOSER and R. LESSING (*Monatsh.*, 1924, **45**, 323—337).—Zirconium salts are precipitated by sodium arsenate from boiling hydrochloric acid solutions as a hydrated normal arsenate,  $\text{Zr}_3(\text{AsO}_4)_4$ , whilst from strong nitric acid solutions a zirconyl salt,  $\text{ZrO} \cdot \text{HAsO}_4$ , is obtained which is more easily filtered. Fractional precipitation of a commercial "pure" zirconium preparation, by the latter method, gave fractions in which the equivalent of the metal varied from 98.68 to 90.56, which shows that hafnium is precipitated with zirconium and that its arsenate is still less soluble than that of zirconium. Conditions have been

worked out and tested in detail for the use of this precipitation of zirconium as arsenate in separating it from titanium, cerium, and thorium. In presence of titanium and cerium, an excess of hydrogen peroxide must be present to ensure their conversion into pertitanic acid and cerous salts respectively. The separation from thorium is satisfactory only when the acidity of the solution is adjusted within a narrow range near 1.13*N*-nitric acid.

G. M. B.

**Precipitation of Gold and Silver by Metallic Sulphides.** [Detection of Traces of Gold and Silver in Solution.] A. STEIGMANN (*Chem.-Ztg.*, 1925, 49, 423).—For the detection of traces of gold in a solution, hydrogen peroxide is added followed by solutions containing (a) sodium sulphite and "metol" and (b) sodium sulphite and silver nitrate. The characteristic colour of the colloidal solution of silver obtained from the reagents added is considerably modified by the presence of gold and the colour also develops much more rapidly. Traces of silver may be detected in a solution by the same process, except that the silver nitrate in the reagents is replaced by mercuric chloride.

A. R. P.

**Elementary Analysis of Organic Substances by Combustion with Copper Oxide in a Vacuum.** J. ŠVĚDA and O. PROČKE (*Chem. Listy*, 1925, 19, 163–167).—A small quantity of the substance is introduced in a small platinum boat into a hard glass combustion tube one end of which is packed with copper oxide wire. The tube is then filled with alternate layers of copper oxide and reduced copper obtained from copper oxide wire and finally each end of the tube is plugged with copper gauze. After weighing, the whole is introduced into a silica tube, which is then connected by well fitting stoppers and stopcocks to a manometer, a drying tube containing phosphorus pentoxide, and a Sprengel vacuum pump. After evacuation, the tube is heated at 750–800° in an electric furnace and the gases evolved (carbon dioxide and nitrogen) are withdrawn into a eudiometer for analysis. Hydrogen is determined from the loss in weight of the glass combustion tube and its contents after making allowance for the oxygen required for the combustion of the carbon and for the weight of the substance.

A. R. P.

**Proving Identity of Two Organic Compounds.** E. MURMANN (*Oesterr. Chem.-Ztg.*, 1925, 28, 86–87).—Where very small quantities only are available, the m. p. and behaviour towards a large number of solvents are compared for the substance under examination and the substance with which it is suspected to be identical. Figures are allotted to the behaviour with each solvent, and the succession of these is usually sufficient to prove identity or otherwise.

S. I. L.

**Determination of Alcohol.** M. MARTINI and A. NOURISSON (*Ann. Falsif.*, 1925, 18, 235–237).—The alcohol is distilled into an oxidising potassium dichromate solution, the excess of dichromate reduced by potassium iodide, and the liberated iodine titrated with sodium thiosulphate solution. [Cf. *B.*, 1925, 520.]

D. G. H.

**Micro Determination of Sugar or Reducing Substance in Blood.** L. LORBER.—(See i, 852.)

**Determination of  $\alpha$ -Cellulose.** C. G. SCHWALBE (*Papier-Fabr.*, 1925, **23**, 232—233).—A discussion of Jentgen's method (*Kunststoffe*, 1911, **1**, 165) and various modifications, e.g., washing with sodium hydroxide solution after draining off the first filtrate and the prolongation of the time of treatment. Mechanical kneading is not recommended. [Cf. *B.*, 1925, 539.] J. F. B.

**Determination of Pentosan.** F. W. KLINGSTEDT (*Z. anal. Chem.*, 1925, **66**, 129—160).—All carbohydrates and vegetable substances that give hexoses on hydrolysis yield, on distillation with 12% hydrochloric acid, hydroxymethylfurfuraldehyde and probably also other compounds which form condensation products with phloroglucinol, so that under certain conditions the determination of pentosans by this method will give very erroneous results. The solubilities of the phloroglucides of furfuraldehyde and its derivatives in alcohol vary considerably; thus the methylfurfuraldehyde compound is readily soluble in warm alcohol, even after it has been dried for 8 hours, whilst the furfuraldehyde compound is insoluble after drying, but slightly soluble when moist. Hydroxymethylfurfuraldehyde and *s*-difuryldimethyl ether compounds are almost completely soluble in alcohol when moist, but less soluble when dried. Extraction of a mixed condensation product with alcohol, however, and calculation of the insoluble residue to pentosan invariably yields high results, whether the condensation is carried out at the ordinary temperature or in a warm solution and whether the product is dried or not before extraction. Fairly correct results for pentosan may be obtained by a careful regulation of the distillation, not more than about 150—180 c.c. being collected. When all the furfuraldehyde has distilled, the distillate gives no further green precipitate with a hydrochloric acid solution of phloroglucinol. The condensation should be carried out in cold solutions and the moist precipitate extracted with alcohol. The residue gives the minimum amount of pentosan in the substance tested. [Cf. *B.*, Aug. 7th.] A. R. P.

**Colorimetric Determination of Acetone in Urine.** M. H. P. SITSSEN.—(See i, 855.)

**Determination of Urea in Blood, etc.** P. B. REHBERG, also G. y ROIG and K. HELMHOLZ. (See i, 853.)

**Jaffe's Reaction for Creatinine. II. Effect of Substitution in the Creatinine Molecule and a possible Formula for the Red Tautomeride.** I. GREENWALD.—(See i, 839.)

**Standard Solution for Sahli's Hæmometer.** A. K. J. KOUMANS.—(See i, 851.)

**Determination of Xanthrophyll.** F. M. SCHERTZ.—(See i, 871.)

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## General, Physical, and Inorganic Chemistry.

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**Excitation Maxima for Spectral Lines in the Striæ of the Positive Column of Hydrogen.** E. LAU (*Ann. Physik*, 1925, [iv], 77, 183—194).—Spectrophotometric records have been obtained of the distribution of light-intensity arising from the emission of single lines at various positions in the striæ of the positive column in a hydrogen discharge tube. Similar data have been obtained for the continuous spectrum. An ingenious device was employed to maintain a constant pressure in the stream of hydrogen. The Balmer series lines,  $H\alpha$ ,  $H\beta$ ,  $H\gamma$ , are most intense at different points in the striation. The most important lines in the Fulcher band spectrum, 6430, 6327, 6224, 6121, 6018, and 5656, 5548, 5420, 5302, occur most strongly at different places. The shortest wave-lengths in a band system, *e.g.*, 6018 and 5302, correspond with the smallest electron-velocities. The maximum of the continuous spectrum occurs at the same place for all wave-lengths between 4000 and 5000 Å. The positions of maximum intensity for series lines are reversed when striæ with a lower potential drop are investigated. The probable change of the electron velocity within a striation is only 1 volt. This may mean an acceleration or a retardation according to the type of striation.

The small electron velocity is regarded as due to collisions of electrons with hydrogen molecules. The energy resulting from the loss in velocity reappears as the continuous radiation, which is thus ascribed to a purely collisional mechanism. In the Balmer series and in the continuum, there are two excitation maxima in a double striation, but there is only one maximum for the Fulcher bands. In the first striation from the cathode, whether it be single or double, the lines of the Balmer series (especially  $H\alpha$  and  $H\beta$ ) are much weakened near the cathode. There is no evidence of electrons existing in the positive column with velocities greater than those of the exciting electrons. (Cf. Seeliger and Okubo, *Physikal. Z.*, 1924, 25, 337, who found it necessary to assume that a current of faster electrons traverses the striation.) R. A. M.

**Hydrogen Spectrum of Constant Frequency-difference.** J. W. NICHOLSON (*Month. Not. Roy. Astr. Soc.*, 1925, 85, 656—659).—Among the lines of the secondary spectrum of hydrogen showing a normal Zeeman effect, and therefore probably of atomic origin, a number may be picked out between 3732.25 and 4966.98 Å. which have an approximately constant wave-number difference of 1313. Another large group nearer the red end has a wave-number difference which is nearly the same, namely, 1300. The lines of these two groups, which have certain members in common, are also most characteristically unaffected by the presence of helium. They appear to belong to a series spectrum nearer to the neon than

to the helium type, and they show a certain resemblance to the nebular and to the Wolf-Rayet spectra. Another class of lines previously described (this vol., ii, 468), which show no Zeeman effect, form widely separated bands of molecular origin. M. S. B.

**Hydrogen-like Spectra from the Point of View of the Polarisability of the Atom-core.** E. SCHRÖDINGER (*Ann. Physik*, 1925, [iv], 77, 43—70).—The polarisability of the core of atoms of noble gases has been calculated for the *p*-, *d*-, and *f*-series. It is fairly constant within a series; in many cases it is accurately so. In the same spectrum, the variation from series to series is usually in the sense that the constant polarisability for one series is a multiple of that of another series. The polarisability of the core in outer orbit series may be accepted as fairly constant. Evidence is brought forward showing that the outer orbits of lithium and sodium are weakly bound. The remarkable disturbance of the Bergmann Series for AlII can be explained on the basis of a very great polarisability for exciting frequencies which are smaller than the resonance frequency, and a negative polarisability for frequencies greater than the resonance frequency. This explanation is tentatively extended to the arc spectra of the alkaline earths. All calculations are based on whole number impulse quanta and an attempt is made to state the case for and against this method of treatment. R. A. M.

**Structure of the Band Spectrum of Helium. III. The Doublet Bands.** W. E. CURTIS and R. G. LONG (*Proc. Roy. Soc.*, 1925, A, 108, 513—541; cf. A., 1923, ii, 351).—New data of the doublet bands of helium, which are unique in conforming to a line-series law, have been secured, extending the main series to the eighth member, and their structure has been studied in detail. Previous difficulties of interpretation have been to a large degree overcome. New and much more accurate values of the molecular moments of inertia and separation of the nuclei have been obtained. Support is afforded to Lenz's suggestion (*Verh. d. Phys. Ges.*, 1919, 21, 632) that the structure of the helium molecule may be related to that of the hydrogen molecule. Light is thrown on the nature of the perturbations occurring in two of the bands. The second series of doublets is re-examined, and, although the data are much less extensive, the results of the analysis are closely similar to those obtained from the main series. It is concluded that the two series must originate from the same molecule, but a different radiating electron. L. F. G.

**Characteristic X-Rays from Lithium.** G. K. ROLLEFSON (*Physical Rev.*, 1925, [ii], 25, 740—746).—By photoelectrical determination, values for radiation and ionisation potentials of lithium are, respectively, 39.2, 43.07, 46.0 volts and 48.4 volts. Extension of the Moseley curve for the  $K\alpha$  lines gives, on interpolation, the following wave-lengths: lithium, 286.5 Å; beryllium, 132.8; boron, 74.4; carbon, 49.0; nitrogen, 33.2; oxygen, 24.4; fluorine, 18.6; neon, 14.8 Å. A. A. E.

**Further Spectra Associated with Carbon.** R. C. JOHNSON (*Proc. Roy. Soc.*, 1925, **A**, **108**, 343—355).—The spectra associated with carbon, which are developed in vacuum tubes containing helium and a trace of carbon, have been studied in the ultra-violet. A number of new faint lines are recorded in the region 4000—2400 Å., but it has not been found possible to deduce any general laws governing the alteration of the intensity distribution caused by helium. Several new members of the Comet Tail bands are recorded in the near ultra-violet, and a new spectrum is described which is associated with these bands, and is of similar structure, but degraded in the opposite direction. The new bands lie between 4235 and 3314 Å. Their presence in the cometary spectrum is uncertain. The negative carbon bands were well developed in the same tube, and have been remeasured and arranged in series.

S. B.

**Origin of the Auroral Green Line 5577 Å., and other Spectra Associated with the Aurora Borealis.** J. C. McLENNAN and G. M. SHRUM (*Proc. Roy. Soc.*, 1925, **A**, **108**, 501—512).—In studying the effect of large admixtures of helium or of neon on the spectrum of oxygen, a hitherto unknown line, of wave-length  $5577.35 \pm 0.15$  Å., has been photographed; it is very sharp and is subject to great fluctuations in intensity. Evidence is produced to prove that this line is identical with the auroral green line  $\lambda = 5577.350 \pm 0.005$  Å. This line is attributed to some hitherto unknown spectrum of oxygen, and is not a limiting member of the ordinary band spectrum of this substance. It has been observed faintly in highly-purified oxygen when using currents of high density. Helium has been used to bring out the bands of nitrogen (cf. Merton and Pilley, this vol., ii, 333) with an intensity distribution similar to that found in the aurora. The possibility of metastable helium acting as the exciting agent in the auroral spectrum is discussed. L. F. G.

**Resonance Lines of Neon.** G. HERTZ (*Z. Physik*, 1925, **32**, 933—939).—The spectrum of a low-voltage arc in neon was photographed in a vacuum grating spectrograph and two strong lines were found at 735.7 and 743.5 Å. Their difference in frequency agrees with the difference of the terms  $1s_2$  and  $1s_4$ , and are the combinations of these terms with the ground term. They are resonance lines. The two ionisation potentials of neon are 21.47 and 21.57 volts, in agreement with the value 21.5 obtained by the electron impact method.

E. B. L.

**Spectrum of Sodium at Low Voltages.** F. H. NEWMAN (*Phil. Mag.*, 1925, [vi], **50**, 165—173).—The sodium low-voltage spectrum was determined in a three-electrode discharge tube in which sodium vapour was subjected to electron bombardment by electrons emitted from a heated tungsten wire cathode, and accelerated by a potential difference applied between the grid and cathode. On the basis of Bohr's theory of atomic structure, it is shown that by bombarding the vapour by electrons of increasing energy, lines of the arc spectrum should be emitted by the permitted inter-

orbital transfers, up to an electron energy of 5.12 volts, at which value the whole of the arc spectrum should appear. Photographic observations showed the development of the spectrum in the order of the potentials predicted by theory. At 2.2 volts, wave-lengths 5896 and 5890 Å. only appear. At 4.0 volts, the lines 3303 and 3302 Å. are excited, and the lines 6161, 6154, and 5688, 5683 Å. are emitted at 4.4 and 4.6 volts, respectively. F. G. T.

**Spectra of Doubly and Trebly Ionised Phosphorus.** M. O. SALTmarsh (*Proc. Roy. Soc.*, 1925, A, 108, 332—343).—Observations have been made on the spectrum of phosphorus from a vacuum tube containing the vapour of yellow phosphorus and a variable amount of hydrogen, excited by a condensed discharge with and without self-induction. By making use of the intensity changes with alteration of the discharge, the lines corresponding with the different states of ionisation have been selected. The series system of doubly ionised phosphorus, III, is a doublet system, in accordance with the spectroscopic displacement law. Approximate values of the various series terms have been obtained. Three members of the triplet series of trebly-ionised phosphorus have been identified. It has now been observed that, for three groups of elements, the sharp terms are greater than the diffuse terms with the same Rydberg numbers for the neutral and singly ionised atom, but smaller for the doubly and trebly ionised atom. S. B.

**Intensity Relations of Triplet Components of the Alkaline Earths and Spark Doublets of Calcium.** H. B. DORGELO (*Physica*, 1924, 4, 281—286; cf. A., 1924, ii, 282; Burger and Dorgelo, *Z. Physik*, 1924, 23, 258).—Rules previously given are confirmed. The intensity ratio for the triplets *ps* and *pd* is 5 : 3 : 1, for the *db* triplet 7 : 5 : 3. The spark doublet of the principal and sharp series of calcium has the same ratio (2 : 1) as the arc doublet of the alkali metals. The complex spark doublet  $1\pi-2\delta$  of calcium gave the same value as the complex arc doublet of caesium.

CHEMICAL ABSTRACTS.

**Structure of the Spectrum of Scandium. II.** M. A. CATALÁN (*Anal. Fis. Quím.*, 1924, 22, 497—505; cf. A., 1923, ii, 104).—A revision of the classification of the terms of the spectrum of ionised scandium. Two new multiplets are given. The selection principle as modified by Laporte (A., 1924, ii, 364) is valid for this spectrum. G. W. R.

**Reported  $K\beta_4$  Line in the X-Ray Spectra of Molybdenum and Palladium.** S. K. ALLISON (*Nature*, 1925, 115, 978—979).—No evidence has been obtained, in the case of molybdenum, for the existence of the  $\beta_4$  line described by Leide (this vol., ii, 457); however, in the region in which it should occur, a discontinuity in the general radiation always appeared, due to the absorption by the target of its own radiation. It is possible that the effect might be mistaken for a faint line on the short wave-length side of the  $\gamma$  line. A. A. E.

**Stages in the Excitation of the Spectra of Cadmium.** A. E. RUARK and R. L. CHENAULT (*J. Opt. Soc. Amer.*, 1925, **10**, 653—659).—Errors may be introduced into the determination of the energy of electron impact required for the excitation of a spectrum line, by the occurrence of successive impacts upon a given atom. Tables giving the appearance voltages of lines should therefore be accompanied by data of the current densities at which the observations were made. Such observations are supplied for the cadmium lines developed in a three-electrode tube with applied voltages of 8—65 volts. S. B.

**Nature of the Iodine Line 2062 Å.** L. A. TURNER and K. T. COMPTON (*Physical Rev.*, 1925, [ii], **25**, 791—794).—The authors' experimental results are explicable on the assumption that the iodine line 2062 Å. is not a resonance line, but that the atoms which absorb it are in a state of which the energy level is 0.545 volt above the normal. The existence of a resonance line of atomic iodine between 1750 Å. and 1890 Å. is indicated. A. A. E.

**Tungsten X-Ray Emission and Absorption Spectra.** R. V. ZUMSTEIN (*Physical Rev.*, 1925, [ii], **25**, 747—752).—An investigation of the *M* series lines of tungsten, using a vacuum spectrometer. In the emission spectrum, faint lines  $\eta_1=6.857$  Å. and  $\eta_2=6.789$  Å. have been observed, and Hjalmar's two components of the  $\alpha$  and  $\beta$  lines measured at  $\alpha'=6.948$  Å.,  $\beta'=6.720$  Å. Lines were observed in the absorption spectrum at 6.708, 6.475, 5.416, 4.800, and 4.365 Å. There is also an unpredicted component,  $M_3'=5.380$  Å. A. A. E.

**The Mercury Line 2270 Å. ( $1s-2p_1$ ).** T. TAKAMINE and M. FUKUDA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, **2**, 293—298).—This line, not hitherto observed directly, has been found in the mercury arc spectrum. The wave-length appears to be shifted by about 0.1 Å., according as the line is produced by a condensed discharge or in the side-glow of an arc. W. A. C.

**Rotating Arc between Carbon Electrodes.** PAUTHENIER (*Compt. rend.*, 1925, **180**, 1833—1836).—Details of a new method. R. A. M.

**Complex Structure of Spectra.** S. GOUDSMIT (*Z. Physik*, 1925, **32**, 794—798).—A variation of Pauli's treatment of electron grouping and quantum numbers for an atom under the influence of a strong magnetic field is developed and applied to the spectra of neon and lead. E. B. L.

**Intensities of Lines in Multiplets. I. Theory.** H. N. RUSSELL (*Proc. Nat. Acad. Sci.*, 1925, **11**, 314—322).—Formulae are developed which represent fairly closely all the available data. J. S. C.

**Intensities of Lines in Multiplets. II. Observed Data.** H. N. RUSSELL (*Proc. Nat. Acad. Sci.*, 1925, **11**, 322—328).—The theory developed (preceding abstract) is compared with the observed data, the agreement being close. J. S. C.

**Classification of Enhanced Lines of Various Elements. I.** M. KIMURA and G. NAKAMURA (*Japan. J. Phys.*, 1924, **3**, 197—215).—Examination of the spark spectra of about thirty elements has shown that their enhanced lines may be grouped according to their lengths. All members of a group behaved similarly when either the self-induction, capacity, or spark gap was varied. From consideration of the fact that the larger is the enhanced line the smaller will be the amount of energy required to excite it, a classification of the groups as II, III, IV, or spark, super spark, and super-super spark indicates that the lines in each group are emitted by singly, doubly, and triply ionised atoms, respectively. From these considerations, the number of electrons easily detachable from an atom under an intense electrical discharge increases with the positive valency of the element and reaches a maximum with groups IV or V of the periodic table. A. E. M.

**Classification of Enhanced Lines of Various Elements. II. Spectra of Intermittent Arc Shunted by a Condenser.** M. KIMURA (*Japan J. Phys.*, 1924, **3**, 217—225).—Using an intermittent condensed arc and varying the voltage up to 440 volts, certain classes of enhanced lines appeared in succession. Spark lines appeared first, then super spark, and finally super-super spark. In the cases of zinc and copper, no super spark lines appeared even in the 440 volts arc, whilst with the other elements, antimony, bismuth, platinum, cadmium, and tin, these were obtained easily at 220 volts. Super-super spark lines appeared in the 440 volt arc of lead, but not in the arcs of antimony, bismuth, or tin. A. E. M.

**Doublets and Triplets in the Spectra of Different Elements.** Y. SUGIURA (*Japan J. Phys.*, 1924, **3**, 155—185).—Mathematical. Doublets and triplets are deduced as being emitted by atoms having one and two valency electrons, respectively. Expressions for the wave-number differences of doublets and triplets are obtained from the energy difference due to the intra-atomic magnetic fields set up by the elliptic orbits of the electrons. These calculated values are in good agreement with those observed for the doublets of the alkali elements and for the copper, silver, and aluminium groups. Calculated values of the wave-number differences  $\Delta\nu_p^{2,3}$  and  $\Delta\nu_d^{2,3}$  for the elements of the second column of the periodic table are in fair agreement with observation. The bearing of the work on the orientation of electron orbits in atoms is discussed. A. E. M.

**Spark Spectra in the Schumann Region.** L. and E. BLOCH (*J. Phys. Radium*, 1925, [vi], **6**, 105—120; cf. A., 1921, ii, **3**, 286, 364; Lang, *Phil. Trans.*, 1924, A, **224**, 371).—Valuable additions to the data of spark spectra in the region 1850—1300 Å. have been made by the use of two vacuum spectrographs with fluorite optical parts. In the later model, the fluorite was of very good quality and the absence of fluorescence together with the use of a very fine slit have enabled the authors to obtain plates which show a decided advance in respect of detail. Hundreds of new lines are

recorded and many lines hitherto regarded as simple have been resolved into doublets or triplets. The radical changes involved in the spectra have necessitated the publication of new lists of wave-lengths for iron, nickel, cobalt, and tungsten. Data for copper, silver, gold, platinum, manganese, and chromium will appear later. In the new arrangement, the prism consists of two  $30^\circ$  fluorite prisms and a mirror; in the spark gap, the current of hydrogen employed formerly has been replaced by nitrogen. An important experimental difficulty in the work was the increasing opacity of the fluorite window. An invisible deposit is formed which is only removed by dismounting the window and washing both sides with benzene. The photographs were calibrated by means of the following lines determined by means of a vacuum grating spectrograph. 1807·70, 1751·80, 1657·86, 1561·35, and 1335·70 (carbon); 1935·79, 1930·97, and 1858·13 (aluminium); 1742·81 and 1494·63 (nitrogen). A series of secondary standards in the aluminium spectrum was also used. These may be as much as 0·2 Å. in error. Hence the absolute values of the wave-lengths recorded may be in error owing to uncertainty in the standards, but the intervals between lines are known accurately to within a few hundredths of an ångström. The table for iron extends from 1895·53 to 1505·16; for nickel about 270 new lines are recorded down to 1370·31; cobalt shows 346 lines from 1882·14 to 1424·82, of which 150 are new. The tungsten spectrum shows a very large number of lines down to 1450. (Cf. A., 1924, ii, 214.) R. A. M.

**Theory of the Continuous X-Ray Spectrum.** M. BRONSTEIN (*Z. Physik*, 1925, **32**, 881—885).—It is shown that a small correction should be applied in deducing the sharp edge of the continuous spectrum from Einstein's  $h\nu$  relation, dependent on the angle between the beam of X-rays and the direction of the cathode rays. E. B. L.

**Spectroscopic Evidence of J-Transformation of X-Rays.** M. SIEGBAHN (*Nature*, 1925, **116**, 11—12).—Responsibility is denied for some of the *K* wave-length values ascribed to the author by Khastgir and Watson (this vol., ii, 336). Leide's new and more accurate values yield no trace of such discontinuities as are described by Khastgir and Watson. A. A. E.

**Spectroscopic Evidence of J-Transformation of X-Rays.** W. W. NIPPER (*Nature*, 1925, **116**, 12).—Siegbahn's (preceding abstract) contentions are supported. Although the greatest deviation of the values employed from more recent wave-length determinations occurred, by coincidence, at points corresponding with two of the critical absorptibilities for *J*-transformation of X-rays, there is no spectroscopic evidence for the existence of the phenomenon. A. A. E.

**Spectroscopic Evidence of J-Transformation of X-Rays.** S. R. KHASTGIR and W. H. WATSON (*Nature*, 1925, **116**, 47).—Polemical and explanatory (cf. this vol., ii, 336, and preceding abstracts). A. A. E.

**The Term Problem of Doublet Spectra, with Particular Reference to X-Ray Spectra.** G. WENTZEL (*Ann. Physik*, 1925, [iv], **76**, 803—828).—A complete representation of the terms of the X-ray, as well as of the alkali spectra, can be obtained if the energy of the  $n_k$  orbit is calculated by the separation method, taking into account the relativity effect and penetration into inner electron shells. If the energy is calculated from the relativistic fine structure constant  $\alpha^2 = (2\pi e^2/hc)^2$ , the principal term (non-relativistic) involves fractional azimuthal quantum numbers, as in the suggestion of Heisenberg (this vol., ii, 3). By assuming that the charge on the shell of the atom is very small compared with that on the kernel, the calculation for the X-ray and Millikan ultra-violet spectra is much simplified. The whole of the alkali and X-ray terms may be expressed as functions of two quantum numbers  $n$  and  $k$ , if negative as well as positive values of  $k$  are admitted. The expression found by the author for the screening doublets  $(\Delta\sqrt{\nu}/R)/0.6 = \text{integer}$  (*Z. Physik*, 1923, **16**, 46) is obtained by assuming that  $k^2$  is very small compared with  $n^2$ . The Sommerfeld fine structure theory follows from the application of these ideas to the hydrogen atom. F. G. T.

**X-Rays Terms and Intensities.** H. R. ROBINSON (*Phil. Mag.*, [vi], 1925, **50**, 241—250; cf. A., 1923, ii, 818).—Previous work has been extended and made more accurate by the production of secondary X-ray spectra from targets of uranium oxide, thorium nitrate, gold, arsenic oxide, manganese oxide, and titanium oxide. The general distribution of intensity among the sub-groups of the secondary rays follows closely the results of the previous work, showing clearly that so long as the critical absorption frequency of a group is not too far removed from the frequency of the incident radiation, most of the secondary electrons come from the softer sub-groups. As the critical absorption frequency decreases, the maximum intensity in the sub-groups shifts gradually from the softer towards the harder members. This holds generally in the  $M$  and  $N$  as well as in the  $L$  sub-groups. A comparison of visual and photometric observations of intensities indicates that the former somewhat exaggerates the differences in intensity. The photometer curves especially indicate the diffuseness of the low-velocity side of the lines, due mainly to the straggling of electrons from deeper layers of the target. F. G. T.

**Exact Determination of Characteristic Atomic Frequencies in the Spectral Region between Visible Light and X-Rays.** HOLWECK (*J. Chim. Phys.*, 1925, **22**, 311—318; cf. Holweck, *Compt. rend.*, 1921, **173**, 709).—The critical potentials of some elements have been determined by a modification of the "gaseous anticathode" method of Mohler and Foote. The gas was contained in the chamber of a negatively charged electroscope through which was passed a beam of X-rays, issuing from a molybdenum anode as the result of the collision of a stream of electrons, emitted at a difference of potential  $V$ . If  $V$  is comparatively small the X-ray



radiation forms a continuous spectrum, and the critical potential is indicated by a break in the curve connecting  $V$  with the degree of ionisation. The following values were found for the  $L_{III}$  critical potentials in volts: argon,  $246.5 \pm 1$ ; chlorine,  $203 \pm 1$ ; sulphur,  $163 \pm 1$ ; phosphorus,  $128 \pm 2$ ; silicon,  $98 \pm 2$ ; aluminium,  $68 \pm 2$ . The substances used were argon, hydrogen chloride, hydrogen sulphide, hydrogen phosphide  $PH_3$ , and hydrogen silicide  $SiH_4$ ; for aluminium the beam was passed through a thin sheet of the metal. The author's previous value for aluminium (*loc. cit.*) is in error owing to a wrong correction. W. H.-R.

**Generally Accepted Explanation of the Zeeman Triplet on a Quantum Basis.** W. M. HICKS (*Nature*, 1925, **115**, 978).—In the usual way of applying Larmor's theorem to the explanation of the Zeeman effect, it is tacitly assumed that after the imposition of the magnetic field the rotating system is the same as before, with simply the rotation superposed. This assumption is incorrect, and it is objected that the new orbit ceases to be quantised, and that the total energy is supposed to be altered by the action of a magnetic field on a moving electron. A consideration, however, of actual orbits leads to the result that no effect is to be expected, or if so that the magnitude must depend on the second or higher powers of  $H$ . A. A. E.

**Quantum Theory of Multiplet Structure and the Anomalous Zeeman Effect.** W. HEISENBERG (*Z. Physik*, 1925, **32**, 841—860).—The theory of the interaction between an electron and the atomic core involves the ambiguity that for one definite stationary state of the core and of the outer electrons there are two values for the energy of their interaction, and, conversely, for one value of this energy there are two systems of stationary states for the electron and the core. Schemes are developed which yield an interpretation of some of the observed regularities of multiplets.

E. B. L.

**Intensity of the Components in the Zeeman Effect.** L. S. ORNSTEIN, H. C. BURGER, and W. C. VAN GEEL (*Z. Physik*, 1925, **32**, 681—683).—The intensities of the components of the zinc triplet 4810, 4722, 4680 Å. ( $2p_i$ — $ss$ ) were determined, using a grating spectrograph and a Moll microphotometer. The results show satisfactory agreement with theory (cf. Hönl, *ibid.*, 1925, **31**, 340; Ornstein and Burger, this vol., ii, 340).

E. B. L.

**Polarisation of Resonance Radiation and the Duration of Excited State.** K. R. RAMANATHAN (*Proc. Indian Assoc. Cult. Sci.*, 1925, **9**, 93—102).—The changes of polarisation of the resonance radiation of mercury vapour in weak magnetic fields (Wood and Ellett, *Proc. Roy. Soc.*, 1923, **A**, 103, 396) can be explained by taking into account the Larmor precession of the orbit of the electron round the direction of the magnetic field, and the finite duration of the excited condition of the atom. The duration of the excited state required to explain the decrease of polarisation in mercury vapour resonance when a magnetic field is applied

parallel to the direction of observation, and perpendicular to the incident beam of light, is consistent with Wien's determination of the same quantity (A., 1924, ii, 362). The changes in intensity and polarisation of the resonance radiation when the mercury vapour is mixed with hydrogen, helium, argon, or air (Wood, *Phil. Mag.*, 1922, [vi], **44**, 1107) can be explained by assuming a finite time of excitation of the atom, and that the effect of a collision is either to destroy the radiation or to disturb the polarisation so as to make its direction random. F. G. T.

**Excitation and Ionisation Potentials of Rare Gases.** G. HERTZ and R. K. KLOPPERS (*Physica*, 1924, **4**, 367—372; cf. A., 1922, ii, 733; 1923, ii, 281; *Z. Physik*, 1923, **18**, 307).—The method previously employed is modified by the use of an equipotential nickel cathode. Values of the resonance potentials are: argon, 11.5, 13.0, 13.9 volts; krypton, 9.9, 10.5, 11.5, 12.1 volts; xenon, 8.3, 9.9, 11.0 volts. Ionisation potentials ( $\pm 0.1$  volt) are: argon, 15.4; krypton, 13.3 ( $p=0.07$  mm.); xenon, 11.5 ( $p=0.12$  mm.). These values do not correspond with a single spectral term, but with average values for groups of neighbouring terms.

CHEMICAL ABSTRACTS.

**Experimental Study of Directions of Emission of Photo-Electrons.** P. AUGER (*Compt. rend.*, 1925, **180**, 1939—1941; cf. this vol., ii, 618).—The expression  $P=\sin^3\omega d\omega \cdot \sin^2\lambda d\lambda$  for the probability of emission of a photo-electron in a small solid angle  $d\omega d\lambda$  making an angle  $\omega$  (the colatitude) with the direction of the exciting X-ray pencil was deduced in the earlier paper. The experimental distributions are considered in two stages, as functions of  $\omega$  and  $\lambda$ , respectively. The integral of  $\sin^3\omega$  is expressed as  $\frac{1}{2}(1-\cos\omega)[1-\frac{1}{2}\cos\omega(1+\cos\omega)]$  and that of  $\sin^2\lambda d\lambda$  as  $\frac{1}{2}(\lambda-\sin\lambda\cos\lambda)$ . The experimental and theoretical curves are of the same type. R. A. M.

**Distribution of Initial Velocities among Thermionic Electrons.** L. H. GERMER (*Physical Rev.*, 1925, [ii], **25**, 795—807).—Measurements were made of the number of electrons from a tungsten filament at 1440—2475° Abs. which arrived at a coaxial cylindrical electrode against various retarding potentials. The experiments showed that the thermionic electrons emitted from tungsten into a high vacuum have velocity components distributed according to Maxwell's law for the distribution of velocities in an electron atmosphere in temperature equilibrium with the hot filament. A. A. E.

**Schottky's Method of Determining the Distribution of Velocities among Thermionic Electrons.** C. DAVISSON (*Physical Rev.*, 1925, [ii], **25**, 808—811).—Schottky's formula for the thermionic current from a filament to a coaxial cylinder fails when the potential at any distance  $x$  from the axis is less than  $Vr^2(R^2-x^2)/x^2(R^2-r^2)$ , where  $V$  is the potential of the filament with respect to the cylinder,  $r$  and  $R$  are the radii of filament and cylinder, respectively, and  $r < x < R$ . A. A. E.

**Modification of the Laws of Emission of Ions from Hot Metals by the Quantum Theory.** S. C. ROY (*Proc. Indian Assoc. Cult. Sci.*, 1925, **9**, 61—81).—The probability of identity between photo-electric and thermionic work-functions is discussed.  
W. A. C.

**Vaporisation of Electrons.** N. v. RASCHEVSKY (*Z. Physik*, 1925, **32**, 746—752).—It is assumed that the emission of electrons from a hot body can be treated as being analogous to ordinary vaporisation of molecules, that the electrons behave like a mon-atomic gas, and that energy transference between the electrons and atoms inside the hot body is negligible. In the equation for the thermionic current,  $i = Ae^{-b/T}T^a$ ,  $a$  is only equal to 2 when the energy of the internal electrons is taken as being independent of temperature; if these electrons are regarded as free,  $a = \frac{1}{2}$ ; if they form a lattice,  $a = -1$ .  
E. B. L.

**Electron Reflection in Gases.** H. BAERWALD (*Ann. Physik*, 1925, [iv], **76**, 829—848).—The reflection of electrons in hydrogen has been studied by comparing the total current produced by the passage through the gas of electrons from a hot filament with the current due to electrons reflected on impact with hydrogen molecules. The latter current was measured by means of an annular collector shielded from, and surrounding, the filament. The amount of reflection increases with the gas pressure, but the ratio of reflected to direct current is independent of the velocity of the electrons. The integral and differential curves are given for the variation of both direct and reflected current with change of the electron velocity obtained by varying the grid voltage. The differential curves of the direct current show maxima which flatten and occur with more slowly moving electrons as the gas pressure increases. The reflection is associated with a loss of energy which becomes accentuated when the electrons are accelerated by more than 11 volts. Above 16 volts, positive ions appear in the gas. This ionisation voltage was determined for a number of gas pressures and for varying filament currents. From a consideration of the free paths of the hydrogen molecules in these circumstances it is concluded that energy loss from slowly moving electrons occurs on grazing contact with the sphere of action of the hydrogen molecule.  
F. G. T.

**Isotope Effect in the Spectrum of Silicon Nitride.** R. S. MULLIKEN (*Nature*, 1925, **116**, 14).—The equations previously given (*Physical Rev.*, 1924, [ii], **23**, 554) for the silicon nitride bands are incorrect. The equation  $\nu = 24234.2 + 1016.30 n' - 17.77 n'^2 + 0.41 n'^3 - 0.0049 n'^4 - 1145.00 n'' + 6.570 n''^2$  holds for the position of the null-lines of the  $\text{Si}^{28}\text{N}$  bands,  $n'$  being the vibrational quantum number of the initial,  $n''$  that of the final, state of the molecule. Various abnormalities now disappear, an analogy of the  $\text{SiN}$  bands to the violet  $\text{CN}$  bands is evident, and the isotope effect is normal. In the case of  $\text{SiN}$ , but not in that of  $\text{BO}$ , integral vibrational quantum numbers are preferred.  
A. A. E.

**Band Spectra of Lead Isotopes.** E. S. BIELER (*Nature*, 1925, **115**, 980).—The assumption that the carrier of the band at 4270 Å. is the PbH molecule instead of the Pb<sub>2</sub> molecule affords a satisfactory explanation of the results of Grebe and Konen (*A.*, 1922, ii, 4) on the band spectra of lead isotopes. A. A. E.

**Determination of the Atomic Weight of a Mixture of Lead Isotopes Present in Clevite from Aust-Agdar, Norway.** (MLLE.) E. GLEDITSCH, (MME.) DORENFELDT, and O. W. BERG (*J. Chim. Phys.*, 1925, **22**, 253—263).—Taking the atomic weight of ordinary lead as 207·18, the atomic weight of the mixture of lead isotopes in Norwegian clevite was determined as 206·17 by two different methods: (1) by conversion of a carefully purified chloride into the sulphate, and, (2), more accurately by measuring the densities of saturated solutions of the nitrates, from which the atomic weight can be calculated, if it is assumed that the molecular solubilities are the same. The single result obtained by method (2) agreed with the mean of slightly differing results obtained by method (1). The clevite was remarkable for its small content of thorium.

W. H.-R.

**Number of Ions Produced in a Spherical Volume by Radium Emanation (Radon).** M. W. MUND (*Ann. Soc. Sci. Bruxelles*, 1925, **44**, 336—344).—Theoretical. The total number of ions produced in a spherical volume of gas by the  $\alpha$ -particles of emanation homogeneously distributed in it and of radium-*A* and radium-*C* on the enclosing walls has been calculated. Two cases are considered: one, when the gaseous volume has a larger radius than the ranges of the  $\alpha$ -particles, and the other when this radius is smaller. Equations are given connecting the number of ions produced with the ranges of the  $\alpha$ -particles, the radius of the spherical enclosure, the constant of the gas ionised, and the number of atoms of radium emanation present.

A. S. R.

**Magnetic Spectrum of  $\beta$ -Particles from Radium-*E*.** (MLLE.) I. CURIE and J. D'ESPINE (*Compt. rend.*, 1925, **181**, 31—33).—The upper limit of the principal band is very sharply defined at  $\beta=0\cdot936$  ( $\beta$ =ratio of the velocities of the particle and of light), the lower edge being somewhat indefinite at  $\beta=0\cdot70$ . The portion of maximum intensity between  $\beta=0\cdot86$ — $0\cdot80$  is due to the partial overlapping of a sharply-defined band extending from  $\beta=0\cdot936$ — $0\cdot80$  and a less sharply-defined band extending from  $\beta=0\cdot86$ — $0\cdot70$ . The band corresponding with radiations,  $\beta=0\cdot50$ , is possibly due to some secondary effect. There is also a band corresponding with radiations of higher velocity,  $\beta=0\cdot986$ — $0\cdot97$ .

J. S. C.

**Paramagnetism and the Electronic Configuration of the Atom.** L. C. JACKSON (*Nature*, 1925, **115**, 981).—It is suggested that the different magnetic states of the ions of iron (Fe<sup>+</sup>) and cobalt (Co<sup>+</sup>) may correspond with different internal configurations of the electrons. Thus ordinary ferrous iron would possess the configuration 2, 8, 14, 0, and the other magnetic state might be produced by the transference of one of the 14 electrons in the

incomplete third quantum orbit to the fourth quantum orbit, or by a redistribution of the third quantum orbit electrons among the various levels,  $3_1$ ,  $3_2$ , and  $3_3$ , of this orbit (cf. Russell, this vol., ii, 406).  
A. A. E.

**Structure of Strontium.** H. COLLINS (*Chem. News*, 1925, **131**, 3—6).—Tables of atomic and molecular volumes, heats of formation, of neutralisation and of solution, and magnetic rotation are compiled to support the speculation that the strontium atom is formed by the union of calcium and titanium atoms.  
S. I. L.

**The Statistical Distribution Function in the Theory of Radiation and Atomic Heat.** E. CSÁSZÁR (*Z. Physik*, 1925, **32**, 872—880).—Polemical against Schrödinger (*ibid.*, 1924, **25**, 173).  
E. B. L.

**Quantum Theory of the Laue Effect.** M. BRONSTEIN (*Z. Physik*, 1925, **32**, 886—893).  
E. B. L.

**Application of Quanta to the Electron Theory of Metals.** L. S. ORNSTEIN (*Z. Physik*, 1925, **32**, 673—677).—Expressions are obtained for the conditions of equilibrium between electrons, atoms, and radiation. The theory of metallic conduction is developed from the point of view that the mean free path of an electron ends when it approaches nearer than a certain small distance to a metallic ion. As with other theories, it fails to account for the Hall effect, or for super-conductivity at very low temperatures.  
E. B. L.

**New Light on Two-electron Jumps.** R. A. MILLIKAN and I. S. BOWEN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 329—334; cf. A., 1924, ii, 710; this vol., ii, 342; *Physical Rev.*, 1925, [ii], **25**, 591).—An extension of previous work, the radiating properties of two-valency-electron, and three-valency-electron atoms being investigated. The former systems are characterised by a spectral flag consisting of five nearly equally spaced bars, the central one being about twice as heavy as the others, and systems of the second type are characterised by a flag consisting of four bars, the middle two being fairly close together. These flags are produced by simultaneous jumping of two electrons. The jumps consist in a jump of one of the two electrons between a  $2p$  and a  $2s$  level, or a  $3p$  and a  $3s$  level combined with a simultaneous jump of a second electron between two of the levels:  $2p_1$ ,  $2p_2$ ,  $2p_3$ , or  $3p_1$ ,  $3p_2$ , and  $3p_3$ . The significance of the two-electron jump is considered, a more detailed analysis being promised later.  
J. S. C.

**Physical Interpretation of Bohr's Stationary States.** G. P. THOMSON (*Phil. Mag.*, 1925, [vi], **50**, 163—164).—The stationary states of an electron in the hydrogen atom can be regarded as determined, without postulating waves with a velocity greater than light, by supposing the electron to be attached to the nucleus by a tube of force forming a connexion of limited, although possibly varying, cross-section between the two charges. If the tube possesses mass, and its tension provides the attraction between the electron and the

nucleus, it will be able to transmit waves, and the condition determining the possible states is that the vibrations in the tube shall be in tune with the period of the orbit.

F. G. T.

**Relative Transition Probabilities in the Sodium Atom.** G. R. HARRISON (*Physical Rev.*, 1925, [ii], **25**, 768—782).—Direct precise measurements were made of line absorption intensities, whence the constants  $C_1$  and  $C_2$  in Slater's formula for transition probabilities,  $Nx\hbar\lambda_0 B_{ij} = c\pi \log_e 10 \times \sqrt{C_1/C_2}$  and relative values of  $B_{ij}$  were determined for the various lines 2 to 16 in the principal series of sodium. No decrease in relative probability of the higher numbers with increasing vapour pressure was found. Relative values of  $A_{ij}$  were computed from Einstein's relation  $c^3 A_{ij} = 8\pi\hbar\nu_0^3 B_{ij}$ . In these expressions,  $A_{ij}$  is the probability of a spontaneous transition from state  $j$  to state  $i$  with the emission of radiation,  $B_{ij}$  that of the reverse process,  $c$  the velocity of light,  $N$  the number of absorbing atoms,  $x$  the length of the absorbing path,  $\hbar$  Planck's constant, and  $\lambda_0$  the central wave-length of the absorption line.

A. A. E.

**Methods for Determining Transition Probabilities from Line Absorption.** J. C. SLATER (*Physical Rev.*, 1925, [ii], **25**, 783—790).—A discussion of the various steps encountered in translating the experimental data into atomic constants, and a statement of the formulæ in a form adapted for practical use.

A. A. E.

**Relation of Spectral Lines to Mass Variations within the Atom.** L. B. HAM (*Physical Rev.*, 1925, [ii], **25**, 762—767).—An investigation of the mass variations of the electron and nucleus involved in the transitions represented by Bohr's frequency condition  $\hbar\nu = E_b - E_e$ , on the assumption that the total mass variations of the electron are composed of "kinetic" and "potential" variations. An apparent discrepancy between the quantum theory and the theory of relativity is thus eliminated, and it is shown that the electronic mass may be considered as quantified. The fine structure of the hydrogen doublet is explained, and absolute values of the changes of mass of the electron at aphelion and perihelion for various orbital transitions for  $H\alpha$  are tabulated.

A. A. E.

**Orbits in the Hydrogen Atom as Affected by the Motion of the Nucleus.** E. REICHENBÄCHER (*Z. Physik*, 1925, **32**, 907—917; cf. *ibid.*, 505).

E. B. L.

**Electronegative Hydrogen.** A. E. VAN ARKEL and J. H. DE BOER (*Physica*, 1924, **4**, 382—392).—Electronegative hydrogen (as in lithium hydride) accounts for the properties of  $B_2H_6$  on the basis of Kossel's screening effect. For the hydrocarbons, hydrogen behaves like a small halogen rather than an infinitely small positive charge. Simple rules are given for calculating the b. p. of halogen derivatives of methane; the method is less successfully applied to derivatives of silicon hydride.

CHEMICAL ABSTRACTS.

**Possible Explanation of the Ingersoll Non-magnetic Nickel Film.** C. W. OSEEN (*Z. Physik*, 1925, **32**, 940—941).—A film

of nickel formed by cathode sputtering is not magnetic. If the *M* ring contains 18 electrons the atom would not be expected to be magnetic. If one or more of these electrons has a higher quantum number, which is probable in crystals and in chemical compounds, the atom would be paramagnetic. E. B. L.

**Atomic Structure Factor in the Intensity of Reflection of X-Rays by Crystals.** D. R. HARTREE (*Phil. Mag.*, 1925, [vi], 50, 289—306).—The use is indicated, in examining complicated crystal structures, of *F*-curves, which represent the variation with glancing angle of the factor *F*, the scattering power of an atom, defined as the ratio of the amplitude of the wave scattered by that atom to the amplitude of the wave scattered by an electron. By assuming that the individual electrons in an atom scatter according to classical theory, it is shown that the *F*-curves for any given atom can be calculated from the dimensions of, and the progress of time in, the core orbits. It is possible by a numerical analysis of the terms of the optical and X-ray spectra to determine approximately the field of an atom, and from this the dimensions of the core orbits may be calculated (A., 1924, ii, 2). The results of this analysis indicate that the maximum radii of all non-circular core orbits with the same principal quantum number are very nearly the same. This, in conjunction with the result that the contribution to the scattering power of an atom from a non-circular orbit is a function of the maximum radius of the orbit only, permits all non-circular core orbits of the same principal quantum number to be regarded as equivalent as regards their contribution to the scattering power of the atom. Maximum radii of the core orbits are represented by the formula  $\rho_0 = \kappa / (N - \gamma)$ , where *N* is the atomic number, and  $\kappa$  and  $\gamma$  are constants for core orbits of the same quantum number in different atoms. Values of the constants are given for a number of orbits. Tables are given for the contributions to the scattering power from circular and non-circular orbits, respectively, and the *F*-curves based on Stoner's distribution of electrons are given for the ions Cs<sup>+</sup>, Cu<sup>+</sup>, S<sup>2-</sup>, S<sup>4+</sup>, and O<sup>2-</sup>. In these curves, there is a slow initial decrease of *F* with increasing glancing angle for compact ions compared with that for ions of greater size. For the same element in different states of ionisation there is little difference in value of *F* except for small glancing angles. The observed values of *F* for Na<sup>+</sup> and Cl<sup>-</sup> are smaller than those calculated either from the Bohr or the Stoner electron distribution. F. G. T.

**Interpretation of Intensity Measurements in X-Ray Analysis of Crystal Structure.** W. L. BRAGG (*Phil. Mag.*, 1925, [vi], 50, 306—310).—A discussion of factors to be considered in using Hartree's results for the relative scattering powers of atoms based on a calculation of orbit dimensions (cf. preceding abstract). The influences are of two types, dependent on the glancing angle and the structure factor, respectively. Those dependent on the glancing angle are due to the method and crystal sample used, and on the polarisation of the scattered radiation. The dependence of the

intensity on the structure factor is obscure, but if the observed intensities show a parallelism with the calculated structure factors when both are arranged in order of increasing glancing angle, the assigned structure must be correct. In comparing each plane with the next at a higher angle, a rise of structure factor should correspond with an increased intensity, and *vice versa*. In the discussion of the form of the law relating the intensity of scattered radiation  $I$  to the structure factor  $S$ , it is pointed out that an estimate of the extinction coefficient  $\epsilon$  of rock salt (A., 1921, ii, 477) leads to the relation  $I \propto S^2/(\sigma + \epsilon)$ , where  $\sigma$  is the absorption coefficient. For a crystal in which  $\epsilon$  is much larger than  $\sigma$ , this relationship becomes  $I \propto S^2/(\sigma + \alpha I)$ , where  $\alpha$  is a constant. This assumes the form  $I \propto S$ , or  $I \propto S^2$ , according to whether  $I$  is large or small. The discrepancy between the observed and Hartree's calculated scattering coefficients for sodium, chlorine, and oxygen may be due in part or entirely to the heat motions of the atoms, for which no allowance has been made.

F. G. T.

**Diamagnetism and the Size of Ions.** G. JOOS (*Z. Physik*, 1925, **32**, 835—839).—The distance of the outer electrons from the nucleus is calculated from Langevin's theory and agrees remarkably well with the result obtained from the theory of the crystal lattice.

E. B. L.

**Formation of Band Spectra.** R. MECKE (*Z. Physik*, 1925, **32**, 823—834).—The close relationship existing between the nuclear vibrational and rotational energy of sixteen band spectra is emphasised. For the complete development of a band spectrum the determining factor is probably the interaction between the nuclear oscillations and the electron motions, and not the strength of the non-harmonic bond.

E. B. L.

**Structure and Distribution of Band Spectra.** H. DESLANDRES (*Compt. rend.*, 1925, **180**, 1980—1986; cf. *ibid.*, 1454).—The infra-red absorption of water vapour has been examined and the position of the absorption bands measured. Strong absorption is shown at  $2.661\mu$ ,  $6.26\mu$ , and above  $30.6\mu$ , whilst other weaker bands are present. The frequencies of the bands agree fairly well with those deduced from the formula  $\nu = q/r \times d_1/s$  (Deslandres, *loc. cit.*), where  $d_1$  is a fundamental frequency of  $1062.5$ ,  $s$  is the number of atoms in the molecule which equals 3 for water, and  $q$  and  $r$  are whole numbers. Bands at  $3.154\mu$  and  $6.26\mu$  can be split up, by a suitable prism, into a number of secondary bands the frequencies of which differ by  $d_1/24$  and  $d_1/48$  in the two cases, respectively. The results can be explained on the assumption that the atomic nucleus is surrounded by a cubical zone of protection within which the attractive force on an electron becomes a repulsion. The cubes are perfectly elastic, of side  $2a$ , and emit a fundamental frequency  $d_1$ . Band spectra are produced by the elastic vibrations of the cubes without breaking the protective zone, but when the latter is broken down the ordinary line spectrum is emitted.

W. H.-R.



**Fulcher Hydrogen Bands.** G. H. DIEKE (*Phil. Mag.*, 1925, [vi], 50, 173—179; cf. *Proc. K. Akad. Wetensch. Amsterdam*, 1924, 27, 490).—A comparison of the author's interpretation of the Fulcher bands with that of Curtis (this vol., ii, 351). The former interpretation gives a more satisfactory explanation of the vertical series, of the intensity of the lines, and of the variation of the intensities with temperature. On the other hand, Curtis' value for the moment of inertia of the hydrogen molecule is more acceptable than that based on the author's interpretation. F. G. T.

**Extension of the Negative Band Spectrum of Nitrogen.** T. R. MERTON and J. G. PILLEY (*Phil. Mag.*, 1925, [vi], 50, 195—199; cf. this vol., ii, 333).—The negative band of the spectrum of nitrogen has been remeasured, and the heads of the bands have been arranged in five series. The results do not agree with those of Deslandres (*Compt. rend.*, 1904, 139, 1174), but the constancy of the second differences in the wave-numbers is much closer than with the values of Deslandres. F. G. T.

**Quantum Analysis of New Nitrogen Bands in the Ultra-violet.** R. T. BIRGE and J. J. HOPFIELD (*Nature*, 1925, 116, 15).—A group of strong bands in the predicted position (cf. A., 1924, ii, 803) has been analysed, but the progressions are unexpectedly not related to those of any other analysed group of nitrogen, or of any other substance. The equation for the new group is  $\nu = 68,956.6 + (1681.45n' - 15.25n'^2) - (2345.16n'' - 14.445n''^2)$ , where  $n'$  varies from 0 to 9 and  $n''$  from 0 to 3 only. A. A. E.

**Infra-red Emission and Absorption of Potassium Vapour.** A. L. NARAYAN and D. GUNNAYA (*Proc. Indian Assoc. Cult. Sci.*, 1924, 9, 1—14).—In potassium vapour at 500—700°, the existence of Moll's line at  $3.65\mu$  and Paschen's line at  $2.72\mu$  has been confirmed, and a new line at  $1.2\mu$  found. Below about 600°, the vapour exercises no selective absorption. W. A. C.

**Absorption of Electrically Luminescent Potassium Vapour.** A. L. NARAYAN and G. SUBRAHMANYAM (*Proc. Indian Assoc. Cult. Sci.*, 1924, 9, 15—18; cf. preceding abstract).—In potassium vapour at about 350° rendered feebly luminescent by an electrical discharge, the Bergmann line at  $1.5\mu$  shows distinct absorption. It is maintained that the energy of excitation of the spectral lines increases in the order: principal, diffuse, sharp, Bergmann. W. A. C.

**Effect of Density on the Wave-length of the Absorption Bands of Iodine.** A. PEROT and M. COLLINET (*Compt. rend.*, 1925, 180, 2030—2032).—Known weights of iodine were vaporised in sealed glass tubes at 180° and the wave-lengths of six of the absorption bands were measured. The effect of density is given by the relation  $d\lambda/\lambda = ad\rho$ , where  $\lambda$  is the wave-length of the band,  $\rho$  the density, and  $a = +12 \times 10^{-3}$  and is constant between the limits  $\rho = 0.16 \times 10^{-4}$  and  $\rho = 1.96 \times 10^{-4}$  C.G.S. Results of the same order were obtained when the iodine was vaporised in open tubes, indicating that it is the density of the vapour and not the total pressure that is effective. W. H.-R.

**Luminous Vapour from the Mercury Arc and the Progressive Changes in its Spectrum.** LORD RAYLEIGH (*Proc. Roy. Soc.*, 1925, **A**, 108, 262—279).—When mercury distils away from the arc in a vacuum, the stream of vapour is luminous. An examination of the light shows that the spectrum lines of the arc which are members of known series are in general strongly developed in the vapour stream. An exception is  $1p-1s$ , 1850 Å. The arc lines not hitherto classified into series are faint or absent. The higher members of the various series appear in greater relative intensity in the vapour than in the arc. Their absolute intensity, even, may be greater in the vapour. At greater distances from the arc, the light from the arc changes in many ways. The higher series members lose in intensity, 2537 steadily becomes stronger, and the continuous spectrum of mercury appears. The effect of an electric field is to cause the rapid disappearance of the line spectrum of the vapour. 2537 is more persistent than the other lines, and the continuous spectrum passes on. The observations are discussed in relation to estimates of the life-period of an excited atom etc., and are difficult to reconcile with present views on the origin of spectra. S. B.

**Ultra-violet Absorption Spectra of Dichloroethylenes.** J. ERRERA and V. HENRI (*Compt. rend.*, 1925, **180**, 2049—2050).—The ultra-violet absorption of the *cis*- and *trans*-isomerides of dichloroethylene has been studied, using the pure liquids and also solutions of them in hexane and alcohol. Both isomerides begin to absorb at about 2600 Å., and the absorption increases with diminishing wave-length. The *trans*-isomeride has a higher coefficient of absorption than the *cis*-. The ratio of the two coefficients is the same in both solutions and in the pure liquids, and increases from 1.3 for 2595 Å. to 3.9 for 2200 Å. W. H.-R.

**Fluorescence of Fisetin in the Ultra-violet Light of the Wood Lamp.** L. MEUNIER and A. BONNET (*Compt. rend.*, 1925, **180**, 2038—2040).—Sections of ordinary wood barks used for tanning show no fluorescence, but woods from Quebracho in Colorado, and Tizerah of Morocco, show a brilliant fluorescence on freshly-cut sections. Solutions show a feeble fluorescence only, but if a substance with a large surface such as filter-paper, or, better, cellulose acetate silk, is added to the solution, a brilliant fluorescence is obtained in ultra-violet light, owing to the presence of fisetin in the bark (cf. Perkin, T., 1896, **69**, 1303), whilst the fluorescence is also observed if powdered leather, which has been tanned with extracts from either of these two barks, is treated similarly. The method enables extracts from these woods to be detected in tanning mixtures, and also enables slowly tanned leather to be distinguished from products rapidly tanned with Quebracho extract. W. H.-R.

**Theory of Diminution of Fluorescence.** A. PREDWODITELEW (*Z. Physik*, 1925, **32**, 861—871).—The energy absorbed by a fluorescent substance is partly transformed into heat and partly

radiated as fluorescence. A relationship is exhibited between the amount of fluorescence and the specific heat at constant volume of the active molecules. A method of calculating the mean energy of the resonators is given and its relation to the amount of fluorescence is deduced.

E. B. L.

**Polarised Fluorescence of Dyes.** V. S. J. VAVILOV (*Z. Physik*, 1925, **32**, 721—729; cf. Lewschin, this vol., ii, 629).—The König-Martens spectrophotometer was used to measure the intensity of the polarised fluorescent light from fluorescein in methyl alcohol, water, and glycerol, and of erythrosin in glycerol. At high concentrations, fluorescein in methyl alcohol and in water shows no polarisation. The amount of polarisation is independent of wave-length.

E. B. L.

**Opalescence of Binary Liquid Mixtures.** J. C. K. RAO (*Proc. Indian Assoc. Cult. Sci.*, 1924, **9**, 19—60).—The intensity and polarisation of light scattered by dust-free mixtures of toluene and acetic acid at the ordinary temperature and of methyl alcohol and carbon disulphide over a range of temperatures has been measured. Intensities show maximum values at definite concentrations and temperatures; these maxima are steepest at the critical temperature and very steep indeed at the critical concentration. The degree of polarisation follows a similar course, and at the critical temperature and concentration the scattered light is almost completely polarised. A formula based on Lorentz's electromagnetic theory is developed to express the amount of scattering at right angles to the primary beam.

W. A. C.

**Spectrophotometric Studies of the Glow Discharge.** R. SEELIGER and W. LINDOW (*Physikal. Z.*, 1925, **26**, 393—403).—The distribution of light intensity at various positions along discharge tubes containing (a) oxygen, (b) hydrogen has been measured for various individual lines in the spectra of the two gases. Graphs are given showing the variation in intensity of the lines 4650 Å. (spark), 4520 (band), 4268 (doublet) for oxygen, and the lines 4634, 4177, 4461 for hydrogen with distance in mm. from the cathode. The curve, distance from cathode—intensity, is plotted for single lines at various gas pressures. The relations between distance, intensity, and pressure are also given for the negative glow. The sharp beginning of the negative glow is clearly shown for single lines, but the distance of the intensity maximum as well as the shape of the curve differs widely for different lines. Hence visual recognition of a sharp edge to the glow loses in theoretical significance unless observations are carried out with suitable light-filters. Generally, the intensity—distance curve is flat for higher excitation potentials and shows a sharp maximum for lower excitation potentials. The work may provide a means of classifying the many-lined spectra.

Quantitative data for the absolute intensity gradient at the edge of the dark space are given, and a close approximation to the mean free path of electrons can be made at different pressures.

A theory is advanced which appears to account for many of the phenomena observed in the discharge tube. The authors consider that the primary electrons ionise the gas in the glow and excite the light; the positively and negatively charged entities then fill the space and by their recombination contribute to the light emission. Diffusion plays an important part, since the swift (and slower) primary electrons travelling in a straight line intersect the paths of the secondary electrons and scattering effects occur. Experiments designed to test this mechanism gave results in accord with the theory.

R. A. M.

**Spectroscopic Study of the Combustion of Phosphorus Trioxide and of Hydrogen Phosphide.** H. J. EMELÉUS (*J. Chem. Soc.*, 1925, **127**, 1362—1368).—A modification of Thorpe and Tutton's method for the preparation of phosphorus trioxide is described. The glow of the trioxide appears as a luminous pulse starting at a considerable distance from the surface. Water vapour is essential to the glow and the pulses occur more readily in the presence of a little liquid water. The spectrum of the light from the glow of the trioxide is identical with that obtained in the case of glowing phosphorus by Emeléus and Downey (this vol., ii, 89). The burning of hydrogen phosphide in air shows the same ultra-violet bands, with that at about  $\lambda=3270$  Å. relatively more intense. Ether and acetone inhibit the glowing of phosphorus and of its trioxide, and also prevent the ignition of an hydrogen phosphide-air mixture when the pressure is reduced; benzene, chloroform, coal gas, and ammonia act less effectively. It is suggested that the low-temperature combustions of phosphorus, phosphorus trioxide, and hydrogen phosphide involve some common stage responsible for the chemical anomalies and intimately associated with the characteristic light emission.

W. T.

**Generalisation of the Townsend Theory of Spark Potentials.** W. DÄLLENBACH (*Physikal. Z.*, 1925, **26**, 407—410).—Mathematical. An attempt to formulate more accurately the interdependence of spark-potential and glow discharge.

R. A. M.

**Electrification of Gases by Surface Combustion.** J. DICKINSON (*Phil. Mag.*, 1925, [vi], **50**, 225—241).—The extent of ionisation accompanying gaseous combustion has been determined by measuring the sign, and the rate of growth, of the charge on an iron chamber in which surface combustion is occurring, and on a metal vessel, acting as an electrode, into which the products of combustion were led. When the gas-air mixture is burnt by surface combustion alone, the charge on the burnt gases (flue gases) is negative for mixtures containing originally less than 16% gas. When that percentage is reached, all electrification disappears. For gas percentages above 16%, the products are positively charged. The 16% gas mixture is that corresponding with complete combustion. In the combustion chamber itself, the above electrification signs are reversed. The burning gases in mixtures with less than 16% gas carry positive charges and impart these charges to the

walls of the combustion chamber. When the gas percentage is above 16%, unburnt gas predominates, and imparts a negative charge.

When there is perfect combustion, there is no electrification either on the chamber or on the flue-box, showing definitely that there is then complete equilibrium between the gases and the heated surfaces, all the surplus electrical discharge being wholly taken up by the gases in the combustion chamber, so that there are no ions in the products of combustion. When the gas mixture burns as a flame, the charge on the combustion products is wholly positive for mixtures between 2.6% and 18.5% gas. On the other hand, the sign on the combustion chamber depends on the temperature, changing from negative to positive with increasing temperature in the neighbourhood of red heat. Evidence that the added heat of combustion during surface combustion is not due to currents in the metal tube is found in the fact that the conductivity of the gases in the chamber during flame combustion is approximately seventy times that of the gases during surface combustion in the cases of optimum gas mixtures.

F. G. T.

**Variation of Dielectric Constants of Organic Liquids with Pressure.** M. GRENACHER (*Ann. Physik*, 1925, [iv], 77, 138—158).—A new technique has been devised for investigating at intervals of 10 atm. the variation of dielectric constant with pressures up to 60 atm. for organic liquids. Accurate results were obtained for toluene, ether, chloroform, carbon tetrachloride, nitrobenzene, nitrotoluene, and bromobenzene. Waibel's results on benzene (*ibid.*, 1922, 72, 161) were used to standardise the apparatus. Nitrobenzene, nitrotoluene, bromobenzene, ether, and chloroform show definitely greater variations of dielectric constant with pressure than is the case for toluene, benzene, and carbon tetrachloride. They correspond with Meyer's dipolar liquids (A., 1924, ii, 515). The difference is most marked with ether and chloroform. For the other liquids, there is some uncertainty because data on the compressibility are lacking.

An improved needle-vibration galvanometer has been devised which is prompt in action and much more convenient than other types in use.

R. A. M.

**Variation of Dielectric Constant with Pressure for Organic Liquids at Pressures up to 800 Atmospheres.** (Fr.) C. FRANCKE (*Ann. Physik*, 1925, [iv], 77, 159—181).—A method for producing high pressures in a condenser is described and a complicated circuit has been devised which enables very accurate measurements of dielectric constant to be made at pressure intervals of 50 atm. up to 800 atm. maximum pressure. The following data were obtained: for benzene at 18°  $\epsilon = 2.2765$  at 50 atm. and 2.3412 at 700 atm.; the pressure coefficient varies from  $4.96 \cdot 10^5$  to  $3.34 \cdot 10^5$ ; the Clausius-Mosotti expression  $\epsilon - 1/(\epsilon + 2) \cdot 1/d$ , leads to extreme values of 0.3373 and 0.3297; for hexane,  $\epsilon = 1.8905$  at 50 atm. and 1.9736 at 800 atm.; the coefficient varies from  $7.25 \cdot 10^5$  to  $4.42 \cdot 10^5$ ; for heptane,  $\epsilon = 1.9468$  at 50 atm. and 2.0224 at 800 atm.; the

coefficient varies from  $6.53 \cdot 10^5$  to  $3.55 \cdot 10^5$ ; for carbon tetrachloride,  $\epsilon = 2.2311$  at 50 atm. and  $2.3222$  at 800 atm.; the pressure coefficient varies from  $6.26 \cdot 10^5$  to  $4.26 \cdot 10^5$ . The temperature coefficients employed were those of Isnardi (*Z. Physik*, 1922, 9, 153) and Graffunder (*Ann. Physik*, 1923, [iv], 70, 225). R. A. M.

**Influence of Solvents on Rotatory Power.** R. LUCAS (*Compt. rend.*, 1925, 181, 45—47).—Investigations on the variation with the wave-length of the specific rotatory power of camphor in benzene, cyclohexane, and in a mixture of these two liquids show that over the range studied, 6708—4358, the value of the expression  $[\alpha]_C - [\alpha]_M / [\alpha]_C - [\alpha]_B$ , is constant,  $[\alpha]_C$ ,  $[\alpha]_B$ , and  $[\alpha]_M$  being, respectively, the specific rotatory powers in cyclohexane, benzene, and the mixed solvent. A theory is developed in which the dissolved substance exists in two forms, each characterised by a definite dispersion and rotatory power, the equilibrium between the two forms being determined by concentration, temperature, and the nature of the solvent. J. S. C.

**Rotatory Power of certain Camphor Derivatives.** A. HALLER and R. LUCAS (*Compt. rend.*, 1925, 180, 1803—1806).—The rotatory power of alcohol and benzene solutions has been measured at seven wave-lengths between 4358 and 6708 Å. for the following compounds: benzylidenecamphor, o-chlorobenzylidenecamphor, anisylidenecamphor, and piperonylidenecamphor. For the second compound,  $[\alpha]$  is a little higher in benzene than in alcohol; for the other compounds,  $[\alpha]$  is about 5—6% lower in benzene than in alcohol. The following show much larger differences: benzylcamphor, anisylcamphor, piperonylcamphor. Measurements of  $[\alpha]$  are given in alcohol, benzene, carbon disulphide, and cyclohexane. The rotatory power varies greatly with the solvent. The quantity  $\delta/\Delta = [\alpha]_{C_6H_6} - [\alpha]_{C_6H_5} / [\alpha]_{C_6H_6} - [\alpha]_{CS_2}$  is practically constant for a given solute, and varies little with wave-length. The constancy of  $\delta/\Delta$  follows from Biot's law for a mixture of two active bodies. Hence it is inferred that two different active forms exist in these solutions. R. A. M.

**Rotatory Power and Dispersion in the Terpene Series.** —PARISELLE (*Compt. rend.*, 1925, 180, 1832—1833).—The rotatory dispersions of d- and l-camphene are identical. The author's method (A., 1923, i, 813) for preparing camphene from pinene hydrochloride has resulted in specimens in which  $[\alpha]_D = -79.90^\circ$  and  $[\alpha]_D = +77.10^\circ$ . The additive compounds of camphene always exhibit rotatory power of the opposite sign to that of the original camphene; the rotatory dispersion is always near to that of  $\alpha$ -pinene and is definitely less than that of camphene and therefore of camphor. The camphene nucleus has thus been modified, an observation which confirms the work of Langlois, who has shown that camphene easily gives rise to abnormal compounds by intramolecular migrations. Ninety-eight % formic acid reacts with camphene in the presence of phthalic anhydride to give isobornyl formate, b. p.  $95^\circ$  (14 mm.),  $d_4^{20}$  1.01,  $n_D^{15}$  1.470,  $[\alpha]_D = -3.14^\circ$ . R. A. M.

**Rotatory Dispersive Power of Organic Compounds. XVI. Halogen Derivatives of Camphor. Optical Superposition in the Camphor Series.** J. O. CUTTER, H. BURGESS, and T. M. LOWRY (*J. Chem. Soc.*, 1925, **127**, 1260—1274).—Measurements have been made of the optical rotations over a range of wavelengths of  $\alpha$ - and  $\alpha'$ -chlorocamphor, of  $\beta$ -bromocamphor, and of five isomeric dibromocamphors. The basis of the principle of optical superposition is illustrated by  $\alpha$ - and  $\alpha'$ -chlorocamphor, the rotatory power of which can be represented by  $[\alpha]_{5461} = 65.5^\circ \pm 24.6^\circ$ ; by  $\alpha$ - and  $\alpha'$ -bromocamphor,  $[\alpha]_{5461} = 51.8^\circ \pm 98.9^\circ$ , and by  $\alpha\beta$ - and  $\alpha'\beta$ -dibromocamphor,  $[\alpha]_{5461} = 8.8^\circ \pm 91.9^\circ$ , whereas the means of the rotatory powers of the pairs camphor  $\alpha\alpha'$ -dichlorocamphor, camphor  $\alpha\alpha'$ -dibromocamphor, and  $\beta$ -bromocamphor and  $\alpha\alpha'\beta$ -tribromocamphor are  $[\alpha]_{5461} = 62.1^\circ$ ,  $51.3^\circ$ , and about  $12^\circ$ , respectively. No such regularities were observed with the  $\pi$ -compounds. In nine cases out of ten, the curves of rotatory dispersion are complex, but normal. The rotation increases progressively as the wave-length diminishes, giving rise to quasi-hyperbolic dispersion curves, which do not exhibit any obvious anomalies; the dispersion is not simple, since it cannot be represented by a single term of Drude's equation. The dispersion can be represented satisfactorily by two terms of Drude's equation, except for  $\alpha'\beta$ -dibromocamphor. The dispersions of this substance are more complex, giving imaginary values for the constants of the two-term equation.

In the constants for the Drude equation, the low-frequency term, representing the contribution of the ketonic group to the optical activity of the molecule, is always positive, as in camphor. The high-frequency term, representing the sum of the partial rotations of the fixed asymmetric centres, is negative in camphor, and remains so in  $\beta$ -bromocamphor and in  $\alpha\alpha'$ -dibromocamphor, where no new centre of asymmetry is introduced, and the dispersion is quasi-anomalous. In compounds containing a halogen atom in the  $\alpha$ -position, the large partial rotation of the new asymmetric carbon atom makes the high-frequency term positive, and the dispersion is complex but normal.

In the two  $\alpha'$ -derivatives the fixed negative rotation of the camphor molecule is reinforced by the negative partial rotation of the new asymmetric carbon atom. For  $\alpha'$ -bromocamphor the negative term of the Drude equation predominates over the positive in the visible region, but a reversal of sign is observed in the early ultra-violet region. The dispersion curve becomes totally anomalous, and an inflection at 5455, maximum at 4710, and a reversal of sign at 3890 Å. have been experimentally observed. F. G. T.

**Variation of Rotatory Power of Solutions of Asparagine as a Function of Hydrogen-ion Concentration.** (MLLE.) J. LIQUIER (*Compt. rend.*, 1925, **180**, 1917—1919).—The rotatory power of asparagine between  $p_H$  1.29 and  $p_H$  9.91 is measured by adding varying amounts of strong and weak acids or bases. The dispersion is normal at extreme  $p_H$  values, but anomalous at the intermediate value of  $p_H = 3$ . The rotation at a given  $p_H$  is constant

whether the added acid is weak or strong, showing that a close connexion exists between dissociation and rotatory power. On the basis of a mixture of undissociated molecules and ions, a three-term expression gives quantitatively the rotatory power as a function of hydrogen-ion concentrations and of the two dissociation constants of the amphoteric asparagine. R. A. M.

**Influence of Hydrogen-ion Concentration on the Optical Rotation of Gelatin.** R. H. BOGUE and M. T. O'CONNELL (*J. Amer. Chem. Soc.*, 1925, **47**, 1694—1697).—The specific rotation of 2% solutions of isoelectric and ash-free gelatin at 30° varies with the hydrogen-ion concentration. Within the range examined,  $p_H$  0.3 to  $p_H$  13.4, in which hydrolysis is improbable under the conditions employed (cf. Northrop, A., 1921, ii, 541), the specific rotation exhibits a minimum at the isoelectric point,  $p_H$  4.7, and then rises as the acidity or alkalinity is increased, subsequently decreasing in high concentrations of acid or alkali. There is no indication of a second isoelectric point at  $p_H$  7.7. At  $p_H$  4.7, the specific rotation of pure ash-free isoelectric gelatin in 2% solution at 30° is  $-104^\circ (\pm 4^\circ)$ . R. B.

**Colours Shown by Nobili's Rings.** B. N. CHUCKUBUTTI (*Proc. Indian Assoc. Cult. Sci.*, 1924, **9**, 83—91).—Nobili's rings may be obtained with a variety of cathodes and electrolytes, but the finest display results when a brass plate is used in lead sulphate or manganous sulphate solution. The rings consist of granular particles of metal or oxide and are largest ( $d=500\mu\mu$ ) near the centre and smallest ( $d=275\mu\mu$ ) at the periphery. It is suggested that the colours are due to diffraction by these granules, and the similarity to metal colours produced by heat is pointed out. W. A. C.

**The Significance of Atomic Constants in Additive Properties.** F. SWARTS (*Bull. Soc. chim. Belg.*, 1925, **34**, 161—182).—The existing tendency to ascribe definite values to various groups or atoms in respect of additive properties such as atomic and molecular volumes, magnetic rotation, refractivity, etc., and the establishment of general formulæ which are only verified to a very large degree of approximation is keenly criticised. Such functions, due to the fundamental properties of the electrons within the atom, are profoundly affected, not only by the structure of the molecule, but vary with the proximity of different atoms and the strength of the electromagnetic field within the molecule, and an approximate calculation shows that the latter may be of the order of  $10^3$  gauss, i.e., that of the most powerful field employed in the study of magnetic rotatory power. Real progress can best be made by greater precision in the physical measurements and a determination of the atomic variations rather than the atomic "constants" in relation to compounds the structure of which has been firmly established by chemical means. The author's investigations show that fluorine exhibits the most regular behaviour in organic compounds and often establishes interesting relationships which are masked when the other halogens are used as substituents. The effect of fluorine on molecular dispersion is extremely small, its



spectrum shows the absence of rays in the near ultra-violet, and fluorine derivatives show much less absorption in that region than do the corresponding hydrocarbons themselves, and hence the frequency of the electrons must be very great. J. W. B.

**Heat of Formation of Formaldehyde.** H. VON WARTENBERG and LERNER-STEINBERG (*Z. angew. Chem.*, 1925, **38**, 591—592).—The experimental value of the heat of formation of formaldehyde, 158.8 cal. per mol.  $\text{CH}_2\text{O}$ , is not in accordance with theory; the experimental work has therefore been repeated. No error had arisen from incomplete combustion, but a slight tendency to polymerisation of the formaldehyde on the walls of the containing apparatus was detected. Whilst this error is considered to have been slight, a series of repetitions of the determination gave a final corrected value of 134.1 cal./mol. at constant volume, and this value, which is in fair agreement with that given by calculation (126.7 cal.), is to be substituted for the previous one. C. I.

**X-Ray Crystal Analysis as an Auxiliary in Organic Chemical Research.** R. ROBINSON (*Nature*, 1925, **116**, 45).—A brief account of the successful application, by Shearer, of X-ray analysis to the determination of the length of carbon chains and the position of a carbonyl group. Similar investigations indicate that the acetylenic linking of stearolic acid is hydrated in each of the theoretically possible directions, *i.e.*,  $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CO}\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{H}$  and  $\text{CH}_3\cdot[\text{CH}_2]_8\cdot\text{CO}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$ , when the substance is treated successively with sulphuric acid and water. A. A. E.

**X-Ray Analysis of Solid Solutions of Potassium Chloride and Potassium Bromide.** T. SASAHARA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, **2**, 277—286).—Powder photographs of fusion-mixtures ranging from 22 mol. % to 88 mol. % of potassium bromide indicate complete additivity in the lattice constant; the density also is additive. Although the mean lattice constant is thus a linear function of the concentration, it is probable that the spacing is a little smaller in the neighbourhood of chlorine atoms and a little larger in that of bromine atoms. W. A. C.

**X-Ray Examination of the Inner Structure of Various Calcium Carbonates.** A. ÔSAWA (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 33—41).—X-Ray examination of various forms of calcium carbonate derived from animal and vegetable sources showed that most varieties consisted of the calcite modification, but calcium carbonate from an *Acropora*, a *Favia*, *Septifer bilocularis*, and *Trubo cornutus* consisted of the aragonite variety. The author's aragonite model agrees with that of Bragg (A., 1924, ii, 109). A. R. P.

**X-Ray Analysis of Electrolytic Brass.** H. NAKAMURA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, **2**, 287—292).—Electrolytically deposited brass of 82.48% of copper and cast brass of 82.85% of copper have been examined by the powder method and the lattice constant 3.62 Å. has been found in both cases. In spite of con-

siderable differences in the microscopic structure of the two brasses, their atomic structures must be regarded as identical. After annealing, however, the constant of the electrolytic brass was 3.62 Å. and that of the cast brass 3.61 Å. W. A. C.

**X-Ray Analysis of Copper-Zinc, Silver-Zinc, and Gold-Zinc Alloys.** A. WESTGREN and G. PHRAGMEN (*Phil. Mag.*, 1925, [vi], 50, 311—341).—It is suggested that the fundamental difference between solid chemical compounds and solid solutions lies in their structure. In an ideal chemical compound, structurally equivalent atoms are chemically identical. In an ideal solid solution all atoms are structurally equivalent. Most metallic phases represent intermediate stages between these two extreme types of structure. X-Ray analysis of the above alloys has shown that five different types of structure are common to all three systems, two additional phases occurring in the gold-zinc system. The  $\beta$  and  $\gamma$  phases of the copper-zinc system were investigated in the form of single crystals, the analyses in the other cases being made by the powder method alone. The five structures common to the systems, arranged in order of increasing zinc content, are:  $\alpha$ , face-centred cubic;  $\beta$ , cubic of the caesium chloride type;  $\gamma$ , cubic, with 52 atoms in the elementary cube;  $\epsilon$  and  $\eta$ , close-packed hexagonal with axial ratios of 1.55—1.60 and 1.80—1.90, respectively. A gold-zinc phase,  $\gamma_1$ , stable at the ordinary temperature, and containing about 50% zinc, was cubic, with about 32 atoms in the elementary cube; another phase,  $\gamma_2$ , stable only at higher temperatures and obtained by quenching gold-zinc alloys containing 53—54% zinc, was apparently cubic with about 90 atoms in its elementary cube. The  $\alpha$ ,  $\eta$ , and very probably the  $\epsilon$  phases represent ideal solid solutions as above defined, the first having copper, silver, or gold, and the others zinc as solvent. The other phases are regarded as solid solutions in chemical compounds, the solvents of the  $\beta$  phases being CuZn, AgZn, and AuZn. The formulæ  $\text{Cu}_4\text{Zn}_9$ ,  $\text{Ag}_4\text{Zn}_9$ , and  $\text{Au}_4\text{Zn}_9$  are proposed for the bases of the  $\gamma$  phases, and it is most likely that the  $\gamma$  phase of the gold-zinc system corresponds with  $\text{AuZn}_3$ .

F. G. T.

**X-Ray Examination of Inner Structure of Strained Metals.**  
**III. Copper and Aluminium under Extension, Compression, and Torsion.** A. ONO (*Mem. Coll. Eng. Kyushu*, 1925, 3, 195—224).—An X-ray analysis of copper and aluminium, under strain due to extension, compression, or torsion, has been made. The effect of annealing strained aluminium has also been determined. The crystal rearrangement due to slip and rotation is discussed from the point of view of the behaviour of single crystals under distortion observed by previous investigators. [Cf. *B.*, 1925, 594]. M. S. B.

**X-Ray Examination of Iodosuccinimide.** (MISS) K. YARDLEY (*Proc. Roy. Soc.*, 1925, A, 108, 542—547).—There are 4 mols. per unit cell of this substance. It does not belong to the ditetragonal pyramidal class, as stated by Groth, but to the tetragonal pyramidal polar class (cf. following abstract). L. F. G.

**Crystallographic and Optical Properties of Iodosuccinimide.** A. E. H. TUTTON (*Proc. Roy. Soc.*, 1925, A, 108, 548—552; cf. preceding abstract).—The results of a detailed examination of these properties are given. Density determinations have also been made. The substance is optically active, but it was not possible to determine the angle of rotation. Miss Yardley's conclusion as to the crystallographic class is confirmed. L. F. G.

**Quantum Theory of the Intensity of the Modified Band in the Compton Effect.** G. E. M. JAUNCEY (*Physical Rev.*, 1925, [ii], 25, 723—736).—The theory already developed (this vol., ii, 368) is extended to scattering by *L* and *M* electrons and by electrons in elliptical orbits. Experiments are in qualitative agreement with the required increase of the intensity of the modified band relative to that of the unmodified band as the angle of scattering is increased, and (for a given angle of scattering) with its required decrease as the atomic number of the scatterer increases. Curves show the intensity of the modified bands when molybdenum  $K\alpha$  X-rays are scattered by carbon and sulphur at 30° and 90°.

A. A. E.

**Dependence of the Intensity of the Compton Effect on the Atomic Number.** B. DAVIS (*Physical Rev.*, 1925, [ii], 25, 737—739).—The integrated intensity of the scattered radiation is proportional to  $b/z^3\lambda^3$ , where *z* is the atomic number and *b* the fraction of orbital electrons taking part in the scattering. All the orbital electrons appear to take part equally in the scattering effect. The relative intensities for molybdenum  $K\alpha$  radiation for paraffin, aluminium, sulphur, and calcium, respectively, are 8, 1.25, 0.7, and 0.35.

A. A. E.

**Lattice Constants of Metals.** W. P. DAVEY (*Physical Rev.*, 1925, [ii], 25, 753—761).—Precision measurements of the lattice constants  $a \times 10^{-8}$  cm., by comparison with sodium chloride ( $a = 2.814 \text{ \AA}$ .) and the corresponding calculated densities are tabulated respectively as follows: aluminium,  $4.046 \pm 0.004$ ,  $2.688 \pm 0.008$ ; iron,  $2.855 \pm 0.003$ ,  $7.93 \pm 0.03$ ; nickel,  $3.499 \pm 0.003$ ,  $9.04 \pm 0.03$ ; copper,  $3.597 \pm 0.004$ ,  $9.01 \pm 0.03$ ; molybdenum,  $3.142 \pm 0.003$ ,  $10.21 \pm 0.03$ ; palladium,  $3.859 \pm 0.004$ ,  $12.25 \pm 0.04$ ; silver,  $4.079 \pm 0.004$ ,  $10.49 \pm 0.03$ ; tungsten,  $3.155 \pm 0.001$ ,  $19.32 \pm 0.02$ ; platinum,  $3.912 \pm 0.004$ ,  $21.51 \pm 0.06$ ; gold,  $4.065 \pm 0.004$ ,  $19.37 \pm 0.06$ ; lead,  $4.920 \pm 0.005$ ,  $11.48 \pm 0.03$ ; bismuth,  $4.539 \pm 0.005$  (hexagonal axes, axial ratio 2.606),  $9.80 \pm 0.03$ .

A. A. E.

**Atomic Structure of Palladium and Platinum Black containing Adsorbed Gases.** A. OSAWA (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, 14, 43—45).—X-Ray examination of platinum and palladium blacks prepared by different processes show that the metal is crystalline and not amorphous as stated by Kirchner (*Ann. Physik*, 1922, [iv], 69, 59). When the metals adsorb gases a true solid solution is formed, the gases entering into the interspace of the lattice.

A. R. P.

**Crystal Structures of Cæsium Tri-iodide and Cæsium Dibromiodide.** R. M. BOZORTH and L. PAULING (*J. Amer. Chem. Soc.*, 1925, **47**, 1561—1571).—The dimensions of the units of structure of cæsium tri-iodide and cæsium dibromiodide as determined from considerations of spectral and Laue photographs are respectively:  $d_{100}=6.83 \text{ \AA.}$ ,  $d_{010}=9.89 \text{ \AA.}$ ,  $d_{001}=11.00 \text{ \AA.}$ , and  $d_{100}=6.57 \text{ \AA.}$ ,  $d_{010}=9.18 \text{ \AA.}$ ,  $d_{001}=10.66 \text{ \AA.}$  In the crystalline substances there are four molecules in the unit. The structures are based on the simple orthorhombic lattice  $\Gamma_0$  and the crystals belong to the space group  $V_h^6$ . The results of these investigations differ from those of Clark and Duane (*J. Opt. Soc. Amer.*, 1923, **7**, 455). J. S. C.

**Crystal Structure of Mercurous Halides.** R. J. HAVIGHURST (*Amer. J. Sci.*, 1925, [v], **10**, 15—28).—X-Ray analysis of powdered and of single crystals of mercurous halides (cf. this vol., ii, 502) shows that the cell units are tetragonal and contain 2 mols. of  $\text{Hg}_2\text{X}_2$ . The dimensions (in  $\text{\AA.}$ ) are:  $\text{X}=\text{Cl}: a=4.47, c=10.89$ ;  $\text{X}=\text{Br}: a=4.65, c=11.10$ ;  $\text{X}=\text{I}: a=4.92, c=11.61$ . Mauguin's cell unit for calomel is unnecessarily large (cf. A., 1924, ii, 588). The atomic arrangement may be derived from the space group  $D_2^2$ , or others; four mercury atoms are at  $(0, 0, u)$ ,  $(0, 0, \bar{u})$ ,  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-u)$ , and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+u)$  and four halogen atoms at  $(0, 0, v)$ ,  $(0, 0, \bar{v})$ ,  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-v)$ , and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+v)$ .  $u$  and  $v$  are slightly lower than  $\frac{1}{8}$  and  $\frac{3}{8}$ , respectively. The results indicate the existence of the chain molecule  $\text{XHgHgX}$ ; strong positive double refraction is to be expected from crystals of this structure and has been observed. S. K. T.

**Structure of Stearic and Stearolic Acids.** A. MULLER (*Nature*, 1925, **116**, 45).—Stearic acid crystals, obtained from a saturated solution in carbon disulphide, are monoclinic. The dimensions of the unit cell are:  $a \ 5.60, b \ 7.38, c \ 50.9 \text{ \AA.}$ ,  $\beta \ 59.7^\circ$ ;  $d$  slightly above 1.05, indicating four molecules to the unit cell. A crystal of stearolic acid appeared to be triclinic. A. A. E.

**Crystalline Structure of Pentaerythritol Tetranitrate.** I. E. KNAGGS (*Min. Mag.*, 1925, **20**, 346—352).—Pentaerythritol tetranitrate (T., 1923, **123**, 77), examined by the X-ray spectrometer method, was found to be built on the simple tetragonal lattice  $\Gamma_0$ , to belong to the space-group  $D_{2d}^2$ , and to have 4 mols. of  $\text{C}(\text{CH}_2\text{O}\cdot\text{NO}_2)_4$  per unit cell of dimensions  $a=13.2, c=6.66 \text{ \AA.}$  The arrangement of the atoms in the nitro group is thought to be  $-\text{N} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$

or  $-\text{N} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ , and not  $-\text{N}=\text{O}=\text{O}$ . The angles between the linkings from the central carbon atom show a considerable departure from the angle of the regular tetrahedron, and this perhaps causes a strain which contributes to the explosive nature of the compound.

L. J. S.

**Isomorphism of Zirconium Sulphate and Quadrivalent Cerium Sulphate.** L. FERNANDES (*Gazzetta*, 1925, **55**, 290—293).—The compounds,  $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  are

completely miscible and hence able, in all proportions, to form mixed crystals. T. H. P.

**Monoclinic Double Sulphates containing Thallium. Thallium Nickel and Thallium Cobalt Sulphates.** A. E. H. TUTTON (*Proc. Roy. Soc.*, 1925, A, 108, 240—261).—A full crystallographic description is given of these two salts. The results confirm the conclusion previously reached from an examination of thallium zinc sulphate and selenate, that these double salts containing thallium are true members of the isomorphous series of monoclinic hexahydrated double sulphates and selenates  $R_2M(SO_4)_2 \cdot 6H_2O$ . These all crystallise in the holohedral class of the monoclinic system. The small angular changes, which occur on substituting either thallium or rubidium for potassium in the salt, are about equal.

S. B.

**Regular Growth of Crystals of Different Species.** L. ROYER (*Compt. rend.*, 1925, 180, 2050—2052).—Regular growth of crystals of one substance on crystals of another requires an approximate identity of form and dimensions of the two lattices. The growth of crystals of alkali and silver halides on cleavage faces of potassium chloride, galena, and sodium chloride has been studied. Regular growths occur if the differences in the dimensions of the two lattices do not differ by more than 12, 10, and 16% in the three cases, respectively, but if these limits are exceeded the crystals are deposited quite irregularly. No formation of mixed crystals occurs when potassium and sodium chloride are deposited simultaneously.

W. H.-R.

**Crystal Structure and Physical Properties.** A. E. VAN ARKEL (*Physica*, 1924, 4, 286—301).—By passing the corresponding chlorides, together with hydrogen, and nitrogen or carbon monoxide, over a heated tungsten wire, titanium, zirconium, and tantalum nitrides and carbides have been prepared. In the regular system, values of  $d_{100}$  are: titanium carbide, 4.29 Å., nitride, 4.23 Å.; zirconium carbide, 4.71 Å., nitride, 4.59 Å.; tantalum carbide, 4.56 Å. For tantalum nitride (hexagonal, with 2 mols. per unit cell) Ta ( $\frac{1}{3} \frac{2}{3} u$ )( $\frac{2}{3} \frac{1}{3} \bar{u}$ );  $u=0.25$ , axial ratio 1.62, edge of basal hexagon 3.05 Å. Combination of the metal with two oxygen or fluorine atoms still produces the ionic type of lattice, sulphides and selenides being intermediate between ionic and molecular lattices. In the regular system, values of  $d_{100}$  are: zirconium dioxide, 5.08 Å., thorium dioxide, 5.26 Å., uranium dioxide, 5.48 Å., strontium fluoride, 5.86 Å. Zirconium sulphide and selenide crystallise in the rhombohedral hexagonal system, with respective axial ratios 1.59, 1.63; edge of hexagon, 3.68, 3.79 Å.; (1 mol. per unit cell) Zr (000); S (Se) ( $\frac{2}{3} \frac{1}{3} u$ )( $\frac{1}{3} \frac{2}{3} \bar{u}$ ) with  $u=0.25$ , analogous to cadmium iodide. Ferrous and manganous sulphides form ionic space lattices.

CHEMICAL ABSTRACTS.

**Electrical Conductivity of Mixed Crystal Alloys.** G. BOBELIUS (*Ann. Physik*, 1925, [iv], 77, 109—137).—The specific

conductivity of a metal is given according to Drude by the expression (1)  $\chi = \epsilon^2/2m \cdot NL/\mu$ , where  $\epsilon$  is the charge,  $m$  the mass,  $\mu$  the velocity,  $N$  the number per c.c., and  $L$  the mean free path of the conducting electron. Wein regarded  $\mu$  as a constant independent of temperature and characteristic of an atomic movement, and  $N$  as also constant, so that the temperature variation of  $\chi$  would be due to the direct proportionality between energy content and  $L$ . Højendahl (A., 1924, ii, 647) sought an explanation on the basis of the Bohr atom and the independence of the translation velocity of the valency electron with temperature. He considered that the mean free path is constant from atom to atom of the same element, but that atoms of the second component interfere.  $N$  and  $\mu$  were assumed to be constant throughout a series of alloys. The expression  $\chi = \text{constant} \cdot (1/pq - 1)$  ( $p$  and  $q$  are concentrations of components) was deduced and found to be in agreement with experiment for Cu-Ni alloys. The author, however, finds that the agreement is fortuitous, since other series of alloys do not confirm Højendahl's reasoning. The discrepancy is due to the simplicity of the assumptions.  $N$  and  $\mu$  are now assumed to differ for the two components of a mixture, and (1) is rewritten as (2)  $\chi = \epsilon^2/2m(N_1L_1/\mu_1 + N_2L_2/\mu_2)$  and simplified to (3)  $\chi = A'pL_1 + B'qL_2$ , where  $A'$  and  $B'$  are constants characteristic of the two components.

On this basis, it is deduced that the conductivity at absolute zero is given by (4)  $\chi_0 = Ap/q + ap + Bq/p + bq$ , where  $A, B, a, b$  are constants. This assumes random distribution of atoms and a straight line free path ( $a$ ). To test the theory, it is necessary to investigate theoretically the variation of the resistance of alloys with temperature. It is then shown that the resistance  $\rho'$  of an alloy is given by  $\rho' = p\rho_1 + q\rho_2 + \rho_0$ , where  $\rho_1$  and  $\rho_2$  are the specific resistances of the components at the temperature of the alloy,  $p\rho_1$  and  $q\rho_2$  are interpolated linearly, and  $\rho_0$  is a quantity independent of temperature. At the absolute zero,  $\rho_1$  and  $\rho_2$  vanish, so that

$\chi_0 = \frac{1}{\rho_0} = 1/\rho' - p\rho_1 - q\rho_2$ . Thus  $\chi_0$  may be obtained from the experimental data and compared with the value obtained by the use of (4). The theoretical treatment is confirmed by the following systems: Au-Ag, Au-Cu, Pd-Pt, In-Pb, K-Rb. For example, in Au-Ag  $\chi_0 = 27p/q + 80p + 27q/p + 45q \text{ ohm}^{-1} \text{ cm}^{-1} \cdot 10^3$ . The data for the systems Cu-Ni, Au-P, Ag-Pd, Cu-Pd are also considered. The range of validity of assumptions ( $a$ ) is discussed. Further, the results are used to calculate values for the mean free path and for the electron velocity in various elements. Regularities in the values of the constant  $A$  are pointed out which may prove significant when the theory can be tested more rigidly. (Cf. Cuy, this vol., ii, 378.)

R. A. M.

**Electric and Magnetic Spectroscopy.** W. ARKADIEV (*Phil. Mag.*, 1925, [vi], 50, 157-163). It is pointed out that since thermal waves have the same relation to magnetic centres in dielectrics as X-rays to electric centres, somewhere in the intermediate region between thermal oscillations and slow electric

vibrations the disappearance of magnetic behaviour must occur, accompanied by magnetic absorption of the passing rays and strong alteration of the magnetic permeability. This is illustrated by the magnetic spectra of iron and nickel wires in the wave-length region 1 cm. to 1 km. The apparent permeabilities of these substances, calculated from the absorption of waves in ferromagnetic wires, agree with the assumption that the elementary magnets in ferromagnetic metals, under the influence of weak magnetic fields, rotate according to the same laws of viscous-elastic motion adopted for the displacement of electric centres in dielectric bodies.

F. G. T.

**Weiss's Theory of Ferromagnetism.** R. H. DE WAARD (*Z. Physik*, 1925, **32**, 789—793).—The theory fails to account even approximately for the small coercive force necessary to remove residual magnetism in iron and nickel.

E. B. L.

**Magnetisation of Ferro-nickel: Saturation and Atomic Moments.** M. PESCHARD (*Compt. rend.*, 1925, **180**, 1836—1838).—The specific magnetisation of iron and nickel mixtures has been plotted against percentage composition for the three temperatures  $+16^\circ$ ,  $-79^\circ$ ,  $-188^\circ$ . The compound  $\text{Fe}_2\text{Ni}$  is very definitely indicated. The value at  $0^\circ$  Abs. for each saturation is extrapolated by means of the expression  $\sigma = \sigma_0 - KT^2$ . The atomic moments (expressed in magnetons) are plotted against percentage composition and the curve is closely similar to that obtained for specific saturations at absolute zero. Both curves provide evidence for the existence of  $\text{Fe}_2\text{Ni}$ ,  $\text{Fe}_3\text{Ni}_2$ , and  $\text{FeNi}_2$ . The first two have 9 magnetons per atom and the third has a total of 20 magnetons. The magnetisation to saturation point of solid solutions in equilibrium obeys the mixture rule. At each temperature, a hyperbolic function  $\sigma = \sigma_\infty (1 - a/H)$  represents the degree of saturation and the coefficient  $a$  varies from one alloy to another from 1 to 40. Ferro-nickel may exist in the  $\beta$  or  $\gamma$  state and the bearing of this fact on the results is worked out.

R. A. M.

**Optical Constants of Crystals of Selenium and Tellurium between 3000 and 5000 Å.** R. F. MILLER (*J. Opt. Soc. Amer.*, 1925, **10**, 621—634).—When plane polarised light is reflected from the surface of an absorbing medium it becomes in general elliptically polarised, and if the form of the elliptical vibration is determined for some angle of incidence, the optical constants of the medium may be calculated. Such determinations have been made with crystals of selenium and tellurium, with the crystal axis parallel and perpendicular to the plane of incidence, and the corresponding values for the refractive indices and reflecting powers are given. In the parallel position  $\mu$  for selenium is 3.4—4.4, and for tellurium 1.9—2.9, and in the perpendicular position, for selenium 2.3—3.1, and for tellurium 1.7—2.7, over the given range of wave-length. The analysis of the reflected light was made by a photographic method described by Voigt (*Physikal. Z.*, 1901, **2**, 203).

S. B.

**Polymorphic Transformations of Silica.** L. LONGCHAMBON (*Compt. rend.*, 1925, **180**, 1855—1858; cf. A., 1913, ii, 133; 1919, ii, 420).—In the presence of a solvent (tungstate, molybdate, silicate, etc.) between 870° and 1470°, precipitated silica dissolves rapidly and after a few minutes hexagonal tridymite and  $\beta$ -cristobalite appear. The latter is slowly converted into tridymite, the stable form under these conditions. Quartz is converted into tridymite at 870—1470°. Cristobalite is not normally an intermediate product. The condition for its appearance is supersaturation of the solvent. Above 1470°, quartz, tridymite, silica, glass, and precipitated silica all form cristobalite (octahedra). With the precipitated silica numerous droplets of fused silica occur at 1500°,  $d$  (cold) 2.2. Below 870°, precipitated silica dissolves rapidly, giving tridymite and cristobalite, quartz being formed only very slowly. New determinations of  $n$  and  $d$  of cristobalite and tridymite give 1.487, 2.347 and 1.477, 2.266, respectively.

R. A. M.

**Increase of Tensile Strength and Recovery of Zinc Crystals.** E. SCHMID (*Z. Physik*, 1925, **32**, 918—921).—The tensile strength increases with plastic deformation, but this action is partly reversed if the crystal is allowed time to recover.

E. B. L.

**Strengthening and Weakening of Tin Crystals.** M. POLANYI and E. SCHMID (*Z. Physik*, 1925, **32**, 684—712).—Single crystals of tin were subjected to slight tension and the rate of increase of length was measured; the results show increased resistance with deformation. When the stress was removed the crystals recovered, rise of temperature hastening the recovery greatly. Consequently the rate of stretching and the temperature influence the extent to which the crystals gain in strength. The recrystallisation of tin crystals was investigated by etching and by the X-ray spectrograph. Crystals were examined which had been stretched, quickly pulled apart, and compressed. Crystals both with and without cleavage lines were tested, the position at which the nucleus of the new crystal formed and the rate of formation were noted. Crystals which have been slowly and carefully drawn out and their internal energy increased are much less liable to crystallise than such as have been rapidly torn apart.

E. B. L.

**X-Ray Study of Soaps and Fats.** J. J. TRILLAT (*Compt. rend.*, 1925, **180**, 1838—1840; cf. this vol., ii, 640).—When an alcoholic solution of a fatty acid is allowed to evaporate on glass, the crystals are oriented. Metal plates have been substituted for glass. With some metals, the X-ray spectra are the same as with glass; with others, a second spectrum, traced to a film of soap in which the molecules are also oriented, is superimposed. It is intense with plates of lead, tin, and antimony, fairly intense with iron, copper, and bismuth, feeble with nickel, zinc, and molybdenum, and absent with aluminium, palladium, platinum, and gold. All the soaps of palmitic acid have the same maximum distance of 46.3 Å. (except copper, 43.5 Å.). The lead soaps of a series of fatty



acids have been examined. The maximum distances for the stearate (51.3), palmitate (46.3), and myristate (41.2) exhibit constant differences  $\Delta(C_{n+2}-C_n)=5 \text{ \AA.}$ , or  $\Delta d/\Delta N$  ( $N$  is number of carbon atoms) $=1.25 \text{ \AA.}$  This value increases to about  $1.3 \text{ \AA.}$  when  $N$  is smaller. It is smaller than that observed with the fatty acids ( $1 \text{ \AA.}$ ) and nearer to that of the ethers ( $1.22 \text{ \AA.}$ ). Most simple fats and waxes are oriented by simple fusion on glass, *e.g.*, glyceryl margarate has  $d=48 \text{ \AA.}$  Even a compound like lecithin is oriented,  $d=47 \text{ \AA.}$

R. A. M.

**Determination of Avogadro's Number from the Light Diffused by Ethyl Chloride.** P. DAURE (*Compt. rend.*, 1925, **180**, 2032—2034).—Avogadro's number ( $N$ ) is calculated by the equation of Einstein from new measurements of the ratio  $R$  for ethyl chloride, where  $R$  is the ratio between the intensity  $I$  of light diffused at right angles to the primary beam of intensity  $E$  for 1 c.c. of gas. As the light used was not monochromatic, an approximate method of graphical integration was used. The method gives the values  $N=(6.5 \pm 0.65)10^{23}$ , and  $R=(1.06 \pm 0.1)10^{-7}$  for green light.

W. H. R.

**Revision of Weight of Normal Litre of Methyl Chloride Vapour.** T. BATUECAS (*Compt. rend.*, 1925, **180**, 1929—1932),—Methyl chloride vapour obeys the law of limiting densities. The vapour was prepared by two methods (*a*) the reaction between phosphorus trichloride and methyl alcohol (*cf.* T., 1905, **87**, 1592) and (*b*) by thermal decomposition of tetramethylammonium chloride. The highest and lowest values of seven determinations made with suitable precautions were 2.3099 and 2.3072. The final value,  $2.3084 \pm 0.0001$ , is definitely higher than the only other precise measurement 2.3045 (Baume, A., 1908, ii, 372).

R. A. M.

**Revision of the Compressibility of Methyl Chloride and the Molecular Weight of this Gas.** T. BATUECAS (*Compt. rend.*, 1925, **181**, 40—42).—Employing the method previously outlined (A., 1924, i, 1280), the value of the factor  $(1+\lambda)$  for methyl chloride has been determined from measurements of compressibility. As with dimethyl ether, the compressibility decreases in a characteristic manner with decreasing pressure. The value for the weight of a litre of gaseous methyl chloride under standard conditions is 2.3084 g. This leads to a value for the atomic weight of chlorine,  $\text{Cl}=35.47$ .

J. S. C.

**Effect of a Magnetic Field on the Electrical Resistance of Liquid Metals and Alloys.** E. J. WILLIAMS (*Phil. Mag.*, 1925, [vi], **50**, 27—46).—Theoretical. The change in the electrical resistance of a liquid conductor due to the action of a magnetic field is attributed to the sum of a true resistance change, and a change consequent on energy expended in maintaining hydrodynamic currents in the liquid conductor. These currents are set up because the magnetic field and electric current in the conductor are independent, whereas, for the liquid to remain at rest,

it is necessary for the force per unit volume acting on the liquid to be derivable from a single-valued potential function. An expression is obtained by means of dimensional analysis for the resistance change due to this cause. An analysis of the results of Rossi (*Nuovo Cim.*, 1911, [vi], 2, 337) reveals evidence for the existence of a true resistance change in a magnetic field in bismuth amalgams, a 1% amalgam showing a resistance increase of 0.0001% in a field of 4000 gauss. The similar change in molten bismuth (Berndt, *Ann. Physik*, 1907, [iv], 23, 805) is estimated as approximately 0.002% at 420° for a field of 3000 gauss. In other cases, the hydrodynamical effect certainly predominates, and, in most cases, a true change, if present at all, is negligible. The variation of the resistance change with the current traversing the liquid metal conductor, which has been observed in some cases, is explained by supposing that the motion of the liquid in these instances is turbulent. The further theoretical consequences of this supposition are substantiated by the experiments of Jones (cf. following abstract), from which it is shown that in the turbulent motion of liquids in an enclosed space, due to the action of external volume forces, the average stream-lines maintain a constant shape as these forces are varied proportionately at all points. In this respect the average stream-lines of turbulent motion resemble the stream-lines in steady motion. The resistance to the motion is in all cases proportional to (velocity)<sup>1.70</sup>, which is in agreement with the law of resistance in turbulent motion obtained by Osborne Reynolds for the flow of water through straight pipes. F. G. T.

#### Electrical Resistance of Mercury in Magnetic Fields.

T. J. JONES (*Phil. Mag.*, 1925, [vi], 50, 46—60).—In a column of mercury of about 5 cm. diameter, to which a magnetic field varying between 2 and 10 kilo.-gauss is applied perpendicular to the direction of the current, the magneto-resistance change for currents between 0.5 and 5 amp. is given by  $\delta R \propto H^{1.58} d/i^{0.40} b^{0.41}$ , where  $H$ ,  $d$ ,  $i$ , and  $b$  are respectively the field, the diameter of the column, the current in the column, and the distance apart of the poles of the magnet. It was found that the change of resistance is independent of the field resistance, but depends on the temperature, increasing by 12.5% for a rise of 273°. When the magneto-resistance change is measured in wide tubes and with comparatively large fields and currents, the effect is of a different nature from that exhibited by solid metals, with which the resistance change is proportional to the resistance in the field and independent of the current in the conductor. The theory of Williams (cf. preceding abstract) explains all the phenomena observed and gives for the resistance change a relation which is in good agreement with that obtained in the experiments. F. G. T.

**Thermal Variation of Magnetism of Water and of Some Paramagnetic Solutions.** B. CABRERA and A. DUPRIER (*J. Phys. Radium*, 1925, [vi], 6, 121—138).—The Curie-Weiss equation  $\chi(T+\Delta)=C$  for the variation of paramagnetism with temperature is valid over a wide range of temperatures ( $\chi$  is the susceptibility,

$T$  absolute temperature,  $\Delta$  and  $C$  are constants characteristic of the substance). Langevin's expression  $\mu_0 = \sqrt{3RC}$  ( $\mu_0$  is magnetic moment,  $R$  the gas constant) is in accord with experiment and has been justified theoretically by Ehrenfest (*Comm. Phys. Labor. Leiden*, Supp. 44b). Weiss ascribes the origin of  $\Delta$  to a molecular field varying directly as the density of the paramagnetic atoms (A., 1915, ii, 737), but Foex (*Diss., Strasburg*, 1921) has recently investigated certain solutions in which  $\Delta$  appears, but mutual actions of paramagnetic atoms seem unlikely. The authors have measured by a couple the attraction in a non-uniform field and have determined the variation with temperature of the susceptibility of water and of certain solutions. The susceptibility of water between 20° and 80° is given by  $-\delta\chi/\chi = [1.67 + 0.0016(t - 20^\circ)](t - 20^\circ) \cdot 10^{-4}$ . The variation is due to depolymerisation of water molecules, so that addition of a diamagnetic salt like magnesium chloride increases the effect until  $\delta\chi/\chi$  approaches zero. Solutions of manganese chloride, manganese nitrate, and nickel nitrate have been studied at various concentrations. The Curie-Weiss law is borne out by values of  $\Delta$  (Mn<sup>++</sup>, -25; Ni<sup>++</sup>, -2), which are approximately independent of the concentration or the nature of the anion. These values of  $\Delta$  have been used to calculate the number of magnetons of the two cations and the results Mn<sup>++</sup>  $28.06 \pm 0.08$ , Ni<sup>++</sup>  $15.96 \pm 0.05$  are in the case of nickel identical with the number 16 already known, and in the case of manganese smaller by one than the number found for solid manganese salts. The constant  $\Delta$  is due to a deformation of the surface of the paramagnetic atom by the influence of other atoms in chemical combination with it. The view that in solutions water exerts such a deformation effect is in harmony with the theory of Ehrenfest.

R. A. M.

**Diamagnetism of Nematic Substances.** G. FOEX and L. ROYER (*Compt. rend.*, 1925, **180**, 1912—1913).—The magnetisation coefficient of *p*-azoxyanisole in the solid state is independent of temperature. At 116°, the nematic phase appears and the magnetisation diminishes abruptly by about 17%, owing to orientation of molecules by the magnetic field. The nematic phase (116—134°) shows great variations of the magnetisation coefficient with temperature; the value approaches the original value as the temperature increases and remains constant when the liquid phase is attained. The curve, magnetisation coefficient—temperature may be produced to 95° for the nematic phase and the maximum difference observed between two magnetisations in the liquid and nematic phases is greater than 18%. Whenever the substance solidifies, a different value is observed for the coefficient owing to imperfect distribution of the tiny crystals making up the solid. Anisaldazine gave similar results.

R. A. M.

**Dispersion of Electrical Double Refraction of Some Organic Liquids.** G. BECKER (*Ann. Physik*, 1925, [iv], **76**, 849—862).—The dispersion of the electrical double refraction has been measured by Lyon and Wolfram's method (A., 1921, ii, 6) for the following

liquids at  $20^\circ$ : anisole, *m*-xylene, phenetole, ethylbenzene, acetal, ethyl butyrate, toluene, and ethyl ether. The behaviour of the first four is represented satisfactorily by the Havelock formula (A., 1911, ii, 165)  $Bn\lambda/(n^2-1)^2=\text{const.}$ , where  $B$  and  $n$  are respectively the Kerr constant and the refractive index of the liquid for the wave-length  $\lambda$ . The mean values of the Havelock constant for these four liquids are  $C \times 10^{11}=0.596, 0.485, 0.643$ , and  $0.425$ , respectively. The deviations from the above formula are most marked with ethyl ether and acetal. Owing to the ambiguous behaviour of toluene and ethyl butyrate, the conclusion that the Havelock formula does not hold for substances with low optical dispersions cannot be confirmed.

F. G. T.

**Black Body for Optical Pyrometer Calibration.** H. S. ROBERTS (*J. Opt. Soc. Amer.*, 1925, **10**, 723—724).—Details are given for the construction of a black body for use in the calibration of optical pyrometers from the fusion point of a metal. A small piece of the metal is heated to fusion at the bottom of a graphite or porcelain tube of suitable shape, and the "matching" is done as the metal is observed to melt. The advantages of the procedure are that it gives a direct determination of the temperature of the black body and that very little of the standard metal is required.

S. B.

**Latent Heat Determinations.** A. W. SMITH (*J. Opt. Soc. Amer.*, 1925, **10**, 711—722).—A summary of the methods proposed for determinations of the latent heats of fusion and evaporation.

S. B.

**Automatic Control of Low Temperatures.** T. S. SLIGH (*J. Opt. Soc. Amer.*, 1925, **10**, 691—693).—A short review, with references, of the methods used for attaining constant low temperatures.

S. B.

**Thermal Conductivity of Wires and Rods.** T. BARRATT and R. M. WINTER (*Ann. Physik*, 1925, [iv], **77**, 1—15).—The expression  $K=H^2/pqhV^2 \coth^2 \alpha l$  gives the conductivity of a wire or thin rod, and is simplified to  $K=H^2/pqhV^2$  when the length  $l$  is great ( $K$  is the thermal conductivity of the wire,  $p$  the circumference of the rod,  $q$  the cross-sectional area,  $h$  the emissivity of the surface,  $V$  the temperature of the hot end, and  $\alpha=\sqrt{hp/qk}$ . Of these quantities,  $h$  is the most difficult to measure. Accordingly, the experimental methods are designed to secure accurate values for  $H$  (the heat supplied in calories per sec. to the hot end of the wire) and  $V$ , and the theoretical treatment is designed so that  $h$  may be eliminated entirely from the calculations. The technique is based on earlier work (*Proc. Phys. Soc.*, 1914, **26**, 347). Values of  $K$  are given for platinum, iridium, rhodium, gold, tantalum, molybdenum, various alloys, and for glass, ebonite, graphite, and various woods.

The mathematical treatment includes a solution of the equation for the fall of temperature along a rod enabling  $K$  to be evaluated

from  $H$ ,  $V$ ,  $q$ , and the temperature at any point along the rod. Various cases are discussed and simple formulæ deduced so that the result of the work is to place on a sound theoretical basis the experimental methods developed by the authors for the measurement of  $K$ , using very small samples of material. R. A. M.

**Specific Heats.** S. WIESNER (*Ann. Physik*, 1925, [iv], 76, 802; cf. this vol., ii, 275).—A correction. The refractivities previously used were the Gladstone and Dale values; thus  $u$  signifies the specific refraction and not the specific atomic volume. When the Lorenz and Lorentz values are used  $r\sqrt{d}$  is in the neighbourhood of 1.5, instead of 3, as previously given. The elements silver, potassium, phosphorus, mercury, and sodium which gave abnormal results, now give values of  $r\sqrt{d}$  between 0.87 and 0.68. F. G. T.

**Molecular Heats of Gases at Low Temperatures.** F. A. GIACOMINI (*Phil. Mag.*, 1925, [vi], 50, 146—156).—The molecular heats at constant volume of ammonia, methane, and hydrogen were determined at temperatures down to 83° Abs. by observing the pressure increase on heating the gases in a closed vessel by an inductive electrical impulse in a small piece of constantin foil placed near the centre of the gas-container. The pressure was recorded by a sensitive membrane manometer. The determination of  $C_v$  by this principle presupposes a non-uniform temperature distribution in the gas. The validity of this type of measurement was supported by the direct observation of development and evolution of heat clouds in the gas, of the rate of heat evolution from, and the temperature attained by, the foil, and by the pressure-increase curves for various gases for varying heat changes, and under different pressures and temperatures. A theoretical consideration of the principle assumes the pressure development to occur in two idealised stages, an isochoric heating of a small volume of the gas round the foil, followed by the adiabatic compression of the rest of the gas. From these assumptions the condition for obtaining trustworthy results is  $[RQ/V_0C_vP_0]^2 \leq 1$ , where  $Q$ ,  $V_0$ , and  $P_0$  are, respectively, the heat supplied, and the initial volume and pressure of the gas. The pressure maxima for carbon dioxide were constant over a range of from 1 to 0.1 atm., the duration of the maximum decreasing with decrease of pressure. The molecular heats of methane and ammonia sink with falling temperature below the value corresponding with rigid molecules, the fall with ammonia being especially rapid.  $C_v=5.30$  cal. for methane at 83° Abs., and  $=5.55$  cal. for ammonia at 229° Abs. F. G. T.

**Microscopic Study of the  $\alpha\beta$ -Transformation of Natural Cristobalite.** R. WEIL (*Compt. rend.*, 1925, 180, 1949—1951).—Cristobalites from different places have been examined. From San Cristobal the transformation begins at 180—195° and ends at about 205—210°; from Tehema County: 175—210° or 230°; from Chauffefour: two regions exist, 175—190° and 217—245°; from Blaue Kuppen: 220—230° or 250—255°; from Cottenheim: 220—230°. Pseudomorphic tridymite-cristobalite crystals from

Chaudfour showed a transformation point at 180—200°; tridymite from Mt. Egmont shows points between 170—190° and 235—250°.

R. A. M.

**Heat of Sublimation of Carbon Dioxide.** J. W. ANDREWS (*J. Amer. Chem. Soc.*, 1925, **47**, 1597—1602).—Experiments in which a definite quantity of carbon dioxide was sublimed by means of an electric current, the energy input and the volatilised substance being measured, lead to a value for the heat of sublimation of 6205 cal. There is a difference of 2.64 units between the entropies as calculated from thermal and equilibrium data on carbon, oxygen, and carbon dioxide, and from the thermal data for carbon dioxide itself. The possible sources of error are discussed. J. S. C.

**Additive Properties of Boiling Points.** A. E. VAN ARKEL and J. H. DE BOER (*Physica*, 1924, **4**, 392—399; cf. this vol., ii, 734).—From the general additivity of the b. p., it is found that  $\Sigma\sqrt{a}/\Sigma b$ , representing the cohesion pressure at the b. p. ( $a$  and  $b$  being the van der Waals' constants) has a constant value for all tetra-halogen derivatives of methane. The results lead to an atomic volume for hydrogen of 9.20% less than that of fluorine. For compounds containing hydrogen, the external action of the central atom is not entirely screened, and van Laar's rules no longer apply. Also, when the size of the central atom is increased, individual differences in the screening efficiency of the halogens appear, leading to the existence of co-ordination complexes, e.g.,  $K_2SiF_6$  and  $K_2SnCl_6$ .

CHEMICAL ABSTRACTS.

**Influence of Hydrogen and Substituted Halogens on the Properties of Organic Compounds, especially on their Boiling Points.** A. E. VAN ARKEL and J. H. DE BOER (*Rec. trav. chim.*, 1925, **44**, 675—692).—In each group of organic compounds, for each halogen the value of  $\sqrt{\alpha}$  per halogen atom is proportional to the volume,  $\alpha$  being the constant in van der Waals' equation of state. The values of  $\sqrt{\alpha}$  are different in different groups, and are smaller the greater the number of other atoms in proximity to the halogen atom. In the paraffin series, the central atom is surrounded by halogen and hydrogen atoms, and exerts no influence beyond these, but in the ethylene, benzene, and silicon series this is not so. As the surrounding of the central atom by other atoms will obviously be more perfect the greater the volume of the latter, it follows that the ethylene and chloroethylene compounds readily form additive compounds, whilst ethylene tetraiodide is formed from carbon tetraiodide by removal of iodine, and compounds such as silicon tetrabromide show no tendency to complex formation. It is shown that fluorine falls into line with the other halogens. Hydrogen, however, has a variable value of  $\sqrt{\alpha}$ . It is smallest in the hydrocarbons, and is greater the more halogens there are attached with hydrogen to a carbon atom. The introduction of halogens into other carbon groups also exerts an influence (although smaller) on the value of  $\sqrt{\alpha}$  for hydrogen.

L. L. B.

**Variation with Pressure of the Boiling Points of Naphthalene, Benzophenone, and Anthracene.** J. L. FINCK and R. M. WILHELM (*J. Amer. Chem. Soc.*, 1925, **47**, 1577—1582).—The variation with pressure of the b. p. of naphthalene, benzophenone, and anthracene has been investigated over the range of pressure 700—800 mm. of mercury, the data for the first two substances being intended for use in thermometry. Two purified samples of anthracene differed in their normal b. p. by about 0.5°. The experimental data are satisfactorily represented by the equation  $t_p = t_{760} + A(t_p + 273.1) \log(p/760)$ , in which  $t_p$  represents the temperature corresponding with pressure  $p$  (mm. of mercury),  $t_{760}$  the normal b. p., and  $A$  a constant characteristic of the substance. The following are the respective values of  $t_{760}$  and  $A$ : naphthalene 217.95° and 0.2075, benzophenone 305.84° and 0.194, anthracene 340.36°, 339.87°, and 0.201. J. S. C.

**Melting Point of Carbon.** H. ALTERTHUM, W. FEHSE, and M. PIRANI (*Z. Elektrochem.*, 1925, **31**, 313—316).—The authors have applied their method for the determination of the m. p. of difficultly fusible metals (cf. Pirani and Alterthum, A., 1923, ii, 125) to the determination of the m. p. of graphite. The graphite, in the form of a rod 140 mm. long and 37 mm. diameter, broadened at each end and with a hole (18 mm. deep and 3 mm. diameter) bored at an angle to the axis of the rod, is surrounded by a water-cooled jacket through which hydrogen at 800 mm. pressure is passed, and is heated by an alternating current (8000 amp. and 9 volts). The m. p. is 3760° Abs.  $\pm 65^\circ$ , a value in good agreement with other determinations. J. W. B.

**Temperature Scale and M. p. of Molybdenum.** A. G. WORTHING (*Physical Rev.*, 1925, [ii], **25**, 846—857).—Values are tabulated and plotted for the spectral emissivities of molybdenum as a function of temperature from 300° Abs. to 2800° Abs., and the relations between true, brightness, and colour temperatures examined. Molybdenum has m. p.  $2895 \pm 10^\circ$  Abs. A. A. E.

**Cryoscopy of Diphenyl Ether.** J. T. DURAND and E. ROUGÉ (*Bull. Soc. chim.*, 1925, [iv], **37**, 697—700).—Discrepancies observed in the m. p. of samples of diphenyl ether obtained by Sabatier and Mailhe's method (A., 1910, i, 669) are due to the relatively high cryoscopic constant (80) of this substance, which renders its m. p. much more sensitive to traces of impurities. The purest diphenyl ether obtainable has m. p. 26.9° in the cryoscope, and experiments with cyclohexane, benzene, toluene, and naphthalene give the values 78.8, 79.8, 79.7, and 80.0, respectively, for the cryoscopic constant. Naphthalene gives the most constant results, cyclohexane the most erratic. From these results, the latent heat of fusion is calculated to be 22.65 cal. R. B.

**Constitution of Aromatic Substances and their Physical and Chemical Properties. II. Melting Points of Benzene Derivatives.** I. A. PASTAK (*J. Chim. Phys.*, 1925, **22**, 264—279; cf. this vol., i, 531).—A review of the m. p. of polysubstituted benzene

compounds containing two different groups, R and r, of which R occurs once only, and r once or more times. Substituent groups are divided into two main classes: (1) basic groups including H, CH<sub>3</sub>, (Cl), (Br), OH, NH<sub>2</sub> . . . , and, (2), acidic groups including H, CO<sub>2</sub>H, NO<sub>2</sub> . . . . The fundamental principle is that in disubstituted compounds, C<sub>6</sub>H<sub>4</sub>Rr, if R and r belong to the same class (see above), the normal position possessing the lowest m. p. is the meta, and the m. p. are in the order para > ortho > meta. If, however, R and r belong to different classes, the normal positions are the ortho and para, and the m. p. order is para > meta > ortho, the para position always having an abnormally high value. Polysubstituted compounds can be divided into two classes: (1) "Alphabetical isomerides," for which no simple rules exist for m. p., and in which the different r groups are in the ortho or para positions relative to one another; and (2) the "ompa" isomerides, in which the r groups are relatively in the meta position. In the "ompa" isomerides, two r groups in the meta position to one another resemble one group in the position midway between the two. Thus the isomeride of the compound C<sub>6</sub>H<sub>3</sub>Rr<sub>2</sub> with the r groups in the 1:3 positions resembles the compound C<sub>6</sub>H<sub>4</sub>Rr' with the r' in the meta position, and in this way polysubstituted compounds can be reduced so as to correspond with the disubstituted compounds for which the fundamental principle (above) holds.

W. H.-R.

**The Group of Volatile Hydrides.** F. PANETH and E. RABINOVITSCH (*Ber.*, 1925, 58, [B], 1138—1163).—The hydrides are classified as volatile hydrides (*e.g.*, HCl), salt-like hydrides (*e.g.*, LiH), and metal-like hydrides (*e.g.*, CuH); the first group is mainly considered in the present communication. Simple volatile hydrides containing only one atom of the central element in the molecule are formed by elements occurring in one to four places before a rare gas in the periodic system. Many of these elements form also more complex hydrides which generally resemble closely the simpler compounds, so that they are readily considered in a somewhat broader group.

[With W. HAKEN.]—Older determinations of the b. p. and m. p. of germanium hydride have given values which are widely divergent from those predicted from its association with the tetrahydrides of carbon, silicon, and tin. Pure germanium hydride is conveniently prepared by the electrolysis of a solution of germanium dioxide in sulphuric acid between lead electrodes, condensation of the gaseous products by liquid air, and fractionation of the condensate in Stock's vacuum apparatus; it has b. p.  $-88.5^{\circ}$ , m. p.  $-164.5^{\circ}$ , mol. heat of evaporation 3.65 kg.-cal. The value for the b. p. is in good agreement with that found recently by Schenk and Imker (*this vol.*, ii, 279; cf. A., 1922, ii, 855), with whose views on the instability of the hydride in the presence of mercury the authors do not concur. It is shown that the m. p. and b. p. of the hydrides rise with increase in the number of the period in all groups of the periodic system and that the rise is linear to a first approximation. All the graphs



are parallel to the graphs of the m. p. and b. p. of the rare gases placed at the end of the periods. A distinct departure from the linear nature is caused by neon; among hydrides of the corresponding period methane alone is suitable for comparison, since ammonia, water, and hydrogen fluoride are markedly associated. Between the constants of methane and monosilane, however, the same discrepancy is noticed as between those of neon and argon, whilst, also, a similar discrepancy is observed in the b. p. of the halogens. An exceptional position is taken also by radium emanation, the m. p. of which appears to require redetermination. In every period the hydrides of the fourth group resemble the rare gases most closely in volatility; the mono-, tri-, and di-hydrides are increasingly less volatile in the given order. It follows therefore that the constants of the hydrides can be deduced from the position of the central element in the periodic system whereby the b. p. of the hydrides of lead, bismuth, and polonium are calculated to be  $-13^{\circ}$ ,  $+22^{\circ}$ , and  $+37^{\circ}$ , respectively. The exceptional positions occupied by the hydrides of fluorine, oxygen, and nitrogen may be attributed to the established association of hydrogen fluoride and water, but this has not been placed beyond doubt for ammonia; in general, the adequacy of molecular association as an explanation of abnormal b. p. is open to question. Graphic representation of the heats of evaporation (at the b. p.) of the hydrides gives a picture similar to that derived when the b. p. is used, but in which the irregular exceptions are rather more sharply defined. In addition to the hydrides of fluorine, oxygen, and nitrogen, hydrogen chloride and sulphide give "high" values. The tendency towards association among volatile hydrides diminishes towards the left and downwards from fluorine, so that in the first period it extends to the third member,  $\text{NH}_3$ , whereas in the second only to the second member,  $\text{SH}_2$ . With m. p., the same departures from linearity are in general observed as with the b. p., but the "abnormally high" m. p. of methane and hydrogen iodide shows the anomaly to extend to the fourth member. The remaining constants of the volatile hydrides are not generally known with sufficient exactitude to permit accurate comparison, but the graphs for the molecular volume at the b. p. and for refractive index are generally similar to those just discussed. The thermostability decreases as the periodic number increases, the maximum instability being exhibited in the sixth group of the periodic system. In general, the volatile hydrides behave as a homogeneous family. As far as their properties can be numerically expressed, the data vary very regularly within the separate periods and groups of the natural system. Their physical constants present unmistakable similarity to those of the rare gases.

Comparison shows that those elements which form volatile hydrides give also volatile or readily melted halogen or alkyl compounds, provided that the central element functions with the same valency. The alkyl derivatives appear to fall into the same two classes as the hydrides, since the alkali alkyls are solids at the atmospheric temperature, whereas those of the elements which

yield volatile hydrides are liquids and volatilise readily. The power of yielding volatile alkyls is more widely distributed in the periodic system, extending as far as zinc and mercury. The same parallelism between conductivity and volatility is encountered among hydrides, halides, and alkyls, volatility and poor conductivity occurring simultaneously. In every period, the hydrides and halides of the fourth group have the lowest m. p. and b. p., whereas those of the sixth group have the highest constants. The m. p. and b. p. of the compounds of a given element with hydrogen, chlorine, bromine, and iodine vary parallel to the constants of the free halogens with which hydrogen must be reckoned in this connexion. According to their physical constants, the volatile hydrides must be regarded as the lightest of the volatile halides.

Physically the hydrides resemble closely the rare gases, and their physical properties are most clearly expressed by considering their molecules to have the hydrogen nuclei "buried" and to present a "rare-gas" surface. The possibility of assigning a similar molecular structure to the volatile halides is considered. It is obvious that the volatile hydrides and halides in the right groups of the periodic system belong to the same structural type and that in the left groups the salt-like hydrides are in all respects comparable with the typical salts.

H. W.

**Atomic Volume of Manganese.** A. N. CAMPBELL (*J. Chem. Soc.*, 1925, **127**, 1487).—The curve of atomic volumes shows in the neighbourhood of manganese two minima, one at manganese and the other at cobalt. With the new value of the density of manganese (Campbell, T., 1923, **123**, 2323), the two minima persist, but the first minimum is shifted from manganese to chromium.

W. T.

**Density-changes of Tungsten with Working.** W. GEISS and J. A. M. VAN LIEMPT (*Ann. Physik*, 1925, [iv], **77**, 105—108; cf. *B.*, 1925, 361).—Cold working of tungsten leads to a limiting value of 19.35 for the density. This agrees with the value deduced from X-ray measurements, so that there is no evidence of compression of the space lattice by hammering or rolling.

R. A. M.

**Expansion of Water while Freezing.** A. P. LAURIE (*Trans. Faraday Soc.*, 1925, **20**, 509—510).—On the assumption that the tetrahedral structure of ice is formed from liquid triangular molecules of trihydrol, the triangles meeting at the centre of the tetrahedron, the increase in volume on crystallisation is calculated. The dimensions of the molecules of trihydrol are determined from the atomic diameters of oxygen and hydrogen in the solid state. The calculated specific gravity for ice is 0.918, the experimental value being 0.917.

F. G. S.

**Trouton's Rule as a Criterion of Association.** C. WAGNER (*Z. Electrochem.*, 1925, **31**, 308—309).—A mathematical paper in which it is shown that by integrating the Clausius-Clapeyron equation and combining the result with the Nernst formula the value of the Trouton coefficient ( $\lambda/T$ ) is approximately 28 for

liquids in which bimolecular association occurs. This value may therefore be employed as a criterion for such association. The cases of water, and ethyl and propyl alcohols ( $\lambda/T$  26.0, 27.1, and 26.9, respectively) are cited as examples. J. W. B.

**Surface Tension of Water, Benzene, Methyl Alcohol, and Ethyl Alcohol.** B. ALI (*Proc. Indian Assoc. Cult. Sci.*, 1925, **9**, 155—178).—The capillary tube method of measuring surface tension is modified by determining, instead of the rise of liquid in the capillary, the pressure which must be applied to the surface of the meniscus in order to depress it to the level of the horizontal surface of the liquid outside the tube, or to an arbitrary mark at a known distance below the free surface of the liquid. The pressure was measured by a sensitive differential manometer. The values of the surface tension of the above four liquids at 29.5° were, respectively, 71.32, 28.10, 23.30, 21.32 dynes/cm. The advantages of the method are discussed, and the average error in measurement is estimated as 1 part in 9000 parts. F. G. T.

**Compressibilities of Some Organic Liquids.** J. HEBEISEN (*Ann. Physik*, 1925, [iv], **77**, 206—224).—Röntgen's measurements (*ibid.*, 1888, **33**, 644) for the absolute compressibility of water are taken as standards and the compressibilities of various organic liquids have been determined relative to that of water by a differential method. The technique has been described by Schmidt (*ibid.*, 1925, **76**, 571). The variation of compressibility with temperature is given by  $x \cdot 10^6 = a + bt + ct^2$  ( $a$ ,  $b$ , and  $c$  are constants). The true compressibilities ( $x \times 10^6$ ), mean error (e%), temperature coefficient  $dx/dt \cdot 10^6$ , and density  $d$  for the following liquids at temperatures  $t^\circ$  are as follows:

	$x \cdot 10^6$ .	e%.	$dx/dt \cdot 10^6$ .	$d_{18}$ .	$t^\circ$ .
Paraldehyde .....	82.144	2.30	+1.051	0.9988	12.13
Anisole .....	60.416	1.01	+0.365	0.9956	11.87
Benzyl alcohol .....	46.429	1.38	+0.13	1.0486	17.85
Ethyl benzene .....	82.364	0.99	+0.443	0.8721	17.89
<i>m</i> -Cresol .....	49.914	0.079	+0.154	1.0359	17.78
Aniline .....	44.714	2.23	+0.104	1.0236	17.95
Acetone .....	121.182	1.05	+0.540	0.7961	18.32
Nitromethane .....	69.440	1.90	0.327	1.1398	18.36

R. A. M.

**Thermal Separation in Gaseous Mixtures.** G. A. ELLIOTT and I. MASSOW (*Proc. Roy. Soc.*, 1925, **A**, **108**, 378—385).—If a gaseous mixture is kept in two communicating vessels maintained at different temperatures, the composition of the mixture will differ in the two vessels, owing to thermal separation. The amount of the separation with one vessel at 0° and the other at 500° has been measured for the gases hydrogen, helium, and carbon dioxide, taken in pairs. It was found that in each case the constituent of higher molecular weight becomes more concentrated in the colder part of the mixture. The greatest differences in composition observed exceed 10% in hydrogen-carbon dioxide mixtures, 12%

in helium-carbon dioxide mixtures, and approach 4% in helium-hydrogen mixtures. For each pair of gases there is an "optimum" mixture for which the separation is a maximum. The separations attained are about 0.7 of those predicted by Chapman for molecules behaving as rigid elastic spheres, and are higher than those previously recorded by Ibb. S. B.

**Physical Properties of Binary Liquid Mixtures in the Region of the Critical Miscibility Point.** N. PERRAKIS (*J. Chim. Physique*, 1925, 22, 280—310; cf. Gay and Perrakis, this vol., ii, 669).—The results previously obtained (Gay and Perrakis, *loc. cit.*) for binary liquid mixtures near the critical point are tested by reference to new and older data. At constant temperature, the vapour tension of binary mixtures is independent of composition over the whole interval of non-miscibility. The freezing-point curves for binary mixtures of ethyl alcohol with phenol, *o*-cresol, and phenyl oxide have been determined, and also those of mixtures of benzene with methyl, ethyl, *isopropyl*, and *n*-butyl alcohols. If two liquid layers are formed, the freezing point remains constant over a range of concentrations, and if the freezing-point curve only falls slightly with change of concentration—as in the mixtures of benzene with alcohols, or of ethyl alcohol with phenyl oxide—it is an indication that the region of non-miscibility is being approached even although two liquid phases are not actually formed. In the mixtures of ethyl alcohol with phenol or *o*-cresol, the freezing-point curve falls very sharply, indicating good miscibility. In these cases, the liquid becomes highly viscous and tends to vitrify without crystallisation; theory shows that this abnormal increase in viscosity is characteristic of mixtures far removed from the zone of non-miscibility. Existing data confirm the deduction that, in the neighbourhood of and below the critical point, the surface tensions of each of the two liquid phases, in mutual equilibrium with air, are themselves equal.

Properties not common to the two liquid phases, such as specific heat, heat of mixing, and volume changes on mixing, are not independent of concentration over the region of non-miscibility, but vary directly with the concentration over this region. If the graph connecting these properties with concentration shows an approximately linear portion, it may be concluded that the region of non-miscibility is being approached. This is confirmed by new measurements of these properties for the above-mentioned systems, and the effect of the addition of water to mixtures of benzene with alcohols is also studied. W. H.-R.

**Physical Chemical Properties of Mixtures of Ethyl and *iso*Propyl Alcohols.** G. S. PARKS and K. K. KELLEY (*J. Physical Chem.*, 1925, 29, 727—732; cf. A., 1924, i, 930).—When ethyl and *isopropyl* alcohols are mixed there is an evolution of heat, which is never more than 13 cal. per mol., but is about  $2\frac{1}{2}$  times as great as the heat effect of mixing ethyl and propyl alcohols. The volume shrinkage is only 0.01%, and the vapour pressures and refractive indices agree closely with those calculated for perfect solutions.

Kendall's cube root equation for the viscosity of mixtures gives results which are, on an average, 0.4% too high, whilst the logarithmic equation gives values 0.9% too low. A. G.

**Certain Physico-chemical Properties of Mixtures of Water and Acetone.** C. SANDONNINI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 448—453).—The results of measurements for water-acetone mixtures of the specific heats at 14—20°, the heats of mixing at 15°, and the specific gravities, viscosities, and surface tensions at 25° render probable the existence of molecular complexes of water and acetone, although the maxima of viscosity and heat of mixing do not correspond with any stoichiometric relation between the constituents. T. H. P.

**Specific Heats of Binary Mixtures.** J. W. WILLIAMS and F. DANIELS (*J. Amer. Chem. Soc.*, 1925, 47, 1490—1503).—The variation of the specific heat with changes in composition of the binary liquid mixtures benzene-toluene, chloroform-carbon tetrachloride, chlorobenzene-bromobenzene, benzene-carbon tetrachloride, and chloroform-acetone has been investigated over the temperature range 20—60°. The first four pairs form solutions which are almost ideal. The partial molal heat capacities of the components have been calculated. The experimental data are critically discussed and the questions of "deassociation" and compound formation considered. The variations of the specific heats at constant pressure,  $C_p$ , with temperature, of acetone, bromobenzene, and chlorobenzene are represented by the equations:  $C_p = 0.5042 + 0.00030t + 0.0419t^2$ ,  $0.3043 + 0.000101t + 0.0544t^2$ , and  $0.2273 + 0.000042t + 0.0525t^2$ , respectively, where  $t$  is the temperature. J. S. C.

**Molecular Contraction in Solution.** J. N. RAKSHIT (*Z. Electrochem.*, 1925, 31, 320—323; cf. this vol., ii, 288).—Further measurements of the change in volume which occurs when various substances are dissolved in water and other solvents are made, the results of which are in agreement with the theory that association between solute and solvent occurs on dissolution and varies with dilution. J. W. B.

**Viscosity of Solutions.** N. DE KOLOSSOWSKY (*Bull. Soc. chim. Belg.*, 1925, 34, 190—201).—A formula representing the specific heats of dilute solutions, based on kinetic considerations and particularly taking into account the work necessary to overcome the viscosity of the medium with rise of temperature, is given and tested by the determination of the viscosities of sodium chloride, trichloroacetic acid, oxalic acid, sodium carbonate, and lead acetate solutions. The specific heats of these solutions calculated from the formula are in every case in good agreement with the experimental values. J. W. B.

**Molecular Compounds of the Phenols.** V. Vapour Pressure Curves. G. WEISSENBERGER and F. SCHUSTER (*Monatsh.*, 1924, 45, 437—448; cf. this vol., i, 538).—Where an equimolecular complex has been inferred from the position of maximum deviation

of the vapour pressure-composition curve of mixtures of two substances, it is shown that the vapour pressure, at a concentration  $c$  of one component should be given by  $Pc/(c+1) + Pkc/(c+1)^2$ , where  $k$  is a constant. If the complex formed is of the type 1 mol. : 2 mols. the second term of the expression becomes  $Pkc/(c+1)^3$ . These formulæ are in satisfactory agreement with the observed figures for mixtures of *cyclohexanol*, *o*-, *m*-, and *p*-cresols, 2-, 3-, and 4-methyl*cyclohexanol* with benzene, of *cyclohexanol* with ethyl acetate, and of *o*-, *m*-, and *p*-cresols with ethyl alcohol. But with mixtures of *o*-, *m*-, and *p*-cresols with acetone or ethyl ether, respectively, second order differences are found, which are represented with satisfactory accuracy by the addition of a further term  $k_2Pc^2/(c+1)^5$  to the above expression, and are interpreted as due to the formation of the two complexes 2 mol. : 1 mol. and 1 mol. : 1 mol. A similar second order deviation occurring in the case of mixtures of *cyclohexanol* with acetone and methyl alcohol, respectively, is attributed to association in one of the components. The values obtained for the system *cyclohexanol*-chloroform are too complex for interpretation.

G. M. B.

**Molecular Compounds of the Phenols. VI. Behaviour of the Naphthols, the *ar*-Tetrahydronaphthols, and Related Substances.** G. WEISSENBERGER, F. SCHUSTER, and N. MAYER (*Monatsh.*, 1924, **45**, 449—455).—Measurements are recorded of the vapour pressure at 18° of solutions of various concentrations of  $\alpha$ -naphthol in methyl alcohol,  $\beta$ -naphthol in acetone, *ar*-tetrahydro- $\beta$ -naphthol in ethyl alcohol and in acetone, tetrahydronaphthalene in ethyl alcohol, acetone, ether, benzene, *n*-hexane, and chloroform, *cyclohexanone* in ethyl alcohol, acetone, benzene, and chloroform, and of anethole in ethyl alcohol and chloroform, respectively, the figures being compared in each case with those calculated from the van't Hoff relation. The depression of vapour pressure caused by  $\beta$ -naphthol is less than that found with phenol, but the tetrahydro derivative gives depressions of the same order as phenol. In the solutions of tetrahydronaphthalene, the observed vapour pressures are higher than the calculated values in all cases with the exception of the solutions in chloroform, where experiment gives a lower value. *cycloHexanone* causes a depression of vapour pressure only in the solutions in chloroform where complex formation occurs, probably through the oxygen atom of the keto group just as it occurs through the oxygen atom of the phenols. Anethole, again, gives a depression of vapour pressure with chloroform only.

Surface tension and viscosity measurements are also recorded for these mixtures.

G. M. B.

**Boiling Points of Mixtures of Water, Benzene, and Ethyl Alcohol under a Pressure of 760 Mm. of Mercury.** J. BARBAUDY (*Compt. rend.*, 1925, **180**, 1924—1926).—Young (T., 1902, **81**, 707) found a constant mixture boiling at 64.85° containing 18.5% alcohol, 74.1% benzene, and 7.4% water, and indicated the possibility of dehydrating alcohol by distillation in the presence of benzene. The author has worked out the ternary diagram at

760 mm. The critical point 39% alcohol, 42% benzene is ill-defined. The lowest b. p. is confirmed as 64.8–64.9°, at which temperature the distillate separates into two layers.

	t°.	% Alcohol.	Benzene.	Water.	% of layer in distillate.
Upper layer .....	65	16.3	81	2.7	90.6
Lower layer .....	65	39.6	5.9	54.5	9.4

On cooling, the lower layer increases in amount and in alcohol content at the expense of the upper layer. R. A. M.

**Vapour Pressure of Aqueous Solutions of Nitric Acid.** G. B. TAYLOR (*Ind. Eng. Chem.*, 1925, **17**, 633–635).—Previous data on the partial pressures of water and nitric acid vapours over solutions of nitric acid have been correlated by plotting  $\log p$  against  $1/T$ . The best lines were drawn through the experimental values and the results are tabulated for 20–100% nitric acid and for temperatures of 0–125°. M. B. D.

**Vapour Pressures of Glycerol–Water and Glycerol–Water–Sodium Chloride Solutions.** A. R. CARR, R. E. TOWNSEND, and W. L. BADGER (*Ind. Eng. Chem.*, 1925, **17**, 643–646).—The vapour pressures of glycerol–water mixtures containing 10–96% of glycerol have been measured between 60° and 160°. Measurements were also made for similar mixtures when saturated with sodium chloride. M. B. D.

**Some Physical Properties of Silicate Glasses and their Possible Bearing on the History of Igneous Rocks.** W. E. S. TURNER (*Trans. Faraday Soc.*, 1925, **20**, 481–488).—A discussion of the density, thermal expansion, compressibility, viscosity, and the weathering of silicate glasses, and of the solubility of gases in the molten and hardened glass. Water is regarded as the chief cause of the weathering or corrosion of glass and figures are given showing that a rough proportionality exists between moisture absorption and corrosion. The corrosion increases with decrease of silica concentration and with increase of alkali oxide concentration. F. G. S.

**Solid Solutions of Water and Oxygen.** N. S. KURNAKOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 482).—Striking examples of series of compounds of continuously-changing composition are the iron compounds such as micas, tourmalines, phosphates, and borates. With such compounds, the gradual absorption of oxygen and the conversion of ferrous into ferric oxide do not affect the homogeneity of the crystals but result in continuous variation in the colour and optical properties. The mineral vivianite, consisting of a hydrated ferrous phosphate, may also be produced synthetically, and in the first stages of its formation is composed of almost colourless crystals, which retain their form and uniformity, but gradually become blue as absorption of oxygen proceeds. The proportion of water in vivianite crystals may also change continuously, owing to the formation of solid solutions of the mineral with water. T. H. P.

**Dilatometric Anomaly of  $\alpha$ -Solid Solutions of Copper and Aluminium.** P. CHEVENARD (*Compt. rend.*, 1925, **180**, 1927—1929).—The dilatation curves of aluminium bronzes show a discontinuity at 265° (heating) and 250° (cooling) which is not due to phase changes. The temperature at which the anomaly occurs is independent of aluminium content, but the amplitude of the discontinuity reaches a maximum at 9.3% aluminium. This agrees with Stockdale's value 9.8% for the limit of  $\alpha$ -solid solutions. The anomaly decreases on further increase in aluminium content and disappears at 16% when  $\gamma$ -solid solutions appear. R. A. M.

**Inner Crystalline Structure of Ferrite and Cementite in Pearlite.** N. T. BELAIEV (*Proc. Roy. Soc.*, A, 1925, **108**, 295—306).—The inner crystalline structure of ferrite and cementite in pearlite has been studied by examining sections under a magnification of 4000 diameters. The cementite lamellæ are petal-like in shape and curvature, but the edge is composed of rectangular steps. The ferrite lamellæ appear to be composed of a multitude of small cubes of uniform size and suitably oriented. The production of these peculiarities is attributed to the stresses imposed on the lamellæ during the change of the iron from the face-centred to the cube-centred lattice. S. B.

**Volumetric Measurement of the Mutual Solubility of Liquids. Mutual Solubility of the Systems Ethyl Ether-Water and isoAmyl Alcohol-Water.** I. A. KABLUKOV and V. T. MALISCHEVA (*J. Amer. Chem. Soc.*, 1925, **47**, 1553—1561; cf. Hill, A., 1923, ii, 467).—A method for the measurement of the mutual solubilities of liquid pairs is described, in which the quantity of each liquid and the volumes at equilibrium are measured. In cases of low solubility, e.g., water in ether, the volumetric method fails to give accurate results due to the error in reading the volumes of the layers in the measuring tubes. The mutual solubilities of ether and water and of isoamyl alcohol and water were determined between 10° and 30°. Methods of increasing the accuracy of the determinations are discussed. The untrustworthiness of the refractometric method of solubility determination is emphasised. J. S. C.

**The Solubility of Sulphur Dioxide in Water and in Aqueous Solutions of Potassium Chloride and Sodium Sulphate.** J. C. HUDSON (*J. Chem. Soc.*, 1925, **127**, 1332—1347).—The solubility of sulphur dioxide has been determined in water (cf. Schonfeld, *Annalen*, 1855, **95**, 1; Sims, *J. Chem. Soc.*, 1862, **14**, 1; Lindner, A., 1912, ii, 825; Smith and Parkhurst, A., 1922, ii, 398) and in aqueous potassium chloride containing up to 30 g. of salt per 100 g. of water between 10° and 90°, and also, between 20° and 50°, in aqueous sodium sulphate containing up to 20 g. of salt per 100 g. of water. The solubility in aqueous potassium chloride increases linearly with the salt concentration. The curves for sulphur dioxide in sodium sulphate solutions exhibit distinct maxima. The increase of the solubility in salt solutions is probably due to



combination between the salt and the gas (cf. Péchard, A., 1900, ii, 398; Fox, A., 1902, ii, 645), whilst a decrease of the solubility is due to hydration of the salt. An improved method of iodometric titration of sulphur dioxide is described. F. G. S.

**Miscibility of Mixtures of Water, Ethyl Alcohol, and *iso*-Butyl Alcohol.** P. BRUN (*Compt. rend.*, 1925, **180**, 1745—1747).—Mixtures of *isobutyl* alcohol and water containing less than 8% or more than 83% of the alcohol are not miscible at any temperature. When the percentage of *isobutyl* alcohol is 12—83%, the mixtures become homogeneous by use of temperature. From 8—12% the mixtures are homogeneous at the ordinary temperature, separate into layers by heating and on further heating again become miscible. The critical point is at 123.5° and 37.5%. The ternary system water-ethyl alcohol-*isobutyl* alcohol is characterised at 0° by a critical mixture of the composition: 31.6% *isobutyl* alcohol, 15.7% ethyl alcohol, 52.7% water. For *n*-butyl alcohol, the corresponding figures are 23%, 16%, and 61%. R. A. M.

**Solubility of Sucrose.** P. MONDAIN-MONVAL (*Compt. rend.*, 1925, **181**, 37—40; cf. A., 1923, ii, 131, 295; this vol., ii, 654).—The values of the limiting heat of solution,  $L$ , as determined by the direct and indirect methods are  $-1.84$  and  $-1.76$  Cal., respectively. The value of the coefficient  $i$  as obtained from vapour pressure measurements is 1.79. The solubility in water has been determined over the temperature range 0.9—30.5°, the solubilities at the two extremes being, respectively, 180.5 g. and 218.0 g. per 100 g. of water. The value of  $L$  as calculated from the solubility equation,  $500LdT/T^2 + idc/C = 0$ , is  $-1.77$  Cal. at 18°. The eutectic mixture contains 166 g. of sucrose per 100 g. of water, the eutectic temperature being  $-13.9^\circ$ . J. S. C.

**Solubility of Bi-bivalent Salts in Solutions containing a Common Ion.** O. J. WALKER (*J. Chem. Soc.*, 1925, **127**, 61).—The solubilities of the succinates and malonates of calcium, strontium, and magnesium have been determined in water and in solutions containing a common ion at 25°. The solubilities in the mixed solutions are always greater than those calculated from the solubility product. They are, however, in qualitative agreement with the theories of Debye and Hückel and of Noyes, and magnesium oxalate shows a fairly satisfactory quantitative agreement. R. W. L.

**Solubility of Oxygen in Silver.** N. PARRAVANO and G. MALQUORI (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 417—423).—The absorption of oxygen by silver depends in marked degree on the time of contact, so that the m. p. of silver determined in the ordinary way in air or oxygen cannot have a constant value. When the contact between oxygen and silver is prolonged, both at 875° and at 1050° constant values are obtained for the ratio between the concentration of the oxygen in the metal and the square root of the pressure of the gas, the oxygen dissolving even in the solid metal in the monatomic form. The view that the velocity of absorption

of the oxygen is a function of the velocity with which the gas diffuses into the interior of the metal is supported by the fact that the velocity of absorption increases with the surface of contact.

T. H. P.

**Molecular Condition of Phenol in Benzene Solution.** J. C. PHILIP and C. H. D. CLARK (*J. Chem. Soc.*, 1925, **127**, 1274—1277).—The distribution of phenol between benzene and water (cf. Rothmund and Wilsmore, A., 1902, ii, 447; Philip and Bramley, A., 1915, ii, 236) has been measured over the range 0.438—112.7 g. phenol per litre of the benzene phase. The distribution ratio ( $=C_W/C_B$ , where  $C_W$  and  $C_B$  represent the g. phenol per litre of the aqueous layer and the benzene layer, respectively) is constant up to  $C_B=2.8$  and then departs from constancy at higher concentrations. Since the molecular weight of phenol in water is approximately normal, the condition of phenol in benzene corresponds with simple  $C_6H_5\cdot OH$  molecules so long as the distribution ratio is constant. The contradictory results obtained by the freezing-point method (Auwers, A., 1893, ii, 133) are due to the separation of a solid solution of phenol in benzene (Garelli, A., 1897, i, 26). It is probable that in a concentrated solution of phenol in benzene triple molecules as well as double molecules exist (cf. Herz and Fischer, A., 1905, ii, 304).

F. G. S.

**Adsorption of Polonium by Various Substances and its Reversibility.** J. H. BRENNEN (*Ann. Chim.*, 1925, [x], **3**, 390—418).—Polonium is adsorbed reversibly by silver and ferric hydroxide sols, the equilibrium attained being the same whether the polonium is added before or after precipitation. The same applies to certain substances insoluble in hydrochloric and acetic acids (e.g., glass, charcoal) and to salts sparingly soluble in water; in these cases the adsorption increases with decreasing hydrogen-ion concentration, attaining a maximum in neutral solution. The polonium, which is adsorbed almost instantaneously, is liberated only with great difficulty. Freundlich's adsorption isotherm holds for the adsorption of polonium with an activity of 2.24—27 *E.S.U.*

S. K. T.

**Adsorption Phenomena exhibited by Tricalcium Phosphate.** P. JOLIBOIS and J. MAZE-SENCIER (*Compt. rend.*, 1925, **181**, 36—37).—Although immediate analysis shows that the precipitates obtained on treating solutions of phosphoric acid with an excess of lime water are practically pure tricalcium phosphate, on leaving them in contact with the solution for 48 hrs. a considerable adsorption of calcium oxide is observed. On agitating the liquid immediately after precipitation, a colloidal solution is obtained which deposits precipitates of the same composition as those obtained when the tricalcium phosphate is left in contact with the corresponding solutions without agitation for 48 hrs. Similar results are obtained when pure tricalcium phosphate, previously heated at 1000°, is agitated with lime water.

J. S. C.

**Application of X-Ray Methods to the Problem of Imbibition.** J. R. KATZ (*Physikal. Z.*, 1924, **25**, 659—666).—A general review of the possibilities of X-ray technique as a means of elucidating the problems associated with the phenomena of imbibition.

R. W. L.

**Vapour Pressure-Water Content Diagrams and Adsorption Power of Aniline Black.** G. STADNIKOFF (*Kolloid-Z.*, 1925, **36**, 352; cf. *ibid.*, 1922, **31**, 19, and 1924, **35**, 228).—A reply to the criticisms of Kosakewitsch (*ibid.*, 1925, **36**, 82). E. M. C.

**Unimolecular Films between Liquids: Butyric Acid between Water and Hexane, and Acetic Acid between Water and Benzene.** W. D. HARKINS and H. M. McLAUGHLIN (*J. Amer. Chem. Soc.*, 1925, **47**, 1610—1613).—The number of molecules in a unimolecular film of butyric acid between water and hexane is  $2.78 \times 10^{14}$ /sq. cm. and the area per molecule 32 sq. Å. These are the quantities previously found for this acid between water and benzene and between water and water vapour (A., 1919, ii, 324). The films are tightly packed and the number of molecules in unit area depends on the dimensions of the molecules as they lie oriented in the film, the carboxyl groups being towards the aqueous phase and the hydrocarbon chains toward the air or organic phase. The expanded film of acetic acid on water, 50 sq. Å., is reduced to 38.7 sq. Å. with benzene as upper phase. Tables are given representing the partition of butyric acid between water and hexane and of acetic acid between water and benzene together with the interfacial tensions of the two systems. The partition data show that butyric acid forms double molecules in hexane.

J. S. C.

**Foaming Power and Surface Tension, especially of Humus Sols.** W. OSTWALD and A. STEINER (*Kolloid-Z.*, 1925, **36**, 342—351).—There is no necessary relationship between foaming power and lowering of the surface tension. The independence of these properties is particularly striking in the case of humus sols, which foam strongly but have little surface activity. With sols of humus from peat, addition of alkali increased, and of acid decreased the foaming, but the surface tension remained unchanged. With sols prepared from *Acidum huminum* (Merck) the foaming increased markedly in the order alkaline, slightly acid, strongly acid, whilst the surface tension also increased slightly. The alkaline humate sols have no structural viscosity, but the acid and especially the partly flocculated suspensions have a high structural viscosity which follows an exponential equation (this vol., ii, 392). No single fundamental property is associated with foaming power. The essential feature is the formation of a skin at the liquid-air surface. A simple apparatus is described for the quantitative measurement of skin formation by comparing the rates of movement within a graduated capillary tube of a freshly-formed and an aged meniscus. With an acid humus suspension which foams strongly the rate of movement with an aged meniscus is much

slower than that with an alkaline humate sol of much lower foaming power.

E. M. C.

**Superficial Solutions and the Law of Gay-Lussac.** A. MARCELIN (*Compt. rend.*, 1925, **180**, 2022—2023; cf. A., 1924, ii, 594).—The equation  $pS=KT$  is applicable to films of benzyl benzoate and oleic acid on the surface of water, where  $p$  and  $S$  are the pressure and surface area, and  $T$  is the absolute temperature. The value of the constant  $K$  depends on the particular liquid, and is from 20 to 60 times less than the constant  $R$  of the gas equation. Molecules in the surface film are probably partly dissolved and are polarised on the surface of the water.

W. H.-R.

**Extension of the Law of Gay-Lussac to Superficial Solutions.** R. DELAPLACE (*Compt. rend.*, 1925, **180**, 2024—2026; cf. preceding abstract).—The value of the constant  $K$  of the equation  $pS_M=KT$  (Marcelin, *loc. cit.*) has been determined at 15° and 27° for films of benzyl benzoate on water, alcohol, benzene, ether, and chloroform.  $K$  is independent both of the temperature and of the nature of the solvent, and equals  $0.126 \times 10^7$ , or about 1/60 of the value of the gas constant  $R$ . The low value is not due to polymerisation, but a superficial colloid may be formed. In the evaporation of volatile liquids such as alcohol, benzene, ether, or chloroform from the surface of water, a superficial pressure is first produced, but this gradually dies away.

W. H.-R.

**Explanation of "Intertraction" Phenomena between Solutions, and Molecular Significance of Surface Tension.** N. K. ADAM and G. JESSOP (*Proc. Roy. Soc.*, 1925, **A**, **108**, 324—331).—It has been suggested that the development of streamers at the interface of two liquids, during mixing, is due to a special force of "intertraction" which aids the mixing. The present experiments are entirely at variance with this view, and it has been found that the so-called "intertraction" phenomena only occur if the solutions are placed one above another, and not side by side, and if there is a difference in the rates of diffusion between the solutes in the two solutions. Quite different phenomena are observed when the faster replaces the slower as the uppermost solution, and regular streaming only occurs with the slower diffusing solution uppermost. It is concluded that the movements at the interface are due to the hydrostatic equilibrium of the layers being upset by the diffusion of the solutes across the interface at different rates. Negative surface tension means that those forces of cohesion perpendicular to the interface which act when there is positive surface tension, restraining the diffusion of molecules away from the interface, become negative. This state is manifested by the diffusion of one liquid into the other.

S. B.

**Freezing Points of Very Dilute Solutions of Electrolytes.** F. HOVORKA and W. H. RODEBUSH (*J. Amer. Chem. Soc.*, 1925, **47**, 1614—1624).—The freezing-point depressions produced by the electrolytes of different valency types, viz., potassium chloride, caesium nitrate, potassium sulphate, barium nitrate, magnesium

sulphate, cupric sulphate, and lanthanum sulphate, at concentrations between 0.01 and 0.001*M*, are in very close agreement with the values derived from the equations of Debye and Hückel (A., 1923, ii, 459; Rodebush, A., 1924, ii, 825). J. S. C.

**Quantitative Absorption Measurements in the Ultra-violet in Very Dilute Solutions.** R. SUHRMANN and P. HUPPERT (*Z. physikal. Chem.*, 1925, **116**, 319—331).—Dilute solutions of salicylic acid in alcohol ( $8.57 \cdot 10^{-5}$ — $8.57 \cdot 10^{-8}$  mol./litre) and potassium nitrate in water ( $1.112 \cdot 10^{-2}$ — $4.65 \cdot 10^{-4}$  mol./litre) exhibited marked deviations from Beer's law in the region 248.2—365.5  $\mu\mu$  (cf. Ghosh and Bisvas, A., 1924, ii, 523; Halban and Ebert, *ibid.*, 824). It is considered that the molecular extinction coefficient is subjected to two opposing influences which alter with the concentration. Beer's law holds only in the concentration range where these forces nearly compensate each other. The influence of the dielectric constant of the solvent on electrical forces conditioning absorption is discussed. L. F. G.

**Measurement of the Viscosity of Solutions of Cotton in Aqueous Cuprammonium Hydroxide and its Significance as a Test of Textile Quality.** F. D. FARROW and S. M. NEALE (*J. Text. Inst.*, 1924, **15**, T, 157—172).—A method for determining the viscosity of solutions of cotton materials in ammoniacal copper oxide solution is described. For comparative purposes 2% solutions are convenient, but equations which have been tested over the range 0—3% may be used to convert the viscosities for other concentrations into a 2% or other standard. These equations are  $1 + C/m = 11/\log(\eta_m/\eta_B)$  and  $1 + C/n = 11/\log(\eta_n/\eta_B)$ , where  $m$  is the weight of cotton in the solution used the viscosity of which is  $\eta_m$ ,  $\eta_B$  is the viscosity of the solvent, and  $n$  is the weight of cotton in a solution of standard concentration the viscosity,  $\eta_n$ , of which is required. The falling sphere viscosimeter is recommended.

In the paper, the log viscosities for 2% solutions of a large range of cotton materials are reported. Whilst it does not yet seem possible to propose standards of viscosity with which cotton should conform at any normal stage of manufacture, comparisons of the viscosities of the material before and after a treatment afford an extremely sensitive indication of the inception of structural change in the cellulose. For example, such processes as boiling cotton with alkali in the presence of air, or boiling with extremely dilute acids, or immersion in oxidising solutions, produce distinct falls in viscosity which also run parallel with falls in tensile strength. Mercerisation, however, being merely a swelling phenomenon, does not cause any noteworthy diminution in viscosity. J. C. W.

**Dielectric Constants of Solutions of Electrolytes. II.** P. WALDEN, H. Ulich, and O. WERNER (*Z. physikal. Chem.*, 1925, **116**, 261—290; cf. this vol., ii, 512).—The dielectric constants, mostly at 20°, of the undermentioned solutions have been determined by an apparatus previously described, slight modifications being introduced when using solvents of higher dielectric constant

than 10 : tetrapropylammonium iodide in chloroform, ethylaniline, aniline, *o*-dichlorobenzene; *s*.-tetrachloroethane, pyridine, *m*-nitrotoluene, and water; diethylamine hydrochloride in chloroform, aniline, and pyridine; tetraethylammonium picrate in *o*-dichlorobenzene; potassium chloride, barium chloride, and cadmium bromide in water. Measurements in chlorobenzene, bromobenzene, and ethylene dichloride gave only qualitative results. Successive small additions of solute to solvent cause the dielectric constant to fall towards a minimum, beyond which it rises. This rise was not observed with the solution of tetrapropylammonium iodide in *m*-nitrotoluene, owing to the small solubility of the solute, nor in any of the aqueous solutions, as here the measurements could not be carried far enough. The results are discussed theoretically.

L. F. G.

**Effect of Light on Settling of Suspensions.** C. G. T. MORISON (*Proc. Roy. Soc.*, 1925, **A**, **108**, 280—284).—It has been observed that the passage of a beam of light through soil or kaolin suspensions contained in a rectangular tank causes the suspensions to stratify, the layers running parallel to the surface. The distance between successive strata appears to vary with the wave-length of the light traversing the tank, but the strata produced by white light are quite sharp. The stratification persists while the illumination is continued, and slowly disappears when it is cut off.

S. B.

**Use of Scattered Light in the Determination of the Distribution of Size of Particles in Emulsions.** A. J. STAMM and T. SVEDBERG (*J. Amer. Chem. Soc.*, 1925, **47**, 1582—1596).—A method for the determination of the distribution of size of particles using scattered light is developed and applied to benzene-in-water emulsions in presence of soaps. After a period of sedimentation the systems are illuminated from the two sides in a narrow cell with dark opaque background and the variation in the intensity of the scattered light with the height is recorded photographically, the densities on the plate being determined with a photometer. The theoretical and practical derivations of the distribution of the size of particles from the density-height relationship are developed. The ratio of the average sizes of the particles in disperse systems, the average diameters of the particles of which are not less than two or three times the wave-length of light, may be obtained from the slopes of intensity-concentration curves. Mass distribution curves obtained for emulsions in presence of sodium, potassium, and caesium palmitates are in good agreement with those from microscopic measurements. The position of the mass maxima is not shifted by using different alkali soaps, although there is an increase in the number of small particles in passing from sodium to potassium to caesium soaps. An exponential increase in the radius corresponding with the mass maxima is caused by increasing the benzene concentration, the concentration of stabiliser remaining constant. Increase of the concentrations of benzene and stabiliser, their ratio remaining constant, gives maxima corresponding with a larger size of particles.

J. S. C.

**Method of Determination of the Granular Distribution of Disperse Systems.** R. AUDUBERT and H. RABATÉ (*Compt. rend.*, 1925, **180**, 1663—1665).—A method is described for measuring the size and granular distribution of solid particles by observations of the rate of sedimentation. The intergranular liquid is placed in two vertical tubes which communicate near the lower ends and a small portion of the disperse phase is introduced at the top of one of the vertical tubes, causing a difference of pressure, which diminishes as the grains fall; this difference is measured at regular intervals. If the relation between the mass ( $m$ ) of the grains and their diameter ( $r$ ) is of the form  $dm = F(r)dr$ , application of the Stokes law leads to the relation  $F(r) = K't^{3/2}dp/dt$ , where  $p$  is the difference of pressure after time  $t$ , and  $K'$  is a constant depending on the form of the apparatus and on the Stokes constant  $A$ , where  $r^2t = A$ .  $F(r)$  is thus calculated for each value of  $t$ , from which the number of grains can be obtained as a function of the diameter. W. H. R.

**Reduction Velocity and Growth of Particles in the Preparation of Colloidal Gold Solutions.** R. ZSIGMONDY and E. HÜCKEL (*Z. physikal. Chem.*, 1925, **116**, 291—303).—An attempt to correlate the autocatalysis of the reduction of gold salts by formaldehyde with increase of size of the particles. Solutions of gold salts were reduced either alone or in the presence of definite quantities of a red gold hydrosol. The times taken to attain a standard colour were observed. Reduction is accelerated by rise of temperature, and, to a certain extent, by increase in the amounts of formaldehyde and of added hydrosol. In some cases, the phenomena suggest that the velocity of linear increase of the particles is constant; where growth is very rapid, however, there appears to be an acceleration of the linear increase. Reduction takes place in the immediate neighbourhood of the gold particles. The concentration of the reactants is increased in this region by adsorption; this enhanced concentration, and not the mean concentration of the solution, controls the course of the reaction. L. F. G.

**Preparation of Well-defined Silicic Acid Sols.** W. GRUND-MANN (*Kolloid-Z.*, 1925, **36**, 328—331).—Almost identical silicic acid sols can be prepared by attention to the following factors. The same quantities of hydrochloric acid and sodium silicate must be used and the mixture transferred at once to collodion membranes of the same thickness and freshly-prepared for each sample. Only distilled water is used for the dialysis and the rate of its addition must be the same in all cases. The sols should be protected during dialysis from atmospheric contamination. The difficulty of preparing concentrated sols in summer (cf. Lösenbech, A., 1922, ii, 695) and the readiness with which these flocculate especially after storms, are ascribed to the action of atmospheric impurities. E. M. C.

**Preparation of Colloidal Silver by Reduction with Chloroform.** V. MORÁVEK (*Chem. Listy*, 1925, **19**, 195—203).—To prepare colloidal silver, using gelatin as protective colloid, the

author employs 8 millimols. of silver nitrate, 435.2 millimols. of ammonia, 50 millimols. of chloroform water, and 20 millimols. of chloroform to give 12.5 c.c. of a mixture in which the silver : gelatin ratio is 0.11 : 1. The mixture is warmed for 15–20 mins. on a water-bath at 90°, dialysed, and evaporated in a vacuum, the colloidal silver being obtained in solid, cold water-soluble form. The reducing action is increased in the presence of sodium or potassium hydroxide. Measurements are recorded of the size of the colloid particles, and of the resistance of the solution towards coagulating electrolytes. B. F.

**General Colloid Chemistry. XIV. Constitution and Stability of Iron Oxide Sols. IV.** N. KÜHNEL and W. PAULI (*Koll. Chem. Beihefte*, 1925, 20, 319–337; cf. A., 1924, ii, 740).—Ferric hydroxide sols prepared by peptisation of precipitated hydroxide with ferric chloride contain on the average ten times as much iron and twenty times as much chlorine as those prepared by hydrolysis. The ratio of active to total chlorine is from 1 : 5 to 1 : 6 in hydrolysed sols and is little affected by dialysis; but it decreases from 1 : 3 to 1 : 17 on dialysis of peptised sols, whilst the total oxychloride per colloid equivalent increases more than sixfold. The extent to which chlorine is substituted by sulphate and oxalate anions on coagulation is throughout considerably higher for hydrolysed than for peptised sols. By dialysis, the oxychloride portion of the sol-substance is progressively diminished, more markedly so in hydrolysed sols. Transport numbers are much the same for both varieties. W. A. C.

**General Colloid Chemistry. XIV. Structure of Heteropeptoids. I. Aluminium-Iron Oxide Sols.** N. KÜHNEL and W. PAULI (*Koll. Chem. Beihefte*, 1925, 20, 338–355; cf. preceding abstract).—When precipitated aluminium hydroxide is peptised with ferric chloride, or ferric hydroxide with aluminium chloride, brown sols are obtained containing roughly equivalent amounts of aluminium and iron, the proportions varying with the mode of preparation. In the replacement of chlorine by coagulating anions, and in the relations exhibited by the transport numbers, and the size of particles, these sols resemble pure ferric hydroxide peptised sols. It is suggested that the sol particles have the same constitution as mixed crystals (solid solutions). W. A. C.

**Viscosity of Reversible Emulsions.** S. S. JOSHI (*Trans. Faraday Soc.*, 1925, 20, 512–519; cf. A., 1924, ii, 529, 731).—The viscosities of water-in-oil emulsions prepared from castor oil, olive oil, and paraffin oil have been determined, using sodium oleate, potassium palmitate, oleate, and stearate as emulsifying agents. The viscosity, which is independent of the concentration and nature of the emulsifying agent, increases with increase of the disperse phase and falls suddenly on inversion of the emulsion to the oil-in-water type. The viscosities calculated from the equations of Arrhenius (A., 1888, 336), Hatschek (A., 1911, ii, 98), and Einstein (A., 1921, ii, 19) are compared with the experimentally determined



values. The suggestion is made that an increment in the size of the grains of the water-in-oil emulsions with increase in the proportion of the aqueous phase may be one of the factors causing deviation of the calculated from the observed values. F. G. S.

**Alteration of Viscosity of Disperse Systems with the Velocity of Shear.** A. DE WAELE (*Kolloid-Z.*, 1925, **36**, 332—333).—Herschel's equation (cf. Ostwald, *ibid.*, 249) for the viscosity of disperse systems under varied velocities of flow is discussed and a new equation suggested to include the dynamic and static behaviour both of peptised and flocculated substances. E. M. C.

**Theory of the Colour of Colloidal Metal Suspensions.** G. JOBST (*Ann. Physik*, 1925, [iv], **76**, 863—888).—Mathematical. The theory of Mie (*ibid.*, 1908, **25**, 378) is developed. A radiation formula is deduced for a disperse system of completely reflecting spheres suspended in a transparent medium, and applied to the case of gold suspensions. The absorption and emission spectra are calculated for a number of systems consisting of particles with diameters from 100—600 $\mu\mu$ . These curves are in very approximate agreement with those calculated by the original theory of Mie. As the diameter of the particles increases, the maxima in these curves flatten. This flattening in the absorption spectra curves illustrates the gradual change in colour of transmitted light from greenish-blue to green. The curves for the emission spectra indicate the change in colour of gold sols from yellow, through reddish-yellow, to the characteristic red, with increase of particle size. The latter colour occurs only with particles of considerable size. F. G. T.

**Velocity of Ice Crystallisation through Supercooled Gelatin Gels.** E. H. CALLOW (*Proc. Roy. Soc.*, 1925, **A**, **108**, 307—323).—The velocity has been followed by seeding a supercooled gel with ice, and measuring directly the movement of the crystal boundary. Experiments with the gels at  $-3^{\circ}$  showed that the presence of more than 1% of gelatin greatly reduces the velocity of crystallisation. Thus in a 1% gel of  $p_H$  1.50, the velocity was half that through distilled water and in a 1.5% gel it was twenty-four times slower still. Smaller quantities of gelatin have not a proportionate effect. When the hydrogen-ion concentration of the gels is altered, the velocity of crystallisation shows a minimum at the isoelectric point of gelatin. The velocities were greater if the gel had been previously boiled for some hours,  $\beta$ -gelatin having apparently less influence on the rate than the normal gelatin.

Opaque gels offer less resistance to a falling body than do clear gels of equal concentration. It is suggested that the opaque gels owe their turbidity to the presence of fibrils, which take no part in the gel structure. S. B.

**Relation between Swelling of Gelatin and Hydrogen-ion Concentration.** W. OSTWALD, A. KUHN, and E. BÖHME (*Koll. Chem. Beihefte*, 1925, **20**, 412—433; cf. Kuhn, A., 1922, i, 183).—The swelling produced by acids when added to gelatin which has been brought to the isoelectric condition ( $p_H=4.7$ ) by repeated extraction with water diminishes in the order: hydriodic, gly-

cerophosphoric, sulphosalicylic, hydrochloric, sulphuric. The same order is observed in presence of salts of the respective acids. As a rule, at equal values of  $p_H$ , the swelling by pure acids is greater than that by mixtures of acids and salts. In certain cases, however, where the anion has a marked swelling action, buffer mixtures exert a much greater effect than the pure acids, although the salts alone tend to diminish swelling. Dibasic acids have a stronger swelling effect, within certain limits of  $p_H$ , than monobasic. W. A. C.

**Influence of Very Small Quantities of Foreign Substances on the Stability of Colloidal Solutions.** A. BOUTARIC and (MME.) Y. MANIÈRE (*Compt. rend.*, 1925, **180**, 1841—1842; cf. this vol., ii, 394, 526).—The stability of colloidal solutions against a particular electrolyte may be increased or decreased by the addition of small amounts of other substances. If  $\alpha$  is the maximum amount of an electrolyte which fails to bring about any flocculation and if the value is  $\beta$  after addition of another substance, the expression  $\beta - \alpha/\alpha$  measures the new stability. The phenomenon has been studied in detail, using an arsenic sulphide sol. Small amounts of salts or of ammonia or potash increase the stability when the alkali chlorides are used as flocculating agents. If the salts of bivalent elements are used, the stability is increased if alkali chlorides were added first, but decreased if the preliminary addition consisted of chlorides of bi- or ter-valent elements, or of sodium silicate, ammonia, or potash. If aluminium chloride is used as coagulating agent, the previous addition of chlorides decreases the stability, but a preliminary treatment with a trace of silicate or of ammonia or potassium hydroxide makes the quantity  $\beta - \alpha/\alpha$  positive, i.e., protection occurs.

R. A. M.

**Coagulation of Prussian Blue and Ferric Hydroxide Sols.** S. GHOSH and N. R. DHAR (*J. Physical Chem.*, 1925, **29**, 659—678; cf. *ibid.*, 435).—Further evidence that there is a close relation between abnormal behaviour on dilution, abnormality towards mixed electrolytes, and acclimatisation has been obtained by studying the coagulation of sols of Prussian blue and of positively charged ferric hydroxide, both of which behave abnormally. These phenomena are believed to be due mainly to the adsorption of ions carrying the same charge as the sol. Ferric hydroxide behaves normally when coagulated by potassium chloride or bromate, and arsenic trisulphide is normal towards silver nitrate. The former is, however, abnormal when coagulated by ferric chloride or aluminium nitrate, because the positive ions of these salts are absorbed. Similarly, ferric hydroxide is abnormal towards mixtures containing ferric chloride or aluminium nitrate, but can be acclimatised to these salts. It is normal towards mixtures of potassium bromate and oxalate and of potassium chloride and sulphate.

Some experiments on the influence of non-electrolytes are included.

A. G.

**Coagulation of Colloids by Electrolytes. I. Arsenic Trisulphide Sols and Barium Chloride.** A. J. RABINOVITSOH (*Z. physikal. Chem.*, 1925, **116**, 97—110).—The "total" and the

"free" hydrogen-ion concentrations in arsenic trisulphide sols were determined by the method of Pauli and Semler (A., 1924, ii, 333). The sols were then coagulated by barium chloride solutions. In the filtrate from each coagulum the total hydrogen-ion concentration was found to be unaltered, after correcting for dilution by the barium chloride solutions, but now equalled the free hydrogen-ion concentration, *i.e.*, the filtrate was more acid than the original sol. The increase of acidity rises with the concentration of the sols. Arsenic trisulphide sols are considered to be fairly strong complex acids, dissociating as follows:  $(\text{As}_2\text{S}_3)_n\text{SH}_2 \rightleftharpoons (\text{As}_2\text{S}_3)_n\text{SH}^- + \text{H}^+ \rightleftharpoons (\text{As}_2\text{S}_3)_n\text{S}^- + 2\text{H}^+$ ; the second dissociation constant is less than the first. In the coagulum it was found that the hydrogen had been completely replaced by an equivalent amount of barium; there was no chlorine present.

L. F. G.

**Emulsions. III. Double Reversal of Oil Emulsions by the Same Electrolyte.** W. SEIFRIZ (*J. Physical Chem.*, 1925, 29, 738—749; cf. A., 1924, i, 127).—Petroleum distillates (*d* 0.828—0.857) are not emulsifiable with aqueous casein, but on the addition of sodium or barium hydroxides, water-in-oil emulsions are formed which are converted into oil-in-water emulsions by more of the reagent. Similarly, when sodium hydroxide is added to an oil-in-water emulsion of olive oil, stabilised with agar-agar, it is reversed to a water-in-oil emulsion, and further addition again reverses it to the oil-in-water type; if the stabiliser is gelatose, the first reversal is only partial, but the effect is then also produced by barium hydroxide. Readily reversible petroleum emulsions frequently consist of both oil-in-water and water-in-oil systems; these may exist side by side, or one within the other, in which the drops of the primary emulsion are emulsions of the opposite type. These latter systems may be termed "bimultiple," and more complex emulsions, up to quinquemultiple, have been observed. When an emulsion is stabilised by an organic substance, the films surrounding the drops are often microscopically visible, solid membranes.

A. G.

**Simple Kinetic Principle of Colloidal Processes.** J. ALEXANDER (*Kolloid-Z.*, 1925, 36, 334—337).—The behaviour of heated steel and iron illustrates the general principle that maximum colloidal properties are developed when both the specific surface and the kinetic activity have medium values. Absence of colloidal properties may be caused by either too low a specific surface or too high a kinetic activity.

E. M. C.

**Viscosities of Aqueous Solutions of Pure Soaps and their Variations with Temperature.** N. A. JAJNIK and K. S. MALIK (*Kolloid-Z.*, 1925, 36, 322—327).—The viscosities of solutions of pure sodium palmitate and sodium stearate have been measured at 60°, 70°, and 80° in a constant pressure viscosimeter of the type used by Scarpa (A., 1911, ii, 16) and Farrow (T., 1912, 101, 347). The viscosity increases rapidly with the concentration. Sodium palmitate solutions have a lower viscosity than those of sodium stearate, but the differences become very small for solutions more dilute than *N*/20, especially at 60°.

E. M. C.

**Moisture Relations of Cotton. I. Taking up of Water by Raw and Soda-boiled Cotton at 20°.** A. R. URQUHART and A. M. WILLIAMS (*J. Text. Inst.*, 1924, 15, T., 138—143).—Investigation of the absorption and desorption of water by cotton at  $20 \pm 0.5^\circ$ , in atmospheres of about 1% to 98% relative humidity has shown definitely that there are at least two possible values for the moisture content of a sample of cotton which has been exposed to an atmosphere at a fixed temperature and degree of humidity. A higher value is obtained when the cotton was initially wetter than the atmosphere, and a lower value if it was initially drier. Further experiments show that if cotton is previously heated at  $110^\circ$  it is less able to absorb water vapour, and that scouring the cotton also reduces its capacity for taking up moisture when placed dry in a wet atmosphere. Soda-boiled cotton shows a greater hysteresis than raw cotton.

J. C. W.

**Moisture Relations of Cotton. II. Absorption and Desorption of Water by Soda-boiled Cotton at 25°.** A. R. URQUHART and A. M. WILLIAMS (*J. Text. Inst.*, 1924, 15, T., 433—442; cf preceding abstract).—An improved method has been devised for investigating the complete absorption-desorption curves for a sample of purified cotton at  $25^\circ$ . In the absorption experiments, a bulb containing the cotton was connected to a manometer readable to 0.01 mm. and to a pipette readable to 0.02 c.c., from which any desired quantity of water could be transferred to the cotton by evaporation. In the desorption experiments, the water pipette was replaced by a phosphorus pentoxide tube which could be detached and weighed. It is found that soda-boiled cotton absorbs 22.6% of water at  $25^\circ$  from a saturated atmosphere. The results again show that the absorption curve lies lower than the desorption curve. Contrary to previous statements, however, the curves do not meet at zero humidity, but at a point corresponding with 1.8% relative humidity. Nor do the curves meet at 100% R.H. A possible explanation of the phenomenon of hysteresis in cotton is advanced which is not inconsistent with botanical views of the structure of the cotton hair, and which leads to the figure  $13 \times 10^{-8}$  cm. as the dimension of the smallest pores.

J. C. W.

**Moisture Relations of Cotton. III. Effect of Temperature on the Absorption of Water by Soda-boiled Cotton.** A. R. URQUHART and A. M. WILLIAMS (*J. Text. Inst.*, 1924, 15, T., 559—572).—Measurements of the absorption of water by cotton have been made up to  $130^\circ$ . The apparatus was that described in the preceding abstract, with small modifications in the means for reading the higher pressures, and the material was the same. The results show that when the relative humidity is constant at less than 80%, increase of temperature from  $10^\circ$  to  $110^\circ$  decreases the moisture content of the cotton. When, however, the relative humidity is constant at more than 80%, a similar decrease in moisture content only occurs from  $10^\circ$  to  $50^\circ$ , whilst above  $60^\circ$  the moisture content may actually increase with rise of temperature. Furthermore, the hysteresis also decreases with rise of temperature, and the isosteres are apparently con-

current near the critical temperature and pressure of water. The change which sets in at about  $60^{\circ}$  is explained as due to swelling and the consequent exposure of new surface. Processes which depend for their success on the swollen state of cotton will therefore become easier above  $60^{\circ}$  at high humidities, and the most suitable conditions for attaining maximum moisture content in cotton appear to be  $100^{\circ}$  and 100% R.H.

J. C. W.

**Moisture Relations of Cotton. IV. Absorption of Water by Cotton Mercerised without Tension.** A. R. URQUHART and A. M. WILLIAMS (*J. Text. Inst.*, 1925, **16**, T, 155—166; cf. preceding abstracts).—The variations in the water-fixing power of mercerised cotton with the concentration of the alkali hydroxide employed are found to bear a close resemblance to the variations in dimensions in the single cotton hairs. For example, when mercerised with 15% sodium hydroxide or 28% potassium hydroxide, which are known to cause maximum swelling, the cotton also has a maximum hygroscopicity. On the other hand, the ratio between the moisture contents of the mercerised and unmercerised, scoured cottons at the same atmospheric humidity is independent of the degree of humidity. When mercerised with 15% sodium hydroxide, for example, the moisture content of cotton when absorbing moisture is 1.57 times and when losing moisture 1.46 times the corresponding values for the unmercerised cotton, no matter what the prevailing humidity may be. The results indicate that mercerisation increases the accessible surface of cotton in proportion to the ratio between the moisture contents (the "mercerisation ratio"). A determination of this ratio should afford a measure of the increased capacity of a mercerised cotton, not only for water, but also for dyes. It is calculated that the diameter of the smallest pores in mercerised cotton is equal to or less than  $8 \times 10^{-8}$  cm. as against  $13 \times 10^{-8}$  cm. for soda-boiled cotton.

J. C. W.

**Swelling of Cotton Cellulose. II. Cotton Hairs in Solutions of Potassium Hydroxide.** G. E. COLLINS and A. M. WILLIAMS (*J. Text. Inst.*, 1924, **15**, T, 149—156).—In extension of work on the alteration in dimensions of cotton hairs in sodium hydroxide solutions (A., 1923, i, 1065), similar measurements are now recorded for potassium hydroxide. Although contractions in length are about the same for the two alkalis, increases in diameter are less than half in potassium hydroxide solutions of what they are in sodium hydroxide solutions of the same concentration. Maximum swelling occurs in 28% potassium hydroxide solution, which is the solution of maximum electrical conductivity.

J. C. W.

**Swelling of Cotton Cellulose. III. Cotton Hairs in Solutions of Lithium, Rubidium, and Cæsium Hydroxides.** G. E. COLLINS (*J. Text. Inst.*, 1925, **16**, T, 123—126).—Previous results (cf. preceding abstract) suggested that the solution of alkali having the maximum swelling power might be that of maximum electrical conductivity (and in the case of sodium hydroxide of maximum heat of formation). The data for the other alkalis afford

no support for this connexion. On the other hand, there seems to be a correlation between the degree of hydration of the metal ion and maximum swelling power. For example, there is a maximum on the swelling curve at LiOH 6.6%, or LiOH : 17H<sub>2</sub>O, NaOH 15.5% (12H<sub>2</sub>O), KOH 38% (7H<sub>2</sub>O), RbOH 49% (6H<sub>2</sub>O).

Changes in length produced by the rare alkalis are small; in caesium hydroxide, cotton hairs are actually elongated, even in the most concentrated solutions. The increments in diameter are only about half those attained in solutions of sodium hydroxide.

New physical data are recorded for the rare alkalis, as follows : lithium hydroxide : solubility, 10.73% at 20°,  $d_4^{20}$  of saturated solution 1.115; rubidium hydroxide : solubility, 65% at 20°,  $d_4^{20}$  of saturated solution 2.022; caesium hydroxide : solubility, 81.2% at 20°,  $d_4^{20}$  of saturated solution 2.939. Measurements of the electrical conductivities are also recorded.

J. C. W.

### **Hygroscopic Capacity of Wool in Different Forms and its Dependence on Atmospheric Humidity and other Factors.**

S. A. SHORTER and W. J. HALL (*J. Text. Inst.*, 1924, **15**, T, 305—327).—The moisture contents of various samples of wool have been measured by direct weighing after keeping them sufficiently long in a room at constant temperature, and with a controlled degree of humidity. The data are trustworthy to  $\pm 0.1\%$ . Raw wools differ considerably in their absorption of moisture, owing to the grease and other foreign matter, but, after scouring, their behaviour is fairly uniform. The curves connecting moisture content with atmospheric humidity are sigmoid. The paper deals largely with the influence of various technical processes.

J. C. W.

**Mercerisation of Cellulose.** K. HESS (*Z. Electrochem.*, 1925, **31**, 316—319).—Mainly a polemical review in which the author discusses his own results and conclusions (cf. Hess, Weltzien, and Messmer, A., 1924, i, 142; Hess and Wittelsbach, A., 1920, i, 584) with the opposing views of Herzog and his collaborators (cf. Herzog and Londberg, A., 1924, i, 373, 619) and Katz and Mark (this vol., i, 640). Increase in the accuracy of measurement of the Röntgen diagrams of natural cellulose and hydrocellulose (*loc. cit.*) has shown that the deviation is systematic, the diagrams being very similar, but not identical. The author believes that mercerisation is caused by the salt-forming ability of the amphoteric cellulose and not by a change in the chemical structure of the molecule. The original crystal lattice of the fibre is converted by salt formation into a kind of ion-lattice, the displacement of the C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> groups caused by the inorganic component being irreversible.

J. W. B.

**Dispersion of Different Kinds of Cellulose by Mechanical Means and by the Action of Aqueous Salt Solutions.** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **36**, 338—341; cf. A., 1921, i, 847).—The dispersion of cellulose in concentrated salt solutions is accompanied by hydrolysis with the production of substances in true solution. The rates of dispersion and hydrolysis depend on the form of cellulose used. The dispersion of resistant forms of cellulose

is greatly accelerated by a preliminary mechanical treatment such as grinding at the temperature of solid carbon dioxide or liquid air.

E. M. C.

**Effect of Treatment with Sulphuric Acid on the Breaking Load of Cotton.** P. D. VINCENT (*J. Text. Inst.*, 1924, **15**, T., 281—290).—When cotton is soaked in sulphuric acid it suffers loss of strength, which is generally ascribed to the formation of “hydrocellulose.” It is now shown that with the single cotton hair this “tendering” is a linear function of the concentration of the acid, complete disruption occurring in a solution containing 77 g. per 100 c.c.

J. C. W.

**Elasticity and Tensile Strength of Starch.** S. M. NEALE (*J. Text. Inst.*, 1925, **15**, T, 443—452).—Dried films of pure starch pastes, and pastes containing modified starch and other ingredients common to the practice of sizing have been tested at 20° and 34% or 66% relative humidity in a special apparatus which traced the load-extension diagrams. The general behaviour of starch films resembles that of a ductile metal. Maize, potato, and sago starch films have almost identical elastic properties, but weaker films are produced by oxidation or hydrolysis of the starch, or by the addition of acids, alkalis, or soap to the paste.

J. C. W.

**Ammonia Solutions.** F. E. C. SCHEFFER and (MISS) H. J. DE WIJS (*Rec. trav. chim.*, 1925, **44**, 655—662).—The work of Moore (T., 1907, **91**, 1377) on the equilibrium  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\cdot\text{OH}$  is criticised on the ground that certain values in his equation are contradictory. It is considered that the equilibrium constant can only be determined in terms of the total concentration of ammonia in the liquid, as the  $\text{NH}_3$  and  $\text{NH}_4\text{OH}$  cannot be separately determined. The constant in the equilibrium  $(\text{NH}_3)_{\text{gas}} \rightleftharpoons (\text{NH}_3)_{\text{diss.}}$  cannot be determined, but as  $k_{\text{mol.}} = C_{\text{NH}_4\text{OH}}/C_{\text{NH}_3}$ , then  $C_{\text{NH}_3}/C_{\text{am}} = C_{\text{NH}_3}/(C_{\text{NH}_3} + C_{\text{NH}_4\text{OH}}) = 1/(k_{\text{mol.}} + 1) = \text{constant}$ . The equilibrium constant of  $(\text{NH}_3)_{\text{gas}} + x\text{H}_2\text{O} \rightleftharpoons [x\text{NH}_4\text{OH} + (1-x)\text{NH}_3]_{\text{diss.}}$  is determinable by means of the ratio  $p_{\text{NH}_3}/C_{\text{am}}$ , where  $p_{\text{NH}_3}$  is the pressure of the gas above the liquid, and  $C_{\text{am}}$  is the total concentration of the ammonia (corrected for the small ionic concentration). Henry's law was found to hold for concentrations up to about 0.2*N*. The pressure of ammonia (gas) could be expressed as a function of the total concentration by the formula  $p = 12.9C_{\text{am}}(1 + 0.046C_{\text{am}})$ . The addition of a constant small quantity (0.15 mol.) of ammonium nitrate to varying concentrations of ammonia was found to have no influence on the agreement of the ratio  $p/C_{\text{am}}$  with Henry's law or the above equation; but the addition of increasing quantities of the salt to small concentrations of ammonia was found to be represented by  $p = 12.9C_{\text{am}}(1 + 0.019C_n + 0.0085C_n^2)$ , where  $C_n$  is the ammonium nitrate concentration. The thermodynamic potential of the ammonia molecules in the solution is discussed.

L. L. B.

**Hydrolysis of Alkali Cyanides in Aqueous Solution.** R. W. HARMAN and F. P. WORLEY (*Trans. Faraday Soc.*, 1925, **20**, 502—507).—The degree of hydrolysis of sodium and potassium cyanides

in aqueous solution (cf. Worley and Browne, A., 1918, i, 60; Meyer, A., 1921, i, 501) has been determined by the method previously employed by Worley and Browne (*loc. cit.*). The molar concentration,  $C$ , of the cyanide was varied from 0.01 to 1.0 mol. per litre and the results obtained for the mass law expression  $P^2C/100(100-P)$ , where  $P$  is the percentage hydrolysis, are in satisfactory agreement. The mean hydrolysis constants found for sodium and potassium cyanides at 25° are  $2.51 \times 10^{-5}$  and  $2.54 \times 10^{-5}$ , respectively, and the heat of hydrolysis of potassium cyanide, calculated from measurements at various temperatures is  $2.95 \times 10^3$  cal.

F. G. S.

**Homogeneous Equilibria in Magmatic Melts and their Bearing on the Processes of Igneous Rock Formation.** P. NIGGLI (*Trans. Faraday Soc.*, 1925, 20, 428—441).—The formation of igneous rocks of Pacific, Mediterranean, and Atlantic types is discussed with reference to equilibria in the magma and the processes of silicification and desilicification, complex decomposition reactions, substitution reactions with formation of new molecular types, formation of double salts, and polymerisation. The importance of the study of such homogeneous equilibria for the systematic classification of rock types is emphasised.

F. G. S.

**Kinetic and Electromagnetic Definition of the Thermodynamic Temperature of a Gas.** E. WERTHEIMER (*Z. Physik*, 1925, 32, 596—619).—The thermodynamic temperature of a gas may be defined by means of either the thermal agitation of the molecules or the electromagnetic energy of radiation. In the latter case, although the actual energy is quantitatively of no account, yet the temperature can be defined as that at which the medium is in equilibrium with black body radiation of temperature  $T$ .

E. B. L.

**Kinetic Theory of Evaporation.** D. B. MACLEOD (*Trans. Faraday Soc.*, 1925, 20, 525—543).—On the assumption that the ratio of the densities of vapour and liquid in equilibrium is equal to the ratio of the number of the molecules with sufficient speed to escape from the liquid to the number with insufficient speed, the minimum escaping speeds of molecules of a number of liquids at various temperatures have been calculated. It is found that for unassociated substances the minimum kinetic energies of escape fall off linearly with the temperature to within 20° or 30° of the critical temperature. They then decrease rapidly to zero. The minimum energies of escape for acetic acid and the alcohols are not so simply related to the temperature. It is shown that for unassociated liquids the minimum energy of escape is practically directly proportional to the molecular surface energy as is required by the theory, whilst definitely associated liquids do not show this proportionality. The latent heats of evaporation of six unassociated liquids, calculated over a range of temperature by evaluation of the difference between the total kinetic energy of 1 g. of the escaping molecules and the total



kinetic energy of 1 g. of the general mass of molecules, are in very good agreement with the values determined experimentally.

F. G. S.

**Dissociation of Several Metallic Oxides.** F. BORN (*Z. Elektrochem.*, 1925, **31**, 309—311).—A theoretical paper in which by means of the Nernst heat theorem and existing data for the melting points, boiling points, latent heats of vaporisation, and heats of formation, the dissociation pressure of the oxygen and the degree of dissociation of several metallic oxides at  $2000^{\circ}$  and  $3000^{\circ}$  Abs. are calculated. Calcium oxide is practically completely dissociated at its b. p. ( $3120^{\circ}$  Abs.), as are probably magnesium oxide and zirconium oxide which have b. p. above  $3500^{\circ}$  Abs. Silica and chromic oxide are largely dissociated, aluminium and thorium oxides only slightly. The dissociation pressures obtained respectively for aluminium, calcium, chromic, magnesium, silicon, thorium, titanium, tungsten, and zirconium oxides, are at  $2000^{\circ}$ , 25, 0.2, 3, 0.3, 2, about  $3 \times 10^{-3}$ , 3, 760, about  $6 \times 10^{-4}$  mm.; at  $3000^{\circ}$   $>760$ , 700,  $>760$ , 750,  $>760$ , about 16,  $>760$ ,  $>760$ , about 16 mm. J. W. B.

**Vapour Pressure of the Volatile Constituents of Glass at the Ordinary Temperature.** F. BORN (*Z. Elektrochem.*, 1925, **31**, 312).—By means of the Nernst vapour pressure formula and equilibrium equation the vapour pressures of the volatile constituents of glass (oxides and silicates of the alkali metals) at the ordinary temperature are calculated to be of the order of  $10^{-16}$ — $10^{-20}$  and  $10^{-25}$ — $10^{-30}$  mm., respectively; the calculated partial pressure of the oxygen is less than  $10^{-40}$  mm., and the combined effects produce a vapour pressure of  $10^{-16}$ — $10^{-20}$  mm. J. W. B.

**Relationships Existing between Hydrogen and Palladium.** B. LAMBERT and S. F. GATES (*Proc. Roy. Soc.*, 1925, **A**, **108**, 456—482).—Pressure-concentration equilibria were investigated at  $75^{\circ}$ ,  $103^{\circ}$ , and  $120^{\circ}$ . Different equilibrium pressures, with the same concentrations of hydrogen in the solid phase, were obtained when the method of approaching equilibrium was varied. There is some evidence, however, in each series of experiments, for the existence of the compound  $\text{Pd}_2\text{H}$ . The contention that metallic palladium exists in at least two allotropic forms is supported. L. F. G.

**Equilibrium Conditions of Magnesium Carbonate in Ammoniacal Solutions.** G. H. LAFONTAINE (*Compt. rend.*, 1925, **180**, 2045—2047).—Solutions of magnesium hydrogen carbonate were treated with known quantities of ammonia and ammonium hydrogen carbonate, and the composition of the solid phase determined after prolonged stirring at  $30^{\circ}$ . The solid phases consist of the following compounds: (1) the neutral hydrated carbonate  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ , (2) a double carbonate,  $\text{MgCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3 \cdot 4\text{H}_2\text{O}$ , (3) a basic carbonate,  $\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , and (4) a second basic carbonate,  $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O} + 5(\text{MgCO}_3 \cdot 3\text{H}_2\text{O})$ , which is not a mixture, but a definite compound forming minute spheroids which are optically inert. The approximate limits of concentration in which these

compounds are precipitated, either singly or in pairs, have been determined.

W. H.-R.

**System Sodium Nitrate-Sodium Sulphate-Water and the Minerals Darapskite and Nitroglauherite.** H. W. FOOTE (*Amer. J. Sci.*, 1925, [v], 9, 441-447).—Solubility data for the system have been determined at 0°, 25°, and 35°. No evidence in favour of the existence of double salts other than darapskite,  $\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ , was obtained (cf. Massink, *Z. physikal. Chem.*, 1918, 92, 364). The mineral nitroglauherite is shown to be essentially a mixture of sodium nitrate and darapskite. The quintuple point temperatures, at which the three solid phases are sodium nitrate, sodium sulphate decahydrate, darapskite, and anhydrous sodium sulphate, sodium sulphate decahydrate, and darapskite, respectively, are 13.5° and 24.5°. The double salt is formed above 13.5° and still exists at the highest temperature investigated, although evidence was obtained of another quintuple point in the region of 50°, above which darapskite does not form.

J. S. C.

**Equilibria in the Systems: Ammonium Chromate-Ammonium Sulphate-Water, and Ammonium Chromate-Potassium Chromate-Water at 25°.** S. ARAKI (*Mem. Coll. Sci. Kyōtō*, 1925, 8, 213-222).—The solubility curves for each pair of salts consist of two branches and show that two series of solid solutions are formed in each case. No solid solutions exist when the molar percentage of ammonium chromate is between 2.90% and 21.50% in the former system, and between 16.75% and 55.50% in the latter. The molar percentages of ammonium chromate in the total dissolved salts in the liquid solutions which are in equilibrium with these two series of solid solutions are 8.56% and 61.66%, respectively.

J. W. B.

**Equilibrium in the Ternary System Bismuth Oxide, Hydrochloric Acid, Water.** G. WARIS (*J. Indian Chem. Soc.*, 1925, 1, 307-310).—Analyses of the liquid and solid phases of the ternary system at 25° show that no hydrate of bismuth oxychloride exists at this temperature; the solid phase which separates out from solutions containing 25-33.67% of hydrogen chloride is normal bismuth oxychloride.

J. W. B.

**Nature of Aluminium-Magnesium Alloys.** G. G. URAZOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, 2, 480-481).—Investigation of the m. p. diagram and microstructure of alloys of magnesium with aluminium shows that these two metals form three series of solid solutions. In the first aluminium dissolves up to 11 at.-% Mg; in the second magnesium dissolves up to 7 at.-% Al; whilst the third contains between 37 and 59 at.-% Mg. The m. p. diagram consists of three branches, corresponding with the temperatures at which the first crystals of the three series of solid solutions appear.

T. H. P.

**Equilibrium Diagram of the Aluminium-Zinc System.** T. ISIHARA (*Science Rep. Tōhoku Imp. Univ.*, 1925, 13, 427-442).—The equilibrium diagram of the aluminium-zinc system was

redetermined by the electrical resistance method, in conjunction with microscopic, dilatometric, and X-ray measurements. The form of the liquidus agrees with the results of previous investigations. For the  $\gamma$ -phase the solidus occurs at a higher temperature than that previously obtained, but for the  $\beta$ -phase Hanson's result (*Engineering*, 1922, **113**, 538) is confirmed. The eutectic at  $380^\circ$  contains 5% Al. The solubility of aluminium in the  $\alpha$ -phase varies from 1% at  $380^\circ$  to 0.3% at the ordinary temperature. A transformation in the  $\beta$ -phase is found at  $340\text{--}350^\circ$ , corresponding with the  $A_2$  transformation in iron. There is no change in the Laue diagram taken above and below this range. The solubility of zinc in aluminium at the ordinary temperature is found to be 32.5%, showing a large divergence from previous results. The diagram generally confirms that of Hanson. C. S.

**Copper-Antimony Alloys.** N. S. KURNAKOV and K. F. BELOGLAZOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 490—492).—Reimann's observation that the maximum m. p. for copper-antimony alloys occurs at 71 at.-% of Cu is in moderately good agreement with the authors' result, namely, 72 at.-% Cu (*Z. Metallkunde*, 1920, **12**, 321), but does not justify the conclusion that the  $\beta_2$ -phase consists of a definite compound Cu : Sb = 5 : 2. Within the limits of stable existence of the  $\beta_2$ -phase, no evidence for this is afforded by the m. p. diagram, the electrical conductivity isotherms, or the curve of temperature coefficient of conductivity. Between  $400^\circ$  and  $600^\circ$  these curves are continuous and show no singularity at Cu : Sb = either 3 : 1 or 5 : 2. Analogous relations are observed for the electrical conductivity and hardness diagrams of the  $\beta_1$ -phase (74—80 at.-% Cu), which is the product of the polymorphous transformation of  $\beta_2$  below  $410^\circ$  and is stable at the ordinary temperature. The  $\beta_1$ - and  $\beta_2$ -phases must therefore be regarded as of variable composition. T. H. P.

**Constitution of Aluminium-Copper Alloys.** G. MASING and L. KOCH (*Wiss. Veroff. Siemens-Konzern*, 1925, **4**, [1], 109—112).—By diffusion experiments with  $\text{CuAl}_2$  and an alloy in the  $\alpha$  region the existence of the two crystalline phases  $\delta$  and  $\eta$  has been confirmed. Since X-ray investigation failed to detect these phases, it would seem that they have the same lattice structure. A. R. P.

**Equilibrium Diagram of the System Iron-Carbon-Titanium.** K. TAMARU (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 25—32).—In ternary alloys of iron, carbon, and titanium containing less than 4% Ti the whole of the titanium is retained in solid solution in the ferrite. Titanium decreases the carbon content of the iron-carbon eutectic and the solubility of graphite in austenite at high temperatures. [Cf. *B.*, 1925, 593.] A. R. P.

**Ternary System, Lead-Cadmium-Thallium.** C. DI CAPUA (*Gazzetta*, 1925, **55**, 280—290).—The solidification phenomena observed with the alloys Cd-PbTl<sub>2</sub> indicate that the alloy corre-

sponding with the maximum in the m. p. curve of lead-thallium alloys behaves as a compound and with cadmium gives mixtures which may be regarded as a series of binary alloys,  $\text{PbTl}_2$ -Cd. Thus the ternary system may be divided into two regions, Cd-Pb $\text{Tl}_2$ -Tl and Pb-Cd-Pb $\text{Tl}_2$ , the alloys of each region constituting a separate ternary system. In neither of these partial ternary systems do solids appear other than those of the three limited binary systems. The possible solids in the system Pb $\text{Tl}_2$ -Pb-Cd are, therefore, mixed crystals Pb $\text{Tl}_2$ Pb and Cd, the ternary diagram showing two surfaces of primary separation meeting along a curve of secondary separation stretching from the eutectic Pb-Cd to the eutectic Pb $\text{Tl}_2$ -Cd. The diagram for the other partial system, Pb $\text{Tl}_2$ -Cd-Tl, is more complex, since Pb $\text{Tl}_2$ -Cd and Cd-Tl exhibit a eutectic without mixed crystals in appreciable amount, and Pb $\text{Tl}_2$ -Tl gives a diagram resembling Roozeboom's type IV, except that the concentration of the mixed crystals rich in thallium which are formed at  $312^\circ$  from those poorer in thallium virtually coincides with that of the liquid which at  $312^\circ$  is in equilibrium with the two solids. Three solids are possible in this case, namely, two species of binary mixed crystals and cadmium; there should, therefore, be a point of invariant equilibrium in which three univariant curves meet, but one of these is a curve of transformation and does not correspond with deposition of two solids and the invariant point becomes a transformation point and not a eutectic point.

T. H. P.

**Theory of Crystallisation in Rock Magmas.** C. H. DESCH (*Trans. Faraday Soc.*, 1925, **20**, 469—473).—The difference in behaviour of molten metallic and silicate systems is ascribed to the high viscosity of the latter. This high viscosity probably accounts for the comparative rarity of eutectic structures in igneous rocks. Bowen's views (*J. Geol.*, 1922, **30**, 177), which involve reaction between solid and liquid phases and exclude the eutectic conception, are criticised and similarities in the structure of certain igneous rocks and alloys are pointed out.

F. G. S.

**Graphic Methods of Representing Equilibria in Systems of Three Components.** G. G. URAZOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 482—483).—The author develops methods for the graphic analysis of the equilibrium in systems of three components characterised by the existence either of a stable chemical compound or of a compound melting with decomposition, the formation of solid solutions between the components being excluded in both cases. Application of the method of "crystallisation paths" permits of the determination of the composition of any point within the projected triangular system, and of the order in which solid phases are deposited; it is also possible to foretell the number of breaks in the cooling curve for a mixture of any composition.

T. H. P.

**A Property of van't Hoff's Plane Diagram.** K. F. BELOGLAZOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 502—504).—It is shown that van't Hoff's diagram (*Vorlesungen über theor.*

*u. phys. Chemie*, **1**, 161) representing the isothermal crystallisation of solutions of two salts may be adapted to crystallisation at variable temperature, the saturation isotherms for different temperatures being brought into relation to one set of axes. Crystallisation and the inverse process of dissolution correspond in the diagram with curves combining the isotherms for the initial and final temperatures of the process. For such curves, in conformity with Kurnakov's terminology, the name "crystallisation paths" is suggested.

T. H. P.

**Thermodynamics of the Capillary Layer.** G. BAKKER (*Ann. Physik*, 1924, [iv], **75**, 685—710; cf. A., 1924, ii, 23).—Mathematical. The formation of the capillary layer is imagined to occur in two steps: homogeneous phases of liquid and of vapour are first formed, and interaction between these leads to the formation of the stable capillary layer. The energy change in the first step is  $\frac{1}{2}(\rho_1 - \rho_2)r_i/(\rho_1 + \rho_2)$  and in the second  $\epsilon - \frac{1}{2}(\epsilon_1 + \epsilon_2)$ , where  $\rho_1$ ,  $\rho_2$  are the densities and  $\epsilon_1$ ,  $\epsilon_2$  the energies of the liquid and vapour, respectively,  $\epsilon$  is the energy of the capillary layer, and  $r_i$  the internal heat of evaporation. A discussion of the energy relations leads to the equation  $\left(H - T \frac{dH}{dt}\right)S = \epsilon - \frac{1}{2}(\epsilon_1 + \epsilon_2) + \frac{1}{2}(\rho_1 - \rho_2)/r_i(\rho_1 + \rho_2)$ , where  $H$  is the surface tension and  $S$  the surface of the capillary layer. From this is derived the expression  $d\epsilon - Td\eta + p_T dv = H v (\delta s / v \delta t - 1/R \cdot \delta w / v \delta t) dt$ , where  $\eta$  is the entropy,  $R$  the radius of curvature,  $v$  the volume per unit mass of the capillary layer,  $p_T$  the average pressure along the capillary layer, and  $w$  a function of the volumes of the liquid and vapour phases. For isothermal changes this expression reduces to one derived earlier (*loc. cit.*):  $Td\eta = d\epsilon + p_T dv$ .

A calculation is made of the thickness of the capillary layer of two drops of liquid and of a vapour bubble of carbon dioxide at 20°. Experiment and theory agree fairly well.

A. S. R.

**Thermodynamics of Water Absorption by Textile Materials.** S. A. SHORTER (*J. Text. Inst.*, 1924, **15**, T, 328—336).—The Clapeyron-Clausius equation is applied to the absorption of moisture by textile materials, giving a connexion between the heat change and the mode of variation with temperature of the humidity-regain relationship. The heat changes are calculated for cotton, silk, and wool at various regains, from Schlöesing's data. The calculated values vary in accordance with theory, becoming large in the neighbourhood of zero regain, and approaching zero in the neighbourhood of saturation. The values of the "heat of wetting" are calculated by integrating the heat of absorption. The calculated value for cotton at a regain of 5.1% is found to be in close agreement with the experimental value obtained by Barratt and Lewis (A., 1922, i, 526). The theory is applied to a critical consideration of the results obtained by Hartshorne (*Trans. Nat. Assoc. Cotton Manuf.*, 1905, **79**, 194; 1911, **90**, 281) for the influence of temperature on the regain of cotton and wool. Values of the heat of absorption calculated from Hartshorne's data

do not show a rapid increase in the neighbourhood of zero regain, although this is to be expected on theoretical grounds and is shown to be so by the values calculated from Schlöesing's data. Harts-horne's conclusions are therefore not acceptable; the invalidity would seem to be due to the neglect of the influence of temperature on the relative humidity given by his control solutions of sulphuric acid.

J. C. W.

**Calculation of Specific Affinity.** T. DE DONDER (*Compt. rend.*, 1925, **180**, 1922—1924).—Mathematical. R. A. M.

**Activity Coefficients.** E. WILKE and O. KIENIGER (*Z. physikal. Chem.*, 1925, **116**, 215—226).—The influence of high concentrations of hydrochloric acid and of sodium chloride on hydrogen and chlorine electrodes has been examined. Whilst the *E.M.F.* of hydrogen cells, in the presence of hydrochloric acid alone, are in approximate agreement with the Nernst formula, the chlorine cells do not obey this formula, the *E.M.F.* with 5*N*-hydrochloric acid in the variable half cell being about four times as great as the calculated value. The *E.M.F.* of hydrogen-chlorine cells were measured as a check, and found to be the same as those calculated from the single potentials of their electrodes. The effect of applied currents on the individual electrode potentials in hydrogen-chlorine cells was measured; with the same current, the potential shift of the hydrogen electrode increases with dilution of acid or neutral salt, the reverse occurring with the chlorine electrode. This is ascribed to the superior mobility of the hydrogen ion. The heats of solution of chlorine in water, hydrochloric acid solutions, sodium chloride solutions, and mixed hydrochloric acid-sodium chloride solutions were measured.

L. F. G.

**Heats of Solution and Heats of Incomplete Reactions.** (MLLE.) BÉRENGER and A. TIAN (*Compt. rend.*, 1925, **180**, 1907—1910).—If a chemical reaction occurs in the presence of a solvent the heat effect is given by  $X=Q+Q_1-Q_2$ , where  $Q$  is the heat released in the thermochemical experiment,  $Q_1$  is the heat of solution of reactants (1), and  $Q_2$  the heat of solution of resultants (2), and  $X$  is the required heat of reaction. For completed reactions  $Q_1$  and  $Q_2$  are easily measured. They are also measurable for incomplete reactions which can be studied calorimetrically in dilute solutions, for  $Q_1$  and  $Q_2$  are given by the algebraic sum of the heats of solution of all the components of (1) and (2) in a large volume of solvent  $S$ . The problem is quite different if the reaction has to be carried out in concentrated solutions. Many organic reactions, e.g., esterification, can only be carried out slowly in concentrated solutions, and are incomplete. Whilst the equation is still theoretically valid, practically the measurement of  $Q_1$  and  $Q_2$  is possible only when the reaction is either (a) purely catalytic and the catalyst is not in concentrated solution, or (b) the reaction is very slow. Methods are indicated whereby approximate values for  $Q_1$  and  $Q_2$  can be obtained under these conditions.

R. A. M.

**Heats of Solution and Dilution of Salts.** I. J. WÜST and E. LANGE (*Z. physikal. Chem.*, 1925, **116**, 161—214; cf. Richards and Rowe, A., 1921, ii, 380).—An electrical adiabatic calorimeter is described by means of which the heats of solution and dilution of the chlorides, bromides, and iodides of sodium and potassium were determined at 25°. The concentrations of the solutions were varied over a wide range.

L. F. G.

**Theory of Specific Heats of Solutions.** N. DE KOLOSSOWSKY (*J. Chim. physique*, 1925, **22**, 225—252).—Assuming, (a), that the specific heat ( $k$ ) of a solution is an additive property of the specific heats of all the constituents, and, (b), that the specific heats of dissolved molecules or ions are given, as in the gaseous state, by the relation  $C_p = 2N + 3$ , where  $N$  is the number of atoms in the molecule, the following equation is deduced :

$$k = \{\mu mc + 2n + 3(1 - \gamma + i\gamma) - (mc - 2x)v\} / (M + \mu m) \quad (1)$$

Here  $m$  and  $M$  are the molecular weights of the solvent and solute, respectively,  $\mu$  is the number of molecules of the solvent containing 1 mol. of the solute,  $c$  the specific heat of the solute,  $n$  and  $x$  are the numbers of atoms contained in the molecules of the solute and the solvent, respectively,  $\gamma$  is the degree of dissociation,  $i$  the number of ions given by the dissociation of one solute molecule, and  $v$  the number of solvent molecules combined with one solute molecule as, e.g., hydrate. By placing  $\gamma$  equal to zero or unity, the equation is applicable to cases where dissociation is either entirely absent or complete. Existing data are in general agreement with the equation for both electrolytes and non-electrolytes except when  $n$  is greater than 10, in which case assumption (b), above, is unjustified, but the error is only slight. The specific heat of an equimolecular solution increases with increase of  $n$ , but diminishes with increase of  $M$ . The effects of dissociation of the solute or of association of the solvent are usually insignificant. By a suitable transposition, the equation enables  $v$  to be calculated from the specific heat of a solution, and in this way the numbers of water molecules associated with 1 mol. of a large number of salts, acids, and bases in aqueous solution have been calculated. They are usually not whole numbers, but the nearest integer often agrees with a known hydrate, although the method gives no indication of how the water molecules are distributed among the different ions.

W. H.-R.

**Electrical Conductivity of Potassium Iodide in Bromine-Iodine Solutions.** W. PLOTNIKOV (*Z. physikal. Chem.*, 1925, **116**, 111—118).—The conductivities of potassium iodide in mixtures of bromine and iodine have been determined at 25°. The solubility of potassium iodide in bromine is greatly increased by the addition of iodine. In spite of the low dielectric constant of bromine, the solutions have a considerable conductivity. The specific conductance increases very rapidly on the addition of iodine or of potassium iodide to solutions of medium concentration, but only slowly on the addition of potassium iodide to solutions already nearly saturated with that substance. These effects are explained by the formation

of polyiodides which dissociate to form complex ions. The calculated molecular conductivities of the substances  $KI_9$  and  $KI_{11}$  decrease rapidly on dilution.

L. F. G.

**Ionisation of Aromatic Nitro Compounds in Liquid Ammonia.** I. (MISS) M. J. FIELD, W. E. GARNER, and C. C. SMITH (*J. Chem. Soc.*, 1925, **127**, 1227—1237).—From observations of the electrolysis of solutions of *m*-dinitrobenzene in liquid ammonia it is concluded that ionisation occurs through the formation of organic anions, and cations consisting of ammonia molecules carrying one, or possibly two, positive charges. The equations  $R(NO_2)_2 + xNH_3 \rightleftharpoons R(NO_2)_2 \cdot xNH_3 \rightleftharpoons R(NO_2^{--})_2 + xNH_3^+$  are suggested for this process, the nitro compound possibly behaving as a colloidal particle of high mobility. Similar solutions of isomeric nitrobenzenes and -toluenes were found to exhibit slow increases of conductivity, due to the ionisation of an additive compound with ammonia. For *m*-dinitrobenzene, 2 : 4- and 2 : 6 : dinitrotoluenes the conductivity increases from zero with a velocity which corresponds with a unimolecular charge. For *o*- and *p*-dinitrobenzenes, and for 2 : 5-, 3 : 4-, and 2 : 3-dinitrotoluenes, the small initial conductivity increases linearly with time, at a rate independent of the concentration, the solution becoming yellow. The above changes occur simultaneously with 3 : 5-dinitrotoluene. The first type of change is characteristic of compounds with two nitro groups in the *m*-position to one another, the additive compounds being blue or purple. The second type, which is probably due to the production of a pseudo-acid, is characteristic of compounds with two nitro groups in the *o*- or *p*-position. The maximum conductivity of these compounds is regarded as a measure of the electronegative character of the nitro groups, and, except for 2 : 6-dinitrotoluene, the nitro groups in the *m*- are much more electronegative than those in the *o*- and *p*-derivatives. The methyl group in *m*-position lowers, and in the *o*- and *p*-positions raises, the negative character of the nitro groups.

F. G. T.

**Displacement of Some Organic Acids from their Sodium Salts as shown by Electrical Conductivity.** J. BUREAU (*Compt. rend.*, 1925, **181**, 42—44).—On titration of aqueous solutions of sodium salts of monobasic acids,  $K \leq 10^{-5}$ , with hydrochloric acid, the electrical conductivity being determined after each addition, 1% accuracy is obtained provided the dilution be not greater than  $N/400$ . Greater accuracy is attained if the salt solution be added to the acid. Using salts of dibasic acids,  $K_1 = 10^{-2} - 10^{-3}$ ,  $K_2$  being much smaller ( $10^{-5}$ ), the formation of acid salts is indicated with an error varying from 2 to 4%. More exact results are obtained by adding the salt solution to the acid. On titration of salts of dibasic acids for which the  $K$  values do not differ greatly, the total displacement of the organic acid is indicated with an error of 5—6%, the accuracy being not much improved by adding the salt to the acid.

J. S. C.

**Electrical Transport in a Ferric Oxide Hydrosol.** H. PUIGGARI (*1st. S. Amer. Congress Chem.*, 1924).—Ferric oxide



hydrosol ( $p_H$  3.8) was prepared by gradually adding ammonia solution (90 g. of 28% ammonia solution in 180 c.c. of water) to 1000 g. of ferric chloride hexahydrate in 2000 c.c. of water, and dialysing for 264 hrs. For 0.003 amp., the *E.M.F.* across the electrodes was about 23 volts at 17°. The amount of spongy, dark-orange coloured coagulum which separated on the platinum cathode was directly proportional to the current, averaging  $304 \times 10^{-5}$  g. per amp. sec. for currents of 0.003—0.01 amp., irregularly and progressively smaller for 0.036—0.065 amp., and invisible for less than 0.0003 amp. The electrical transport is increased by rise of temperature. A new similarity between electrolytic and colloidal solutions is thus exhibited.

CHEMICAL ABSTRACTS.

**Dissociation of Weak Electrolytes in Water-Alcohol Solutions.** L. MICHAELIS and M. MIZUTANI (*Z. physikal. Chem.*, 1925, **116**, 135—159).—The dissociation of the following substances in mixtures of ethyl alcohol and water has been investigated by a potentiometric method: acetic acid, phosphoric acid, lactic acid, salicylic acid, benzoic acid, carbonic acid, aminoacetic acid, *o*-, *m*-, and *p*-aminobenzoic acids, and ammonia. L. F. G.

**Physical Significance of Electrolytic Solution Tension.** J. HEYROVSKÝ (*Compt. rend.*, 1925, **180**, 1655—1658).—By means of a reversible cycle of operations the following equation is deduced for the reversible electrode potential ( $\pi$ ), of a univalent metal in contact with a solution containing its ions; (1)  $\pi = RT/F \cdot \log P_M + I + H/F + RT/F \log [M^+]$ . Here  $R$ ,  $T$ , and  $F$  have their usual significance,  $P_M$  is the vapour pressure of the metal at temperature  $T$ ,  $H$  is the free energy of hydration of the ions, and  $[M^+]$  the concentration of the ions in the solution, whilst the affinity of electrons for the metallic ions is given by the relation  $IF = \log P_M/P_{M+} \cdot P_e$ , where  $P_{M+}$  is the partial pressure of the ions in the vapour, and  $P_e$  the pressure of the electrons in the solid metal. The first three terms in equation (1) thus replace the single term for the Nernst electrolytic solution pressure and give a physical significance to the latter. In the few cases in which the terms in equation (1) are known, the calculated and experimental values of  $\pi$  agree as well as can be expected. W. H.-R.

**Method of Studying Electrode Potentials and Polarisation.** H. D. HOLLER (*Bureau of Standards Sci. Paper*, No. 504).—A resistance-coupled thermionic valve amplifier is used to operate an oscillograph under conditions which permit of observations of the variations in the potential when no current is taken from the electrode under investigation. The electrode is put in series with the grid battery, variations in the anode current, as recorded by the oscillograph, being proportional to variations in the electrode potential over the range employed. The electrode is used in conjunction with a standard electrode to form a cell through which direct current is passed, and changes in potential whilst opening and closing the circuit are recorded. When the polarisation disappears slowly, the *E.M.F.* of polarisation and the potential difference due to

resistance can be distinguished. By superposing alternating current on the cell, and using a separately excited wattmeter, the true resistance of the electrode can be determined. The results show that the electrode potential as measured by the potentiometer method may be more than 0.2 volt too high because of the potential drop due to resistance. Preliminary results indicate that the so-called transfer resistance between electrode and electrolyte may be due to gas. C. S.

**Standard Values in the Calculation of the Hydrogen Exponent from Measurements with the Hydrogen and Quinhydrone Electrodes.** I. M. KOLTHOFF (*Chem. Weekblad*, 1925, 22, 332—339).—Recent work on the calculation of the hydrogen-ion concentration from the potentials of the hydrogen, calomel, and quinhydrone electrodes in various solutions is reviewed and discussed, and formulæ for the calculation of  $p_H$  values from measurements made with the hydrogen and quinhydrone electrodes in conjunction with the various forms of calomel electrode are put forward. S. I. L.

**Electrometric Behaviour of Aluminium.** A. SMITS and H. GERDING (*Z. Elektrochem.*, 1925, 31, 304—308; cf. *ibid.*, 1924, 30, 423).—The potentials of aluminium amalgams of varying composition in saturated acetylacetone solution were measured against the normal calomel electrode. An increase in the atomic percentage of mercury from 0 to 0.35% causes a continual increase in the negative potential, the mercury being a positive catalyst for the establishment of internal equilibrium in the aluminium, which is not attained until the latter concentration of mercury is reached. Further increase in the mercury concentration up to 0.78 atomic % causes a straight line decrease in the negative potential; at the latter concentration, separation of a liquid phase occurs, and the potential remains constant up to 99.97 atomic % of mercury. Extrapolation of the straight line curve obtained between 0.35 and 0.78 atomic % of mercury back to the axis gives the true potential of pure aluminium when it is in internal equilibrium, this value being 1.520 volts, which is 0.130 volt more negative than the two-phase system aluminium+mercury. The potential of the latter system in a normal solution of aluminium chloride relative to the normal hydrogen electrode has a value 1.30 volts (Müller and Hölzl, A., 1922, ii, 341) and therefore the potential of pure aluminium in internal equilibrium in a *N* aqueous solution of aluminium chloride must have a minimum value of -1.430 volt relative to the normal hydrogen electrode. A correction is applied to the *E.M.F.* diagrams in the earlier communication (*loc. cit.*), and the results confirm the conclusion that no compound of aluminium and mercury is formed. J. W. B.

**Electronegative Potential Series in Liquid Ammonia.** F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1925, 47, 1503—1507).—Kraus (*Trans. Amer. Electrochem. Soc.*, 1924, 45, 175) has shown that the elements may be arranged in two electro-affinity series depending

on whether the element functions as an anion or as a cation. Replacement reactions in liquid ammonia solutions show that in the following series an element will in general replace any previous element when this is present as a homo-atomic anion: lead, bismuth, tin, antimony, arsenic, phosphorus, tellurium, selenium, sulphur, iodine. J. S. C.

**Potentials of Metals against Pure Water.** A. SMITS, H. GERDING, and (MISS) R. KROON (*Rec. trav. chim.*, 1925, **44**, 638—642).—From theoretical considerations, the expression  $E = -0.058/\nu F \cdot \log L_M/M_L^\nu - 2.784$  is obtained for the potential of a metal in pure water, assuming that the metal exists in equilibrium with a hydrogen phase at 1 atm. pressure.  $L_M$  is the solubility product of the metal and  $M_L^\nu$  is the ionic concentration. For silver, this gives  $E = -0.406$  volt. The potential of a hydrogen film on a metal electrode which is not developing hydrogen is equal to that outside the electrode, and can be calculated from the electron concentration outside the surface layer, or from the hydrogen ion concentration of the liquid. From an ion-electron equation which is derived theoretically,  $E$  for the hydrogen potential in pure water is found to be  $-0.406$  volt. Measurements of the electrode potential of silver and copper in pure water gave equilibrium potentials of  $-0.411$  and  $-0.410$ , respectively. The potential of silver was found to be influenced by light. A study of the influence of temperature showed that an increase rendered the silver more negative and the copper more positive. L. L. B.

**Electrical Charges Arising at a Liquid-Gas Interface.** H. W. GILBERT and P. E. SHAW (*Proc. Physical Soc.*, 1925, **37**, 195—214).—The various methods of studying electrification produced when a liquid is in contact with a gas are discussed under nine headings: one or both at rest, cataphoresis of gas bubbles, passage of gas over a liquid, fall of a liquid in an unbroken column through a gas, liquid jets, waterfall electricity, bubbling, shattering of drops in an air stream, and spraying. Explanations are given in terms of the modern theory of orientation and polarisation at the surface, but emphasis is laid on the discrepancies between the results of different observers. A summary is given of established results in regard to the three properties of a gas-liquid interface: potential difference, surface tension, and balloactivity. E. B. L.

**Surface Potential in Solutions of Inorganic Electrolytes.** W. WESSEL (*Ann. Physik*, 1925, [iv], **77**, 21—43).—Theoretical. The equilibria of inorganic ions in the surface layers of liquids have been investigated statistically. A formula is deduced showing the connexion between surface potential and concentration. Complete dissociation is assumed and the theory leads to correct values for the magnitude and sign of the surface potential of various acids and salts. Differences in behaviour are traced to differences in ionic volumes. R. A. M.

**Contact *E.M.F.* between the Solid and Liquid Phases of the same Metal and between the Outgassed Surfaces of two Dissimilar Metals.** P. H. DOWLING (*Physical Rev.*, 1925, [ii], 25, 812—825).—No definite change in contact *E.M.F.* at the m. p. of tin, Wood's metal, or a tin-lead alloy (25% Pb) could be observed. Any such change, if it exists, is at most of the order of 0.005 volt, and may possibly have been masked by the gas-effect. After removal of gas, the contact potential between copper and nickel reaches a limiting value of 0.25 volt (nickel positive to copper). When tin cools in a glass vessel, audible clicks are observed, accompanied by large electrical effects; this is apparently a tribo-electric phenomenon.  
A. A. E.

**Electromotive Force of Filtration.** L. RIETY (*Compt. rend.*, 1925, 180, 2026—2027; cf. A., 1924, ii, 528).—Solutions of ferrous, ferric, and copper salts were forced through glass tubes, and the potential difference between the entering and issuing solution was measured. For salts of monobasic acids the issuing solution has a negative charge, whilst for salts of di- and tri-basic acids the charge is positive; iron lactate is an exception. The results are due to the dissolving of alkali silicate from the glass with resulting hydrolysis of the iron or copper salts. Mercuric cyanide and chloride resist hydrolysis and with these salts high positive potentials are produced.  
W. H.-R.

**Specific Electro-kinetic Effects between Solid Phases and Dissolved Electrolytes.** R. LABES (*Z. physikal. Chem.*, 1925, 116, 1—64).—The conditions for electro-kinetic phenomena are reviewed and discussed mathematically (cf. Stern, *Z. Elektrochem.*, 1924, 30, 508). Electro-kinetic phenomena are influenced by the solubility products for the anion components of the solid phase and the cations of the electrolyte on the one hand, and the cation components of the solid phase and the anions of the electrolyte on the other. The smaller the solubility products, the greater is the effect. Endosmotic experiments with barium sulphate, zinc oxalate, and silver chloride, in contact with various solutions, confirmed the above conclusions.  
L. F. G.

**Decomposition Potentials of Solutions of Metallic Bromides in Molten Aluminium Bromide.** W. ISBEKOV (*Z. physikal. Chem.*, 1925, 116, 304—312).—Current-voltage data have been obtained for solutions of zinc, cadmium, silver, mercuric, antimony, and bismuth bromides in molten aluminium bromide. The decomposition potentials of the salts are in the above order, the nobility increasing from left to right. This order is different from that in aqueous solutions (zinc, cadmium, antimony, bismuth, mercuric, silver), but is the same as that of the equivalent heats of formation. Also, any metal in this series will precipitate any subsequent member from the bromide solution. Data were also obtained for sodium and potassium bromides. Their decomposition potentials are the same, and indicate that aluminium is here the primary product of electrolysis.  
L. F. G.

**Potentials of the Alkali Metals Determined by the Measurement of Decomposition Voltages of Molten Alkali Chlorides, Bromides, and Iodides.** B. NEUMANN and H. RICHTER (*Z. Elektrochem.*, 1925, **31**, 287—296).—The authors have determined or redetermined the decomposition voltages of a large number of molten alkali halides at various temperatures by a slightly improved modification of the method previously employed (cf. Neumann and Bergve, A., 1915, ii, 817) and hence calculated the temperature coefficients and the absolute potentials of the alkali metals. Mixtures of the halides of two alkali metals show two points of inflection on the curve corresponding with the decomposition potentials of the two salts and hence small quantities of other alkali metal halides present in the caesium, rubidium, and lithium salts employed do not affect the accuracy of the values obtained. The temperature coefficients for all halides of a metal (with the possible exception of fluorides) have the same value, as also have all the alkali metal halides with the exception of lithium. The following values are obtained as the mean of a large number of concordant determinations with different halides and with mixtures of halides at different temperatures: absolute potentials, caesium 2.909, rubidium 2.744, potassium 2.614, sodium 2.454 (cf. Trümpler, A., 1924, ii, 526 gives 2.72), lithium 2.091 volts. The discrepancy between these values compared and those obtained by other investigators working in aqueous solution is due to the untrustworthy absolute potential of the hydroxyl and sulphate ions. Temperature coefficients for sodium halides  $1.487 \times 10^{-3}$ , potassium halides  $1.500 \times 10^{-3}$ , rubidium halides  $1.50 \times 10^{-3}$ , caesium halides  $1.544 \times 10^{-3}$  (mean  $1.501 \times 10^{-3}$ ), and for lithium halides,  $1.347 \times 10^{-3}$ . The decomposition voltages for rubidium and caesium salts, not determined in the earlier work (*loc. cit.*) are: rubidium chloride 2.93 at 783°, bromide 2.67 at 738°, iodide 2.29 at 675°, caesium chloride 3.28 at 647°, iodide 2.56 at 595° (volts).  
J. W. B.

**Potentials of Metals of the Alkaline Earths and the Rare Earths Determined by Measurement of the Decomposition Potentials of the Molten Chlorides, Bromides, and Iodides.** B. NEUMANN and H. RICHTER (*Z. Elektrochem.*, 1925, **31**, 296—304).—The method previously employed with the halides of the alkali metals (cf. preceding abstract) has been extended to the measurement of the decomposition voltages of the fused halides of the alkaline-earth and rare-earth metals and of aluminium chloride. Measurements were made at various temperatures in each case with a mixture of the pure anhydrous halide with either potassium or sodium chlorides, and the temperature coefficient and the absolute potential of the metal calculated as previously. As with the alkali halides, the temperature coefficient of the group is practically constant with the exception of the first member, *i.e.*, beryllium and aluminium, respectively. The following values were obtained for the decomposition voltage: beryllium chloride 1.47 at 737°, temperature coefficient  $0.965 \times 10^{-3}$ ; magnesium chloride 2.23 at 783°, *t. c.*  $0.712 \times 10^{-3}$ ; calcium chloride 2.82 at 638°, *t. c.*  $0.704 \times 10^{-3}$ ;

strontium chloride  $2.99$  at  $633^\circ$ , t. c.  $0.7143 \times 10^{-3}$ ; barium chloride  $3.06$  at  $647^\circ$ , t. c.  $0.7143 \times 10^{-3}$ ; the absolute potentials for the metals beryllium, magnesium, calcium, strontium, and barium being,  $0.811 \pm 0.003$ ,  $1.422 \pm 0.001$ ,  $1.903 \pm 0.002$ ,  $2.075 \pm 0.002$ ,  $2.154 \pm 0.005$  volts. Further decomposition voltages are: thorium chloride  $1.70$  at  $765^\circ$ , t. c.  $1.875 \times 10^{-3}$ ; cerium chloride  $2.10$  at  $738^\circ$ , t. c.  $1.875 \times 10^{-3}$ ; lanthanum chloride  $1.65$  at  $783^\circ$ , t. c.  $1.882 \times 10^{-3}$ ; neodymium chloride  $1.55$  at  $800^\circ$ , t. c.  $1.852 \times 10^{-3}$ ; praseodymium chloride  $1.45$  at  $737^\circ$ , t. c.  $1.862 \times 10^{-3}$ ; aluminium chloride  $1.49$  at  $640^\circ$ , t. c.  $1.132 \times 10^{-3}$ ; the absolute potentials for the metals cerium, thorium, lanthanum, neodymium, praseodymium, and aluminium being  $2.097 \pm 0$ ,  $1.747 \pm 0$ ,  $1.748 \pm 0.002$ ,  $1.645 \pm 0$ ,  $1.436 \pm 0.002$ ,  $0.845 \pm 0.006$  volts.

J. W. B.

### Concentration and Polarisation at the Cathode during Electrolysis of Solutions of Copper Salts. W. L. MILLER

(*J. Franklin Inst.*, 1925, **199**, 773—783).—The overvoltage obtained when a solution of a copper salt is electrolysed between copper electrodes has been determined by subtracting from the total potential difference between the electrodes, measured by means of an oscillograph element, the internal resistance drop through the cell and the concentration voltage. The internal resistance drop, or instantaneous fall in potential difference when the current is stopped, was equal, in the experiments under consideration, to the product of the current into the resistance of the leads, electrodes, and electrolytes, indicating the absence of any "transport resistance" or of a non-conducting film on the electrodes. The concentrations at the electrodes during electrolysis were calculated from the equations developed by Rosebrugh and Miller (A., 1911, ii, 181) on the basis of Weber's diffusion theory. Measurements of the time required to liberate hydrogen from acid solutions of copper salts by constant, interrupted, successive, and sinusoidal currents have all confirmed the validity of these equations. Concentration changes at the anode were found to be trifling compared with those at the cathode, and measurements with auxiliary electrodes showed that the overvoltage was almost exclusively cathodic. An expression for the overvoltage,  $A + (B - 0.03) \log z_0/z$ , where  $z_0$  is the copper concentration in the body of the electrolyte and  $z$  that at the cathode, has been deduced.  $A$ , the "instantaneous overvoltage," has hitherto been considered as the true overvoltage. It is independent of the copper concentration, but increases with increasing acidity. It falls to zero with the current density and reaches a constant maximum value in 7.5 *N*-sulphuric acid at 0.7 amp. per sq. dm.  $A$  depends on the previous history of the cathode, and not on some reaction in solution such as dehydration of ions. It has less than its normal value for a measurable time after the electrode has been the anode, so that lower values of  $A$  are obtained with alternating than with direct or interrupted currents. The rapidity with which the overvoltage falls when the current is interrupted shows that it cannot be studied successfully by the com-

mutator method.  $B$  is independent of the copper concentration, current density, and sulphuric acid concentration. M. S. B.

**Dissolution of Nickel in Sulphuric Acid under the Influence of an Alternating Current.** A. P. ROLLET (*Compt. rend.*, 1925, 180, 2047—2049).—An alternating current of 50 periods was passed through two nickel electrodes immersed in sulphuric acid. The solution was stirred and large volumes used to minimise the effects of the products of electrolysis. The hydrogen evolved corresponds exactly with the weight of nickel dissolved. The yield increases with increasing speed of stirring. As the temperature is raised from  $0^{\circ}$ , the yield rises to a maximum at  $30^{\circ}$  and then falls, until at  $70^{\circ}$  it is less than at  $0^{\circ}$ . With low current densities the yield increases rapidly with the concentration of the sulphuric acid and then becomes constant, but with high current densities concentration has a more gradual effect, and the yield only reaches a constant value in very concentrated solutions. The yield rises with the current density up to a value between 0.7 and 1.5 amp. per sq. cm.; under these conditions hydrogen only is evolved. Above this limiting current density the yield falls rapidly and both oxygen and hydrogen are given off. W. H.-R.

**Theory of Reaction Rate.** G. N. LEWIS and D. F. SMITH (*J. Amer. Chem. Soc.*, 1925, 47, 1508—1520).—Theoretical and mathematical. The theory that the rate of a chemical reaction is governed by the concentration of activated molecules, the latter being defined as all those molecules possessing more than a minimum energy, is discussed. The classical Arrhenius equation is exactly true in certain simple cases and is in all cases a very close approximation. Observed reaction velocities can be satisfactorily accounted for both by collision and by radiant energy. An equation representing the number of encounters between molecules and the quanta of light necessary for activation is developed. Whilst there is no serious drawback to the general radiation theory, the simple theory assuming activation by nearly monochromatic light is untenable. A subsequent paper will give reasons for believing that radiation, and not collision, is the important factor in the promotion of chemical processes. J. S. C.

**Mechanism of Chemical Reaction.** R. C. TOLMAN (*J. Amer. Chem. Soc.*, 1925, 47, 1524—1553).—A theoretical and mathematical paper in which the various suggested mechanisms of activation of molecules prior to their participation in chemical processes are discussed. As typical examples of homogeneous reactions proceeding entirely in the gaseous phase the unimolecular decomposition of nitrogen pentoxide (Daniels and Johnston, A., 1921, ii, 249) and the bimolecular reaction, decomposition of nitrous oxide (Hinshelwood and Burk, A., 1924, ii, 751) are considered in an attempt to find out whether the various proposed mechanisms are sufficiently rapid to account for the observed rates of reaction and whether they lead to a velocity expression of the proper order. Activation by collision cannot take place fast enough to account for the unimole-

cular process, but might be a possibility for bimolecular processes if each of the molecules of the reacting species brings an appreciable fraction of the total energy of activation, or if both activation and immediate reaction are a result of the same collision. Activation by collision with a molecule which is itself in an activated state, resulting in a transfer of energy, although of importance in certain types of reactions is not the primary method of activation for reactions of constant order. The simple radiation theory cannot satisfactorily explain unimolecular reactions and leads to incorrect predictions of the active frequency. In the case of bimolecular reactions activation may occur sufficiently rapidly to account for the observed rates provided that each of the reacting molecules brings an appreciable fraction of the energy of activation. Activation by the simultaneous absorption of more than one frequency is not a probable mechanism. An elaborated form of the radiation theory involving the existence of a series of activated states of nearly the same energy content rather than a single activated state, probably provides a satisfactory mechanism for unimolecular and bimolecular reactions and also explains why absorption lines are not found in the positions calculated from the simple theory. The simultaneous absorption and emission of quanta may be a definite step in a chemical process but there is no evidence that such stages are of primary importance in accounting for known rates of reaction. A large number of references to the published work of various authorities are given.

J. S. C.

**Gaseous Combustion at High Pressures. V. Explosion of Hydrogen-Air and Carbon Monoxide-Air Mixtures at Varying Initial Pressures up to 175 Atmospheres.** W. A. BONE, D. M. NEWITT, and D. T. A. TOWNEND (*Proc. Roy. Soc.*, 1925, **A**, **108**, 393—418; cf. *A.*, 1924, ii, 398).—Hydrogen-air mixtures ( $2\text{H}_2 + \text{O}_2 + 4\text{N}_2$ ) and carbon monoxide-oxygen-diluent mixtures ( $2\text{CO} + \text{O}_2 + 4\text{R}$ , where  $\text{R} = \text{CO}$ ,  $\text{A}$ , or  $\text{N}_2$ ) were studied at higher initial pressures (75—175 atm.) than those previously employed. The time taken for the attainment of maximum pressure in the explosions diminished as the initial pressure increased, except in the case of the mixture  $2\text{CO} + \text{O}_2 + 4\text{N}_2$ , where the reverse occurred; this exceptional behaviour gives further confirmation of the activation of nitrogen on the explosion of carbon monoxide-air mixtures, the activation increasing with initial pressure. The ratio, maximum pressure attained during explosion : initial pressure, increased with the initial pressure; this is possibly due to the increasing opacity of the gaseous medium to the radiation emitted during the explosion. No evidence of "after-burning" was observed with this initial pressure range. Previous views on carbon dioxide dissociation are revised. The degree of carbon dioxide dissociation at the maximum temperature attained was probably 15—25% with  $2\text{CO} + \text{O}_2 + 4\text{A}$  mixtures, and about 5% with  $2\text{CO} + \text{O}_2 + 4\text{N}_2$  mixtures. When carbon monoxide is the diluent, it suppresses such dissociation. Secondary formation of nitric oxide in the carbon monoxide-air explosions was inconsiderable except when excess of air was present;



in this connexion, mixtures containing 25, 50, and 60% of excess air were studied. With excess of air, and 125 atm. initial pressure, amounts of nitrogen peroxide largely in excess of those predicted on thermodynamical grounds were obtained, thus confirming the view that the primary nitrogen activation is more a pressure than a temperature phenomenon. In the explosion of the hydrogen-air mixtures, the amount of water dissociation at the maximum temperatures attained never exceeded about 1%, nor could any nitrogen activation be detected.

L. F. G.

**Detonation Limits in Explosive Gas Mixtures.** R. WENDLANDT (*Z. physikal. Chem.*, 1925, **116**, 227—260).—The conditions obtaining in and near the zone of pseudo detonation (cf. this vol., ii, 135) are investigated. It is assumed that, with progressive dilution of the explosive mixture, chemical reaction finally becomes so slow that it is not consistent with the high velocity of normal detonation, *i.e.*, a volume element would remain for too short a time in the normal wave zone for complete chemical change to take place. With greater dilution the change becomes still more incomplete, the retardation being accentuated by decrease in temperature and pressure in the wave zone. Data previously obtained are examined and shown to conform with this assumption, correlated with the equations of Riemann, Hugoniot, and Jouguet (cf. Becker, *Z. Physik.*, 1922, **8**, 321). Reaction velocities at high temperatures can be calculated from experimental data obtained in this region.

L. F. G.

**Rate of Decomposition of Nitrogen Pentoxide at Low Concentrations.** J. K. HUNT and F. DANIELS (*J. Amer. Chem. Soc.*, 1925, **47**, 1602—1609).—The various theories which have been put forward to explain unimolecular reactions are critically discussed. The decomposition of nitrogen pentoxide is shown to be unimolecular. The rate of decomposition has been determined at 35°, 45°, and 55° at pressures ranging from 280 to 0.01 mm. The specific rate of reaction is independent of concentration over the range investigated and is not influenced by nitrogen dioxide or by the presence of a large excess of nitrogen.

J. S. C.

**Chemical Deposits of a Regular Form.** J. M. MULLALY (*Phil. Mag.*, 1925, [vi], **49**, 1222—1225).—Ammonia and hydrogen chloride were allowed to diffuse steadily from opposite ends of a tube of uniform bore. The distribution of ammonium chloride crystals along the tube was measured (by the thickness of the salt deposited along an axis of the tube) by means of a travelling microscope. The results may be represented by the combination of two error curves, with a common origin at the point on the axis where the deposit is thickest. If  $m_0$  is the maximum thickness at  $l=0$  and  $m$  the thickness at a point  $l$  distant from the origin the equations are:  $m/m_0=e^{-k_1 l^2}$  and  $m/m_0=e^{-k_2 l^2}$ , where  $k$  and  $k_1$  are constants for a given tube. Within limits  $k$  and  $k_1$  are independent of time and of the bore of the tube.

R. A. M.

**Velocity of the Synthesis of Hydrogen Bromide by Capacity Change.** A. BRAMLEY (*Physical Rev.*, 1925, [ii], 25, 858—864).—The dielectric constant of bromine vapour at  $180^{\circ}$  is 1.0128, evidently corresponding with the molecular aggregate  $(Br_2)_6$ . When investigated by the capacity method, the formation of hydrogen bromide from hydrogen and bromine is shown to be practically zero in the dark at  $18^{\circ}$ ; activation by illumination is four times as effective with blue light as with red. At  $58^{\circ}$  the reaction proceeds in the dark, the thermal predominating over the photochemical effect. A. A. E.

**Chemical Activity.** P. PETRENKO-KRITSCHENKO, D. and B. TALMUD, W. BUTMY-DE-KATZMAN, and A. GANDELMAN (*Z. physikal. Chem.*, 1925, 116, 313—318).—The velocities of reaction of halogen derivatives of methane and ethane with various reagents were measured. A periodicity in the reactivities was observed, minima occurring with compounds of the type  $C_2H_5X$ ,  $CH_3 \cdot CHX_2$ , and  $CX_4$ , and maxima with compounds of the type  $CH_2 \cdot X \cdot CH_2 \cdot X$ , and  $CHX_3$ . L. F. G.

**Is the Hydrolysis of Esters Derived from Strong Acids Accelerated by Hydrogen Ions?** S. C. J. OLIVIER and G. BERGER (*Rec. trav. chim.*, 1925, 44, 643—651).—A reply to the criticism by Skrabal (this vol., ii, 139) of the views advanced by the authors that the hydrolysis of esters of the above type is not accelerated by hydrogen ions. Small quantities of trichloroacetic acid are not decomposed under the conditions of the experiment. L. L. B.

**Reactions of Benzoic Acid at the Boundary of Two Liquid Phases.** (MLLE.) A. KLEIN (*Roczniki Chemji*, 1925, 5, [1—3], 101—109).—The mechanism of the reaction between benzoic acid dissolved in carbon tetrachloride and aqueous sodium hydroxide is shown to be in agreement with the diffusion theory. The velocity of the reaction is greatly accelerated by stirring and by rise in temperature,  $10^{\circ}$  increasing the velocity by 32%. Benzoic acid in carbon tetrachloride solutions of more than 0.04*N* exists in the form of double molecules. The partition coefficient of benzoic acid between the two solvents used is 0.00126. R. T.

**Relation between Rapidity of Stirring and Velocity of Reaction in Heterogeneous Systems.** (MLLE.) A. KLEIN (*Roczniki Chemji*, 1925, 5, [1—3], 138—147; cf. preceding abstract).—For reactions in heterogeneous systems the following equation is shown to hold:  $(K-a)/n = \text{const.}$ , where  $K$  is the velocity of reaction with stirring,  $a$  the velocity without stirring, and  $n$  the number of revolutions of the stirrer per minute. The value of  $K$  also depends on the shape and exact position of the stirrer, and is not constant for the same apparatus, but only for each experiment. R. T.

**Reactions between Liquid Amalgams and Aqueous Solutions.** (MLLE.) A. KLEIN (*Roczniki Chemji*, 1925, 5, [1—3], 110—137).—The velocity of reaction of amalgams of sodium and

zinc with water, acids, alkalis, and salts is investigated. The results obtained are not constant if with sodium amalgam water, alkaline, or sodium chloride solutions are used; for other solutions, the velocity falls with increase in the sodium-ion concentration. With neutral or alkaline solutions a temperature rise of  $10^{\circ}$  increases the velocity by 46%, whilst the rate of stirring has no effect on the speed of reaction. The latter, for acid solutions, consists of the sum of two components, one of which is the velocity of reaction in neutral solution, the other being at any moment proportional to the concentration of acid, to the rate of stirring, and to the temperature (a  $10^{\circ}$  rise increasing the coefficient of proportionality by 7%), but not to the concentration of amalgam. In the case of zinc amalgam, the velocity of reaction with hydrochloric acid appears to be proportional to the 4.6th power of the concentration of the latter, and is doubled by a  $10^{\circ}$  rise in temperature. The presence of zinc ions in the supernatant liquid diminishes the velocity of reaction. R. T.

**Thermal Decomposition of Silver Carbonate.** M. CENTNERSZWER and B. BRUŽS (*J. Physical Chem.*, 1925, 29, 733—737).—The velocity of decomposition of heated crystalline silver carbonate is normal, diminishing according to the unimolecular equation, but the amorphous carbonate, prepared from silver nitrate and potassium hydrogen carbonate, behaves abnormally. The velocity at first falls rapidly, then remains constant, and finally falls exponentially. This is explained by the formation of an unstable oxycarbonate as an intermediate product; the reaction velocity diminishes with rising temperature between  $245^{\circ}$  and  $260^{\circ}$ , and it is concluded that the oxycarbonate is a catalyst, but that above  $260^{\circ}$  no such intermediate product is formed. A. G.

**Thermal Dissociation of Calcium Carbonate, and the Differential Method.** II. L. ANDRUSSOV (*Z. physikal. Chem.*, 1925, 116, 81—96; cf. this vol., ii, 538).—The above reaction was investigated by means of a slight modification of the differential method previously described. Reaction velocities were determined and were found to be affected considerably by moisture. The equation for the reaction isochore was constructed, and was in agreement with the Nernst equation. Extrapolated values for the dissociation pressures of calcium carbonate on each side of the experimental range ( $500$ — $900^{\circ}$ ) were determined by means of the isochore. The chemical constant of carbon dioxide is  $1.035 \pm 0.1$ . Advantages of the differential method are discussed. L. F. G.

**Nephelometry. Suggested Sensitive Test for the Stability of Explosives.** A. F. C. POLLARD (*Trans. Opt. Soc.*, 1924—25, 26, 63—73).—Colloidal solutions of silver oxide, prepared by adding small quantities of 0.001*N*-sodium hydroxide to a great excess of 0.1*N*-silver nitrate solution, are exceedingly sensitive to traces of nitrogen peroxide, the colloidal particles disappearing. Purified air is drawn over finely-divided cordite or guncotton and through the solution contained in one tube of a nephelometer

similar to that described by Kingslake (this vol., ii, 821); the disappearance of the colloidal particles reduces the scattering of the light, the effect being measured by the movement of the standard tube necessary to restore photometric equality. The test is not sufficiently delicate to measure directly the time rate of evolution of nitrous gases, which is a measure of the stability of an explosive, but by carrying out two tests at an interval which need not exceed 10 hrs., the amount of nitrogen peroxide accumulated during the interval may be determined. The test is superior to the Abel test, since the explosive does not require to be heated. S. I. L.

**Spark Photography as a Means of Measuring Rate of Explosion.** J. E. SMITH (*Physical Rev.*, 1925, [ii], 25, 870—876).—The explosive is placed in a cartridge having openings at definite intervals, additional charges being placed at the openings. Automatic spark illumination enables photographs to be obtained of the shadows of the sound waves associated with a particular opening. Rates of explosion for various charges of lead styphnate, mercury fulminate, and gunpowder were determined. [Cf. B., 1925, Aug.] A. A. E.

**Titanous Chloride and Nitric Acid.** M. COBLENS and J. K. BERNSTEIN (*J. Physical Chem.*, 1925, 29, 750—752; cf. A., 1924, ii, 605).—Like nitric acid, nitrous acid is reduced to nitric oxide by titanous chloride, whilst hyponitrous acid is reduced to nitrous oxide; stannous chloride reduces all three acids to hydroxylamine. The formation of the gaseous oxides is a catalytic effect of titanous chloride and they are reduced to ammonia when shaken with the reagent. A. G.

**Catalytic Action. XIV. Comparative Study of the Catalytic Activity of Reduced Copper, Reduced Nickel, and Thoria. II.** S. KOMATSU and C. TANAKA.—(See i, 905.)

**Catalytic Action. XV. Catalytic Activity of Reduced Copper. II.** S. KOMATSU and M. KURATA.—(See i, 942.)

**Mechanism of Catalytic Decomposition.** F. H. CONSTABLE (*Proc. Roy. Soc.*, 1925, A, 108, 355—378).—The theory of the dehydrogenation of alcohols at a copper surface is discussed in the light of previous experimental results (A., 1924, ii, 843; this vol., ii, 311). It is concluded that the mechanism of the change is the loss of neutral hydrogen atoms, and that activation of the alcohol molecule by the copper consists in increasing the distance between the hydrogen atom and the oxygen atom of the hydroxyl group. The quantitative deductions from this point of view are not in agreement with experiment unless it is assumed that only a part of the copper surface is catalytically active, *i.e.*, that "reaction centres" exist.

These centres are treated as being some characteristic grouping of copper atoms, and the variation in the activity of the catalyst with its temperature of preparation is discussed from this point of view.

S. B.

**Poisoning of Nickel Catalyst by Thiophen and Action of a Copper Catalyst.** B. KUBOTA and K. YOSHIKAWA (*Sci. Papers Inst. Phys. Chem. Res.*, 1925, **3**, 33—50).—The toxic influence of thiophen on the catalytic reduction of benzene to cyclohexane in presence of reduced nickel is investigated. It is considered that unstable nickel hydrides,  $H(Ni)_nH$ , coexist in the catalyst in proportions depending on the conditions under which the catalyst is prepared. The most active hydride,  $H \cdots HNiH \cdots H$ , alone is capable of hydrogenating an aromatic nucleus and is the only one poisoned by thiophen. A nickel catalyst thus poisoned will still reduce phorone to valerone with yields equal to those obtained with the most active catalyst, because the unpoisoned  $H(Ni)_2H$  is present. Copper catalysts will not catalyse the hydrogenation of aromatic nuclei and copper is not poisoned by thiophen, which supports the above theory. In the reaction studied, the thiophen nucleus is reduced and nickel sulphide is formed progressively throughout the catalyst. The percentage of active nickel formed decreases rapidly the higher the temperature at which the oxide is reduced; the temperature of preparation of the latter from the nitrate has little effect.

Valerone semicarbazide melts at  $121^\circ$ , higher than previously recorded. S. K. T.

**Action of Promoters in Catalysis.** M. C. BOSWELL and C. H. BAYLEY (*J. Physical Chem.*, 1925, **29**, 679—692).—When ferric oxide containing ceric oxide is reduced by hydrogen the volume of hydrogen retained by the oxides, compared with the amount of water removed, is greater than in the absence of ceric oxide, and the addition of potassium hydroxide has a similar effect on platinum. It is therefore concluded that the action of promoters is to increase the concentration of charged hydrogen and hydroxyl in the surface layer (cf. A., 1923, ii, 231; this vol., ii, 215; *Proc. Roy. Soc. Canada*, 1923, **17**, III). The promoter probably (1) enables the surface film to be formed more rapidly on reduction, (2) acts as particles throughout the reduced layer around which dissociated water can accumulate at higher concentrations, and (3) increases the stability of the catalytic film so that it is not lost, at high temperatures, as water. A. G.

**Reciprocal Excitation and Inactivation of Catalysts.** A. QUARTAROLI (*Gazzetta*, 1925, **55**, 252—264; cf. this vol., ii, 53).—The catalytic effect on the decomposition of hydrogen peroxide produced by copper hydroxide prepared from a copper salt and sodium hydroxide in presence of the peroxide increases enormously as the concentration of the hydrogen peroxide is diminished; under certain conditions, diminution of such concentration sixteen-fold results in more rapid liberation of oxygen. Ferric hydroxide, precipitated with the copper hydroxide, greatly increases the catalytic activity of the latter, although alone its effect is negligible; a mixture of these two hydroxides in presence of alkali is far superior to colloidal platinum as a catalyst for the peroxide in very dilute solution. On the other hand, nickel and magnesium hydroxides,

similarly precipitated, weaken the action of copper hydroxide, whilst the effect of aluminium hydroxide may be in either direction according to the concentration of the copper in the solution.

T. H. P.

**Positive and Negative Catalysts of the Dehydration of Cupric Hydroxide.** A. QUARTAROLI (*Gazzetta*, 1925, 55, 264—270).—Addition of as little as 1 part of hydrogen peroxide per  $2 \times 10^8$  parts of solution appreciably increases the velocity with which cupric hydroxide, in presence of a small amount of alkali, changes colour at  $50^\circ$  to green and ultimately to black. The traces of the peroxide present in ordinary distilled water are possibly the cause of such change. Even in amounts very small compared with the quantity of cupric hydroxide itself, various electrolytes, particularly magnesium salts, markedly retard the alteration of the hydroxide. The blackening of copper hydroxide suspended in alkaline solution appears to be, not a simple dehydration, but a complex phenomenon composed of oxidations and reductions, with formation of saline hydrates containing copper atoms of different degrees of oxidation.

T. H. P.

**Low-temperature Oxidation at Charcoal Surfaces. I. Behaviour of Charcoal in the Absence of Promoters.** E. K. RIDEAL and W. M. WRIGHT (*J. Chem. Soc.*, 1925, 127, 1347—1357).—Oxygen may be adsorbed on a charcoal surface to form at least three types of surface compounds: (i) the autoxidisable fraction formed by the readily detachable atoms not in the regular space lattice; (ii) strong adsorbing surface from which carbon dioxide can be evolved only at high temperatures (non-catalytic surface); (iii) a fraction forming unstable oxygen complexes, which may in time pass over into the more stable form; the oxygen on this is activated. Attempts have been made to measure the areas of these different surfaces on the charcoal. The autoxidisable fraction was measured by determining the amounts of poison (potassium ferricyanide and amyl alcohol) adsorbed per 100 mg. of charcoal to arrest autoxidation; it was found to be 0.38% of the surface. Aqueous solutions of substances containing but one polar group (alcohol, formic, acetic, and the higher fatty acids) do not undergo oxidation at the surface of charcoal; substances containing two adjacent polar groups (one of which may be a mobile hydrogen atom) are readily oxidised. Reaction velocities of acid oxidation were much higher than the autoxidation, and  $k_{50^\circ}/k_{40^\circ}$  was 2.0 against 1.8 for the latter. Hence oxidation is proceeding on another portion of the charcoal greater in extent than that undergoing autoxidation. The two reactions are not coupled reactions, and the autoxidisable areas can be poisoned without influencing catalytic oxidation. The velocity of oxidation increases with the concentration of the acid and then falls; the maximum rate corresponds with a higher concentration of acid if the oxygen pressure is increased, the optimum being independent of the temperature. This corresponds with a suitable stoichiometric proportion of the reactants on the catalytic surface. From

the amount of amyl alcohol adsorbed to prevent oxidation it was concluded that 40.5% of the total area is active. W. T.

**Decomposition of Hydrogen Peroxide by Cobaltic Hydroxide.** F. G. TRYHORN and G. JESSOP (*J. Chem. Soc.*, 1925, 127, 1320—1330).—The cobaltic hydroxide was prepared by the addition of ammonia to a mixture of hydrogen peroxide and cobalt chloride solution. Low concentrations gave a stable brown sol; higher concentrations gave unstable sols which soon coagulated. The catalyst activity  $kA$  has been calculated by means of the equation for a catalysed unimolecular reaction:  $kA = 1/(t_2 - t_1) \log \{(a - x_1)/(a - x_2)\}$ . The activity appears to be subject to a dual change: an irreversible fall, and a simultaneous reversible increase inversely dependent on the hydrogen peroxide concentration. The irreversible fall seems to be due to a change in the nature of the catalytic surface, resulting in an orientation of the molecules in a position of minimum potential energy, which orientation probably corresponds with a minimum activity. This fall is made negligible by previous treatment of the catalyst with excess of hydrogen peroxide or by allowing it to form slowly by the hydrolysis of a cobaltamine salt. The promoter effect of ammonia is attributed to hydroxyl ions. High concentrations of ammonia decrease the activity due to dissolution of the catalyst. The activity of the catalyst is at first proportional to its concentration; at higher concentrations, it increases more rapidly than catalyst concentration. The catalytic activity is an inverse linear function of the concentration of hydrogen peroxide. A mechanism is suggested for the reaction in which the decomposition of the peroxide occurs in a unimolecular film on the catalyst surface, a distortion of the intramolecular force field on adsorption rendering one hydrogen atom of the peroxide molecule removable by the impact of a hydroxyl ion. The peroxide ion thus formed decomposes to give oxygen and hydroxyl ions. An equation derived on this basis agrees with experimental data and is applicable to other cases of catalysis. W. T.

**Electrolytic Preparation of Hydrogen Sulphide and Sulphides.** P. FISCHER (*Z. Elektrochem.*, 1925, 31, 285—286).—In order to obtain satisfactory yields of hydrogen sulphide and metallic sulphides by the electrolytic method, the cathode must (i) possess as large a conductivity as possible, (ii) have as large a sulphur content as possible, (iii) be of simple composition. The resistance of homogeneous mixtures of silver, arsenic, and copper sulphides, and copper pyrites, stibnite, and galena, with excess of sulphur were determined, but only in the case of copper sulphide was the mixture a conductor, the greatest specific conductivity being obtained with a 50% mixture of the two components. Using this electrode as the cathode, a pure cadmium anode, sodium sulphate solution as electrolyte, and a current density of 0.05 amp./cm.<sup>2</sup>, the yield of cadmium sulphide is practically theoretical, both yellow and orange forms being produced. With a current density of 0.005 amp./cm.<sup>2</sup>, only the yellow form is obtained.

Since the current-potential curve for a 0.1N solution of sodium hydroxide using this cathode and a platinised-platinum anode is a straight line showing no decomposition potential, no evolution of hydrogen occurs, but the sulphur passes directly into solution as an ion.

J. W. B.

**Electrolytic Preparation of Selenides and Iodides.** P. FISCHER (*Z. Elektrochem.*, 1925, **31**, 286—287).—Metallic selenides and iodides may be prepared electrolytically by methods similar to those employed for the preparation of sulphides (cf. preceding abstract). In the case of selenides the cathode consists either of a rod of selenium round which is wound a platinum wire, or, better, an alloy of zinc (5 parts) and selenium (1 part), since in the latter case no hydrogen is evolved and no disintegration of the cathode occurs, the anode being a zinc or copper plate, the electrolyte a solution of sodium sulphate, and the current density 0.1—0.2 amp./cm.<sup>2</sup>. With a silver anode, mainly polyselenides were formed. The valency of the selenium in solution varies with the nature of the anode, the nature and concentration of the electrolyte, current density, etc. For the formation of iodides, the cathode may be either a rod of silver iodide or a platinum plate coated with a thick layer of solid iodine, the electrolyte a solution of potassium nitrate, and the anode a platinum or lead plate; with the latter, crystalline lead iodide separates during the hydrolysis. Lead iodide is also formed when a lead plate and an iodine-coated platinum plate dipping into a 5% solution of potassium nitrate are connected by a copper wire. Varying amounts of free iodine also pass into solution.

J. W. B.

**Electrodeposition of Zinc from Sulphate Solutions.** A. L. MARSHALL (*Trans. Faraday Soc.*, July 1925, advance proof, 7 pp.).—The efficiency of deposition of zinc from pure sulphate solutions increases with rise in temperature more rapidly the lower the zinc and the higher the acid concentration. The potential of a zinc electrode against a 3.51N-solution of sulphuric acid increases with the current density rapidly at first, then slowly to a maximum of about -1.36 volt at 20° and -1.25 volt at 41—59°; these values are considerably reduced by the addition of zinc sulphate to the solution and still more so by the presence of even minute amounts of antimony. The current efficiency of zinc deposition is decreased very greatly by the presence of copper, ferrous, or manganese sulphates, especially at the higher temperatures, but antimony has the most marked effect of any impurity, even 1.0 mg. per litre reducing the efficiency by 10%.

A. R. P.

**Electrolytic Oxidation of Alcohols. II. Electrolytic Chlorination of Ethyl Alcohol.** S. KOIDZUMI (*Mem. Coll. Sci. Kyōtō*, 1925, **8**, 155—166).—The electrolytic chlorination of ethyl alcohol in potassium chloride solution is studied. A special electrolytic cell is described, and the effects of temperature, current density, and electrolyte are determined. Using a carbon plate



anode and a copper cathode, both anolyte and catholyte being a solution of potassium chloride, saturated at 70°, at a temperature of 70–80° and a current density of 0.08 amp./cm.<sup>2</sup>, the main products are chloral hydrate and alcoholate, monochloroacetic acid, ethyl acetate, monochloroacetaldehyde hydrate and alcoholate, and chloroether, the last three products representing intermediate stages in the production of chloral. In the formation of monochloroacetic acid, the alcohol is first oxidised to aldehyde, which is then chlorinated, and the chlorinated aldehyde then undergoes further oxidation to the acid. By limiting the time of passage of the current, corresponding dichlorinated products are isolated. The yield of monochloroacetic acid is increased and that of chloral decreased by interruption of the electrolysis, the best yield (61.2%) of the latter being obtained by addition of the alcohol drop by drop to the potassium chloride electrolyte, the concentration of which is maintained as high as possible, the electrolysis being carried out at 70–80°. In no case was chloroacetal produced.

J. W. B.

**Life Period of Activated Molecules in Thermal and Photochemical Reactions.** N. R. DHAR and B. K. MUKERJI (*Z. Elektrochem.*, 1925, **31**, 283–285).—The authors have applied Turner's formula for the calculation of the average life of an activated molecule (A., 1924, ii, 362) to a number of thermal and photochemical reactions in dilute solutions, the concentration of the reacting substances being substituted for the gaseous pressure in the original equation. The value of  $\tau$  is found to be of the same order ( $10^{-8}$ – $10^{-9}$  sec.) in each type of reaction, thus confirming the authors' opinion that there is no fundamental distinction between thermal and photochemical reactions.

J. W. B.

**Experimental Technique of Photochemistry. II. Determination of Energy Distribution and Total Energy in Radiation from Quartz Mercury Lamps.** R. G. FRANKLIN, R. E. W. MADDISON, and L. REEVE (*J. Physical Chem.*, 1925, **29**, 713–726; cf. this vol., ii, 234).—Details are given of the apparatus used for the determination of energy distribution. It is shown in detail that, whatever the widths of the telescope and collimator slits, and whatever the nature of the line, whether simple or complex, its relative energy is obtained by dividing the area of its energy distribution diagram by  $d\lambda$ ; the energy distribution diagram is obtained by plotting the galvanometer deflection against the wave-length and  $d\lambda$  is the wave-length range embraced by the telescope slit. Total energy is measured by comparison with a Hefner lamp; care must be taken that the mercury lamp is in the position in which it is to be used subsequently, and the field illuminated by the lamp must be explored by the thermopile in order to obtain a correct mean value. Corrections are applied for reflection at the surfaces of lenses etc. and for the infra-red radiation passing through the water-cell. The radiant energy of any wave-length is calculated from the total energy and the energy distribution.

A. G.

**Change of Mass of Silver Halides on Intense Illumination.** P. P. KOCH and B. KREISS (*Z. Physik*, 1925, **32**, 384—396).—Grains of silver halides prepared in a variety of ways were suspended by means of an electrical field between the plates of a condenser and the light from a "pointolite" lamp focussed on them. Silver bromide lost about 25% of its weight, and silver chloride rather less. The loss with silver iodide was doubtful. E. B. L.

**Ripening of Photographic Emulsions from the Point of View of Ionic Deformation.** H. SCHMIDT (*Z. wiss. Phot.*, 1925, **23**, 201—216).—"First-ripening" (*i.e.*, during emulsification) and "after-ripening" (*i.e.*, after washing) are considered. The former results in increase of grain size and no increase in sensitiveness, and it determines the lattice-form of the grains. In "after-ripening" there is no apparent change in grain size, but the individual lattice-forms are made more sensitive to light by the elimination of adsorbed bromide ions, which leads to a change in the deforming forces in the silver halide grains. The quantum jumps are then no longer reversible, but become irreversible and form atomic bromine and silver. The adsorption forces vary in magnitude, and are dependent on the structure and size of the grains, and therefore on the "first-ripening." The extent of "after-ripening" is determined by the "first-ripening" and the resulting lattice form. In "after-ripening" the forces holding the adsorbed bromide ions are overcome by the adsorption of the gelatin, which can be assisted by addition of certain salts, *e.g.*, nitrates, by heating, or by dehydrating with alcohol. "After-ripening" is accelerated catalytically by hydroxyl ions, and ripening-agents act by forming hydroxyl ions by hydrolysis or dissociation, or else by reacting chemically with bromine. The bromide ions removed during ripening are taken up by the gelatin, and the degree of "first" and "after-ripening" depends on the gelatin used. Chemical fog is due to excessive displacement of adsorbed bromide, and is identical in nature with the latent image. With emulsions prepared with excess of silver instead of excess of bromide, silver ions are adsorbed to the lattice bromine ions and increase their deformation, thus giving enhanced sensitivity. On "after-ripening" or keeping, these emulsions fog, owing to reduction by the developer of the silver ions removed from the lattice. W. C.

**[Photographic] Ripening Process. IV.** LÜPPO-CRAMER (*Z. wiss. Phot.*, 1925, **23**, 227—232; cf. this vol., ii, 574).—The sensitiveness of a Lippmann emulsion is enormously increased by digestion at 60°, and the ripened emulsion can be markedly desensitised by treatment with chromic acid, although the minimum sensitiveness thus attainable is higher than that of the unripened emulsion. With coarser-grained emulsions, the sensitiveness can be reduced to that of the original emulsion. The difference is due to the light absorption of the ripened Lippmann emulsion being much higher than that of the unripened emulsion, whereas with coarser grained emulsions, the absorption is not so different in the

two cases. Conclusions of Weigert and Schöller (A., 1922, ii, 10), that in a silver chloride print-out emulsion not the silver chloride but adsorbed silver is the sensitive material, are criticised. Their experimental results are in accordance with the usual view of chemical sensitisation by silver salts etc. The preparation and properties of "photometer-papers" are considered. The behaviour of emulsions to printing-out is in no way parallel with their ordinary photographic sensitiveness. W. C.

**History and Theory of the Latent Image. III.** LÜPPO-CRAMER (*Z. wiss. Phot.*, 1925, 23, 216—226).—Evidence for the mechanical and chemical views of the action of light on the photographic plate is discussed, prominence being given to older observations with iodised silver, and to physical development and "development by light." (Cf. this vol., ii, 575.) W. C.

**Effect of Light on the Interaction of Water and Sodium and Potassium Amalgams.** S. S. BHATNAGAR, M. PRASAD, and D. M. MUKERJI (*J. Indian Chem. Soc.*, 1925, 1, 263—272).—The effect of light on the rate of evolution of hydrogen when sodium or potassium amalgam reacts with water is measured. The amalgams react in the dark, but the rate of evolution of the hydrogen is increased by the action of light from a carbon arc ( $\lambda=366-525\mu\mu$ ). The increase is greater the greater is the percentage of metal in the amalgam up to a certain point, after which the difference decreases with an increase in the concentration of the sodium or potassium. J. W. B.

**Effect of Light on the Thermoelectric Power of Selenium.** R. M. HOLMES (*Physical Rev.*, 1925, [ii], 25, 826—834).—Illumination causes a decrease of about 5% in the thermoelectric power of selenium, corresponding with a five-fold increase in conductivity. The effect may be explained by assuming that a decrease in the potential energies of electrons in the interatomic space causes an increase in the mean free path of conducting electrons. A large thermal *E.M.F.* is developed in a circuit formed entirely of selenium homogeneous in every respect except that a region of temperature gradient of one sign is illuminated whilst that of the other sign is in darkness; the illuminated selenium is positive at the cold junction. A. A. E.

**Photo-activation of Chlorine.** W. TAYLOR (*Phil. Mag.*, 1925, [vi], 49, 1165—1168).—On the assumption that the photosynthesis of hydrogen chloride measures the activation of chlorine, the reaction velocity has been determined for different spectral ranges. If  $h\nu = \delta E = E_m - E_n$ , the incident light, if it is active, must furnish  $\delta E$ . If the final state  $E_m$  is not quantified,  $\nu$  will be a threshold frequency. The activating region of the spectrum actually corresponds with that of the general absorption of chlorine itself, *i.e.* the threshold frequency is about 4900 Å., and it would seem as if the vibratory motions are not quantified. The Ribaud fine structure bands do not correspond with the activating region. R. A. M.

**Mechanism of Photosynthesis of Hydrogen Chloride in the Visible Spectrum.** J. CATHALA (*Compt. rend.*, 1925, **181**, 33—36).—The reaction schemes as proposed by Coehn and others (A., 1923, ii, 206; this vol., ii, 142) are not in agreement with experiment. A more probable mechanism is suggested. Collision is only followed by reaction when the encounters occur within the active zones surrounding the molecules of water vapour. The catalytic activity of water vapour is directly proportional to the intensity of illumination. The following reaction scheme is suggested: (i)  $\text{Cl}_2 + h\nu = 2\text{Cl}$ ; (ii)  $\text{Cl} + \text{Cl}_2 = \text{Cl}_3$ ; (iii)  $\text{Cl} + \text{O}_2 = \text{ClO}_2$ ; (iv)  $\text{Cl}_3 + \text{O}_2 = \text{ClO}_2 + \text{Cl}_2$ ; (v)  $\text{Cl}_3 + \text{H}_2 = 2\text{HCl} + \text{Cl}$ . The expression representing the rate of formation of hydrogen chloride from considerations of the kinetics of the above reaction scheme is:  $d[\text{HCl}]/dt = K' \cdot I^{3/2} [\text{Cl}_2]^{3/2} \cdot [\text{H}_2]/[\text{O}_2][K_1[\text{Cl}_2] + K_2I[\text{H}_2] + K_3[\text{O}_2]]$ , where  $K'$ ,  $K_1$ ,  $K_2$ ,  $K_3$  are constants and  $I$  the intensity of the illumination. The above formula is in excellent agreement with the experimental data of (Mrs.) Chapman (T., 1923, **123**, 3062). The mechanism suggested is further supported by the work of Baly and Barker (T., 1921, **119**, 653). J. S. C.

**Action of Light on Dyes Applied to Cotton Fabrics. Summary of the Literature.** P. W. CUNLIFFE (*J. Text. Inst.*, 1924, **15**, T, 173—194).—A review under the headings: comparative tests of fading; absolute measurements; sources of light; influence of the atmosphere; influence of the colour of the light; relation between active rays and absorption spectra of the dyes; influence of temperature; influence of added substances and the protection of dyed fabrics from fading; theories of fading action; and the relation between chemical constitution and fading. J. C. W.

**Xenon Hydrate.** DE FORCRAND (*Compt. rend.*, 1925, **181**, 15—17).—A crystalline hydrate containing 6 or 7 molecules of water is readily formed on introducing xenon and water into the tube of a Cailletet apparatus. The dissociation pressures of the hydrate have been measured over the temperature range 1.4—23.5°, 24° being the critical temperature of decomposition. The heat of formation from liquid water is 18.266 cal. The stabilities of the hydrates of the inert gases increase with increasing molecular weight of the gas, the dissociation pressures expressed in atms. at 0° for the respective hydrates being: xenon 1.15, krypton 14.5, argon 98.5. Neon hydrate is not obtained even under pressures as high as 260 atm. at 0°. Hydrate formation is the only chemical process in which the inert gases participate. J. S. C.

**Artificial Magnesium Silicate.** A. DAMIENS (*Compt. rend.*, 1925, **180**, 1843—1845).—The magnesium silicate obtained by the reaction of magnesium sulphate and alkali silicates is always contaminated with alkali; this occurs to the extent of 1% even when excess of magnesium salt is employed. The product is partly colloidal and is especially so when the silicate solution is in excess. When the silicate used is  $\text{Na}_2\text{Si}_2\text{O}_5$ , the larger particles of precipitate

correspond with the formula  $(\text{Na}_2\text{Mg})\text{Si}_2\text{O}_5$ , and the smaller colloidal particles after prolonged fractionation vary from  $1.48 (\text{Na}_2\text{Mg})\text{O}, 2\text{SiO}_2$  to  $(\text{Na}_2\text{Mg})\text{Si}_2\text{O}_5$  or  $(\text{Na}_2\text{Mg})\text{SiO}_3$ . The last formula (mixed metasilicate) corresponds with the maximum percentage of sodium obtained in the experiments. At the moment of precipitation the larger particles of magnesium silicate absorb sodium silicate to form the salt  $(\text{Na}_2\text{Mg})\text{Si}_2\text{O}_5$ , whereas the smaller, negatively charged particles adsorb sodium ions. The limiting composition  $(\text{Na}_2\text{Mg})\text{SiO}_3$  is reached by the finest particles. If instead of  $\text{Na}_2\text{Si}_2\text{O}_5$  the salt  $\text{Na}_2\text{Si}_3\text{O}_7$  is substituted, the larger particles correspond with  $(\text{Na}_2\text{Mg})\text{Si}_3\text{O}_7$  and if  $\text{Na}_2\text{SiO}_3$  is used the large grains consist of  $(\text{Na}_2\text{Mg})\text{SiO}_3$ . The potassium silicates behave similarly.

R. A. M.

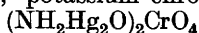
**Thermal Behaviour of Hydrated Barium Aluminate.** G. MALQUORI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 445—448).—Barium aluminate pentahydrate,  $\text{BaAl}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ , prepared by boiling precipitated alumina with saturated barium hydroxide solution in absence of carbon dioxide, loses 3 mols. of water at  $190^\circ$ , becomes anhydrous at  $310^\circ$ , and exhibits two arrests in the heating curve, at  $725^\circ$  and  $1040^\circ$ , respectively, corresponding with two stages in the decomposition of the compound.

T. H. P.

**Mercury-Ammonia Compounds.** P. RAY and P. C. BANDO-PADHYAY (*J. Indian Chem. Soc.*, 1925, 1, 235—246).—By the action of ammonia and ammonium carbonate on mercuric chloro-iodide and of potassium thiocyanate, chromate, and arsenate on infusible white precipitate, several new mercury-ammonia compounds and derivatives of Millon's base are prepared. The addition of a solution of mercuric chloro-iodide (obtained by saturating a solution of mercuric chloride with mercuric iodide) dropwise to a concentrated ammonia solution yields the compound



orange-yellow, whilst by the addition of dilute ammonia to an excess of the mercuric chloro-iodide solution the compound  $4\text{NH}_2\text{HgCl}, \text{NHg}_2\text{Cl}, 2\text{HgCl}_2$ , white, is formed. Addition of an excess of ammonium carbonate solution to mercuric chloro-iodide solution yields the compound  $\text{NHg}_2\text{Cl}, 2\text{HgCl}_2, \text{NH}_3$ ; whilst the reverse procedure yields the compound  $\text{NH}_2\text{HgCl}, \text{HgCl}_2, 2\text{NH}_3$ . Addition of the corresponding mercuric bromo-iodide to ammonia yields mixtures of variable compositions, the reverse process yielding dimercurammonium bromide, which is also obtained by the action of ammonium carbonate. The action of potassium salts on infusible white precipitate (cf. Balestra, A., 1893, ii, 278) proceeds through the formation of a stable intermediate compound to form derivatives of Millon's base, potassium thiocyanate yielding the compound  $\text{NHg}_2\text{SCN}$ ; potassium chromate yields



(cf. Hensgen, A., 1887, 218); potassium bromide and iodide yield the dimercurammonium bromide and iodide, respectively. Potassium arsenite reduces an infusible white precipitate, but the compound  $(\text{NH}_2\text{Hg}_2\text{O})_3\text{AsO}_4 \cdot 3\text{H}_2\text{O}$ , which may be regarded as the

arsenate of Millon's base, is obtained when freshly-prepared mercuric arsenate is digested with ammonia. Nitrogen trioxide passed into a cold aqueous suspension of infusible white precipitate forms a double salt of mercuric chloride and ammonium nitrite which could not be isolated in the pure state. Zinc and cadmium ammonium chlorides react with infusible white precipitate to produce fusible white precipitate. J. W. B.

**Chemical Compounds of Salts in the Electric Arc.** T. PECZALSKI and G. MOKRZYCKI (*Compt. rend.*, 1925, **180**, 1829—1831).—Two carbon poles are maintained at a fixed distance apart and connected to a constant voltage supply. One pole tapers to a point and in the crater of the other mixtures of definite composition are placed. The fall of potential across the arc is measured. Using known mixtures of lime and alumina, the observed voltage is plotted against the percentage of either constituent. On the same graph, the m. p. curve of mixtures is plotted. On both curves two minima are observed corresponding with the compounds  $\text{Al}_2\text{O}_3, \text{CaO}$  and  $3\text{Al}_2\text{O}_3, 5\text{CaO}$ . Further results indicate the existence of a compound  $3\text{KCl}, \text{NaCl}$  which would only be formed at the temperature of the arc. The higher is the m. p. or b. p. of the salt in the crater, the less is the energy needed to maintain the arc. Thus, as in thermal analysis, whenever maxima or minima occur in the potential-composition curves, these correspond with mixtures of which the m. p. or b. p. are sharply different from those of neighbouring mixtures, *i.e.*, the discontinuities may correspond with definite compounds. R. A. M.

**Hydrolysis of Mica.** P. A. ZEMIATTSCHENSKI (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1925, **2**, 484—485).—When heated with water, muscovite undergoes energetic hydrolysis and gradually approaches kaolinite in composition. The extent to which this change takes place depends on the duration of the action and on the fineness of the mica; the change may be accelerated and rendered complete by raising the temperature. Muscovite is decomposed more readily than kaolinite when treated with 10% hydrochloric acid solution. Slight hydrolytic decomposition of muscovite doubtless plays a large part in the process of the decay of mica. T. H. P.

**Stannic Iodide Complexes.** V. AUGER and T. KARANTASSIS (*Compt. rend.*, 1925, **180**, 1845—1847).—Stannic iodide is gradually hydrolysed in dilute hydriodic acid solution and more readily in aqueous solution. Addition of sodium, potassium or ammonium iodide to these solutions does not modify their properties, but addition of rubidium or caesium iodides or of the hydriodides of strong bases leads to the formation of stable complex salts, of which the following  $(\text{X}_2\text{SnI}_6)$  are described: *rubidium stannic iodide*, *caesium stannic iodide*, *tetramethylarsonium stannic iodide*. Mixed crystals of the composition  $\text{K}_2[\text{SnBr}_{5.35}\text{I}_{0.25}]$  and  $\text{NH}_4[\text{SnBr}_{5.35}\text{I}_{0.65}]$ , respectively, are obtained on adding potassium or ammonium iodide to concentrated solutions of stannic bromide. L. F. H.

**So-called Lead Suboxide.** A. E. VAN ARKEL (*Rec. trav. chim.*, 1925, **44**, 652—654).—An examination of the X-ray spectrum of lead suboxide, obtained by carefully heating lead oxalate, shows this to be a mixture of tetragonal lead oxide and the metal. The dimensions of the unit cell of the tetragonal lead oxide existing in this mixture are : length of base, 3.87 Å., and height, 5.02 Å.

L. L. B.

**Imino Group.** E. OLIVERI-MANDALÀ (*Gazzetta*, 1925, **55**, 271—279).—Consideration of Schmidt's results (A., 1924, i, 721) in the light of the work of the author since 1913 shows that, in Schmidt's reactions, not addition of the imino radical resulting from the decomposition of the azoimide by the action of the sulphuric acid, but rather a preliminary addition of the azoimide to the carbonyl group of the aldehyde or ketone, with initial formation of the corresponding azides, must be assumed. These azides are then readily able to undergo further changes to yield the compounds obtained by Schmidt. That such addition of azoimide can occur may be proved by the fact that anhydrous solutions of azoimide in a ketone or an aldehyde often form crystalline deposits, presumably of the additive compounds.

T. H. P.

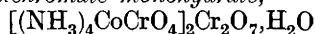
**Complex Salts of Antimony Trichloride.** S. MIYAKE (*Mem. Coll. Eng. Kyushu*, 1925, **3**, 187—193).—Equilibria in the system, potassium chloride : antimony trichloride : 10.55% aqueous hydrochloric acid solution, have been determined at 25°. The solubilities of potassium chloride in water and 10.55% hydrochloric acid solution are 26.27% and 12.75%, respectively, and of antimony trichloride 90.90% and 90.07%. Two complex salts,  $2\text{KCl}, \text{SbCl}_3$  and  $7\text{KCl}, 3\text{SbCl}_3$ , have been shown to exist, but no mixed crystals such as found by Jordis (A., 1903, ii, 603).

M. S. B.

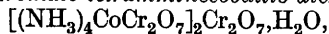
**Selenic Acid and the Selenates.** V. LENHER and E. J. WECHTER (*J. Amer. Chem. Soc.*, 1925, **47**, 1522—1523).—The selenites of potassium, sodium, lithium, rubidium, caesium, barium, and strontium are converted into selenates on roasting in the air. Selenates are also formed when the corresponding carbonates are roasted with selenium dioxide or selenium. Solutions of selenic acid may be obtained by treatment of aqueous suspensions of barium selenate or solutions of potassium selenate with sulphuric or perchloric acids, respectively. Selenic acid of a high degree of purity is obtained by the latter method.

J. S. C.

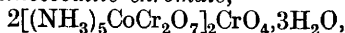
**Cobalti-ammine Chromates and Chromato-cobalti-ammines.** P. RAY and P. V. SARKAR (*J. Indian Chem. Soc.*, 1925, **1**, 289—296; cf. Briggs, T., 1919, **115**, 67).—The action of chromic acid on carbonato-tetrammine- and carbonato-pentammine-cobaltic salts is investigated. The following new co-ordination compounds are prepared and evidence for their constitution is given : *chromato-tetramminecobaltic dichromate monohydrate*,



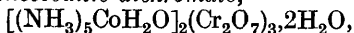
(anhydrous compound obtained by drying over sulphuric acid), by the action of the carbonato-tetramminecobaltic nitrate on chromic acid: *dichromato-tetramminecobaltic dichromate*,



is obtained when a larger proportion of chromic acid is employed; *dichromato-pentamminecobaltic chromate*,



and *aquopentamminecobaltic dichromate*,



are obtained under corresponding conditions from the carbonato-pentammine salt. By the action of ammonium dichromate and ammonia on freshly-precipitated cobalt hydroxide *chromato-pentamminecobaltic chromate*,  $[(\text{NH}_3)_5\text{CoCrO}_4]_2\text{CrO}_4, 2\text{H}_2\text{O}$ , is obtained which on recrystallisation from dilute acetic acid yields the *aquo-pentamminechromate dichromate*,  $[(\text{NH}_3)_5\text{CoH}_2\text{O}]_2\text{CrO}_4(\text{Cr}_2\text{O}_7)_2, \text{H}_2\text{O}$ .

J. W. B.

**Reaction Products of Ruthenium Tetroxide and Hydrochloric Acid.** S. AOYAMA (*Sci. Rep. Tōhoku Imp. Univ.*, 1925, 14, 1–24).—Ruthenium tetroxide reacts with dry hydrogen chloride to form very hygroscopic, reddish-brown needles of *tetrachlorodioxyruthenic acid*,  $\text{H}_2\text{RuO}_2\text{Cl}_4, 3\text{H}_2\text{O}$ . This compound is very soluble in water and alcohol; the dilute aqueous solution rapidly hydrolyses giving a black colloidal precipitate. With ammonium chloride a black, crystalline precipitate of a mixture of ammonium hexachlororuthenate and pentachlororuthenite is formed and the mother-liquor contains ruthenium tetroxide. When heated with an excess of ammonia the solution deposits violet crystals of a new *ruthenium ammine*,  $\text{Ru}(\text{NH}_3)_3(\text{H}_2\text{O})_2\text{Cl}_2$ . Concentrated hydrochloric acid and chlorine convert tetrachlorodioxyruthenic acid into hexachlororuthenic acid which yields a brown, crystalline ammonium salt,  $(\text{NH}_4)_2\text{RuCl}_6, 0.5\text{H}_2\text{O}$ , readily soluble in water, but insoluble in concentrated hydrochloric acid. *Ammonium hexachlororuthenate* solutions slowly give a violet-black precipitate with hydrogen sulphide, precipitation of the ruthenium being complete in 24 hrs.; no blue intermediate compound is formed in this reaction. *Potassium hexachlororuthenate*,  $\text{K}_2\text{RuCl}_6$ , obtained in a similar way to the ammonium salt, crystallises in dark brown octahedra, readily soluble in water, giving a yellow solution which yields a black precipitate of ruthenium tetrahydroxide when boiled with sodium hydroxide. When potassium hexachlororuthenate is heated at  $540^\circ$  in a current of hydrogen chloride, a new *potassium pentachlororuthenite* ( $\text{K}_2\text{RuCl}_5$ ) is obtained which differs in many properties from those described by Howe (A., 1904, ii, 490) and earlier workers. Its aqueous solution is much paler in colour and more stable than those of the other two forms, and gives a deep blue colour with sodium hydroxide which changes, on keeping, to a greenish-yellow, and finally a black precipitate is deposited. With hydrogen sulphide, the solution slowly becomes bright green, then azure-blue, and finally colourless. When tetrachlorodioxyruthenic acid is heated at  $400^\circ$  in a stream of oxygen,



ruthenium dioxide is obtained as a lustrous, black mass resembling graphite.

A. R. P.

**Preparation of Conductivity Water.** I. BENCOWITZ and H. T. HOTCHKISS, jun. (*J. Physical Chem.*, 1925, **29**, 705—712).—A still has been designed which supplies, practically continuously, water of a conductivity of  $0.06-0.07 \times 10^{-6}$  ohm<sup>-1</sup>. Twenty litres of tap water are digested near the b. p. with alkaline permanganate and distilled into a second boiler where carbon dioxide is removed by passing a current of purified air through the hot water. This water is in turn distilled and the vapour enters a preliminary air condenser and steam trap, where about 20% is collected; 80% of the steam passing this is condensed in a warm water condenser and constitutes the conductivity water. The still is constructed of copper and block tin and is completely water-sealed against influx of laboratory air.

A. G.

**Preparation of Selenic Acid and of certain Selenates.** V. LENHER and C. H. KAO (*J. Amer. Chem. Soc.*, 1925, **47**, 1521—1522).—The halogen acids formed in the preparation of selenic acid by oxidation of selenious acid by chlorine or bromine are best removed by addition of silver carbonate in quantity slightly in excess of that necessary to precipitate the halogen. The small amount of soluble silver selenate is decomposed by hydrogen sulphide. The acid solution can be concentrated on the water-bath to about 80% and to higher concentrations under diminished pressure. From the mixed acid solution obtained by chlorination of selenious acid, selenates may be prepared by neutralisation with metallic carbonates. The sparingly soluble selenates of lead, barium, strontium, and calcium are obtained as precipitates. In the case of soluble selenates, metallic chlorides are removed by treatment with alcohol or acetone, the residue being redissolved in water and reprecipitated by either of these solvents.

J. S. C.

**Molybdenum Pentoxide.** W. WARDLAW and F. H. NICHOLLS (*J. Chem. Soc.*, 1925, **127**, 1487).—Molybdenum pentoxide can be prepared by heating the oxysulphate (A., 1924, ii, 766) or the oxyoxalate (J., 1925, **127**, 1311) of tervalent molybdenum in a current of nitrogen:  $\text{Mo}_2\text{O}(\text{SO}_4)_2 = \text{Mo}_2\text{O}_5 + 2\text{SO}_2$ ;  $\text{Mo}_2\text{O}(\text{C}_2\text{O}_4)_2 = \text{Mo}_2\text{O}_5 + 4\text{CO}$ .

W. T.

**Hydrogen Electrode.** F. VLÈS and C. VELLINGER (*Bull. Soc. chim.*, 1925, [iv], **37**, 771—772).—The apparatus, which is designed for  $p_{\text{H}}$  measurements, consists of two vessels connected by a three-way cock with a lateral discharge tube. The liquid under test (about 3 c.c.) is placed in the upper vessel, which is slightly conical in form and carries a thermometer, in addition to the platinum spiral forming the hydrogen electrode. The level of the liquid is adjusted by opening the cock to the discharge tube so that the platinum spiral is immersed about 2—3 mm. below the surface of the liquid, whilst on the four or five spirals remaining above the liquid a current of hydrogen impinges from a side tube, the gas escaping by a second side tube in the upper part of the vessel. The

lower vessel serves as the calomel electrode and is connected by a side tube with a reservoir containing saturated potassium chloride solution, a second side tube admitting the wire contact with the mercury. R. B.

**Apparatus to Measure the Coefficient of Deviation from Boyle's Law. Determination for Acetylene.** J. T. HOWARTH and F. P. BURT (*Trans. Faraday Soc.*, 1925, **20**, 544—549).—Improvements in the design of the apparatus used by Whytlaw-Gray and Burt (T., 1909, **95**, 1659) for measuring the compressibility of gases are described. The compressibility at 0° of acetylene after very careful purification has been measured for pressures from 105.42 mm. to 757.34 mm. of mercury. The relation between  $p_v$  and  $p$  over the experimental pressure range is linear and the coefficient of deviation from Boyle's law ( $(d(pv)/dp) \cdot 1/p_0v_0$ ) between 0 and 1 atm. is -0.00884. Experiments indicate that the variation of the sorption of acetylene on the glass walls is negligible. F. G. S.

**Spiral Springs of Quartz.** H. G. SMITH (*Nature*, 1925, **116**, 14—15).—A description of the method of making spiral springs of silica for use in the measurement of sorption. A. A. E.

**Substitute for a Liquid Air Trap for Mercury Vapour in Vacuum Systems.** A. L. HUGHES and F. E. POINDEXTER (*Nature*, 1925, **115**, 979).—About 1 g. of sodium or potassium is placed in a trap between the diffusion pump and the apparatus to be exhausted and, after evacuation, is distilled on to the walls. The method is as efficient as that employing liquid air, the lowest pressure obtained,  $5 \times 10^{-9}$  mm., being probably due to insufficient heat treatment of the ionisation gauge and connecting tubes. A. A. E.

**Simple Circulation Pump for Gases.** A. W. C. MENZIES, E. M. COLLINS, and P. L. TYSON (*Science*, 1925, **61**, 288).—Mercury droplets are carried to an upper reservoir by means of an air blast; in the fall-tube (2.5 mm. bore), the droplets paddle the gas round a closed system the walls of which are of glass and mercury only. The apparatus requires about 7 c.c. of mercury, and will operate against back pressures corresponding with a head of 30 cm. of water at a rate of 2 litres per hr.; if the back pressure or resistance is negligible, 8 litres per hr. may be circulated. A. A. E.

**Hydrogen Liquefying Cycle and Cryostat for the Maintenance of Low Temperatures.** W. M. LATIMER, R. M. BUFFINGTON, and H. D. HOENSHEL (*J. Amer. Chem. Soc.*, 1925, **47**, 1571—1576).—A combined hydrogen liquefier and cryostat, suitable for use in the determination of physical constants at very low temperatures, is described. Electrolytic hydrogen may be freed from oxygen by passing first over concentrated sulphuric acid to remove alkali spray and then through a tube containing a nickel catalyst. A convenient catalyst is obtained by soaking small pieces of porous brick in nickel nitrate, heating to convert into oxide and later reducing to nickel in the catalyst tube. By this means the oxygen content may be reduced to 0.01%. Small amounts of oxygen may be determined by bubbling a known volume of gas through an

alkaline solution of pyrocatechol and ferrous sulphate, the resulting red tint being compared with those obtained from known oxygen-hydrogen mixtures. Permanent standards for comparison may be prepared from known concentrations of ferric salt. J. S. C.

**Ionisation and Catalysis Experiments suitable for Lecture Demonstrations.** I. M. KOLTHOFF (*Chem. Weekblad*, 1925, **22**, 356—357).—The substance most suitable to illustrate association of ions of a salt in solution, and consequent precipitation, on addition of another solution containing either the cation or the anion, is silver salicylate. A 0.01*N*-solution of mercuric chloride in 0.1*N*-mercuric nitrate gives no precipitate with silver nitrate unless a large excess of the latter is added. Many well-known experiments suitable for illustration of catalytic reactions are mentioned.

S. I. L.

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## Mineralogical Chemistry.

**Chemical Classification of the Mica Group. I. Acid Micas.** A. F. HALLIMOND (*Min. Mag.*, 1925, 20, 305—318).—Analyses selected from the literature are calculated to molecular proportions with  $(\text{Si,Ti})\text{O}_2=600$ . In the soda and potash micas  $\text{K}_2\text{O}+\text{Na}_2\text{O}$  is then near 100. The molecular proportions of  $\text{R}_2\text{O}_3$  plotted against RO give points along a line from

$\text{K}_2\text{O}, 3\text{Al}_2\text{O}_3, 6\text{SiO}_2, 2\text{H}_2\text{O}$   
(muscovite) to  $\text{K}_2\text{O}, 2\text{Al}_2\text{O}_3, \text{RO}, 6\text{SiO}_2, 2\text{H}_2\text{O}$  (phengite), showing a replacement of  $\text{R}_2\text{O}_3$  by RO, as previously suggested for glauconite (A., 1922, ii, 861). In the lithia micas  $\text{SiO}_2=600$ ,  $\text{K}_2\text{O}=100$ ,  $\text{Li}_2\text{O}=100$ , and  $\text{R}_2\text{O}_3$  plotted against RO gives two series :  $\text{K}_2\text{O}, \text{Li}_2\text{O}, 2\text{Al}_2\text{O}_3, 6\text{SiO}_2, 2\text{H}_2\text{O}$  (lepidolite) to

$\text{K}_2\text{O}, \text{Li}_2\text{O}, \text{Al}_2\text{O}_3, \text{RO}, 6\text{SiO}_2, 2\text{H}_2\text{O}$   
(cryophyllite), and lepidolite to  $\text{K}_2\text{O}, \text{Li}_2\text{O}, 2\text{Al}_2\text{O}_3, 3\text{RO}, 6\text{SiO}_2, 2\text{H}_2\text{O}$  (protolithionite). Abbreviated graphical formulæ are given for these.  
L. J. S.

**Tourmalinisation in the Dartmoor Granite.** A. BRAMMALL and H. F. HARWOOD (*Min. Mag.*, 1925, 20, 319—330).—The various modes of occurrence of tourmaline in the Dartmoor granite mass are described (A., 1923, ii, 777). Little of it seems to be a primary constituent of the rock, and it has been largely developed at the expense of the felspar and biotite by pneumatolytic processes connected with the later more acid types of intrusion. Dark nodules consisting of an intimate intergrowth of tourmaline and quartz represent basic clots in the magma.  
L. J. S.

**Potash-oligoclase from Mt. Erebus, Antarctic, and Anorthoclase from Mt. Kenya, East Africa.** E. D. MOUNTAIN (*Min. Mag.*, 1925, 20, 331—345).—Loose crystals of felspar, previously referred to anorthoclase, from the crater of Mt. Erebus, are of two types with respect to their crystal habit. They have  $d\ 2.620$ , refractive indices  $\alpha\ 1.536$ ,  $\beta\ 1.539$ ,  $\gamma\ 1.541$ , and gave analyses

I and II, corresponding with  $\text{Or}_{18}\text{Ab}_{64}\text{An}_{18}$  and  $\text{Or}_{19}\text{Ab}_{64}\text{An}_{17}$ , respectively. The felspar crystals from Mt. Kenya also occur in tuffs in the crater; these have  $d$  2.602, refractive indices  $\alpha$  1.526,  $\beta$  1.530,  $\gamma$  1.532, and gave analysis III, corresponding with  $\text{Or}_{27}\text{Ab}_{63}\text{An}_{10}$ .

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{CaO}$ .	$\text{MgO}$ .
I. ....	62.79	22.12	0.36	0.41	3.76	—
II. ....	62.49	21.86	0.30	1.31	3.74	0.16
III. ....	64.33	20.94	0.20	0.58	2.01	—

	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O} + 110^\circ$ .	$\text{H}_2\text{O} - 110^\circ$ .	Total.
I. ....	7.35	2.98	0.19	0.07	100.03
II. ....	7.20	3.26	0.04	—	100.36
III. ....	7.22	4.71	0.27	0.10	100.36

These and certain other felspar analyses taken from the literature when plotted on a triangular diagram with Or, Ab, An at the three corners fall along a line between  $\text{Ab}_{65}\text{Or}_{35}$  and  $\text{Ab}_{65}\text{An}_{35}$ . The physical constants (cleavage-angle, extinction-angles, refractive index, optic axial angle, and density) are plotted against the composition for these felspars. Those towards the  $\text{Ab}_{65}\text{An}_{35}$  end are called potash-oligoclase, whilst those towards the  $\text{Ab}_{65}\text{Or}_{35}$  end are called anorthoclase. The nomenclature of the felspars as representing a three-component system is discussed, and the bearing of this on petrographical nomenclature is pointed out. L. J. S.

**Chalk and Flint.** G. LINCK and W. BECKER (*Chemie der Erde*, 1925, 2, 1—14).—An outline is given of the various views on the formation of flint in chalk. Experiments were made with solutions of colloidal silica (containing 0.5—0.8%  $\text{SiO}_2$ ) in the presence of precipitated calcium carbonate (vaterite and calcite). The amount of silica adsorbed is greater with smaller sizes of grain of the calcium carbonate. Precipitates obtained from solutions of calcium hydrogen carbonate in the presence of soluble silica contain up to 17%  $\text{SiO}_2$ , the amount depending on the concentration of the solutions. Treatment of these precipitates, after heating at 50—200°, with dilute solutions of sodium chloride, sodium hydroxide, ammonia, etc., causes a portion of the adsorbed silica to pass into solution again. It can be again coagulated by the action of magnesium carbonate or of calcium carbonate solution in the presence of sodium chloride. The conclusion is therefore reached that in the formation of chalk the silica was originally distributed throughout the material, as a pellicle around the minute grains of calcium carbonate. The re-dissolution of the silica in the presence of alkali and ammonia from organic remains would leave the calcium carbonate with a loose open texture. Migration and coagulation in cavities and crevices would give rise to nodules, bands, and veins of flint. Analyses of chalk from Rügen show 0.81—1.54%  $\text{SiO}_2$ , the amount varying with the distance from the bands of flint.

L. J. S.

**Chemical Alteration of Granite beneath Peat.** E. BLANCK and A. RIESER (*Chemie der Erde*, 1925, 2, 15—48).—A detailed review and discussion is given of the literature on the formation of

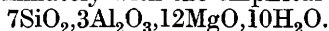
clay or kaolin by weathering processes, more particularly in association with peat and lignite deposits. Analyses are compared of fresh granite, from the Harz Mts., and of the weathered rock taken from below a layer of peat and from the surface. There is no evidence of the formation of kaolin under these conditions. Sulphuric anhydride was found in the weathered products, in peat, sphagnum-moss, and moor-waters; and it is concluded that this has some action in the weathering processes. L. J. S.

**Weathering of Sandstone by Circulating Solutions.** F. KLANDER (*Chemie der Erde*, 1925, 2, 49—82).—The peculiar forms of weathering shown by the sandstones of Saxon Switzerland and the Palatinate are attributed to the action of circulating solutions containing humus compounds and sulphates derived from the surface vegetation. Analyses are given of the portions extracted by water from the rocks and from the soils derived from them. L. J. S.

**Chemical Constitution of the Gehlenite-Melilite Group.** B. GOSSNER (*Chemie der Erde*, 1925, 2, 103—113).—The isomorphous mixing of such complex molecules as suggested by Buddington (A., 1922, ii, 155) is regarded as improbable; and the author traces a connection between the minerals of the gehlenite-melilite group and the monoclinic ("pseudo-tetragonal") pyroxenes. They are regarded as double compounds  $\text{CaO} + \text{pyroxene}$ , of the form  $\text{CaO}[\text{SiO}_3\text{Ca}, \text{SiO}_3\text{Mg}]$ , where  $\text{SiO}_3\text{Mg}$  is replaceable by  $\text{Al}_2\text{O}_3$ , and  $\text{Si}_2\text{O}_6\text{MgCa}$  by  $\text{Si}_2\text{O}_6\text{AlNa}$ . Gehlenite is written  $\text{CaO}[\text{SiO}_3\text{Ca}, \text{Al}_2\text{O}_3]$  and melilite as  $2\text{CaO}[\text{Si}_2\text{O}_6\text{MgCa}, \text{Si}_2\text{O}_6\text{AlNa}]$ . Åkermanite approaches  $\text{CaO}[\text{SiO}_3\text{Ca}, \text{SiO}_3\text{Mg}]$ . L. J. S.

**Relations between Hydrocarbons and Carbonates in Silex and Phtanites.** J. DE LAPPARENT (*Compt. rend.*, 1925, 180, 1858—1859).—In certain siliceous carbonates, the carbonate appears to have been destroyed, leaving a liquid inclusion probably of hydrocarbons. Small rhombohedra of carbonates are often found. The liquid inclusion has a polyhedral contour made up of faces of crystals. R. A. M.

**White Chlorite from Madagascar.** J. ORCEL (*Compt. rend.*, 1925, 180, 1672—1674).—A description of a white chlorite found in the form of very large crystals in Madagascar. The composition corresponds approximately with the empirical formula



The crystals are very good electrical insulators,  $d\ 2.735$ ,  $n_D = 1.5904$ ;  $n_{Dm} = 1.5754$  (calc.);  $n_{Dp} = 1.5749$ . W. H. R.

### **Analytical Chemistry.**

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**New Type of Nephelometer.** R. KINGSLAKE (*Trans. Opt. Soc.*, 1924—25, 26, 53—62).—Concentrated light from a small source is reflected upwards into two vertical glass tubes, one long

one containing a standard and the other, a short one, the solution to be examined. The incident light passes vertically upwards, the scattered light being observed from the front; a Nutting prism is employed to bring the two fields into optical contact. The long tube containing the standard is moved vertically up or down until the fields balance. As standards, known equivalent amounts of silver nitrate and sodium chloride in pure water, boiled and filtered sterilised soap solutions, and silica gels are suggested.

S. I. L.

### **New Method of Quantitative Analysis by Means of X-Rays.**

E. DELAUNEY (*Compt. rend.*, 1925, **180**, 1658—1661).—If a monochromatic beam of X-rays is passed through an aqueous solution contained in a cell of standard size, the absorption may be represented by a relation of the type  $I = I_0 e^{-(a_1 m_1 + a_2 m_2 + \dots)}$ , where  $I$  and  $I_0$  refer to the solution and to pure water, respectively,  $m_1, m_2 \dots$  are the weights of the different elements dissolved in unit volume of the solution, and  $a_1, a_2 \dots$  are characteristic constants for the elements concerned for the particular wave-length used. Hence if  $a_1, a_2 \dots$  are previously determined for various wave-lengths, measurements of X-ray absorption will enable the concentrations of the different elements in a solution to be determined. In general, if  $n$  elements are present,  $n$  different wave-lengths must be used so as to make the number of equations equal to the number of unknown quantities, but in practice the relatively small absorption of some elements enables these to be neglected and may simplify the problem, whilst in cases of single salts the molecular absorption may be substituted for that of the different elements. When tested with solution of barium and strontium chlorides, and of alkali halides, the relative error found varied from 10% to <1%.

W. H.-R.

### **Modified Electrometric Method for the Determination of Hydrogen-ion Concentration.**

S. GLASSTONE (*Analyst*, 1925, **50**, 327—330).—A small platinised platinum cathode placed in the solution of which the hydrogen-ion concentration is required was found to have the same potential as that of an ordinary hydrogen electrode in the same solution, if a small polarising current is applied until the evolution of bubbles just commences. The hydrogen-ion concentration may then be determined from the equation

$$e = RT/F \log_e [H^+],$$

that is,  $e = 0.058 \log_{10} [H^+]$  at 18°. By this method the apparatus necessary for the supply of pure hydrogen is eliminated and equilibrium may be rapidly attained, and with alkaline solutions the superiority of the method is very marked. It is necessary that the  $p_H$  value of the solution should be less than 3 or more than 11 unless the solutions are well buffered.

D. G. H.

**Application of the Quinhydrone Electrode to the Measurement of  $p_H$  Values in Solutions Containing Copper Ions and Other Bivalent Ions.** J. B. O'SULLIVAN (*Trans. Faraday Soc.*, July 1925, advance proof, 3 pp.).—The quinhydrone electrode may



be used for determining the  $p_H$  of many solutions of metallic salts where the hydrogen electrode on account of its greater reducing power is inapplicable, *e.g.*, in solutions of nickel, copper, lead, and cadmium salts. By the use of this electrode the  $p_H$  of a 0.1N-copper sulphate solution made from salt of A.R. quality was found to be 4.14 and the degree of hydrolysis 0.072%.  
A. R. P.

**Determination of Organically Combined Halogen.** M. BUSCH (*Z. angew. Chem.*, 1925, **38**, 519—521).—In alcoholic potash solution hydrazine can be decomposed by a suitable catalyst into nitrogen and hydrogen. If this reaction is carried out in the presence of an organic halogen compound, the halogen is completely eliminated and can be determined. The catalyst is prepared by treating calcium carbonate with a solution of palladium chloride. The method cannot be used for compounds containing sulphur, phosphorus, arsenic, or mercury, owing to their poisonous effect on the catalyst. A series of results is given in which the accuracy of the method is established.  
F. R.

**Micro Determination of Chlorides, Bromides, and Iodides together.** R. STREBINGER and I. POLLAK (*Mikrochem.*, 1925, **3**, 38—59).—Whilst macrochemical separation of iodine from chlorine and bromine by means of thallous iodide is quantitative, the solubility of the latter is sufficient to affect microchemical determinations, even in presence of ammonium salts, alcohol, pyridine, or acetone. The best results are obtained with acetone and water (1:2 by vol.), using 5% thallous sulphate solution, but are 1—2% too low. The electrolytic determination of halogens, using a silver anode, is also found unsuitable for micro determinations. The insolubility of palladium iodide, however, affords a suitable basis for accurate microanalysis. Palladium chloride is added in the cold, the whole left 6—8 hrs., and filtered slowly; the precipitate is washed with warm water, then with alcohol, and dried in a current of air at 90—95°. Accurate results are obtained for quantities down to 0.3 mg. of iodine. The method is suitable for micro determinations of chlorine and iodine and of bromine and iodine together; in the latter case, precipitation is carried out in presence of concentrated hydrochloric acid, in both cases the total halogen being determined by the ordinary silver method. Chlorine and bromine together are determined microchemically by precipitation as silver salts; the dried and weighed precipitate is dissolved in 3—4% potassium cyanide solution, the solution diluted to 1%, and electrolysed. Corrosion of the platinum electrodes is reduced by addition of 1 drop of alkali hydroxide. A special washing arrangement is necessary to prevent access of air when removing the electrode for weighing, as silver is readily redissolved by the cyanide in presence of oxygen. The exact procedure necessary to secure accurate results is described in detail.  
S. I. L.

**Rapid Separation of Sulphur Precipitates in Analytical Reactions.** M. AWSCHALOM (*Anal. Asoc. Quím. Argentina*, 1924, **12**, 461—462).—Finely-divided sulphur precipitated in analytical operations, *e.g.*, by the action of hydrogen sulphide on ferric

salts, may be removed by shaking with a small quantity of ether. The sulphur is brought to a flocculent state in which it can readily be removed by filtration.

G. W. R.

**Inhibition of Bumping in the Determination of Nitrogen in Soil.** F. E. HANCE.—(See i, 1032.)

**Gunning-Arnold and Winkler Boric Acid Modifications of the Kjeldahl Method for the Determination of Nitrogen.** K. S. MARKLEY and R. M. HANN (*J. Assoc. Off. Agric. Chem.*, 1925, **8**, 455—467).—Detailed examination of the boric acid absorption modification of the official Gunning-Arnold method, showed it to be as accurate as the latter, provided water-cooled condensers were used and the temperature of the receiving flasks did not rise above 50°. Bromophenol-blue proved satisfactory as an indicator by artificial light.

A. G. P.

**Determination of Phosphoric Acid as Magnesium Ammonium Phosphate.** G. JØRGENSEN (*Z. anal. Chem.*, 1925, **66**, 209—224).—Polemical. Repetition of McCandless and Burton's procedure (this vol., ii, 157) gave precipitates contaminated with  $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$  from ammoniacal solutions and with magnesium molybdate and normal phosphate from neutral solutions. Balareff's criticism (*A.*, 1921, ii, 518) of the author's method (*A.*, 1906, ii, 579) is based on the results of experiments conducted with solutions of greatly different concentration from those used in ordinary analyses. [Cf. *B.*, 1925, 574.]

A. R. P.

**Determination of Phosphorus and Magnesium.** C. P. STEWART and W. ARCHIBALD (*Biochem. J.*, 1925, **19**, 484—491).—By a micro-Neumann method for the determination of phosphorus, it is possible to determine within 3% 0.05 mg. of phosphorus in 20 c.c. of fluid. A smaller error is obtained with higher concentrations. In determining magnesium in blood or serum the calcium is removed by Kramer and Tisdall's method (*A.*, 1921, ii, 595) and the magnesium is precipitated as ammonium magnesium phosphate, in which compound the phosphorus is determined as above.

S. S. Z.

**Determination of Carbon Monoxide by Hæmoglobin Absorption.** M. NICLOUX (*Compt. rend.*, 1925, **180**, 1750—1753; cf. *A.*, 1923, ii, 578).—By slight modifications of the method of passing air containing carbon monoxide through blood containing a preservative and a reducing agent, better contact between the gas and the liquid is obtained, and carbon monoxide to the extent of 0.00001% may be detected, using 500 c.c. of air. The application of the law of mass action to the reaction between carbon monoxide and hæmoglobin under anaërobic conditions is questioned.

L. F. H.

**Determination of Carbon Dioxide and Carbon Monoxide.** P. LEBEAU and P. MARMASSE (*Compt. rend.*, 1925, **180**, 1847—1850).—The amount of carbon dioxide present in a gaseous mixture is determined by condensation of the carbon dioxide by means of

liquid air, measurement of its volume, and absorption by barium hydroxide as a check. Carbon monoxide is determined by first removing condensable gasses by cooling, then oxidation of the carbon monoxide present by passage over heated iodine pentoxide, and determination of the carbon dioxide formed as above. Presence in the gaseous mixture of a large percentage of hydrocarbons does not interfere with the determination. L. F. H.

**Potentiometric Study of the Reaction between Halogens and the Cyanogen Ion.** E. MÜLLER and A. SCHUCH (*Z. Elektrochem.*, 1925, **31**, 332—334).—The reaction between the halogens and potassium cyanide in solution (0.1*N*) may be followed potentiometrically, a sudden large change in the potential occurring when the equivalent quantities for the equation  $X_2 + CN' = CNX + X'$  are present. The values of this potential (measured in millivolts against a normal calomel electrode) for chlorine, bromine, and iodine, respectively, are +560, 580, 210 when the halogen solution is titrated with the potassium cyanide solution, and 790, 580, and 220 when the reverse procedure is employed, the difference in the chlorine values probably being due to the appreciable reversibility of the reaction. The change in potential is greatest in the case of chlorine, least in the case of iodine, bromine occupying an intermediate position. The method has been applied to the electrolytic preparation of chlorocyanogen to indicate when either component is in excess. J. W. B.

**Determination of Potassium.** R. MEURICE (*Ann. Chim. Analyt.*, 1925 [ii], **7**, 161—163).—Potassium may be precipitated as hydrogen tartrate in the presence of alcohol (99% methyl alcohol containing only traces of acetone was used) and after well washing the precipitate, the potassium is determined by titration with sodium hydroxide solution in the presence of phenolphthalein. If the proportion of potassium chloride be between 1 and 0.8 g., dissolution of the precipitate in the alcohol is negligible and results are accurate to 0.5%. The presence of nitrates and magnesium does not affect the results, and sulphates merely lengthen the time of precipitation. [Cf. *B.*, 1925, 615.] D. G. H.

**Separation of Small Quantities of Calcium from Large Amounts of Magnesium.** BACH (*Chem.-Ztg.*, 1925, **49**, 514).—Contrary to the statements of Rodt and Kindscher (this vol., ii, 158) small quantities of calcium may be accurately separated from much magnesium by means of ammonium oxalate provided the correct conditions are observed. The solution should either be very dilute and contain at least 3% of ammonium chloride, or, alternately, an excess of ammonium oxalate equal to 100 times the weight of magnesium present is added in the form of a hot concentrated solution. A. R. P.

**Determination of Small Quantities of Zinc in Materials of Organic Nature: Microchemical Method based on the Fluorescence of Zinc Salts with Urobilin.** R. E. LUTZ (*J. Ind. Hygiene*, 1925, **7**, 273—290).—A method for determining zinc in amounts from 0.01 to 0.5 mg., to within 10%, is to compare the

green fluorescence obtained on adding standard urobilin solution with the fluorescence obtained in a control test. The zinc solution is obtained in the necessary state of freedom from other salts by a process involving the entrainment of the sulphide precipitate by means of copper, with subsequent elimination of the copper. [Cf. *B.*, 1925, 615.]  
D. G. H.

**Use of Potassium Ferrocyanide in Gravimetric Analysis. [Determination of Cadmium.]** G. LUFF (*Chem.-Ztg.*, 1925, 49, 513—514).—Cadmium is quantitatively precipitated as cadmium ammonium ferrocyanide by the addition of potassium ferrocyanide to the warm cadmium solution containing 10 g. of ammonium chloride and 20 c.c. of ammonia (*d* 0.92) per 100 c.c. After keeping the solution for 4 hrs. at 80°, the crystalline precipitate is collected in a Gooch crucible, dried at 100°, and weighed as  $\text{Cd}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$ .  
A. R. P.

**Detection and Determination of Cobalt by Spectroscopy and Colorimetry.** G. DENIGÈS (*Compt. rend.*, 1925, 180, 1748—1750).—The blue colour shown when hydrochloric acid is added in excess to solutions of cobalt salts furnishes an excellent absorption spectrum (4 bands) easily perceptible at great dilution with a direct vision spectroscope. In any aqueous solution of metallic salts (other than those of iron and copper) cobalt may be determined colorimetrically by addition of concentrated hydrochloric acid and comparison with standards. If the solutions contain iron or copper, reduction is effected by stannous chloride in order to render the method applicable. The method is specially suitable for determining traces of cobalt in commercial nickel salts.  
R. A. M.

**Separation and Determination of Tin in Alloys.** B. S. EVANS (*Analyst*, 1925, 50, 330—334).—The tin may be determined by effecting a preliminary separation of tin, antimony, and arsenic from the alloy. Since the bromides of these three metals are volatile, they may be obtained free from other metals by cautiously acting on the powdered alloy with bromine, and distilling the resulting liquid. No appreciable quantities of the bromides of copper, iron, lead, nickel, cadmium, manganese, or zinc are carried over, and these metals may be determined in the residue. [Cf. *B.*, 1925, 636.]  
D. G. H.

**Separation of Cesium [Hafnium] and its Arc Spectrum.** J. BARDET and C. TOUSSAINT (*Compt. rend.*, 1925, 180, 1936—1938).—The mixture of sulphates is dissolved in concentrated sulphuric acid and enough 80% phosphoric acid is added to precipitate about 20% of the oxides. 1.5 Volumes of water are added slowly, with stirring, so that a slow precipitation of phosphates occurs in a strongly acid medium. After keeping over-night, the acid is decanted off, 3 volumes of water are added to the precipitate, which is then filtered. The filtrate is added to the decanted acid, which is then heated until sulphur trioxide is evolved. The procedure is repeated with this liquid. The phosphate precipitates are converted into sulphates by fusion with alkali carbonates followed by treatment

with sulphuric acid. The fresh phosphates are decomposed by concentrated sodium carbonate solution. The sulphates are then submitted to the original process. Spectroscopic methods are used to control the experiments. The arc spectrum of hafnium has been measured between 2300 and 3500 Å. All the lines found by Hansen and Werner (A., 1924, ii, 79) are confirmed and a certain number of important lines have been added. Forty-eight lines are tabulated with an accuracy of 0.05 Å.

R. A. M.

**Platinum and Palladium Dimethylglyoximes.** R. A. COOPER (*J. Chem. Met. Min. Soc. S. Afr.*, 1925, 25, 296—297).—Platinum dimethylglyoxime forms a fine blue, crystalline precipitate having a characteristic metallic bronze lustre when sodium formate is added to a slightly acid solution of platinic chloride containing an alcoholic solution of dimethylglyoxime. Precipitation is quantitative, but the compound cannot be ignited to metal without loss, although it can be dried at 100° to  $C_8H_{14}O_4N_4Pt$  for weighing. When sodium hydroxide is added to water in which platinum dimethylglyoxime is suspended, it dissolves completely, but an excess causes precipitation of a purple unstable compound; palladium dimethylglyoxime dissolves in sodium hydroxide and is not further affected by excess.

A. R. P.

**Generally Applicable Method of Conducting an Elementary Organic Analysis by the Wet Way.** G. VORTMANN (*Z. anal. Chem.*, 1925, 66, 272—275).—The substance is heated with an excess of potassium iodate and sulphuric acid and the carbon dioxide evolved is collected in the usual absorption tube. The potassium iodate remaining unattacked is determined by diluting the acid liquid and titrating in the usual way. From this, the amount of oxygen consumed in the combustion may be calculated and this figure together with the weight of carbon dioxide produced supplies the data for calculating the composition.

A. R. P.

**Paramœcial Method for Determining the Phenol Coefficient of Disinfectants.** A. SCHNEIDER.—(See i, 1006.)

**Nitrosomethylurethane as a Reagent for Pyrocatechol Tannins.** W. VOGEL (*Collegium*, 1925, 189).—Pyrocatechol tannins give a heavy precipitate with nitrosomethylurethane, whereas pyrogallol tannins, with the exception of chestnut and algarobilla, give no precipitate. Chestnut and algarobilla extracts give a slight turbidity. When pyrogallol tannins are treated twice with nitrosomethylurethane and then with iron alum and sodium acetate, they give the typical blue coloration, whereas pyrocatechol tannins treated similarly gives no coloration. The nitrosomethylurethane test is better than the formaldehyde-hydrochloric acid test.

D. W.

**Rapid Determination of Small Amounts of Dextrose in the Urine in Diabetes.** J. R. WILLIAMS and G. U. CASEY.—(See i, 998.)

**Determination of Invert-sugar in presence of Sucrose.** N. SCHOORL (*Chem. Weekblad*, 1925, **22**, 285—286).—The amount of potassium iodide required in the author's method (this vol., ii, 445) may be reduced to one-tenth of the amount given by addition of potassium thiocyanate after acidifying the reduced liquor. By the procedure given, 1 mg. of invert-sugar requires 0.33 c.c. of 0.1*N*-thiosulphate solution; no increase in reducing action due to the presence of sucrose could be detected. S. I. L.

**Rapid Determination of the Acid Value of Oils.** S. SOMAZZI (*Boll. Ind. Pelli*, 1923, **1**, 44; from *Chem. Zentr.*, 1924, ii, 1530).—Exactly 1 g. of oil is shaken in a graduated pipette with an equal volume of ether and alcohol to complete solution, when the acid is titrated with 0.1*N*-sodium hydroxide, using phenolphthalein as indicator. R. B.

**Bromometric Determination of Thiocyanates and Cyanides.** F. OBERHAUSER (*Z. anorg. Chem.*, 1925, **144**, 257—262).—Thiocyanates may be determined bromometrically if excess of bromine is added and, after keeping for 10 min., the titration completed with arsenious acid and bromine; the reaction is represented by the equation:  $\text{KCNS} + 8\text{Br} + 4\text{H}_2\text{O} = \text{KBr} + \text{BrCN} + \text{H}_2\text{SO}_4 + 6\text{HBr}$ . This process may be utilised for the determination of copper by precipitating as thiocyanate and titrating the precipitate; any nitric acid must first be removed. Cyanides may be determined according to the equation:  $\text{KCN} + \text{Br}_2 = \text{CNBr} + \text{KBr}$ , and ferrocyanides by oxidation with bromine to ferricyanides. Ferricyanides are quantitatively reduced by arsenious acid if a zinc salt is added to precipitate the ferrocyanide as soon as formed; the excess of arsenious acid is then determined by titration with bromine, the insoluble ferrocyanide being unaffected. Complex cyanides may also be determined by converting into mercuric cyanide and proceeding as above. A. G.

**Determination of Indole and Skatole in Bacterial Cultures.** C. R. FELLERS and R. W. CLOUGH.—(See i, 1015.)

**Electrocapillary Analysis of Colloidal Colouring Matters.** W. KOPACZEWSKI (*Compt. rend.*, 1925, **180**, 1530—1533).—By measuring the rise of colloidal dyes (natural and synthetic) up strips of filter-paper, it is found that the rise of electrolytes is independent of their charge. Electro-negative colloids rise as high as water, the upper portion of the filter-paper being more deeply coloured; electro-positive colloids rise scarcely at all, whilst the point of contact with the liquid is the most deeply coloured. Ampho-teric colloids show bands of light and deep colour, and substances of low surface tension rise considerably on the filter-paper irrespective of their charge. By their behaviour when placed on filter-paper, therefore, a qualitative determination of the charge of a colloidal dye may be made. L. F. H.

## General, Physical, and Inorganic Chemistry.

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**Continuous Hydrogen Spectrum.** H. SCHÜLER and K. L. WOLF (*Z. Physik*, 1925, **33**, 42—47).—The intensity of the continuous spectrum observed in the positive column, which begins at 4800 Å., is shown to be unrelated to that of the Balmer series or of the many-lined spectrum. Its intensity is increased by an electric field. As the long wave-length limit corresponds with the heat of dissociation of the hydrogen molecule, the spectrum is attributed to the combination of the atoms in an electric field. Possibly the radiation emitted may also depend on the state of excitation of the hydrogen atoms. E. B. L.

**Further Spectra Associated with Carbon.** R. T. BIRGE (*Nature*, 1925, **116**, 207).—The final states of the six new "double-double-headed" bands described by Johnson (this vol., ii, 723) are identical with the initial states of the comet-tail bands, thus proving the correctness of the author's assignment of vibrational quantum numbers (this vol., ii, 836). The comet-tail bands must have a double electronic level in the initial state, of spacing  $\Delta\nu=126$ . Each band has a double "origin" given by the heads of the two *Q* branches, according to Baldet's analysis. Similarly, the new bands each have a double origin with the same spacing.

A. A. E.

**Doublet Separation in C II and Si IV.** R. J. LANG and S. SMITH (*Nature*, 1925, **116**, 244).—A brief account of work to be published elsewhere.

A. A. E.

**Arc Spectrum of Scandium.** S. PIÑA DE RUBIES (*Compt. rend.*, 1925, **181**, 108—110).—The wave-lengths and intensities are tabulated of 185 lines of the arc spectrum of scandium between 2232 and 3394 Å.

F. G. T.

**Spark Spectra in the Schumann Region.** L. BLOCH and E. BLOCH (*J. Phys. Radium*, 1925, [vi], **6**, 154—165).—Full lists are given of the spark-spectrum wave-lengths for manganese between 1869 and 1464 Å., chromium between 1926 and 1505, copper between 1930 and 1359, silver between 1889 and 1389, gold between 1919 and 1342, and platinum between 1991 and 1330 Å. Lines are noted which may be due to contamination with iron or carbon. W. A. C.

**Low-voltage Arcs in Rubidium and Cæsium Vapours.** F. H. NEWMAN (*Phil. Mag.*, 1925, [vi], **50**, 463—470; cf. this vol., ii, 450).—The voltages required to strike an arc and to maintain it in rubidium and cæsium vapours have been measured at temperatures between 160° and 300°. The arc was struck between an anode of sheet metal and a tungsten-filament cathode heated by passing a

suitable current. The electrodes were enclosed in an evacuated bulb containing sufficient of the metal to form saturated vapour at the highest temperature used. The bulb was heated in an electric furnace. With rising temperature, the striking voltage diminishes; thus for rubidium it is 7.3 volts at 185° and falls to 3.2 volts at 289°. At constant temperature it decreases with increase of the filament current. The same rules apply to the voltage required to maintain the arc, which in all cases is slightly less than the striking voltage. The mechanism of the arc is briefly discussed. A. B. M.

**Electromagnetic Susceptibility of the Iodine Atom. Change of Intensity in the Line Spectrum.** W. STEUBING (*Z. Physik*, 1925, **33**, 113—127).—The spectrum was produced in discharge tubes with carbon electrodes excited either by 10,000 volts direct current, or by alternating current with a periodicity of 50, both with and without capacity. The electromagnet gave a field up to 15,000 gauss. In addition to photographs, the spectrum was recorded by means of a Moll thermopile and galvanometer. The arc and spark lines behave quite differently in the magnetic field; the former vary in intensity but remain sharp, whilst the latter become less sharp and are broadened on the red side. New lines also appear, but no Zeeman effect could be noticed. The loss in sharpness is ascribed to the molecular Stark effect; it increases with increase in pressure of the iodine vapour and also in the presence of foreign gases. The intensity of the spectrum is reduced by the presence of a foreign gas, the effect being greater the higher the molecular weight and the greater its chemical affinity. In a mixture of helium and neon, faint diffuse lines can be resolved into components, and strong new lines appear, presumably due to collisions of the second kind. E. B. L.

**X-Ray Radiation from Hot Sparks.** A. BJÖRKESEN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 413—415).—In a high-potential condensed discharge in a high vacuum stripped atoms emit strong spectrum lines, and the hot sparks radiate X-rays. The X-radiation exhibits all the known characteristic lines in the *L* series for silver and the *K* series for aluminium, silicon, sulphur, and copper. No new lines were observed nor was any shift or broadening noticeable in the known lines. The X-rays are thus not produced by the stripped atoms in the vapour; they originate at the solid electrodes, and apparently the multiple ionisation which gives rise to the enhanced X-ray lines of the *K*-series must be due to simultaneous ejection by a single impact. R. A. M.

**Quantum Explanation of the Zeeman Effect.** A. M. MOSHARRAFA (*Nature*, 1925, **116**, 96—97; cf. Hicks, this vol., ii, 729). A. A. E.

**Quantum Explanation of the Zeeman Effect.** A. W. CONWAY (*Nature*, 1925, **116**, 97). A. A. E.

**Theory of the Zeeman Effect.** G. GIANFRANCESCO (*Nature*, 1925, **116**, 207—208). A. A. E.



**Stark Effect Patterns in Helium.** J. S. FOSTER (*Nature*, 1925, **116**, 135).—New observations prove that the simple displacements (1/1) reported by Stark and Nyquist for the members of the sharp and principal series of helium are correct (cf. Takamine and Kokubu, A., 1919, ii, 379). A new weak perpendicular component of the parhelium combination line 4384 Å. has been observed. Two examples of the pattern 2/3 are mentioned. A. A. E.

**Multiplet Structure.** A. BRAMLEY (*Phil. Mag.*, 1925, [vi], **50**, 375—381).—From the equations of motion of an electron describing a path about a central charge the author deduces an expression for the frequency separation of the components of multiplets in the optical spectra of elements with more than one electron in the atom. The closeness of agreement between computed and experimental frequency differences is illustrated by data from the spectra of potassium and calcium. A. B. M.

**Optical Screening-constant Regularities.** A. C. MENZIES (*Phil. Mag.*, 1925, [vi], **50**, 414—422).—The screening-constant  $s$  in the relativity doublet formula  $\delta\nu = K(Z-s)$  has been calculated from the doublet separations  $\delta\nu$  in the optical spectra of a number of the elements. The following are the principal observed regularities: (1) The values of  $s$  for the alkaline-earth spark spectra are approximately nine-tenths those of the corresponding alkali arc spectra. (2) For the same sub-groups of the periodic table  $s$  varies directly as the atomic number  $Z$ . (3) The  $s$ - $Z$  curves for different sub-groups have almost the same slope; for additions to  $Z$  of 8, 18, and 32, the additions to  $s$  are 5, 13, and 23, respectively. These regularities are to be expected from simple theoretical considerations. The evidence is considered as favouring a magnetic rather than a relativistic origin of multiplets. A. B. M.

**Red Limit and Work of Escape of Photo-electric Electrons.** R. SUHRMANN (*Z. Physik*, 1925, **33**, 63—84).—The curves of photo-electric sensitivity for platinum, gold, and silver near the red limit were measured with the most delicate instruments possible. All three metals show the influence of surface films, but only platinum and gold show any considerable diminution in emission after continued heating at a high temperature in order to remove occluded gas—probably hydrogen in the case of gold and platinum, oxygen in that of silver. From the curves characteristic constants can be deduced by applying the theory of thermionic emission, and the value for the work of escape and the red limit can be calculated for absolute zero. A temperature scale can be constructed and the photo-electric cell may be used as a total radiation pyrometer. E. B. L.

**The Photo-electric Effect in Potassium Vapour as a Function of the Frequency of the Light.** E. O. LAWRENCE (*Phil. Mag.*, 1925, [vi], **50**, 345—359).—The photo-electric effect in potassium vapour has been measured for incident light between 2200 and 3200 Å. A stream of potassium vapour from a reservoir of the metal heated at about 300° traversed the previously evacu-

ated ionisation chamber, condensing on a surface cooled by liquid air on the opposite side. The source of light was a Pfund iron arc, combined with a monochromator. The beam of light passed through the stream of vapour and the positive ions formed were measured. The intensity of the light was determined by a potassium photo-electric cell. Light of wave-length greater than  $2610 \text{ \AA}$ . produces no effect. For shorter wave-lengths, the effect increases with diminishing wave-length, the relation between wave-length of incident light and photo-electric effect being nearly linear over the range investigated. The discrepancy between the observed photo-electric threshold and that required by the Bohr theory is regarded as due probably to a molecular state of the vapour. A. B. M.

**Ionic Mobilities in Ethyl Ether as a Function of Pressure.** L. B. LOEB (*Proc. Nat. Acad. Sci.*, 1925, **11**, 428—435).—In permanent gases, newly-formed positive ions have higher mobilities than the positive ions a few hundredths of a second old, the higher value being equal to the mobility of the negative ion. In ethyl ether, the mobility is small because of the high dielectric constant and the mobility of the positive ion does not equal that of the negative ion. The positive mobility falls from a higher value to a constant lower value in 0.03 sec.; in air this takes about 0.004 sec. The most satisfactory explanation is given by Erikson, that the change in mobility of the positive ion with time is due to a change in the diameter of the ion with increasing complexity; possibly that the newly-formed ions are unimolecular, whilst the aged positive ions are bimolecular. R. A. M.

**Selective Photo-electric Effect on Strontium.** R. DÖPEL (*Z. Physik*, 1925, **33**, 237—245).—The strontium was deposited as a mirror on glass by distillation and full precautions were taken to exclude any hydrogen or moisture. The maximum photo-current was produced at  $350\mu\mu$ , distinctly shorter than that for barium, and showed the characteristic change with the angle of incidence of the plane of the polarised light. E. B. L.

**Electric Charges Carried by Individual Microscopic Particles.** T. SEXL (*Physical Rev.*, 1925, [ii], **26**, 92—96; cf. following abstracts).—A criticism of Derieux' computation by Millikan's method of the elementary electrical charge on mercury droplets. A. A. E.

[**Electric Charges Carried by Individual Microscopic Particles.**] J. B. DERIEUX (*Physical Rev.*, 1925, [ii], **26**, 97—98).—A reply to Sexl (preceding abstract). A. A. E.

**Nature of the Evidence for the Divisibility of the Electron.** R. A. MILLIKAN (*Physical Rev.*, 1925, [ii], **26**, 99—104; cf. preceding abstracts).—Polemical. A discussion of the criticisms of Sexl and others. A. A. E.

**Ionisation Produced in Air during the Complete Absorption of Slow Electrons.** J. F. LEHMANN and T. H. OSGOOD (*Nature*, 1925, **116**, 242).—Approximate determinations show that the

ionisation per electron in air increases steadily with the initial energy of the ionising electron over the range 100 to 1000 volts. The average energy expended per ion-pair decreases from 35 volts (initial energy 200 volts) to 22 volts (initial energy 1000 volts). The behaviour of helium is similar. A. A. E.

**Isotopes of Mercury.** F. W. ASTON (*Nature*, 1925, **116**, 208).—Preliminary results for mercury indicate that the mass numbers and corresponding approximate intensities of the most important constituents of mercury are : 198 (4), 199 (5), 200 (7), 201 (3), 202 (10), 204 (2), in agreement with the accepted atomic weight. Gold, if obtainable by the transmutation of mercury, should have an atomic weight at least as high as 198. A. A. E.

**Isotope Effect in Band Spectra. III. Spectrum of Copper Iodide as Excited by Active Nitrogen.** R. S. MULLIKEN (*Physical Rev.*, 1925, [ii], **26**, 1—32).—By the action of active nitrogen on the vapours of the copper halides, the band spectra are characterised by sharpness and clearness of the heads; the mechanism involved is probably (1) the dissociation of  $\text{Cu}_2\text{X}_2$  or  $\text{CuX}$  molecules giving neutral, unexcited atoms which are subsequently excited by impact with  $\text{N}_2'$  molecules, and (2) dissociation yielding the ions  $\text{Cu}^+$  and  $\text{X}^-$ . Band spectra of cuprous fluoride, chloride, bromide, and iodide were obtained using cupric fluoride, cuprous and cupric chloride, cupric bromide, and cuprous iodide, and some observations are recorded on the excitation by means of active nitrogen of the spectra of lead iodide, mercuric iodide, and mercuric bromide; in the latter case, process (1) (above) is even more definitely indicated. The author discusses the nature of excited electronic states in copper halide molecules, and the band spectra of polar compounds; the formation of  $\text{CuX}_2$  molecules is correlated with the excitation of  $\text{CuX}$ . The absence of electronic band spectra for the hydrogen, silver, and alkali halides is possibly due to the non-occurrence of compounds of the type  $\text{NaCl}_2$ ; its presence in the case of the alkaline-earth halides leads to the assumption that the real emitter is then of the type  $\text{MX}$ , the spectrum of which is excited by the addition of  $\text{MX}_2$  to a flame in a manner analogous to the excitation of the sodium *D* lines (*i.e.*, spectrum of M) by the use of sodium chloride (*i.e.*,  $\text{MX}$ ).

Complete data for the cuprous iodide band spectrum and an analysis of the results are tabulated, the wave-lengths of about 260 heads between 5650 and 3890 Å. being measured; no other bands are present between 1900 and 7000 Å. Every  $\text{Cu}^{63}\text{I}$  band was found, wherever of sufficient resolution and intensity, to be accompanied by a weaker  $\text{Cu}^{65}\text{I}$  band. The  $\text{Cu}^{63}\text{I}$  bands fall into five systems, one in the green, and the others in the blue and violet. So far as data could be obtained, the calculated and observed values of the isotopic displacement are in complete agreement, within the experimental error, for the entire range of values of the vibrational quantum numbers  $n'$  and  $n''$  in all the systems. For cuprous iodide (and probably for the chloride and bromide), the equations indicate that the five (six, or four) systems all correspond with a common

final electronic state, probably the normal state of the molecule. An energy level diagram is given for the cuprous iodide molecule. Numerically large values of  $n''-n'$  are associated with large values of  $n'$ , causing the maximum intensity in band sequences (having the same value for  $n''-n'$ ) to shift from the first to higher members as the sequence considered is further away from the system-origin.

A. A. E.

**Stopping Power of Hydrogen Atoms for  $\alpha$ -Particles.** R. H. FOWLER (*Proc. Camb. Phil. Soc.*, 1925, 22, 793—803).—Bohr calculated the stopping power of light atoms for  $\alpha$ -particles on the basis of classical principles. About one-half of the loss of energy by the  $\alpha$ -particles comes from transfers to electrons in distant atoms of amounts less than the energy required to transfer those atoms to their next higher stationary state. The author has calculated the mechanical transfer of energy from an  $\alpha$ -particle to an electron moving in its normal circular orbit in a hydrogen-like atom. The calculation depends on perturbation theory carried to a second approximation. In Bohr's calculations the equation  $-dT/dx = 4\pi LN^2e^4/mV^2 \cdot \log \gamma mV^3/2\pi Ne^2\omega$  was deduced;  $-dT/dx$  is the rate of loss of energy by an  $\alpha$ -particle of charge  $Ne$  and velocity  $V$  moving through a gas containing  $L$  atoms with a single electron (mass  $m$ , charge  $-e$ ) per c.c. The frequency of these elastically bound electrons is  $\omega$ , and  $\gamma$  is a constant, 1.123. In the present calculation,  $\omega$  is the orbital frequency of revolution and  $\gamma$  is the constant 2.42. The equation is unchanged in form. Gurney's results (this vol., ii, 256) are used to test the calculation. If  $\gamma$  is taken as 1 instead of 2.42, the results are in almost exact agreement with experiment. The reasons for this change are discussed.

R. A. M.

**Theory of the Influence of Magnetic Fields on the Stopping Power of Gases for  $\alpha$ -Particles.** R. DE L. KRONIG (*Proc. Camb. Phil. Soc.*, 1925, 22, 773—776).—A calculation following on the work of Fowler (preceding abstract) of the influence of space quantisation on the stopping of  $\alpha$ -particles by matter.

R. A. M.

**Long-range Particles Emitted by the Active Deposits of Radium.** N. YAMADA (*Compt. rend.*, 1925, 181, 176—178; cf. Bates and Rogers, A., 1924, ii, 84; Pettersson, *ibid.*, 380; Rutherford and Chadwick, *ibid.*, 814).—Radium-C emits only long-range particles of range 9.3 cm., the reported particles of longer range being probably hydrogen nuclei, since they can be eliminated by preliminary careful heating in a vacuum to remove traces of water vapour etc. There are approximately 20 particles of 9.3 cm. range per  $10^6$   $\alpha$ -particles of ordinary range.

J. S. C.

**Variations of Range, Initial Velocity, and Ionising Power of the  $\alpha$ -Particles from Polonium.** (MLLE.) I. CURIE (*Ann. Physique*, 1925, [x], 3, 299—401).—A connected account of work already published, with minor changes in detail (cf. A., 1922, ii, 606; *Compt. rend.*, 1923, 176, 1462; *J. Phys. Radium*, 1923, [vi], 4,

170; A., 1923, ii, 207; this vol., ii, 175, 348, 621). The initial velocity of the  $\alpha$ -particles from polonium is  $1.593 \times 10^9$  cm./sec. and the range at  $15^\circ$  and 760 mm. is 3.87 cm. in air. Maximum ionisation occurs 4.5 mm. from the end of the range in air at  $15^\circ$  and 760 mm.; the velocity at that point is  $0.57 \times 10^9$  cm./sec.

A. S. R.

**Proposed Model for the  $\alpha$ -Particle, and some Nuclear Series.** R. HARGREAVES (*Phil. Mag.*, 1925, [vi], 50, 470—491).—The nucleus is taken to be a structure of positive and negative electrons, rotating about a common axis, with their relative positions unaltered, under attractions and repulsions following the simple electrostatic laws. The model proposed for the helium nucleus is discussed in detail, and it is shown how the same type of model may be extended to represent the nuclei of elements of higher atomic weight.

A. B. M.

**Effective Wave-length of  $\gamma$ -Rays.** D. SKOBEŁTZYN (*Nature*, 1925, 116, 206—207).—Polemical (cf. Gray, this vol., ii, 84).

A. A. E.

**Transmutation of Mercury into Gold.** H. NAGAOKA (*Nature*, 1925, 116, 95—96).—The formation of ruby glass is successfully used to detect the production of gold from mercury, employing a discharge between tungsten and mercury electrodes in paraffin oil, in which a potential difference of  $1.5 \times 10^5$  volts/cm. could be maintained.

A. A. E.

**Chemical Properties of Atoms according to the Bohr Theory.** H. A. KRAMERS (*Naturwiss.*, 1924, 47, 1050—1054).—An account of the development of the Bohr atom and the formulation of the periodic table in terms of quantised atoms and groups of electrons.

E. B. L.

**Quantum Theory and the Bohr Atom.** A. SOMMERFELD (*Naturwiss.*, 1924, 47, 1047—1049).—A general account of the ideas underlying the application of the quantum theory in the Bohr atom and a discussion of outstanding problems.

E. B. L.

**Theory of Emission in the Rutherford-Bohr Atom.** J. PALACIOS (*Anal. Fís. Quím.*, 1925, 23, 259—276).—Assuming that emission in the Bohr atom gives rise to trains of undamped waves and that the escape of electrons is regulated by the laws of chance, a theory is developed by which the measurements of Wien with canal rays can be explained. From this theory and from the experimental data, it follows that the  $H\beta$  and  $H\gamma$  rays have the same emission time. It follows from this that Planck's constant  $h$  may be considered as the product of two universal constants, namely, a time quantum and an energy quantum, the magnitudes of which, calculated from the experimental data, are given. The theory in question makes it possible to deduce the degree of stability of the different orbits, starting from the damping observed in the luminescence of the canal rays.

G. W. R.

**The Epstein-Sommerfeld Quantum Rule.** L. KORDYSCH (*Z. Physik*, 1925, **33**, 214—218).—The quantum theory of the Zeeman effect is based on the Epstein-Sommerfeld empirical rule; it depends on a use of the principle of selection which is not free from objection. The quantum rule for the polarisation is derived by considering the meridional and equatorial motion and selecting from the possible forms those which do not contradict the quantum hypothesis.

E. B. L.

**Atomic and Molecular Collisions and their Chemical Significance.** J. FRANCK (*Naturwiss.*, 1924, **47**, 1063—1068).—Recent progress in the application of quantum theory to collisions between electrons, atoms, and molecules in the normal and in the excited condition is described. An electron or normal atom in colliding with a normal atom may raise the latter to a higher quantum state (collisions of the first type). Conversely, internal energy of excitation may be converted into translational energy by the collision of an excited atom with a slow-moving normal atom or molecule (second type). In the formation of a molecule from two atoms, it will rarely happen that the total energy contributed by the atoms will be precisely what is required for any of the definite quantum states of the molecule which are a condition of its continued existence. The excess energy must therefore be removed, either as radiation or by collision with a third atom or molecule which has not participated in the reaction—a conception which seems to be justified by recent work on reaction velocities (third type).

E. B. L.

**Band Spectra and Molecular Properties.** A. KRATZER (*Naturwiss.*, 1924, **47**, 1054—1058).—A short account of how band spectra yield information concerning the moment of inertia, the nature and strength of linking, the energy of dissociation and other details affecting molecular structure. Consideration of the variation of moment of inertia with temperature as indicated by band spectra has made it possible to express the specific heat of gases from very low to very high temperatures by means of a theoretical curve. Magnetic properties are also discussed.

E. B. L.

**Intensities in Band Spectra.** G. H. DIEKE (*Z. Physik*, 1925, **33**, 161—168).—The rule of Burger and Dorgelo for the intensity of the lines of a multiplet is applied to band spectra and is found to lead to results in agreement with experiment. The *P* branch is stronger in emission than the *R* branch. The course of the intensity is different when the band consists of unresolved doublets from cases in which it consists of really single lines. An explanation is given of the alternation in intensity observed in many bands.

E. B. L.

**Band Spectra Associated with Carbon.** R. T. BIRGE (*Nature*, 1925, **116**, 170—171).—The author has arranged in progressions and assigned vibrational quantum numbers to the thirteen band groups associated with carbon and its compounds. It is probable that both the first negative group and the comet-tail bands are due to ionised carbon monoxide.

A. A. E.

**Absorption Process in Photo-electrically-conducting Sodium Chloride Crystals.** Z. GYULAI (*Z. Physik*, 1925, **33**, 251—260).—The absorption of sodium chloride crystals exposed to intense bluish-green light was compared with the absorption of the unexcited crystal; the absorption curve showed a diminution in the maximum position, but a considerable extension towards the red end. Only 60% of the "centres" could be excited. Light of long wave-length restored the excited crystal to the unexcited condition as a result of the absorption following quantum laws, one quantum of long wave-length light producing a positive current equal to the negative current resulting from the liberation of the electrons.  
E. B. L.

**Absorption of Ultra-violet Light by Inorganic Halides.** F. H. GETMAN (*J. Physical Chem.*, 1925, **29**, 853—864; cf. Crymble, T., 1912, **101**, 266; Brannigan and Macbeth, T., 1916, **109**, 1277; Macbeth and Maxwell, T., 1923, **123**, 370).—The absorption coefficients of a number of chlorides have been measured; the calculated molecular extinction coefficients increase with the atomic weight of the combined metal. The chlorides of calcium, strontium, magnesium, zinc, and aluminium absorb ultra-violet radiation selectively, the wave-length corresponding with the head of the absorption band of each salt being approximately 2730 Å. (cf. Brannigan and Macbeth, *loc. cit.*). The presence of this characteristic absorption band throughout a series of chlorides is shown not to be due to the common ion. Calcium chloride solutions do not follow Beer's law, and from this fact it is doubtful whether the law applies strictly to any strongly polar compounds.  
F. G. S.

**Carbon Disulphide Band at 320m $\mu$ .** G. BRUHAT and M. PAUTHENIER (*Compt. rend.*, 1925, **181**, 104—105).—The extinction coefficients and refractive indices of carbon disulphide in the neighbourhood of, and within, the band at 320m $\mu$  may be represented by formulæ of the Ketteler-Helmholtz type. This band belongs to the type which may be resolved into lines, although when measurements are made with liquid carbon disulphide, it appears continuous. When a vapour possesses large bands and the variations of absorption are regular, the absorption curve may be superposed on a curve representing a  $\delta$  term of the Ketteler formula. This superposition is impossible with carbon disulphide owing to the asymmetry of the curve, and to the fact that the extinction coefficient alters rapidly on the edge, and is markedly constant in the centre, of the band. It is shown that the above band is formed by the juxtaposition of widened lines. A formula derived solely from absorption measurements permits the calculation of the anomalous dispersion, giving values which agree well with those of direct measurement. The interval between the maximum and minimum anomaly has a calculated value of 260 Å., the observed value being 280 Å.  
F. G. T.

**Absorption Spectra of Several Ketones.** J. PLOTNIKOV (*Rec. trav. chim.*, 1925, **44**, 798—799).—Polemical against Langedijk

(this vol., i, 408) and Wegscheider (A., 1923, ii, 49). The author maintains from examples of the photo-chemical decolorisation of dyes that the action depends on the quantity of light absorbed and not on the intensity, and that when heat rays are not superimposed on the true light rays his photo-chemical absorption rule is valid.

J. W. B.

**Spectro-chemistry in the Ultra-red. VII. Absorption of certain Homologous Ketones.** G. B. BONINO (*Gazzetta*, 1925, **55**, 335—340; cf. A., 1923, ii, 711).—The law connecting the values of the maximum molecular absorption coefficients of two compounds in a homologous series with the numbers of hydrogen atoms in their molecules is obeyed also by the series: acetone, methyl ethyl ketone, methyl propyl ketone, and methyl butyl ketone, these compounds showing the ultra-red absorption band assumed to be characteristic of oscillators composed of hydrogen atoms united to carbon atoms.

T. H. P.

**Spectro-chemistry in the Ultra-red. VIII. Absorption of certain Halogenated Hydrocarbons.** G. B. BONINO (*Gazzetta*, 1925, **55**, 341—348; cf. preceding abstract).—With ethyl bromide, *s*-dibromo-, tetrachloro-, and pentachloro-ethane, and di- and trichloroethylene, a maximum value of the molecular absorption coefficient is shown in the ultra-red at  $3.51\mu$ , whilst with tetrachloroethylene and hexachloroethane no such maximum is observed.

T. H. P.

**Absorption Spectra of Benzophenone Derivatives.** T. TASAKI (*Acta Phytochim.*, 1925, **2**, 49—73).—Benzophenone in *M*/10,000 alcoholic solution shows an absorption band at frequency  $4000 \text{ \AA}$ ., uninfluenced by methylation of the benzene nucleus. Ortho- and para-hydroxy substitution have a much greater effect than meta-hydroxy substitution. The *o*-hydroxy derivative shows two bands, whilst *p*-hydroxy substitution has a bathochromic influence which is much stronger in the dihydroxy derivatives. The 2 : 3 : 4-substituted compounds show in general a broad band at frequency 3200. Substitution in both nuclei shows in general a greater effect than substitution in one nucleus. The structural formulæ of the naturally occurring cotoin, phloridzin, and phloretin are confirmed spectrographically.

P. W. C.

**Changes in the Ultra-violet Absorption of Gelatin.** T. T. BAKER and L. F. DAVIDSON (*Nature*, 1925, **116**, 172).—When the  $p_H$  of gelatin is above the isoelectric point ( $p_H 4.7$ ) there is a characteristic increase in absorption from about  $3500 \text{ \AA}$ . towards the red, whereas with a fall in  $p_H$  there is an increase in absorption in the region of shorter wave-lengths.

A. A. E.

**Fluorescence of Cadmium Vapour.** W. KAPUSCINSKI (*Nature*, 1925, **116**, 170).—When a beam of light containing radiation of wave-length below  $3000 \text{ \AA}$ . is passed through heated cadmium vapour, a blue fluorescence, strictly limited to the path of the exciting beam, appears first at  $450^\circ$ , is very pronounced at  $600^\circ$ —



750°, and can be observed with diminished intensity up to 950°. Diffusion of hydrogen through the silica container destroys the effect. The spectrum, which is analogous to the fluorescence spectrum of mercury vapour, shows a continuous band from 5000 to 3950 Å.; the maximal intensity is at approximately 4630 Å.

A. A. E.

**Regularities in the Resonance Spectrum of Iodine Vapour and the Determination of the Moment of Inertia.** A. KRATZER and E. SUDHOLT (*Z. Physik*, 1925, **33**, 144—152).—The fluorescence spectrum excited by the green mercury line is analysed and its term-formula obtained. The value found for the moment of inertia of the normal molecule is  $8.63 \times 10^{-38}$  g. cm.<sup>2</sup>, and the distance apart of the atoms  $2.87 \times 10^{-8}$  cm.

E. B. L.

**Influence of an Alternating Magnetic Field on the Polarisation of Resonance Radiation.** E. FERMI and F. RASETTI (*Z. Physik*, 1925, **33**, 246—250).—The resonance spectrum of mercury vapour was examined under the influence of a weak magnetic field of constant amplitude but variable frequency produced by a thermionic valve circuit. The depolarising effect diminished as the frequency diminished, for frequencies of the order a million per second.

E. B. L.

**Chemical Luminescence with Active Hydrogen.** K. F. BONHOEFFER (*Z. physikal. Chem.*, 1925, **116**, 391—400; cf. this vol., ii, 365).—Wood's active hydrogen produces visible luminescence with mercury, anthracene, the vapour of sodium and other alkali metals, and other substances. Spectrographic investigation showed that (i) Wood's hydrogen itself luminesces in the ultra-violet (3064 Å.); (ii) the hydride band is produced by the action of the gas on liquid mercury, a liquid hydride apparently being formed. The mercury line 2537 Å. also appears as a result of the latter reaction.

L. F. G.

**X-Ray Stimulation of Phosphorescence of Fused Silica.** F. L. HOPWOOD and W. V. MAYNEORD (*Nature*, 1925, **116**, 98).—After exposure to ultra-violet light, castor oil blackens a photographic plate only if the vapour is brought into contact with it. Silica, but not castor oil, when exposed to X-rays blackens a photographic plate, some specimens of silica exhibiting phosphorescence and fluorescence.

A. A. E.

**Light Filter in Interferometry.** J. B. FERGUSON (*J. Washington Acad. Sci.*, 1925, **15**, 279).—Visual acuity in work with the Rayleigh-Zeiss type of interferometer is increased by using the potassium dichromate-neodymium nitrate liquid filter.

R. A. M.

**Ionisation of Hydrogen by Electron Impact as Interpreted by Positive Ray Analysis.** T. R. HOGNESS and E. G. LUNN (*Physical Rev.*, 1925, [ii], **26**, 44—55).—Since at low pressures only H<sub>2</sub><sup>+</sup> ions are formed, the formation of H<sub>3</sub><sup>+</sup> ions increasing in proportion to the increase in pressure (as also did that of H<sup>+</sup>

ions up to 4%), the conclusions of Dempster and Smyth, that the primary process in the ionisation of hydrogen is the ionisation of the molecule without dissociation, are confirmed. The ionisation potential at 16 volts is that for the formation of  $H_2^+$ , a secondary process resulting also in the formation of  $H_3^+$ . The percentage of  $H^+$  ions produced by electron impact in helium containing hydrogen was greater than that of  $H_2^+$  ions, whilst no  $H_3^+$  ions were observed. Evidence was found for the existence of ions  $HeH^+$  and possibly  $HeH_2^+$ . A. A. E.

**Dielectric Constant and Molecular Association of some Liquids.** L. LANGE (*Z. Physik*, 1925, **33**, 169—182).—The dielectric constants of mixtures of organic liquids were determined by Nernst's method at various concentrations and temperatures. Debye's theory of the molecular dipole was applied to the results, and tables of molecular polarisation are given. The curves exhibiting the effect of concentration indicate that association occurred in every case except that of ethyl ether. The effect of increase of temperature is to decrease association, but the dipole moment may increase or decrease according to the type of compound. The values for this moment are given for eight substances of which the molecules are only slightly associated. E. B. L.

**Molecular Volume of Salts at the M. P.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1925, **145**, 88—94).—The molecular volumes of salts at the ordinary temperature are about 0.8 times those at the m. p. The molecular volumes of the alkali halides at the m. p. are only approximately additive. The molecular volumes of alkali halides, carbonates, sulphates, and nitrates increase with increasing atomic weight of the metal or halide and in the order nitrates > carbonates > sulphates. A. G.

**Theory of Colour Production.** J. STIEGLITZ (*J. Franklin Inst.*, 1925, **200**, 35—49).—A lecture, with experimental illustrations, describing the author's theory (cf. A., 1923, ii, 713). F. G. T.

**Calculation of Rotatory Power from Molecular Structure.** R. DE MALLEMANN (*Compt. rend.*, 1925, **181**, 106—108; cf. *ibid.*, 1923, **177**, 427).—Previous suggestions are made more precise by analysing the action of the intermolecular field. Account is taken of the variation of amplitude in the small volume under consideration, and of the particular value of the field at the points considered in evaluating equations of motion of each electron. This more detailed analysis does not modify the general form of the expressions previously obtained for molecular polarisation, refraction, and rotatory power. At the same time, the equations of motion may now be written in a symmetrical form, without this symmetry necessarily existing in the imaginary terms of the total polarisation. By these modifications the optical activity becomes calculable from the configuration of the molecular system. The simplest configuration compatible with optical activity is that of the irregular tetrahedron, and the rotatory power depends on the differences in length of the sides of this tetrahedron, and on the

products of the refractivities of the constituent atoms, taken three at a time. The order of the rotations thus calculated is that of the average experimental values for molecules of normal dimensions. F. G. T.

**The Co-ordination Theory in its Application to the Study of Mordant Dyes.** G. T. MORGAN and J. D. M. SMITH (*J. Soc. Dyers and Col.*, 1925, **41**, 233—241).—A résumé of work already published (cf. T., 1921, **119**, 704; 1922, **121**, 160, 2866; A., 1924, i, 1359. See also B., 1925, 664). W. A. S.

**Tridentate Groups in Complexes of Tetrahedral and Octahedral Symmetry.** J. D. M. SMITH (*J. Chem. Soc.*, 1925, **127**, 1682—1687).—Tridentate groups are those which can be attached at three points to a nuclear atom. They comprise three fused chelate groups represented by ABC to indicate the three chelate groups AB, AC, BC. Tridentate groups are classified according to the number of different chelate groups comprised and are of three types, AAA, AAB, and ABC. With tetrahedral complexes, only one main type is possible, consisting of one tridentate group and one unitary group. The main type gives three classes, (1) AAAb, (2) AABc, (3) ABCd, where the small letter represents the unitary group. Class (1) consists of a single optically inactive form, whilst (2) and (3) each consist of two optically active (enantiomorphous) isomerides. In octahedral complexes (co-ordination number 6), the remaining groups may be either unitary or chelate groups, and if one tridentate group is present there are three main types comprising twenty-four classes, which are tabulated and their isomerism and optical activity indicated. W. H.-R.

**Valency Relations : An Element of Atomic Number Zero with an Atomic Weight of Unity.** F. H. LORING (*Chem. News*, 1925, **131**, 50—52).—It is shown that an element having zero atomic number, zero valency, and an atomic weight of unity can be fitted into the periodic table (cf. Rutherford, A., 1920, ii, 541). The valencies of the elements are discussed in detail. G. M. B.

**Valency in Boron Compounds.** E. MÜLLER (*Z. Elektrochem.*, 1925, **31**, 382—385).—To explain the peculiar series of hydrides of boron, it is suggested that the two inner electrons of the boron atom can play a part in combinations as well as the three outer ones. Assuming that heteropolar hydrides can only be formed when there is no other way of arriving at a rare-gas configuration of the boron atom, it is shown that whilst homopolar  $\text{BH}_3$  cannot exist, homopolar  $\text{B}_2\text{H}_6$  may have one inner electron of each boron atom in common, so that the latter has the neon configuration. In the same way the hydrides  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_6\text{H}_{10}$ , and  $\text{B}_{10}\text{H}_{14}$  may be built up as chain compounds, and  $\text{B}_5\text{H}_9$  and  $\text{B}_5\text{H}_{11}$  as cyclic compounds. To account for the existence of  $\text{BMe}_3$ , one of the carbon atoms is supposed to have an inner electron in common with the boron atom. Among elements having two electron-shells, any two elements can form homopolar compounds by means of the

outer electrons only if the sum of the outer electrons is equal to or greater than 8 (or 5 if hydrogen is involved), but not otherwise; hence the exceptional position of boron. W. A. C.

**Metallo-organic Bases.** F. HEIN and H. MEININGER (*Z. anorg. Chem.*, 1925, **145**, 95—116).—The hydroxides  $\text{Sn}(\text{OH})_4$ ,  $\text{Hg}(\text{OH})_2$ ,  $\text{Pb}(\text{OH})_4$ ,  $\text{Tl}(\text{OH})_3$ , and  $\text{Cr}(\text{OH})_4$  are weak acids or very feeble bases, but, when all the hydroxyl groups except one are replaced by ethyl (or phenyl) radicals, relatively strong bases are obtained; thus the molecular conductivities at a dilution of 64 litres are:  $\text{SnEt}_3\cdot\text{OH}$ , 0.45;  $\text{HgEt}\cdot\text{OH}$ , 1.20;  $\text{PbEt}_3\cdot\text{OH}$ , 8.10;  $\text{TlEt}_2\cdot\text{OH}$ , 140.00;  $\text{CrPh}_3\cdot\text{OH}$ , 212.0. Triphenylchromium hydroxide is nearly as strong a base as sodium hydroxide. The alkalinity of the metallo-organic bases decreases with increasing weight of the organic radical. The nature of the metal has a predominating influence in determining the alkalinity, whilst in the corresponding compounds of sulphur, iodine, nitrogen, and phosphorus the central atom has little influence. This is probably because in the latter compounds the hydroxyl group is in the outer sphere of the co-ordinatively saturated central atom, whilst in the metallo-organic bases the hydroxyl group is more closely connected to the central atom. A. G.

**Lattice Energy of Ammines.** W. BILTZ and H. G. GRIMM (*Z. anorg. Chem.*, 1925, **145**, 63—87).—The lattice energy of ammines is equal to the sum of that of the ammonia-free salt and the heat of formation of the ammine. Ammines with different cations become increasingly similar as the number of ammonia molecules with which the cation is surrounded increases. The relative stability of the ammines of the different halides depends on the nature of the cation; when the heat of formation of the halides increases in the order chloride to iodide, then the stability of the ammines increases in this order also, and this is the case for the metals of the principal series of the periodic system. The heats of formation of the halides of the metals of the secondary series (*e.g.*, silver) increase in the order iodide to chloride, and the stability of the ammines is in this order also. The process of ammine formation may be divided into two stages, the expansion of the molecule of the original salt and the addition of ammonia to the cation. The heat of formation is then equal to the heat of co-ordination less the work done in the separation of the ions of the salt. These two quantities may be roughly calculated; the heat of co-ordination of hexamminepotassium iodide is 14 kg.-cal. per molecule of ammonia, and for salts of the alkaline-earth metals it has double this value. The calculated heat of formation of hexamminecalcium fluoride is negative and this agrees with the fact that it cannot be prepared from gaseous ammonia and crystalline calcium fluoride. A. G.

**Active Hydrogen.** H. COLLINS (*Chem. News*, 1925, **131**, 33—38).—Theoretical. A discussion of the condition of hydrogen in the water molecule in various states; and of various physical constants (thermochemical etc.) of hydrogen. B. F.

**Relationships between Hydrogen and Alkyl Compounds of Non-Metals.** A. VON GROSSE (*Ber.*, 1925, **58**, [B], 1342—1345).—Hantsch and Becker (this vol., ii, 359) have shown that the graph obtained by plotting the absolute b. p. of the alkyl halides against the number of carbon atoms contained in their molecule is a straight line from which the b. p. of the halogen acids can be derived if the value  $n = -1$  is used. This rule is also followed by the completely alkylated derivatives of the elements of the fourth, fifth, and sixth groups of the periodic systems, exceptions being met with in the hydrides of tellurium and polonium and in water and ammonia, which are associated. Similarly, if the molecular volumes of fully alkylated derivatives of elements of the sixth and seventh periods are plotted against  $n$ , a straight line is obtained from which, for  $n = 0$ , values are derived for the molecular volumes of the hydrides which agree well with those observed experimentally.

H. W.

**Refraction and Electron Constraint in Ions and Molecules.** C. P. SMYTH (*Phil. Mag.*, 1925, [vi], **50**, 361—375).—The forces necessary to displace the outer electrons in ions and molecules are calculated from the ionic and molecular refractions. It is shown that the electron constraint increases with increase of nuclear charge when the number of underlying shells remains the same, but with increase of the latter the constraint decreases. The constraint upon an electron in an ion is increased by the proximity of other ions or molecules, particularly if combination occurs. The values of the constraints for the bonding electrons in the group C·C, C·H, H·H, are given as  $9.58 \times 10^5$ ,  $6.79 \times 10^5$ , and  $5.6 \times 10^5$ , respectively. Unsaturation decreases the constraint; the value for the electrons in the C:C bond is  $5.58 \times 10^5$ . The constraints in various other electron groups are discussed.

A. B. M.

**Quantum Hypothesis and Gas Theory.** A. SCHIDLÖF (*Arch. Sci. phys. nat.*, 1924, [v], **6**, 281—293, 381—392).—Expressions are developed for the free energy and the entropy of a molecule of monatomic gas in a volume  $V$ , at a temperature  $T$ , first from the point of view of the generalised phase-space of Boltzmann and Gibbs, and, secondly, with an additional restriction, characteristic of the quantum hypothesis, that each element in the  $\lambda$  dimensional phase-space shall have a "volume"  $h\lambda$ , where  $h$  is Planck's constant. The quantum restriction only introduces a term  $\log 1/h^3$  into the expressions. This theory is open to the objection that both classical and quantum ideas are used which are not strictly compatible. Moreover, the application of quantised motions to a gas molecule would result in velocity "jump," especially if the temperature is low, comparable with the mean velocity given by statistical methods. A deduction of Planck's radiation formula is given. The statistical theory of Bose is applied to eliminate the above difficulties, and it is shown that the formulæ of the kinetic theory of gases are in accord with the quantum theory.

C. W. B.

**Determination of Molecular Dimensions and of Avogadro's Number from Colloidal Solutions.** P. L. DU NOUY (*J. Phys. Radium*, 1925, [vi], **6**, 145—153; cf. *J. Gen. Physiol.*, 1919, **1**, 521).—By the measurement of the force required to lift a platinum ring from the surface of a colloidal solution, surface tensions may be determined continuously from the freshly-agitated down to the static condition of the liquid. The static surface tensions of colloidal solutions, plotted against concentration, show steep and definite minima at definite concentrations. These occur, for sodium oleate at 22°, at 1 in 750,000 (64 dynes/cm.<sup>2</sup>), 1 in 1,220,000 (66 dynes/cm.<sup>2</sup>) and 1 in 1,390,000 (73 dynes/cm.<sup>2</sup>). After allowance is made for the sodium oleate adsorbed by the vessel, the thicknesses of surface-adsorbed oleate are found to be 12·30, 7·56, and 6·64 × 10<sup>-8</sup> cm., respectively. The three figures are considered to represent the dimensions of the sodium oleate molecule, which is oriented along its longest axis at the first and along the others at the second and third minima. Hence the volume of the sodium oleate molecule is calculated to be 617·44 × 10<sup>-24</sup> c.c.; the value of Avogadro's number,  $N$ ,  $6\cdot004 \times 10^{23}$ , follows directly. W. A. C.

**Precision X-Ray Measurements by the Powder Method.** F. C. BLAKE (*Physical Rev.*, 1925, [ii], **26**, 60—70).—Corrections were applied for (a) the unequal shrinking of the photographic films and the influence of humidity on their length, and (b) the influence of the substance examined on the absorption of the X-rays. The lattice constant for iron is  $2\cdot8603 \pm 0\cdot0002$  Å.

A. A. E.

**X-Ray Diffraction Patterns from Plant Fibres.** O. L. SPONSLER (*Nature*, 1925, **116**, 243).—The interplanar spacings 5·80, 3·30, and 2·60 reported by Herzog and Jancke (*Z. Physik*, 1920, **3**, 196) have been resolved, the new values being, respectively, 6·10, 5·40; 3·40, 3·20; 2·62, 2·58. The so-called 2·90 line did not appear when the  $K\beta$  wave-lengths were screened out.

A. A. E.

**Impulse Radiation and Compton's Scattered Radiation.** G. MIE (*Z. Physik*, 1925, **33**, 33—41).—The free electron is supposed to be capable of existing in stationary states of different internal energy; in the lowest or stable state it does not radiate, but in higher states it radiates according to the Bohr  $h\nu$  law. Impulse radiation is then explained as the result of a collision of the first kind (kinetic energy transformed into energy of excitation); the Compton scattered radiation is the reciprocal effect, it is the radiation which, according to the classical theory, must accompany the beginning of the sudden jump of the photo-electron ejected by the X-ray. The Compton electron and the photo-electron have the same origin, they differ merely in that the former completes its radiation and becomes a recoil electron whilst the latter suffers a collision of the second kind and receives kinetic energy instead.

E. B. L.

**Crystal Structure of Chromium and Titanium.** R. A. PATTERSON (*Physical Rev.*, 1925, [ii], 26, 56—59).—Chromium is body-centred cubic,  $a_0$  2·872 Å.; titanium is hexagonal close-packed,  $a_0$  2·951 Å., axial ratio  $c$  1·590; the computed densities are 7·23 and 4·49, respectively. Heat treatment does not affect the crystal form of titanium, but merely changes the size of the crystals.

A. A. E.

**Crystal Structure and Isomorphism of the Fluorides of Lithium and Magnesium.** A. FERRARI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 664—671).—A structure analogous to that of rutile is assigned to magnesium fluoride from X-ray measurements of the powdered crystals. The elementary cell has the dimensions  $a=4\cdot64$  Å.,  $c=3\cdot06$  Å.,  $c/a=0\cdot6596$ . The calculated density, 3·14, is in agreement with the observed. The X-ray intensities were calculated from the above measurements for magnesium fluoride, and from those of Bruni and Levi (this vol., ii, 281) for lithium fluoride. Results equally satisfactory were obtained from the formulæ of Debye and Scherrer, and of Ewald, which assume respectively that the intensities are proportional to the square of the structure factor, and to the structure factor. The volume of the elementary cell of lithium fluoride, containing 4 mols., is  $65\cdot55$  Å.<sup>3</sup>, and that of magnesium fluoride, containing 2 mols., is  $65\cdot85$  Å.<sup>3</sup>. It is suggested from these results that the isomorphism between these salts, of elements of different valency, is explained by the equality of the elementary cell volumes.

F. G. T.

**Crystal Structure of Alkali Monosulphides. I.** A. CLAASSEN (*Rec. trav. chim.*, 1925, 44, 790—794).—The crystal structure of lithium and sodium sulphides is determined by means of Debye-Scherrer photograms and is found to be of the fluorspar (face-centred lattice) type. The lattice parameter for lithium sulphide is 5·70 Å. and the number of lithium sulphide particles per unit cell is four. For sodium sulphide the lattice parameter is 6·53 Å., and hence assuming the fluorspar structure the density of the anhydrous sulphide is calculated to be 1·85, in good agreement with the value 1·89 determined experimentally by the pycnometric method in xylene. The sums of the atomic radii for lithium and sodium sulphides are 2·47 and 2·83 Å., respectively, in good agreement with the values 2·52 and 2·79 Å. obtained by Bragg (A., 1920, ii, 537).

J. W. B.

**Two-stage Transformation of Magnetite into Hämatite.** L. A. WELO and O. BAUDISCH (*Phil. Mag.*, 1925, [vi], 50, 399—408).—The change in magnetic permeability when magnetite is oxidised to ferric oxide at 220° has been measured; an increase in the maximum permeability from 2·93 to 3·39 was observed. When the magnetic ferric oxide was further heated at 550° in nitrogen, the permeability fell to 1·045, the value for the almost non-magnetic normal hæmatite. Magnetite can be heated at 800° in an inert atmosphere without permanent loss of permeability. By considering the crystal structure of magnetite, it is shown that the

extra oxygen required by the change  $2\text{Fe}_3\text{O}_4 \rightarrow 3\text{Fe}_2\text{O}_3$  can be inserted without undue strain, leaving the structure essentially unchanged. It is suggested that this structure represents the magnetic ferric oxide.

A. B. M.

**Magnetic Form of Ferrous Oxide.** J. B. FERGUSON (*J. Washington Acad. Sci.*, 1925, **15**, 279).—Since iron, ferric oxide, and ferro-ferric oxide undergo magnetic changes at  $790^\circ$ ,  $678^\circ$ , and  $530^\circ$ , respectively, ferrous oxide might be expected to behave similarly. Ferrous oxide containing ferro-ferric oxide was reduced to free iron and in the subsequent recombination of the free iron the decrease in magnetic permeability did not correspond with the decrease in the free iron content of the sample. The results indicate that there is a magnetic form of ferrous oxide.

R. A. M.

**Non-magnetic Films of Nickel.** L. R. INGERSOLL and S. S. DE VINNEY (*Physical Rev.*, 1925, [ii], **26**, 86—91).—Nickel films, sputtered in hydrogen with a direct-current generator at 1000 volts, are initially non-magnetic, but when heated at  $300$ — $400^\circ$  become magnetic. X-Ray spectrograms show that the magnetic film has the ordinary face-centred cubic lattice, but that the non-magnetic film is amorphous; it therefore appears that the ferro-magnetism of nickel is a property, not of the individual atom, but of the crystalline aggregate. The original film gave a very small Hall effect; its electrical resistance decreased on heat-treatment.

A. A. E.

**The Four Transverse Effects and their Relations in certain Metals.** E. H. HALL (*Proc. Nat. Acad. Sci.*, 1925, **11**, 416—422).—A theoretical discussion of the Hall and allied effects. The author's theory of electric and thermal conductivity explains qualitatively the four transverse effects and gives approximately the connexion between the values for thermomagnetic and electromagnetic coefficients.

R. A. M.

**Crystal Tempering: Softening of Hard-drawn Tungsten Single-crystal Wire.** F. KOREF (*Z. Metallk.*, 1925, **17**, 213—220).—Fine tungsten wires consisting of a single crystal may be softened by tempering for a short time above  $2100^\circ$  without recrystallisation taking place, provided that the amount of deformation which the metal has undergone does not exceed a certain critical limit depending on the nature of the drawing and the thickness of the wire. Thick wires readily recrystallise after only slight reduction in area, whereas thin wires may be reduced 80% in area before recrystallisation sets in on tempering. All metallic single crystals appear to be strained internally during growth, and unless this strain is removed by suitable tempering the metal works badly and readily recrystallises on subsequent annealing. The density of the wires increases during tempering and the electrical resistance also changes. [Cf. *B.*, 1925, 637.]

A. R. P.

**Electric Moments of the Molecules of Monocarboxylic Acids and their Esters.** C. P. SMYTH (*J. Amer. Chem. Soc.*, 1925, **47**, 1894—1900; cf. *A.*, 1924, ii, 810).—The electric moments



of a number of monocarboxylic acids and their esters have been calculated. The structures are assumed to be formed by the linking of atoms by electron pairs symmetrically located at the apices of regular tetrahedra. The causes of the differences in moments and the influence of chlorine substitution are considered. Support is given to the idea that valency forces are highly localised and directive in character.

J. S. C.

**Electrical Conductivity of Solid Crystal Hydrates.** S. JAKUBSOHN and M. RABINOVITSCH (*Z. physikal. Chem.*, 1925, **116**, 359—370; cf. A., 1923, ii, 822).—The specific conductivities of the hexahydrates of the nitrates of zinc, manganese, cobalt, nickel, and copper were measured both in the solid and liquid states, and by extrapolation of the data relating to the latter state the degree of loosening of the crystal lattice, at 25° below the m. p. of each salt, was calculated. The conductivities of the solid salts increase from zinc to copper. Colour and conductivity are correlated.

L. F. G.

**Distilled Water in Biological Work.** E. CANALS and R. GENEVET (*Bull. Soc. Chim. biol.*, 1925, **7**, 673—677).—Redistillation in glass vessels of water previously distilled from copper vessels, first from chromic acid and then from barium hydroxide, causes successive decreases in its conductivity. Water redistilled from barium hydroxide, and thus having a  $p_H$  nearer neutrality, attacks glass more readily than that distilled from acid. The purest water from an all-glass distillation apparatus had a conductivity of  $1.9 \times 10^{-6}$  and  $p_H$  6.4 at 15°.

H. J. C.

**Spectro-chemistry of Compounds Containing Nitrogen.** K. VON AUWERS and R. KRAUL (*Z. physikal. Chem.*, 1925, **116**, 438—465).—Optical data (refraction and dispersion) and densities are given for aniline, diphenylamine, carbazole, acridine, pyridine, quinoline, and a number of their derivatives. The relations between the chemical constitution and optical properties of these substances are discussed, and correlated with earlier observations.

L. F. G.

**New Determinations with the Micro Bomb Calorimeter.** II. M. PADOA and B. FORESTI (*Ber.*, 1925, **58**, [B], 1339—1342; cf. A., 1923, ii, 737).—Determinations of the heat of combustion of benzoic acid and sucrose show that the authors' method is not inferior to any of those generally employed. The amount of material required in ordinary determinations is 0.01, in precise determinations 0.05—0.03 of that which is customary.

H. W.

**Lattice Energies, Heats of Hydration, and Heats of Solution.** E. LANGE (*Z. physikal. Chem.*, 1925, **116**, 337—349).—Theoretical. Recently obtained data on the heats of solution of six alkali halides (this vol., ii, 791) are used to substantiate Born's formula for the lattice energies. It is probable that the repulsion term,  $n$ , in the formula has not the same value for all sodium and potassium halides. The heats of hydration of the ions in a saturated aqueous sodium iodide solution are calculated approximately and are smaller than those calculated by Fajans for infinite dilution.

L. F. G.

**Determination of the Heat of Dissociation of Mercury Molecules from the Band Spectrum of Mercury Vapour.** E. KOERNICKE (*Z. Physik*, 1925, **33**, 219—230).—The mercury band at 2540 Å., just on the long wave-length side of the bright mercury line, is ascribed to the molecule  $\text{Hg}_2$ . From the strength of this absorption band at various temperatures and pressures the heat of dissociation is found to be 1.4 kg.-cal., the strength of the absorption being taken as an indication of the relative number of molecules present. E. B. L.

**Possible Limits for the Heat of Dissociation of Oxygen.** O. R. WULF (*J. Amer. Chem. Soc.*, 1925, **47**, 1944—1945).—The heat of dissociation of molecular oxygen into atomic oxygen is greater than 56,400 and less than 137,400 cal. per mole. J. S. C.

**Improved Differential Method for the Exact Determination of Specific Heats of Aqueous Solutions; Including Results for Various Salts and Organic Acids.** T. W. RICHARDS and F. T. GUCKER, Jr. (*J. Amer. Chem. Soc.*, 1925, **47**, 1876—1893).—The apparatus and technique for the precise determination of specific heats are described. The specific heats of thirteen solutions have been determined with an accuracy of 1 in 10,000. The results have been recalculated in terms of absolute heat capacity and also reduced to instantaneous heat capacities at 14°, 16°, 18°, 20°, and 22°. The minimum heat capacity of each solution occurs at a temperature lower than that of water. J. S. C.

**M. P. of Inorganic Compounds and of Elements.** E. FRIEDERICH and L. SITTIG (*Z. anorg. Chem.*, 1925, **145**, 251—276; cf. this vol., ii, 374).—Considering uni-, bi-, ter-, and quadri-valent compounds of the type  $\text{AB}_1$  (of which sodium fluoride, calcium oxide, scandium nitride, and titanium carbide may be taken as representatives), it is found that the number of valencies between the two elements exercises a fundamental influence on the m. p. Thus, lithium fluoride has m. p. 1115° Abs., magnesium oxide, m. p. 2920° Abs., titanium nitride, m. p. 3200° Abs., and niobium carbide, m. p. 4100° Abs. In compounds  $\text{A}_1\text{B}_1$  of the same valency, the highest m. p. is found when there is approximate equality of the atomic or ionic volumes of the constituents. If the volume of the cation is small compared with that of the anion, a low m. p. may be expected (e.g., lithium fluoride, chloride, and bromide compared with the corresponding sodium compounds). The magnitude of the volume of the anion of a compound appears to exercise an extreme influence on the position of the m. p., which decreases with increase in size of the anion. The condition for a compound to be gaseous at low temperatures is that the anion must be overwhelmingly great in comparison with the cation. The ratio necessary may be approximately calculated from Henglein's relation between molecular volume and m. p. (cf. A., 1922, ii, 44). The conclusions reached from a study of the m. p. of compounds are applied to the elements, special attention being paid to the influence of valency. The m. p. of elements may be considered as a function

of the force by which the atoms are held together by means of the valency electrons. By plotting *m. p.* against valency, it is concluded that at that region of the periodic system where metal passes into metalloid, the atoms possess the greatest possibility of mutual binding of the electrons, and the highest *m. p.* are also to be found.

L. L. B.

**Structure of Glass.** N. SELJAKOV, L. STRUTINSKI, and A. KRASNIKOV (*Z. Physik*, 1925, **33**, 53—62).—The index of refraction and coefficient of expansion of glass show a maximum near 575°. This is the transition temperature of  $\alpha$ - to  $\beta$ -quartz. Since *X*-ray analysis of glass shows no signs of small crystals of quartz, it is suggested that the peculiarity at this temperature is due to a change in the molecule of the silicate and that glass can truly be regarded as a supercooled, amorphous fluid. The structure of  $\alpha$ -cristobalite is deduced from *X*-ray data and that of  $\beta$ -cristobalite is suggested.

E. B. L.

**Stability Relations of the Modifications of the Polymorphous System  $\text{Al}_2\text{SiO}_5$ .** F. NEUMANN (*Z. anorg. Chem.*, 1925, **145**, 193—238).—From specific heat determinations and the application of Nernst's heat theorem, the *A*—*U* and *U*—*U*<sub>0</sub> relations for andalusite, disthene, and sillimanite have been investigated. Measurements have also been made with mullite, consisting of 62.89%  $\text{Al}_2\text{O}_3$  and 37.11%  $\text{SiO}_2$ . The heats of transformation of the four modifications were determined by measurement of the heats of solution in 40% hydrofluoric acid. The values 90.13, 89.67, 83.42, 83.67 cal./mol. were found for the heats of solution of andalusite, disthene, sillimanite, and mullite, respectively, the experimental temperature being between 14° and 15°. The mean specific heats between the ordinary temperature and 300° to 1300° or 1400° were determined by the calorimetric mixture method, and from the values found the true specific heats were obtained graphically, with a mean error of  $\pm 0.5\%$ . From these, the molecular heats were calculated and plotted against temperature. Molecular heat values are also tabulated for temperatures down to that of liquid hydrogen. The values at low temperatures are proportional to the cube of the absolute temperature, the proportionality factor for andalusite being  $383 \times 10^{-7}$ , for sillimanite,  $310 \times 10^{-7}$ . This holds up to about 25° Abs. The *A*—*U* diagram for the system andalusite-sillimanite shows that, at atmospheric pressure from -273° to 1487°, sillimanite is the stable modification, whilst at higher temperatures andalusite is stable. The diagram for the disthene-sillimanite system shows that disthene is totally unstable. The andalusite-disthene diagram is not given, on account of the small difference between the heats of solution of these modifications. On heating at 1200°, andalusite undergoes a considerable change of structure, being converted into mullite and amorphous silica. Disthene is also converted into mullite and silica by heating at 1400°, but sillimanite undergoes no change on heating at 1300°.

L. L. B.

**Calculation of the Vapour Pressure of a Solution of a Non-volatile Solute.** S. B. MALI (*Phil. Mag.*, 1925, [vi], 50, 141—145).—Theoretical. The case of a solvent which is monatomic in both the liquid and vapour states is considered. Stern's method (*Physikal. Z.*, 1913, 14, 629) is modified by making allowance for the fact that the mutual attraction of the solute molecules and the surrounding solvent molecules results in the distribution of the solvent molecules just around a solute molecule being somewhat different from the distribution at points further away from the solute molecules. Further, owing to the presence of the solute molecules, the general distribution of the solvent molecules at points beyond the immediate influence of the solute molecules will be somewhat different from that in the pure solvent, even although solution is unaccompanied by any volume change. Subject to modifications for these effects, Stern's method leads to the equation  $\log p = -\lambda_0'/kT - 0.5 \log T + \log (2\pi m)^{3/2} \nu^3 / \sqrt{k}$ , where  $\lambda_0'$  denotes the latent heat of evaporation of a gram-mol. of solvent from the solution, and  $m$  and  $\nu$  the mass and vibration frequency respectively of a solvent molecule. This expression differs only in the first term from that of Stern for the vapour pressure of the pure solvent, and, combined with the latter, leads directly to Raoult's law. F. G. T.

**Vapour Pressures of Common Metallic Chlorides and a Static Method for High Temperatures.** C. G. MAIER (*U.S. Bur. Mines, Tech. Paper* 360, 1925).—A static method of determining vapour pressures up to 1250° is described which involves no assumptions relative to the behaviour of the vapour according to the gas laws. Vapour pressure data for the commoner metallic chlorides, accurate enough for technical purposes, are recorded, together with the b. p. and the calculated heats of vaporisation. The vapour pressure of barium chloride is very small; that of calcium chloride is too small to measure. Ferric chloride, manganous chloride, and possibly cobalt chloride show traces of thermal dissociation at about 1000°. At high temperatures, the double salt,  $\text{NaAgCl}_2$ , appears to be formed from the separate chlorides; it has a vapour pressure greater than the sum of the vapour pressures of the separate chlorides at a definite temperature. The results for lead chloride agree with those of Eastman and Duschak (*U.S. Bur. Mines, Tech. Paper* 225, 1919); the vapour pressures of arsenic trichloride do not agree well with those found by Baxter, Bezzenberger, and Wilson (*A.*, 1920, ii, 531). Cupric chloride has no measurable vapour pressure below its decomposition temperature. Anhydrous zinc chloride is prepared by passing chlorine over anhydrous zinc oxide at 600—700°. S. K. T.

**Saturation Pressure of Liquids at Corresponding Densities.** W. HERZ (*Z. anorg. Chem.*, 1925, 145, 378—380; cf. this vol., ii, 494).—The ratio  $p_{T_2} : p_K$ , where  $p_{T_2}$  is the saturation pressure at the absolute temperature,  $T_2$ , at which the density is twice the critical density, approximates to a mean value of 0.464 for a large number of organic liquids and liquefied gases. Notable exceptions are helium (too low), tin tetrachloride (too low), methyl and ethyl

alcohols (too high). Ratios of pressures at temperatures corresponding with densities 2.75 times the critical density are also given, but the agreement is not good. L. L. B.

**Isotherms of Several Gases between  $+400^{\circ}$  and  $-183^{\circ}$ .** L. HOLBORN and J. OTTO (*Z. Physik*, 1925, **33**, 1—11).—Tables of new values of  $pv$  are given for hydrogen and neon, and also tables for helium, nitrogen, air, argon, and oxygen. E. B. L.

**Preparation and Analyses of Constant Mixtures of Air and Carbon Dioxide.** J. JOHNSTON and A. C. WALKER (*J. Amer. Chem. Soc.*, 1925, **47**, 1807—1817).—Marked changes in the direction or velocity of the wind are usually accompanied by variations in the carbon dioxide content of the air. An artificial mixture of air and carbon dioxide in fixed proportion is obtained on allowing air, under a constant pressure-head, to stream past one surface of a thin rubber diaphragm, and carbon dioxide, also under a constant head, to stream past the other surface. Carbon dioxide diffuses through the rubber much faster than the air, and the thin rubber sheet serves to regulate the mixing. The composition of the resulting mixture, under comparable conditions, depends on the effective area of the diaphragm. Certain refinements are introduced into the Pettenkofer method for the determination of carbon dioxide in air. J. S. C.

**Vapours of the System Acetic Acid-Water.** G. POVARNIN and V. MARKOV (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 381—382).—Preliminary results are given for the relation between the b. p. of aqueous acetic acid and the percentages of the acid in the liquid and in the vapour. For the 77% acid, corresponding with  $C_2H_4O_2 + H_2O$ , the vapour contains approximately 62.5% of acid, corresponding with  $C_2H_4O_2 + 2H_2O$ . T. H. P.

**Physical Equilibrium in the System Acetic Acid-Acetic Anhydride.** G. POVARNIN and V. MARKOV (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 375—380).—The relation between the composition of the liquid and vapour phases is given by the equation  $x(100-y)/y(100-x) = 0.419 \mp 0.030$ , where  $x$  and  $y$  denote the percentage concentrations of the anhydride in the vapour and liquid respectively. The b. p. varies linearly with the composition and is given by the expression,  $T = 118^{\circ} + (22.7^{\circ} \pm 1.7^{\circ})y$ . If suitable scales are used, the curve connecting b. p. and composition of the vapour coincides with that showing the relation of composition of vapour to composition of liquid. T. H. P.

**Reversible Anomaly of Copper-Nickel Alloys in the Paramagnetic Region.** P. CHEVENARD (*Compt. rend.*, 1925, **181**, 28—31).—The thermo-electric power, coefficient of thermal expansion, and electrical resistivity of copper-nickel alloys change suddenly at  $450^{\circ}$  in alloys containing about 50% Cu, the maximum effect occurring in the 52% Cu alloy (approximately CuNi).

A. R. P.

**Solubility of Mixtures of Hydrogen and Nitrogen in Liquid Ammonia.** A. T. LARSON and C. A. BLACK (*Ind. Eng. Chem.*, 1925, **17**, 715—716).—The solubilities of hydrogen and nitrogen (3:1) in liquid ammonia have been determined between  $-25^{\circ}$  and  $+22^{\circ}$  at pressures of 50, 100, and 150 atm. The temperature coefficient is positive and the solubility is very nearly proportional to the pressure. [Cf. *B.*, 1925, 669.] D. G. H.

**Solubilities of Sulphur Dioxide and Ammonia in Water.** T. K. SHERWOOD (*Ind. Eng. Chem.*, 1925, **17**, 745—747).—The partial pressures of sulphur dioxide and ammonia over their aqueous solutions have been tabulated and graphed. [Cf. *B.*, 1925, 669.] D. G. H.

**Solubility of the Crystallohydrates of Nickel Sulphate.** N. V. TANCOV (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 335—341).—The solubilities of heptahydrated, blue hexahydrated, and green hexahydrated nickel sulphates per 100 parts of water are, respectively:  $20^{\circ}$ , 37.70, 40.09, 44.37;  $25^{\circ}$ , 40.40, 41.56, 45.36;  $30^{\circ}$ , 43.28, 43.56, 46.56;  $35^{\circ}$ , 47.03, 45.58, 47.76;  $40^{\circ}$ , 50.42, 47.60, 49.16. The corresponding temperature coefficients of solubility at  $30^{\circ}$  are 0.67, 0.49, and 0.24, respectively. The heptahydrate passes into the blue hexahydrate at  $31.55^{\circ}$ , and into the green hexahydrate at  $36.7^{\circ}$ . T. H. P.

**Influence of Pressure on the Solubility of Substances. V. The System Naphthalene-Tetrachloroethane.** E. COHEN, W. A. T. DE MEESTER, and A. L. T. MOESVELD (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 108—118).—The solubility of naphthalene in tetrachloroethane has been measured at  $30^{\circ}$  under pressures up to 1000 atm., the apparatus being similar to that previously described (A., 1923, ii, 386). The results are expressed very closely by the equation  $\log c = 1.54504 - 0.26840 \times 10^{-3}p + 0.0432 \times 10^{-6}p^2$ , where  $c$  is the concentration in g. per 100 g. of solution, and  $p$  is the pressure in atmospheres. The existence of a minimum solubility, shown possible on theoretical grounds, is not established within the range of pressure investigated. A. B. M.

**Solubility Relations of Isomeric Organic Compounds. I.** J. JOHNSTON (*J. Physical Chem.*, 1925, **29**, 882—888).—The study of the equilibrium diagrams of *ortho*, *meta*, and *para* isomerides has been undertaken with a view to determine the relative proportion of these isomerides in reaction mixtures. The theory of ideal solutions is discussed. F. G. S.

**Solubility Relations of Isomeric Organic Compounds. II. Determination of Freezing Temperatures of Binary Mixtures.** D. H. ANDREWS, G. T. KOHMAN, and J. JOHNSTON (*J. Physical Chem.*, 1925, **29**, 914—925).—An apparatus for the accurate determination of time-temperature curves for pure substances and for binary or ternary mixtures is described. The principal advantages are: the effective temperature head is controlled and measured, only small quantities of material are necessary, and the temperature

is measured by means of a thermo-element of small heat capacity and small lag. The theory of cooling curves and the mode of interpretation of such curves for binary mixtures are discussed.

J. S. C.

**Solubility of Ampholytes.** H. VON EULER and K. RUDBERG (*Z. anorg. Chem.*, 1925, **145**, 58—62).—According to Bjerrum's theory (A., 1923, i, 444), the solubility of ampholytes should be increased by the addition of neutral salts. This is not the case for the pairs *l*-tyrosine-sodium chloride, *l*-tyrosine-lithium nitrate, and leucine-sodium chloride, but the solubility of glycylglycine is slightly increased by the addition of sodium chloride. The solubilities of amino-acids should also be greater in the presence of each other, but this is not the case for *dl*-leucine and *l*-tyrosine. In agreement with the theory, methyl-orange is more soluble in a dilute glycine solution than in water. Measurements of the influence of  $p_H$  on the solubility of glycine are in agreement with those of Kolthoff (this vol., i, 296).

A. G.

**Solubility and Size of Grain.** D. BALAREV (*Z. anorg. Chem.*, 1925, **145**, 122—126).—The increase in electrical conductivity of a saturated solution of barium sulphate, which occurs when the crystals are rubbed, is probably due to (1) the presence of barium chloride in the sulphate, (2) the greater solubility of broken than of complete crystals, and (3) the breaking up of atomic complexes. It is doubtful whether the greater solubility of small particles is an important factor. The subsequent fall in conductivity (cf. A., 1901, ii, 493; 1905, ii, 247) may be due partly to the crystallisation of barium sulphate on account of the dissolution of the chloride, but the velocity of crystallisation is much greater than the rate of fall of conductivity and the latter is probably mainly due to the slow restoration of equilibrium between the complete and broken crystals.

A. G.

**Supersaturated Solutions. I. Mechanism of Separation of Salts from Supersaturated Solutions and the Formation of Rhythmic Precipitates in Gels.** W. M. FISCHER (*Z. anorg. Chem.*, 1925, **145**, 311—364).—If supersaturated solutions of salts with valency product 1 are inoculated and shaken, crystallisation occurs immediately for the smallest degree of supersaturation. When the valency product is greater than 1, there is an induction period for slightly supersaturated solutions, during which no crystallisation occurs. At a certain supersaturation, this period vanishes, and crystallisation occurs immediately after inoculation. Salts which show an induction period possess, under the same conditions, a greater dissolution velocity than crystallisation velocity. The connexion between the length of the period ( $t$ ) and the degree of supersaturation ( $x$ ) is given by the relation  $x/\sqrt{t}=\text{constant}$  [although the author's numerical results and curves show that  $x$  decreases linearly with increase in  $\sqrt{t}$ .—ABSTR.]. The same relation,  $x/\sqrt{t}=\text{const.}$ , applies to rhythmic precipitation, which occurs only with those salts which show an induction period. In the presence of agar-agar, gelatin, and dyes, all sparingly soluble salts can be

obtained as rhythmic precipitates. In accordance with a new theory of rhythmic precipitation, based on the variation of the time of precipitation from supersaturated solutions, periodic precipitates of barium sulphate and strontium sulphate have been obtained. It is found that a relation exists between the length of the induction period for a given degree of supersaturation and the cube of the crystallisation velocity of the salt. The larger the period, the smaller is the cubic crystallisation velocity. L. L. B.

**Equilibrium between two Liquid Phases in the System Aniline-Acetic Acid-Water.** E. ANGELESCU and D. MOTZOC (*Bul. Soc. Chim. România*, 1925, 7, 11—24).—A study of the effect of acetic acid on the mutual solubilities of aniline and water has shown that with certain constant proportions of acetic acid closed solubility curves are obtained having an upper and a lower critical temperature. The formation of these curves indicates that a readily hydrolysed aniline acetate is formed in the solution. A. R. P.

**Adsorption of Water from the Gas Phase on Plane Surfaces of Glass and Platinum.** I. R. MCHAFFIE and S. LENHER (*J. Chem. Soc.*, 1925, 127, 1559—1572).—The adsorption of water on surfaces of glass and platinum has been studied by a new method in which a limited quantity of water was placed in an evacuated vessel of known dimensions, and the pressure measured at different temperatures. Above a certain temperature the pressure-temperature curve is linear, and the total number of water molecules present can be calculated. At lower temperatures, owing to adsorption, the pressure is less than the expected value, and the amount of water adsorbed can be calculated from the decrease in pressure. The adsorption and its accompanying free energy change are much greater on glass than on platinum. The thickness of the adsorbed film varies from 0 to 39 layers of molecules, according to the temperature and pressure. With platinum surfaces, this kind of adsorption begins at a definite pressure, below which no measurable adsorption occurs. W. H.-R.

**Absorption of Hydrogen by Cerium, Lanthanum "Mischmetall," and Cerium-Magnesium Alloys.** A. SIEVERTS and E. ROELL (*Z. anorg. Chem.*, 1925, 146, 149—165; cf. A., 1924, ii, 185).—Using (1) impure cerium containing 95% of cerium and 4% of other rare-earth metals, (2) a lanthanum "mischmetall" containing 10% of cerium, and, (3), cerium-magnesium alloys containing up to 12% of magnesium, the absorption of hydrogen has been studied at temperatures from 20° to 1200°. For hydrogen at atmospheric pressure, the temperature-absorption curves of cerium and lanthanum "mischmetall" follow one another closely and show a marked fall in absorption between 1100° and 1200°. At 1100°, saturation can only be reached by heating specimens previously saturated at a lower temperature or by immediately treating the molten metal with hydrogen. If at 1100° specimens are first treated with hydrogen at low pressure, they will not take up the full amount of hydrogen necessary for saturation if the



pressure is raised. Saturated specimens lose all their hydrogen on prolonged keeping in a vacuum; their pressure-absorption isotherms show the general form previously described (Sieverts, *loc. cit.*), but are not satisfactorily reproducible. Unsaturated products do not lose all their hydrogen in a vacuum, and show normal absorption isotherms. The addition of 12% of magnesium only slightly lowers the absorptive power of cerium. These alloys are pyrophoric, but an alloy containing approximately 80% of cerium, 11% of magnesium, and 6% of aluminium is stable in air. Hydrogen from commercial compressed cylinders is absorbed less than electrolytic hydrogen, probably owing to the presence of organic sulphur compounds. W. H.-R.

**Absorption of Arsenic and Oxalic Acids by Certain Calcined Oxides.** P. P. KOZAKEVITSCH (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, 55, 477—492).—The dependence of the composition of the precipitates formed by the interaction of various oxides with arsenic and oxalic acids on the concentration of the acid in the liquid phase has been investigated (cf. Cox, A., 1904, ii, 563; 1906, ii, 757). T. H. P.

**Adsorption of Silver Salts by Silver Iodide.** J. S. BEEKLEY and H. S. TAYLOR (*J. Physical Chem.*, 1925, 29, 942—954).—Investigations on the adsorption of various uni-univalent silver salts by silver iodide at 25° show that the order of decreasing adsorbability is: benzoate (1.4), acetate (8.2), nitrite (3.2), bromate (1.0), naphthalenesulphonate (4.8), benzenesulphonate (170), nitrate (1860), chlorate (100), ethylsulphate (1540), perchlorate (3240). The figures in parentheses denote the relative solubilities at 25°, the solubility of silver bromate, 0.0081 millimol. per g. of water, being taken as unity. Although there is no quantitative connexion between adsorbability and solubility, the less soluble salts are more strongly adsorbed than the more soluble salts. J. S. C.

**Adsorption and Schulze's Law.** H. B. WEISER (*J. Physical Chem.*, 1925, 29, 955—965).—Schulze's law is merely a qualitative rule. The view of Dhar and others (A., 1924, ii, 737), that ions with the lowest precipitating power are adsorbed the most and *vice versa*, is disproved. The adsorption of barium ion during precipitation of arsenious sulphide sols has been determined from solutions of barium chloride and from mixtures of barium chloride with hydrogen chloride and the alkali metals. The adsorption of barium is reduced by the univalent ions in the order: hydrogen > potassium > sodium > lithium, which gives therefore the order in which these univalent ions are adsorbed. The same series is derived from the precipitation values, the salt containing the most readily adsorbed cation precipitating in lowest concentration. This method of determining relative adsorbabilities is of general application. The amounts of precipitating ion carried down on precipitation of a sol are determined by (i) adsorption by the electrically charged particles during neutralisation, (ii) adsorption by the neutral particles during agglomeration. The amounts of

(i) will, under comparable conditions, be equivalent, but those of (ii) will vary with the nature and concentration of the electrolyte. The adsorption values approach equivalence the less the adsorption capacity of the precipitated particles; thus the values are more nearly equivalent with arsenious sulphide sols than with hydroxide sols which have a large adsorption capacity. J. S. C.

**Capillarity and Wetting.** K. SCHULTZE (*Kolloid-Z.*, 1925, 37, 10—17; cf. this vol., ii, 287).—The height of capillary rise, the influence on the formation of solutions, and the wetting of capillaries of non-circular cross-section are discussed. E. M. C.

**Adsorption Activity and Surface Energy of Solids.** B. ILJIN (*Z. physikal. Chem.*, 1925, 116, 431—437; cf. A., 1924, ii, 663; *Physikal. Z.*, 1924, 25, 369).—Theoretical. Three different methods give the following values for the effective adsorbing surface of 1 g. of charcoal:  $10^5$ ,  $3.3 \times 10^5$ ,  $1.8 \times 10^5$  sq. cm. The heat of adsorption for the same mass of a particular gas on equal areas of quite different surfaces (charcoal, mica) is constant. The surface energy of an adsorbent is correlated with the heat of adsorption, the dielectric constant, and the thickness of the film of the adsorbed gas. L. F. G.

**Theory of Adsorption and Partition.** A. FRUMKIN (*Z. physikal. Chem.*, 1925, 116, 501—503).—Theoretical. The work done in transferring a molecule of a member of an homologous series from one phase to another is a term of an arithmetical progression; the partition coefficient is therefore a term of a geometrical progression. Consideration of the work done in transferring  $\text{CH}_2$  groups from the surface of solutions of fatty acids to the space above leads to the conclusions of Langmuir and of Adam (A., 1922, ii, 687) regarding the orientation of these substances. L. F. G.

**Simple Method of Testing Gibbs' Theorem.** A. FRUMKIN (*Z. physikal. Chem.*, 1925, 116, 498—500).—A dilute solution, of known strength, of lauric acid in light petroleum was added drop by drop to a measured water surface until no further change of surface tension indicated the formation of a saturated adsorption layer. The water surface is saturated by  $5.2 \times 10^{-10}$  mol. of lauric acid per sq. cm., Gibbs' equation giving  $5.7 \times 10^{-10}$  mol./cm.<sup>2</sup> L. F. G.

**Capillary Curves of Higher Fatty Acids and the Equation of State of the Surface Film.** A. FRUMKIN (*Z. physikal. Chem.*, 1925, 116, 466—484).—The surface tensions of octoic, decoic, and lauric acids were measured by Wilhelmy's method; the results are expressed graphically. The difference between the form of the curves for these acids and of those for the lower fatty acids is ascribed to the occurrence of attractive forces and of condensation phenomena in the adsorbed film (cf. Adam, A., 1921, ii, 488; 1922, ii, 687; 1923, ii, 539; this vol., ii, 195; *Proc. Roy. Soc.*, 1922, A,

101, 452), *i.e.*, the adsorbed films approximate in their behaviour to the unimolecular films which the insoluble fatty acids form on a water surface. By the introduction of a term which corrects for the mutual attraction of the adsorbed molecules, Szyzskowski's equation is modified to a form which gives fair agreement with the observed data. A comprehensive theory must allow, however, for the formation of molecular aggregates. L. F. G.

**Effect of Sodium Hydroxide on the Surface Tension of a Solution of Sodium Nonoate.** W. D. HARKINS and G. L. CLARK (*J. Amer. Chem. Soc.*, 1925, **47**, 1854—1856).—The surface tension of 0.1*N*-sodium nonoate at 20°, 20.2 dynes/cm., is increased to 48.8 dynes/cm. in presence of 0.008*N*-sodium hydroxide, further addition of base causing a linear decrease. The results indicate that the extremely low surface tension of sodium nonoate solutions is due to a surface film of the salt together with nonoic acid formed by its hydrolysis. The amount of colloid present in these solutions is by no means negligible (*cf.* McBain and Martin, *T.*, 1914, **105**, 967), and the state of the colloid is dependent on the hydroxyl-ion concentration of the solution. J. S. C.

**Surface Tension of Gelatin Solutions of Different Hydrogen-ion Concentration.** L. DE CARO (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 729—733).—Surface tension measurements of 2% gelatin solutions with varying hydrogen-ion concentrations have been made at 30° by the stalagmometric method. These solutions behave like those of other proteins. With increasing hydrogen-ion concentration, the surface tension rises to a maximum between  $p_H$  8 and 9, falls then to a minimum at about  $p_H$  4.5, and finally, in acid solutions, passes through a second maximum at  $p_H$  3, which is lower than that occurring in alkaline solutions.

The author accepts the explanation advanced by Bottazzi and d'Agostino (*A.*, 1913, ii, 115), according to which the protein lowers the surface tension of the solvent most when it is present in non-dissociated form. F. G. T.

**Surface Concentration of Casein, Crystalline Egg-albumin, and Crystalline Hæmoglobin.** J. M. JOHLIN (*J. Physical Chem.*, 1925, **29**, 897—913).—The changes of surface tension with time of aqueous solutions of casein, egg-albumin, oxyhæmoglobin, reduced hæmoglobin, and hæmoglobin-carbon monoxide and the influence of the addition of acid and alkali on the surface tensions of the first two substances have been investigated at 25° by the capillary rise method. The surface tension decreases with time according to the author's equation (this vol., ii, 388), the behaviour of alkaline solutions of egg-albumin being exceptional in that periodicity is observed. J. S. C.

**Adsorption of the Phosphoproteins of Yeast by Various Adsorbents and the Elution of the Adsorbates.** A. FODOR and R. SCHÖNFELD (*Kolloid-Z.*, 1925, **37**, 37—40).—The phosphoprotein of macerated yeast is readily adsorbed by aluminium and

ferric hydroxides and to a less extent by kaolin. The adsorption results in a loosening of the combination between phosphoric acid and the protein. The phosphoprotein precipitated by acid from macerated yeast gives up small quantities of phosphoric acid on treatment with ammonia. The elution with ammonia of the kaolin adsorbate liberates a considerable amount of phosphoric acid. A second eluate with ammonia of the aluminium hydroxide adsorbate gives a greater quantity of phosphoric acid than does the first, whilst in the case of the ferric hydroxide adsorbate traces only are obtained.

E. M. C.

**Adsorption and Heterogeneous Catalysis.** I. E. V. ALEKSEEVSKI (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 403—433).—Animal charcoal which has been heated and subsequently cooled in a desiccator acts as an extremely active adsorbent towards gases and vapours and retains its properties unchanged for a long period. The adsorption of a vapour is greatly accelerated if air saturated with the vapour is passed over the adsorbent. The results obtained with a large number of liquid organic compounds of various types show that the absorption does not depend on the physical constants, but is influenced greatly by the chemical nature of the compounds. Adsorption of acetylene, ethylene, isobutylene, alcohol, and benzene by catalysts such as floridin, alumina, powdered glass, kaolin, etc., is much less pronounced than by animal charcoal. The influence of charcoal on the reaction between ethylene and chlorine, and on various syntheses in which acetylene participates, has been investigated. T. H. P.

**Hydration and Solution.** H. A. TAYLOR (*J. Physical Chem.*, 1925, **29**, 995—1003).—The present position of the hydrate theory is reviewed and various criticisms are offered. From a study of the partition ratio of hydrochloric acid between benzene and aqueous solutions of various neutral salts and of glycerol, it is concluded that these aqueous solutions behave like pure water, there being no difference between combined and free water. This conclusion is confirmed by a study of the effect of sodium and potassium chlorides at *N* concentration on the partial pressure of hydrogen chloride over its concentrated aqueous solutions.

J. S. C.

**Molecular Weight and Solution.** W. D. BANCROFT (*J. Physical Chem.*, 1925, **29**, 966—972).—A consideration of the similarities and dissimilarities between true and colloidal solutions.

J. S. C.

**Ebullioscopic Measurements in Mixed Solvents.** B. H. CARROLL, G. K. ROLLEFSON, and J. H. MATHEWS (*J. Amer. Chem. Soc.*, 1925, **47**, 1791—1799).—An apparatus for ebullioscopic measurements capable of an accuracy of 1% is described. The values obtained for the change in b. p. of a binary liquid mixture on addition of a non-volatile solute are in fairly satisfactory agreement with those calculated from the equation of Lewis (*A.*, 1906, ii, 524).

J. S. C.

**Effect of a Non-volatile Solute on the Partial Pressures of Liquid Mixtures at the B. P.** B. H. CARROLL, G. K. ROLLEFSON, and J. H. MATHEWS (*J. Amer. Chem. Soc.*, 1925, **47**, 1785—1791).—Quantitative measurements of the changes in partial pressure produced by addition of a non-volatile solute to various binary liquid mixtures at the b. p. show that the diminution of the partial pressure of that component in which the added substance is more soluble is greater than that exhibited by the second component.  
J. S. C.

**Nature of Soap in Alcohol.** W. A. PATRICK, W. L. HYDEN, and E. F. MILAN (*J. Physical Chem.*, 1925, **29**, 1004—1008).—Determinations of the b. p. of anhydrous and moist alcoholic solutions of sodium oleate over the concentration range 0.005—0.15*M* show that the soap is considerably ionised in dilute solution at the b. p.  
J. S. C.

**Composition of a Constant-boiling Solution of Hydrogen Bromide in Water.** D. T. EWING and H. A. SHADDUCK (*J. Amer. Chem. Soc.*, 1925, **47**, 1901—1904).—The constant-boiling mixture of hydrogen bromide and water at 760 mm. contains 47.795% of the former, showing that the distillate is not  $\text{HBr} \cdot 5\text{H}_2\text{O}$  (47.381%  $\text{HBr}$ ), as reported by Calm (*Ber.*, 1879, **12**, 613). The figure is higher than that recently determined by Carrière and Cerveau (*A.*, 1923, ii, 555, 47.5%  $\text{HBr}$ ). The constant-boiling temperature is about 125°. The distillate is 5.9061*N*.  
J. S. C.

**Internal Friction of Aqueous Sulphate Solutions.** H. GRUNERT (*Z. anorg. Chem.*, 1925, **145**, 394—396).—Measurements of the viscosities of ammonium sulphate, sulphuric acid, and ammonium hydrogen sulphate solutions show that the formation of the acid salt is accompanied by an increase of the internal friction.  
L. L. B.

**Viscosity of Acetic Acid Solutions.** N. DE KOLOSOSVSKI (*J. Chim. Phys.*, 1925, **22**, 321—324).—The viscosities of approximately 10% acetic acid solutions have been measured between 11° and 30°. The results confirm those of Davis and Jones (*A.*, 1915, ii, 423), but disagree with Wijkander's figures. Re-calculation of the apparent molecular heat of acetic acid in solution gives a mean value of 41, the observed value being 37. Acetic acid, therefore, is not hydrated in solution.  
S. K. T.

**Diffusion of Water through Collodion Membranes between Solutions of Mixed Electrolytes.** E. F. ADOLPH (*J. Biol. Chem.*, 1925, **64**, 329—368).—The diffusion of water through a collodion membrane, either untreated or saturated with gelatin, is not affected by the presence of a non-electrolyte in one of the solutions separated by the membrane; in the case of plain collodion membranes the effect of electrolytes is small except that multivalent anions increase the rate markedly. With membranes treated with gelatin, the rate of diffusion is much greater in all cases; the magnitude of the effect increases with the valency of the ions, but the

predominating influence is exerted by those ions of which the electrical charge is opposite to that of the protein in the membrane. In the case of mixed electrolytes, some ions tend to depress the action of others, and the ultimate rate of diffusion is determined by the relation between the concentration of "depressing" cations and that of effective anions. The depressing influence of such a salt as sodium chloride on the effect of (*e.g.*) potassium ferrocyanide is still greater when the two electrolytes are on different sides of the membrane than when they are on the same side, with pure water on the other. It is considered that, within the range of variation of concentrations of biological fluids, the effect of the ions in themselves is not sufficient to account for water transport across cell-membranes.  
C. R. H.

**Ionic Antagonism.** R. MINAKAMI (*Biochem. Z.*, 1925, **158**, 306—318).—If the chlorides of various uni- and di-valent radicals are added to soap solutions, there is a marked change in the surface tension. The physiologically antagonistic sodium chloride and calcium chloride exhibit no antagonistic action when added together to a soap solution, whereas lithium and magnesium or lithium and barium show marked antagonism. The relatively coarse-grained structure which is brought about in soap solutions by the addition of a univalent cation, particularly lithium, is changed by very small quantities of calcium or, better, magnesium into a fine-grained structure. This latter state of division can only be achieved by the addition of a definite quantity of magnesium or similar ions, not by diminishing the lithium content without addition of magnesium.  
H. D. K.

**Colloidal Bismuth.** A. GUTBIER and T. KAUTTER (*Z. anorg. Chem.*, 1925, **146**, 166—178; cf. Meyer, A., 1903, ii, 285).—One part of a 10% solution of bismuth nitrate in 88—90% glycerol is treated with 36 parts of 0.45% aqueous gum-arabic, the mixture reduced with 5 parts of 1% aqueous sodium hyposulphite solution, and the whole quickly diluted with 60 parts of water; the resulting colloidal solution is filtered and on careful evaporation a black, metallic residue is obtained which dissolves completely in water to form a colloidal solution. The particles migrate to the anode in Coehn's apparatus. The black residue contains 18% of bismuth and about 1% of sulphur, which is present as colloidal sulphur and not as sulphide. Gelatin and extract of "Tubera Salep" are less satisfactory protective agents for the preparation of colloidal bismuth, which is unstable if prepared by reduction without such an agent.  
W. H.-R.

**Preparation of Colloidal Ferric Hydroxide Solutions by Oxidation of Ferrous Hydrogen Carbonate.** N. N. GAVRILOV (*Kolloid-Z.*, 1925, **37**, 46—50).—The oxidation of ferrous hydrogen carbonate by means of air yields only a precipitate of ferric hydroxide, which is not peptised in presence of small amounts of hydrochloric acid or ferric chloride. With larger quantities of ferric chloride, colloidal ferric hydroxide is formed, but only from the

added ferric chloride. Hydrogen peroxide gives a white precipitate with ferrous hydrogen carbonate, but in the presence of ferric chloride or hydrochloric acid a colloidal solution of ferric hydroxide is rapidly formed. The minimum amount of ferric chloride necessary for peptisation in the oxidation of ferrous hydrogen carbonate is about 7% of the total iron. E. M. C.

**Technical Preparation of Colloidal Ferric Hydroxide Solutions.** G. STADNIKOV and N. GAVRILOV (*Kolloid-Z.*, 1925, **37**, 40–46).—Colloidal ferric hydroxide solution for use as a coagulator in the drying of peat can be prepared by the oxidation of solutions of ferrous hydrogen carbonate by means of chlorine water or hypochlorous acid. The necessary concentration (0.04% of ferrous iron) can be obtained on a commercial scale by the treatment of iron turnings with water and a current of flue gas. A progressive diminution in concentration occurs on repeated treatment with mixtures of air and carbon dioxide when the carbon dioxide content is greater than one-half. [Cf. *B.*, 1925, 711.]

E. M. C.

**Silicic Acid Sol.** H. R. KRUYT and J. POSTMA (*Rec. trav. chim.*, 1925, **44**, 765–789).—Changes in the viscosity and  $p_H$  values of a silica sol with time and length of dialysis have been determined and correlated, and the effects produced by the addition of various electrolytes investigated. The sols were prepared by pouring a solution of sodium silicate into 20% hydrochloric acid and dialysing and were found by cataphoresis measurements to be negatively charged. Poiseuille's law holds good and the sols are more stable at the ordinary than at higher temperatures. By adding a solution of 50 g. of sodium silicate in 200 c.c. of water to 70 c.c. of acid, sols are obtained for which  $p_H=4.5$  and the viscosity of which increases with time; on the other hand, by using a solution of 50 g. of sodium silicate in 150 c.c. of water, the  $p_H$  value is  $>6$  and the viscosity of these sols decreases with time, the latter phenomenon being due to the occlusion of sodium silicate from the more concentrated solution. The addition of hydrochloric acid to the latter sols in quantities sufficient to reduce the  $p_H$  value to 4.5 or less converts these into sols of increasing viscosity, whilst the addition of sodium hydroxide or silicate solutions to sols of the first type causes an initial increase in viscosity on account of the greater electroviscous effect due to the greater negative charge, and then converts them into sols of decreasing viscosity. Addition of hydrochloric acid or salt solutions to a sol of increasing viscosity first removes the negative charge and hence lowers the initial relative viscosity due to the removal of the electroviscous effect, whilst on further addition the sol becomes positively charged and the viscosity rapidly increases with final gelation or flocculation. The initial viscosity is considerably lowered by the addition of 50% of water to the sols, but on account of the dilution, changes in the viscosity of such sols are extremely small. Addition of alcohol to the sols also causes an initial decrease in the viscosity, but in this case the viscosity continues to decrease due to the

slight dehydrating action of the alcohol. The action of hydrochloric acid, barium chloride, and aluminium chloride in producing flocculation of the sols is not the same. The sols take up hydroxyl and chlorine ions, the disappearance of the former on the addition of sodium hydroxide or silicate to the sol being established by  $p_H$  determinations. The larger the number of hydroxyl ions added to the sol, the more sodium chloride but the less barium chloride is necessary to cause gelation; no explanation of this phenomenon is at present forthcoming. J. W. B.

**Elasticity of Ammonium Oleate Solutions and the Variable Viscosity of Two-phase Systems.** E. HATSCHKE (*Kolloid-Z.*, 1925, **37**, 25—26).—The elasticity of ammonium oleate is readily demonstrated. After being rotated, the solution comes to rest by moving in a direction opposite to that of the rotation. The effect is shown by solutions as dilute as  $N/140$  with a relative viscosity of 1.08. A variation of viscosity with the shear-gradient is found with coarse suspensions as well as with emulsoid sols and may be accounted for by postulating a labile sheath of rigid liquid around the particles, the thickness of the sheath depending on the shear-gradient. E. M. C.

**Elasticity of Gelatin in Relation to  $p_H$  and Swelling.** G. W. SCARTH (*J. Physical Chem.*, 1925, **29**, 1009—1021).—The elastic properties of gelatin gels in their dependence on the  $p_H$  value have been examined. The reciprocal of the extension—the resistance to stretch—has a minimum value at  $p_H$  4.7 and maxima at  $p_H$  3 and  $p_H$  11, the alkali maximum being the higher. Young's modulus for isotropic gelatin varies but slightly between  $p_H$  4.7 and 11. Lanthanum nitrate has the same general effect on gelatin at a  $p_H$  of 4.7 as is produced by the addition of acid or alkali to isoelectric gelatin. Volume and resistance to stretch increase up to a concentration of salt  $10^{-2}$ — $10^{-3}M$ , and then decrease. The modulus of elasticity remains constant until fairly high salt concentrations are reached, and then decreases. Variation in  $p_H$  of the surrounding medium affects the elasticity of gelatin in three ways: (1) directly through combination or by adsorption with the reagent, acids reducing the elasticity whilst alkalis in low concentration cause a slight increase and at high concentration a decrease, (ii) by modification of imbibition resulting from such combination, swelling increasing the total resistance to stretch and maintaining the modulus of elasticity constant in spite of dilution, (iii) by causing structural changes entailing a loss of elasticity. Changes (i) and (ii) are reversible, whilst (iii) is partly reversible. Theories of swelling and of protoplasmic contraction are discussed. J. S. C.

**Colloid Filtration.** L. ZAKARIAS (*Kolloid-Z.*, 1925, **37**, 50—58).—The author has studied the relation between the solid support and the semi-solid membrane in ultra-filters of collodion supported on unglazed porcelain. In filtration through unglazed porcelain alone, a considerable resistance is offered by air within the capillaries; the rate of filtration rises to a maximum and rapidly falls.



Evacuation of the plate and the use of air-free water doubles the rate of filtration. For plates of unglazed porcelain of different porosities there is a close proportionality between the rates of filtration before and after treatment with a constant collodion solution. The rate of filtration through plates treated repeatedly with collodion is inversely proportional to the number of treatments. Increase of pressure increases the permeability as well as the rate of filtration for both hydrophilic and hydrophobic colloids, although there is no simple relationship between permeability and rate of filtration. Increase of pore size by swelling of the membrane does not necessarily increase the rate of filtration on account of the compensating effect of the increase in length of the capillaries. A colloid filter with a semi-solid membrane is regarded as an adsorption sieve, capable of swelling, but swelling is not an essential feature of a colloid filter since a porcelain plate stopped by barium sulphate forms a dense filter. E. M. C.

**Swelling. I. Swelling of Agar-agar Gels as a Function of Water Content before Swelling.** B. L. CLARKE (*J. Amer. Chem. Soc.*, 1925, 47, 1954—1958).—The percentage swelling of agar-agar gels in water increases rapidly from about 800% when the gel contains so little water that none is extracted by drying over phosphorus pentoxide, to 3903% when the gel contains 0.313 g. of water per g. of agar. Further increase in water content occasions a sharp fall in swelling power, to a water content of 0.554 g. per g. of agar, the swelling power thereafter diminishing much more slowly with increase in water content of the original gel. Freshly-cast agar-agar gels are opaque, and on drying in thin plates, become transparent sharply at a water content of 0.554 g. per g. of agar, probably indicating a change of phase at the point at which the swelling power commences to increase rapidly with decreasing water content, although no corresponding discontinuity is exhibited by the vapour pressure isotherm (cf. Katz, A., 1917, ii, 245). The above results afford an explanation of the loss of swelling power of agar-agar gels on storage. F. G. W.

**New Pattern Formed by Coloured Salts in Solid Gels.** E. R. RIEGEL and L. WIDGOTT (*J. Physical Chem.*, 1925, 29, 872—874).—Copper ferrocyanide formed by diffusion of copper sulphate in 1—5% aqueous solution into a gelatin cake containing 0.05—0.2% of potassium ferrocyanide, is not evenly distributed throughout the cake but is concentrated into dark red zones separated by clear spaces. Lead chromate formed in a similar way from 0.1% potassium chromate in gelatin and 5% lead nitrate solution gave both the zone pattern and rhythmic banding. The formation of clear zones reaching to the corners when the edges are sharp indicates that the entering soluble salt travels in straight lines perpendicular to the walls of the cake. F. G. S.

**Protection of Colloidal Solutions by the Addition of Electrolytes in Quantities Insufficient to produce Flocculation.** A. BOUTARIC and (MLLE.) G. PERREAU (*Rev. gén. Colloid*, 1925, 3, 129—136, 167—176).—The stability of sols of gamboge, resin-

mastic, and arsenic trisulphide has been studied in the presence of varying amounts of electrolytes. The rate of flocculation of sols containing a given electrolyte has, in particular, been examined when larger quantities of the same electrolyte are added. Differences are shown to exist according to the period of time that has elapsed between the preparation of the sols and the time of the measurement. Sols which originally contained some electrolyte flocculate more slowly than those which were practically free from electrolyte. When the amount of electrolyte is increased the degree of protection at first increases, but further increase in the amount of electrolyte diminishes the protection. Especially interesting results are obtained with ammonium and lithium salts. The behaviour of the sols towards electrolytes other than those used in their preparation shows that the presence of lithium chloride protects arsenious sulphide sol from flocculation by potassium, magnesium, barium, and ammonium chlorides, whilst the flocculation is accelerated by cadmium and aluminium chlorides.

C. I. B. V.

**Influence of Hydrogen-ion Concentration on the Protective Action of Gelatin on Zsigmondy's Standard Gold Sol.** H. V. TARTAR and J. R. LORAH (*J. Physical Chem.*, 1925, **29**, 792—798).—The protective action of gelatin on Zsigmondy's standard gold sol has been measured in the presence of acetic, oxalic, hydrochloric, and phosphoric acids. The concentration of hydrogen ion has little effect on the protective action over the  $p_H$  range 8 to 5, but below a  $p_H$  of approximately 4.7 the protective action decreases very rapidly with increase of hydrogen-ion concentration. F. G. S.

**Studies in Emulsions.** W. SEIFRIZ (*J. Physical Chem.*, 1925, **29**, 834—841).—The effect of hydrogen and barium chlorides and sodium and barium hydroxides on olive oil emulsions stabilised by various emulsifying agents has been studied. Reversal of phases takes place with hydrochloric acid and frequently with barium chloride at a  $p_H$  of 7.2, but the main factor causing reversal cannot be ascribed to the hydrogen-ion concentration, for sodium and barium hydroxides may cause reversal in opposite directions and highly alkaline oil-in-water emulsions may be reversed by barium chloride. The effect of the phase volume ratio on the type, texture, and stability (cf. Robertson, A., 1910, ii, 697) is described using refined petroleum oils and aqueous casein. Reversal frequently occurs on keeping. The behaviour of vegetable oils (cf. Seifriz, A., 1924, i, 127) is compared with that of petroleum oils. All the water-in-oil emulsions of the vegetable oils are readily reversible by sodium hydroxide into stable oil-in-water systems, and may be reconverted into the former by barium chloride or barium hydroxide.

F. G. S.

**Sensitisation of Congo-red by Globulin.** G. ETTISCH and H. RUNGE (*Kolloid-Z.*, 1925, **37**, 26—31).—The sensitisation of Congo-red towards flocculation by salts which is produced by the addition of globulin, as observed by Brossa (A., 1923, i, 397) but not by

Becker (*Z. Immun. Therap.*, 1924, **41**, 378), depends on the reaction and salt content of the two systems. Congo-red should be used immediately after dialysis, since on exposure to air it takes up carbon dioxide, and becomes acid, turbid, and more deeply coloured. The reaction and conductivity of globulin suspensions remain constant only for 3 days. Pure Congo-red does not peptise globulin suspensions. The peptisation of globulin and Congo-red by acid, alkali, or salts is independent. Globulin may be peptised by acid at about  $p_H$  4.0 without causing any colour change of Congo-red. There is no affinity between the micelles of globulin and of Congo-red, and the formation of a turbidity in a Congo-red-globulin mixture is a true protein flocculation. The sensitising action of lecithin towards Congo-red (cf. Beck, this vol., ii, 527) is similarly explained.

E. M. C.

**Theory of Liesegang Ring Formation.** N. R. DHAR and A. C. CHATTERJI (*Kolloid-Z.*, 1925, **37**, 2—9; cf. A., 1922, ii, 627; 1924, ii, 158).—Further evidence is advanced in support of the theory that Liesegang rings are formed by the coagulation of a peptised sol and the adsorption of the same material from adjacent layers. Two types of ring structure are recognised, according as the precipitate layer is followed by a region free from precipitate or one which contains the peptised sol. Mercuric iodide, cadmium sulphide, antimony sulphide, and silver sulphide form the second type of structure, and it is shown that the corresponding sols are not adsorbed by the solid precipitate as is the case for substances giving the first type of ring structure.

E. M. C.

**Molecular Attraction and the Equation of State.** K. K. JÄRVINEN (*Z. physikal. Chem.*, 1925, **116**, 420—430; cf. *ibid.*, 1920, **96**, 367).—Theoretical.

L. F. G.

**Chemical Theory of Corresponding States.** G. BOITARD (*J. Chim. phys.*, 1925, **22**, 349—352).—Theoretical. In the reduced general equation of state,  $F(\pi, \phi, \theta, \alpha, \beta, \dots) = 0$ , the theorem of corresponding states can only hold for fluids for which the parameters  $\alpha, \beta, \dots$  are constant. The latter characterise the chemical type of the fluids, and it is shown that the reduced vapour pressure,  $\pi$ , the reduced molecular volume of vapour,  $\phi_1$ , and of fluid,  $\phi_0$ , the reduced heat of vaporisation,  $\lambda (= L/p_{ev})$ , and the reduced entropy,  $\sigma (= \lambda/\theta)$ , are functions of them. Thus, at a given reduced temperature,  $\theta, \pi, \phi_0, \phi_1$ , and  $\lambda$  are constant for the different members of a chemical family. It is also shown that the change of entropy accompanying evaporation is constant for all fluids of the same chemical family at corresponding temperatures.

S. K. T.

**Molecular Interaction in the Liquid State.** G. N. ANTONOV (*Phil. Mag.*, 1925, [vi], **50**, 265—289; cf. A., 1918, ii, 437).—The previous theory of molecular complexity in the liquid state is extended from liquid-liquid to liquid-gas systems, by assuming that the process of formation of liquids is due to the formation of associated molecules, and that the molecules forming the gaseous phase penetrate the liquid phase without suffering any substantial

change of concentration. The empirical law obtained by the author (A., 1924, ii, 829) for the variation with temperature of the difference between the densities of the liquid and vapour phases of a substance is deduced from the above assumptions, since the difference of the densities then represents the concentration of the associated molecules. The relation becomes  $Ae^{\lambda\delta} = T + B$ , where  $A$ ,  $B$ , and  $\lambda$  are constants,  $T$  is the temperature reckoned from the critical temperature downwards, and  $\delta$  the difference of density. Experimental data show that the  $\delta$ - $T$  curve for ethyl acetate is discontinuous, and consists of several portions, each satisfying the above equation, with different constants for each portion. From the similar behaviour of propyl alcohol and hexamethylene, it is suggested that this is a general law for all liquids, and that the molecular clustering which is assumed in the liquid state takes place according to the law of multiple proportions. Some liquids undergo between their m. p. and the critical temperature a greater number of such changes than other liquids. The relation between temperature and latent heat of evaporation, surface tension, and viscosity is investigated, and it is shown that these curves also are discontinuous, breaks occurring at the same temperatures in the different curves for the same liquid. Each portion of the curves for density and latent heat of evaporation satisfies the above equation, which is general for normal and associated liquids, and holds good for all ranges of temperature. Each portion of the curves for surface tension ( $\alpha$ ) and viscosity ( $\eta$ ) is represented by the equation  $\alpha + B = Ae^{\gamma T}$  or  $\eta + C = De^{\kappa T}$ . Discontinuity is an intrinsic characteristic of liquids, and it is probable that definite molecular changes occur in the several intervals of temperature. F. G. T.

**Parameters Depending on Temperature in Statistics: the Debye Theory of Electrolytes.** P. GROSS and O. HALPERN (*Physikal. Z.*, 1925, 26, 403—407; cf. A., 1923, ii, 459, 724; 1924, ii, 386; this vol., ii, 171, 513).—Theoretical. A mathematical analysis of temperature effects, the results being applied to the Debye-Hückel theory of strong electrolytes. The variation of the dielectric constant with the temperature is considered in reference to the calculated and observed heats of dilution. Within the range imposed by its assumptions the Debye theory is regarded as valid.

R. A. M.

**Derivation of the Fundamental Equation from the Law of Mass Action for Condensed and Heterogeneous Systems.** J. J. VAN LAAR and R. LORENZ (*Z. anorg. Chem.*, 1925, 145, 239—250).—A mathematical development of the equilibrium equation derived by Lorenz (cf. A., 1924, ii, 761) on the basis of the law of mass action, the vapour-pressure theory of van Laar, and the conception of thermodynamic potentials. The equation is applied first to the case of ideal gases, and an equation is obtained which gives the molar potentials of the components of an ideal gas mixture. Similar considerations are also applied to van der Waals' equation of state. L. L. B.

**Third Law of Thermodynamics and Calculation of Entropies.** T. J. WEBB (*J. Physical Chem.*, 1925, **29**, 816—833).—The entropy of cadmium chloride hydrate has been calculated on the assumption of the validity of the third law from the energetics of its formation from silver, lead, or mercurous chlorides, cadmium, and water. The values agree within the limit of experimental error, as do the values of the entropy of cadmium iodide obtained in a similar manner. Direct calorimetric measurements of the total energy change of a chemical reaction is often more accurate than its calculation from the free energy and the temperature coefficient of the free energy. A calorimetric determination of the heat of formation of solid silver iodide from solid silver and solid iodine has been made and the value  $14,975 \pm 50$  cal. obtained. This leads, on the assumption of the third law, to a value of 13.95 for the entropy of iodine as compared with 14.24 from a study of the formation of zinc iodide, and 13.95 obtained from the specific heat data of Lange (cf. this vol., ii, 96). The heat of formation of silver bromide has been determined and its entropy at 25° calculated by two methods. F. G. S.

**Free Energy of Dilution and the Activity of the Ions in Aqueous Solutions of Barium Chloride.** J. N. PEARCE and R. W. GELBACH (*J. Physical Chem.*, 1925, **29**, 1023—1030).—The *E.M.F.* of concentration cells containing barium chloride, with and without ion-transference, have been measured with an accuracy of  $\pm 0.05$  mv. The transference numbers of the barium and chloride ions and the free energy and heat content decrease attending the transfer of 1 mol. of barium chloride from concentration *c* to a concentration 0.10*M* have been calculated. The activity coefficients derived from the *E.M.F.* data are in close agreement with those from f. p. data. J. S. C.

**Dissociation Constants of Selenious Acids.** J. S. WILLCOX and E. B. R. PRIDEAUX (*J. Chem. Soc.*, 1925, **127**, 1543—1546).—Measured volumes of standard sodium hydroxide solution were added to 20 c.c. of a 0.05 *M*-solution of selenious acid in the presence of a suitable indicator. The colours were matched by the addition of the same alkali to 20 c.c. of the B,D.H. "universal" indicator containing the same number of drops of indicator. The hydrogen-ion concentrations were thus obtained, from which the first and second dissociation constants of selenious acid were calculated as  $K_1 = 4.0 \times 10^{-3}$ , and  $K_2 = 0.87 \times 10^{-8}$ . The first end-point gives accurate titrations with *p*-nitrophenol as indicator: cochineal, lacmoid, and resazurin should also be suitable. The second end-point is not so sharp, but fair results are obtained with thymolphthalein (to a full blue). W. H.-R.

**Ionisation of Weak Electrolytes in Water-Alcohol Solutions. II. Relations between Chemical Constitution and Alcohol Sensitivity of Acids and Bases.** M. MIZUTANI (*Z. physikal. Chem.*, 1925, **116**, 350—358; cf. this vol., ii, 793).—Data corresponding with those previously obtained for other substances are

given for dilute solutions of formic, butyric, and *isovaleric* acids, methylamine, dimethylamine, trimethylamine, ethylamine, aniline, methylaniline, dimethylaniline, *o*- and *m*-toluidine, and pyridine. New data for ammonia are given. The effect of alcohol on the ionisation of the aliphatic acids increases with the length of carbon chain. Benzoic acid behaves similarly to *isovaleric* acid. The introduction of a hydroxyl group (*i.e.*, to form lactic or salicylic acid) decreases the sensitivity of acids to alcohol. All the bases are less affected by alcohol than are the acids. Ammonia is the least affected, but substitution of hydrogen by methyl groups greatly increases the sensitivity. Similarly, the toluidines and the methylanilines are more sensitive than aniline, which is very nearly as insensitive as ammonia.

L. F. G.

**Ionisation of two Electrolytes in Alcohol-Water Mixtures ; Influence of Environment on Ionisation.** F. BRADLEY and W. C. McC. LEWIS (*J. Physical Chem.*, 1925, **29**, 782—791).—The ionisation of salicylic and of cyanoacetic acids, at dilutions of 8 to 1024 litres, has been examined in alcohol-water mixtures containing 0—100% of alcohol. A slight decrease of the ionisation constant was observed as the dilution was increased. The formula,  $K = K_1(k_1/k_2)[H_2O]^n e^{(E'_0 - E_0)/DRT}$ , has been deduced, where  $K$  is the ionisation constant,  $D$  the dielectric constant of the medium,  $K_1$  the equilibrium constant of the reaction  $HA + nH_2O = HA, nH_2O$ ,  $k_1$  and  $k_2$  are the velocity coefficients for the ionisation and recombination of the ions, respectively,  $E_0$  is the critical increment of ionisation in a medium of unit dielectric capacity, identified with the electrostatic work of separation of the ions, and  $E'_0$  the sum of the critical increments of the ions, identified with the work necessary to remove the solvent molecules with which the ions are hydrated. The values of the constants  $K_1(k_1/k_2)$  and  $(E'_0 - E_0)$  were found by using two experimentally determined values of  $K$  for different solvent mixtures, and the value of  $n$  was found by trial to be 2. The ionisation constants calculated from the dielectric constants and the above data are in good agreement with the observed results. The critical increment of ionisation deduced for a medium of unit dielectric capacity is of the same order as that of the ionisation of other compounds in the gaseous state.

F. G. S.

**Direction of Spontaneous Crystallisations and Chemical Transformations.** N. V. TANCOR (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 342—367).—A further discussion of this subject (cf. A., 1917, ii, 367).

T. H. P.

**Singular Points in Chemical Diagrams.** N. S. KURNAKOV (*Z. anorg. Chem.*, 1925, **146**, 69—102).—A theoretical discussion of certain features exhibited by equilibrium diagrams.

W. H.-R.

**Singular Points in Chemical Diagrams.** N. S. KURNAKOV (*Ann. Inst. Anal. Physico-Chim. Leningrad*, 1924, **2**, 219—254).—A résumé of the subject.

T. H. P.

**Equilibrium Pressures of Hydrates of Gases.** G. TAMMANN and G. J. R. KRIGE (*Z. anorg. Chem.*, 1925, **146**, 179—195).—The systems sulphur dioxide–water, chloroform–water, and carbon dioxide–water have been investigated by measurements of vapour pressure and of f. p. at high pressures and low temperatures. Sulphur dioxide forms a single hydrate,  $\text{SO}_2 \cdot 6\text{H}_2\text{O}$ , which forms a eutectic with ice at  $-2.6^\circ$ . The dissociation pressures of this hydrate and the influence of pressure on the m. p. and eutectic temperatures have been determined. Chloroform forms a single hydrate containing less water than corresponds with the formula  $\text{CHCl}_3 \cdot 18\text{H}_2\text{O}$  given by Chancel and Parmentier (A., 1885, 363). Carbon dioxide forms a hydrate,  $\text{CO}_2 \cdot 6\text{H}_2\text{O}$ , for which the dissociation pressures have been determined from  $-20^\circ$  to  $43^\circ$ . The gas hydrates  $\text{CO}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{N}_2\text{O} \cdot 6\text{H}_2\text{O}$ ,  $\text{Kr} \cdot 5\text{H}_2\text{O}$ , and  $\text{A} \cdot (5-6)\text{H}_2\text{O}$  form a group for which the logarithmic dissociation pressure–temperature curves are nearly parallel. A second group is formed by the hydrates  $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ ,  $\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ , and  $\text{SO}_2 \cdot 6\text{H}_2\text{O}$ , for which the curves are parallel but of different slope compared with the first group.

W. H.-R.

**System Sodium Sulphite–Sodium Hydroxide–Water.** D. L. HAMMICK and J. A. CURRIE (*J. Chem. Soc.*, 1925, **127**, 1623—1628).—The equilibrium conditions have been investigated by Schreinemakers' residue method at  $0.15^\circ$ ,  $20^\circ$ ,  $25^\circ$ , and  $32^\circ$ . At  $0.15^\circ$ , the solubility of the sulphite in presence of excess of sodium hydroxide is very small, and the coexisting solid phases are sodium sulphite heptahydrate, anhydrous sodium sulphite, and sodium hydroxide tetrahydrate. The isotherms at  $20^\circ$  and  $25^\circ$  are very similar except that sodium hydroxide monohydrate replaces the tetrahydrate. At  $32^\circ$ , however, the sodium sulphite heptahydrate is no longer formed, in agreement with the value  $31.5^\circ$  found by Lewis and Rivett (J., 1924, **125**, 1156) for the transition temperature  $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{SO}_3$ , but contrary to the value  $22^\circ$  found by Hartley and Barrett (T., 1909, **95**, 1178). The discrepancies are possibly due to the existence of anhydrous sodium sulphite in more than one metastable phase.

W. H.-R.

**System Chromium Trioxide–Boric Acid–Water.** L. F. GILBERT (*J. Chem. Soc.*, 1925, **127**, 1541—1542).—The solubility of boric acid has been determined at  $25^\circ$  and  $45^\circ$  in solutions containing from 0 to 62.4% of chromic acid. In all cases the solid phase is boric acid the solubility of which is diminished by increasing content of chromic acid, chiefly owing to the common ion (hydrogen) effect.

W. H.-R.

**Equilibria in Systems, with Solid Phases, Separated by a Semi-permeable Membrane.** IV and V. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 157—165; 166—173).—Theoretical. The osmotic behaviour of ternary liquid systems in which (a) a solid binary compound or (b) a solid ternary compound occurs or (c) in which more than one solid phase may occur, is discussed in reference to phase diagrams.

A. B. M.

**Work of Viscosity and Apparent Molecular Heat of Substances in Solution.** N. DE KOLOSSOVSKI (*J. Chim. phys.*, 1925, **22**, 353—368).—The theoretical formula for the specific heats of solutions previously deduced (this vol., ii, 765, 791) is extended in application by the introduction of a term representing the work necessary to overcome the viscosity of the medium. Mathias' formula for the specific heats of solutions (A., 1889, 4) can be deduced directly from the theory outlined. According to the viscosity data for their aqueous solutions, ethyl and propyl alcohols are combined with  $1\text{H}_2\text{O}$ , laevulose with  $2\text{H}_2\text{O}$ , and acetic acid with  $9\text{H}_2\text{O}$ . The quantity  $\epsilon [=C-(2n+3)$ ,  $C$  being the apparent molecular heat of the dissolved solute and  $n$  the number of atoms in its molecule] is fairly constant for isomeric compounds and increases by about 16.4 for successive members of homologous series. The groups H, OH, and  $\text{CO}_2\text{H}$  have no influence on  $\epsilon$ , which, for chemically analogous substances, appears to be proportional to the molecular weight. The revised formula causes only small changes in the degrees of hydration of the electrolytes previously recorded. Sodium iodide and nitric acid in solution now have 1 and  $1.5\text{H}_2\text{O}$ , respectively; potassium and sodium bromides have, respectively, 4 and  $6\text{H}_2\text{O}$  (cf. this vol., ii, 859).  
S. K. T.

**Thermal Decomposition of Metallic Sulphates. I.** (MLLE.) G. MARCHAL (*J. Chim. phys.*, 1925, **22**, 325—348).—The heats of formation and of solution in various solvents of hydrated and anhydrous beryllium oxide and sulphate are recorded. The molecular heat of solution of the anhydrous oxide in 30% hydrofluoric acid is 23.3 Cal., higher than found by Copaux and Philips (A., 1923, ii, 216); the molecular heat of hydration of the oxide is 2.9 Cal. The molecular heat of formation of anhydrous beryllium sulphate is 273.1 Cal.; the heat of formation of the anhydrous double sulphate,  $\text{K}_2\text{SO}_4\cdot\text{BeSO}_4$ , is 8.4 Cal., and of the hydrated form ( $2\text{H}_2\text{O}$ ), 14.7 Cal.  
S. K. T.

**Heat of Mixture of Condensed Systems.** J. J. VAN LAAR and R. LORENZ (*Z. anorg. Chem.*, 1925, **146**, 42—44).—Theoretical. By means of the thermodynamic potential, a complex expression is deduced for the calculation of the heat of mixture of condensed systems.  
W. H.-R.

**Heats of Adsorption of Sulphur Dioxide and of Water Vapour by Silica Gel at  $0^\circ$ .** W. A. PATRICK and C. E. GREIDER (*J. Physical Chem.*, 1925, **29**, 1031—1039; cf. Patrick and Grim, A., 1922, ii, 122).—The heat of adsorption of water vapour at  $0^\circ$  is given by the equation,  $H=1.091X^{0.914}$ ,  $X$  being the number of mg. of water adsorbed per g. of gel and  $H$  the corresponding heat of adsorption in cal. per g. of gel. The respective values of  $H$  and  $X$  at saturation are 236.2 cal. and 361.2 mg. The net heat of adsorption, assuming the heat of liquefaction of the adsorbed water to be 215.6 cal. (596.8 cal. per g.), is 20.6 cal. The heat of adsorption of sulphur dioxide is represented by the equation  $H=0.316X^{0.860}$ . The respective values of  $H$  and  $X$  at saturation are 69.1 cal. and 525



mg. The net heat of adsorption is 21.2 cal. The difference between heats of adsorption and of liquefaction, *i.e.*, the net heat, may be interpreted in terms of the changes in surface and in surface energy involved.

J. S. C.

**Amendment to the Lyons Decisions (1922) Regarding the Thermochemical Standard Substance.** P. E. VERKADE (*Rec. trav. chim.*, 1925, **44**, 800—804).—In view of the continued improvement in the accuracy of heat of combustion determinations (0.1 per thousand now being obtainable), it is essential that the temperature for which the internationally adopted standard value of benzoic acid (6324 cal.<sub>15</sub> per g. [air]) is valid, should be stated. The temperature coefficients of the molecular heats of combustion of benzoic and salicylic acids are calculated to be  $-29.0$  and  $-27.5$ , respectively, hence the isothermal heats of combustions of these substances decrease by 0.038 per 1000 per  $1^\circ$  rise of temperature; therefore a difference of  $5^\circ$  in the experimental temperature involves an error greater than the experimental error. It is suggested that determinations of heats of combustion should all be carried out at a temperature in the near neighbourhood of  $20^\circ$ , it being assumed that the standard value holds for an isothermal reaction at  $19.5^\circ$ . If other temperatures must be employed, the above coefficients should be taken into account.

J. W. B.

**Conductivity of Electrolytes. II. Mobility of the Hydrogen Ion at  $25^\circ$ .** C. W. DAVIES (*J. Physical Chem.*, 1925, **29**, 973—976).—Use may be made of the linear relationship between conductivity and the square root of concentration (this vol., ii, 541) in the extrapolation of conductivity data. The relationship holds exactly for the strong electrolytes and gives in the case of weak and transition electrolytes the limiting slope at infinite dilution. The value  $351.3 \pm 0.1$  is derived for the mobility of the hydrogen ion at  $25^\circ$  from considerations of the data of Kraus and Parker (*A.*, 1923, ii, 6, 722) for hydrochloric and iodic acids.

J. S. C.

**Conductivity of Electrolytes. III. Correlation of Strong and Weak Electrolytes.** C. W. DAVIES (*J. Physical Chem.*, 1925, **29**, 977—986; cf. preceding abstract).—The changes in conductivity of dilute solutions of electrolytes with increasing concentration is due partly to changes in ionic mobilities and partly to a decrease in the degree of ionisation. In the case of the strong electrolytes only the first of these causes is present. With weak and transition electrolytes the changes in ionic mobilities are given by the equation quoted (*loc. cit.*). Allowing for these mobility changes, the true degree of dissociation is calculable. True ionisation constants for weak and transition electrolytes are obtained by dividing the product of ion activities by the calculated concentration of the non-ionised molecules.

J. S. C.

**Conductivity of Potassium and Sodium Chloride in Aqueous Solution.** R. LORENZ and A. VOIGT (*Z. anorg. Chem.*, 1925, **145**, 277—303).—The conductivity theory of Hertz (*A.*, 1912, ii, 120) is supported by observations made with sodium and potassium

chloride solutions. Considerations based on the relation of the "universal" conductivity curve [*i.e.*, the curve obtained by plotting the values  $\psi(u)$  of the Hertz function against the values of  $u$ ] to the molar conductivity curve, lead to a value for the constant  $A$  which is practically identical with the theoretical value of 18.95 (at 18°). Investigation of the value of  $B$  shows that this is not constant.

L. L. B.

**Measurement of Electrical Conductivity at High Temperatures and its Significance for Explaining the Nature of Solid Solutions.** P. J. SALDAU (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 275—286).—Mostly published previously (cf. A., 1916, ii, 594; this vol., ii, 205). Equilibria in the system gold-cadmium have been investigated. At about 450° the compound  $\text{Au}_3\text{Cd}$  separates from alloys containing about 25 atoms % Cd. Further lowering of the temperature results in the formation of a new phase possessing two modifications:  $\alpha_1$  stable between 450° and 135° and  $\alpha_2$  below 135°. The existence of the compound  $\text{Au}_4\text{Cd}_3$  is not confirmed. Maxima on the conductivity isotherms show the existence of the compounds  $\text{AuCd}$  and  $\text{AuCd}_3$ .

T. H. P.

**Electrical Conductance of Selenium Oxychloride Solutions.** A. P. JULIEN (*J. Amer. Chem. Soc.*, 1925, **47**, 1799—1807).—The specific conductance of selenium oxychloride is  $2.0 \pm 0.3 \times 10^{-5}$  mhos at 25°. The variation of the specific conductance with temperature is represented in a satisfactory manner by the equation  $K_t = K_{25} + 0.0392t - 0.943 - 0.0002(t-12)^2$ , where  $K$  represents conductance. The molecular conductances of solutions of sodium, potassium, ammonium, mercuric, ferric, and barium chlorides at various concentrations in the solvent have been determined. A method for the determination of the water content of selenium dioxide is described: selenium dioxide is volatilised through heated potassium chromate; the oxide combines to form stable compounds, the water being collected and weighed.

J. S. C.

**Basis for the Physiological Activity of certain -onium Compounds. The Mobilities of the -onium Ions. I. Sulphonium Ions.** I. BENCOWITZ and R. R. RENSHAW (*J. Amer. Chem. Soc.*, 1925, **47**, 1904—1916).—Conductivity measurements with trimethylsulphonium iodide and triethylsulphonium bromide, over the concentration range 0.04—1.0 millimole per litre, have been carried out in quartz apparatus. The values of  $\lambda_\infty$  for trimethylsulphonium iodide and triethylsulphonium bromide are 127.49 and 113.49, respectively. On the assumption that the value of  $\lambda_\infty$  at 25° of the iodide ion is 76.12 and that of the bromide ion 77.44, the  $\lambda_\infty$  values for trimethylsulphonium and triethylsulphonium are 51.36 and 36.05, respectively.

J. S. C.

**Transference Numbers of Solutions of Mixed Chlorides.** D. A. MACINNES (*J. Amer. Chem. Soc.*, 1925, **47**, 1922—1927).—A re-examination of the transference data obtained by Braley and Hall (A., 1920, ii, 662) and by Schneider and Braley (A., 1923, ii, 456) for mixed solutions of sodium and potassium chlorides, which were

interpreted as indicating the existence of ionic complexes, leads to the conclusion that the results are in agreement with the view that only simple ions are present. J. S. C.

**Transference Numbers of Sodium and Potassium Chlorides and of their Mixtures.** J. DEWEY (*J. Amer. Chem. Soc.*, 1925, **47**, 1927—1932; cf. preceding abstract).—The experiments of Schneider and Braley (A., 1923, ii, 456) on the transference numbers of the sodium and potassium ions in mixed solutions of the two chlorides at a total concentration of 0.2*N*, have been repeated. No evidence was obtained that with a low proportion of sodium chloride the transference number of the sodium ion falls to nearly zero as reported by Schneider and Braley, and the present data are in good agreement with the assumption of simple ions as opposed to the suggested complexes. J. S. C.

**Electrolyte Threads. I. Behaviour of Electrolyte Threads and their Deflection in a Magnetic Field.** E. MANEGOLD (*Z. anorg. Chem.*, 1925, **145**, 181—192).—A thin thread of a coloured electrolyte (0.1*N*-hydrochloric acid and methyl-orange) was caused to flow through distilled water; the thread was 5.5 cm. long and 1.7 mm. in diameter and the rate of flow of electrolyte was 0.8 c.c. per min. When a current was passed through the thread in the field of an electro-magnet the thread was deflected; the current was varied from 0.0016 to 0.0025 amp., and the deflection was approximately proportional to this and was of the order of 0.5—1 cm. A jet of the electrolyte in air was similarly deflected, but the deflection was less because the rate of flow of the liquid was necessarily greater.

A. G.

**Electrokinetic and Thermodynamic Potentials.** H. FREUNDLICH and G. ETTISCH (*Z. physikal. Chem.*, 1925, **116**, 401—419; cf. Borelius, A., 1916, ii, 512; Freundlich and Rona, *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1920, **20**, 397).—The streaming potential method was used to study the effect of varying the concentrations of dilute solutions of salts on the electrokinetic potentials at glass surfaces. In the typical electrokinetic potential-concentration curve the potential rises to a maximum with increasing concentration, then falls, and finally changes its sign. The maximum may, however, be suppressed, and the inversion point may be approached only asymptotically. The form of the curve is explained by the opposing influences of the two ions adsorbed on the glass. In this connexion, Hardy's rule is shown to hold. The thermodynamic potentials were also measured. Here the curves have none of the above characteristics, and follow courses which can be explained on the usual thermodynamic grounds. L. F. G.

**Phase Boundary Forces at Gas-Liquid Interfaces. III. Electrical Properties of Unimolecular Films of Insoluble Substances.** A. FRUMKIN (*Z. physikal. Chem.*, 1925, **116**, 485—497; cf. A., 1924, ii, 462; this vol., ii, 109).—A method is described similar to that of Guyot (this vol., ii, 403) for measuring potential differences at gas-liquid interfaces, which allows the potential

difference at the interface air-unimolecular adsorbed film of insoluble substance to be easily determined, and, in the case of soluble substances, gives results which agree with those determined by Kenrick's method. Films of fatty acids and allied substances, in most cases on 0.01*N*-hydrochloric acid, have been studied. The observed effects are ascribed to orientation of the molecules according to Langmuir's theory, but the effect per molecule is less for higher members of homologous series than for lower. This is due to closer packing of the molecules in the former case. L. F. G.

**Electrochemical Relation of Free Radicals to Halochromic Salts.** J. B. CONANT, L. F. SMALL, and B. S. TAYLOR (*J. Amer. Chem. Soc.*, 1925, **47**, 1959—1974).—Measurements of the *E.M.F.* of a cell consisting of platinum electrodes immersed in tetrachlorobenzoquinone-tetrachloroquinol and triphenylmethyl-triphenylmethyl sulphate mixtures, respectively, dissolved in a solvent made by mixing glacial acetic acid (15 c.c.), bromobenzene (26 c.c.), and 98% sulphuric acid (15 c.c.), indicate that mixtures of triphenylmethyl and its sulphate give reproducible potentials in accordance with the usual electrochemical equation. The same result is obtained when triphenylcarbinol is titrated with vanadous sulphate in aqueous acetone solution against the above tetrachlorobenzoquinone electrode, and the single electrode potentials of triphenylmethyl, phenylxanthyl, and phenyldimethoxyxanthyl have been evaluated. When the hydrolysis of the halochromic salt is negligible, the potential is independent of the hydrogen-ion concentration. When hydrolysis is complete, the potential is a linear function of the latter, a bend in the potential- $p_H$  curve occurring at the range of decreasing acidity over which the colour of the salt solution fades. Whilst reduction of carbinols to dissociable ethanes is thus reversible, reduction to the non-dissociable ethanes was found to be irreversible.

Reduction of carbinols with vanadous sulphate or chloride, in acetone or acetic acid solution, affords a convenient method for the preparation of the corresponding substituted methyls or ethanes. *Dianisyl-di- $\alpha$ -naphthylethane* crystallises with 1 mol. of acetone. The compound melts at 226° when slowly heated, but when heated rapidly it melts at 180°, then solidifies, and finally melts at 226°.

F. G. W.

**Critical Increment of Chemical Reactions.** C. N. HINSHELWOOD (*Phil. Mag.*, 1925, [vi], **50**, 360—361).—The value of the factor  $P$  in the expression  $k=2 \times \text{total number of collisions} \times e^{-Q/RT} \times P$  for the velocity constant of a bimolecular reaction in a gaseous system is discussed. The author differs from Garner (this vol., ii, 552) in regarding  $P$  as independent of temperature. A. B. M.

**Influence of Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Mixtures of Inflammable Gases and Air.** IV. Influence of Dichloro- and Trichloroethylene on the Limits of Inflammability of Carbon Monoxide-Air Mixtures. W. P. JORISSEN and J. H. A. P. VAN DER VALK (*Rec. trav. chim.*, 1925, **44**, 810—813; cf. this vol., ii, 53, 307).—In a slightly modified apparatus, the limits of inflammability of mix-

tures of carbon monoxide and air at  $14^{\circ}$  were 15.35–72.75%. With various proportions of dichloroethylene vapour, the following limits of inflammability were obtained at this temperature: 5%, 6.65–50.25%; 8%, lower limit 3.2%; 10%, below 1.8–27.8%; 11%, lower limit below 0.5%; 12%, below 1.95–16.5%; 13%, upper limit 12.55%; 14%, 0.75–7.6%; 15%, upper limit 5.65%; 16%, 1.75–3.7%; 17 and 18%, no explosion with 0.5% of carbon monoxide; 20%, no explosion with 0.1%. With 2.5% of carbon monoxide, explosion did not occur with a dichloroethylene concentration greater than 16.6%. Dichloroethylene itself (b. p. 50.6–52.7°/759 mm.) has explosion limits 3.25–15.25%, whilst a specimen of low b. p. (48.2–49°/755.5 mm.) and one of high b. p. (57.5–59.5°/758 mm.) gave limits 8.5–13.5% and 10.5–23%, respectively. With trichloroethylene at  $14^{\circ}$ , the following limits were obtained: 2%, 18.95–52.75%; 3%, upper limit 43.55%; 4%, lower limit 21.45%; whilst the trichloroethylene itself showed no explosion at  $14^{\circ}$  with 5% (air saturated with the vapour contains 5.7% by volume).

J. W. B.

**Influence of Non-inflammable Vapours of Organic Liquids on the Limits of Inflammability of Mixtures of Inflammable Gases and Air. V. Influence of Trichloroethylene on the Limits of Inflammability of Hydrogen-Air Mixtures.** W. P. JORISSEN and B. L. ONGKIEHONG (*Rec. trav. chim.*, 1925, **44**, 814–817; cf. preceding abstract).—Both the upper and lower explosion limits of mixtures of hydrogen and air are lowered by the addition of trichloroethylene vapour. At  $14^{\circ}$ , the explosion limits of mixtures of hydrogen and air (explosion limit 6.3–61.3% in the apparatus used) in the presence of varying quantities of trichloroethylene were as follows: 3%, 5.9–43.3%; 5%, lower limit 5.4%; 6.05% (saturated), 4.9–25.9%. At  $25^{\circ}$ , 0%, 5.9–62.3%, 3%, upper limit 45.7%; 5%, 5.1–42.9%; 10.84% (saturated), 5.1–20.8%. At  $35^{\circ}$ , 0%, 6.1–63.1%; 3%, upper limit 47.2%; 6%, 4.7–41.1%; 8%, upper limit 38.3%; 10%, 4.2–34.9%; 14%, lower limit 6.7%; 15.7% (saturated), no explosions with quantities of hydrogen varying from 4 to 20%. The ratios of hydrogen to oxygen at the various explosion limits are also calculated and confirm the deduction made above.

J. W. B.

**Combustion of Carbon Monoxide Mixtures.** J. H. CROWE and A. H. NEWBY (*Phil. Mag.*, 1925, [vi], **49**, 1112–1131).—Mixtures of carbon monoxide and air were ignited at the centre of a spherical explosion vessel. For any completely diffused mixture of air and carbon monoxide at any pressure the flame travels at a uniform velocity. The curve time-distance is a wavy line and a mean straight line can be passed through the points. The wavy line corresponds with a true oscillation of the flame front. The flame reaches the walls before combustion is completed. The velocity of the flame is a function of flame temperature. Convection currents are unimportant, even in the weaker mixtures. The maximum velocity, pressure, and temperature occur with a rich mixture containing about 40% of carbon monoxide. These

phenomena are explained by dissociation. Combustion does not take place instantaneously at any spherical shell of mixtures of carbon monoxide and air, and probably does not do so with any other gas.

The percentage cooling loss is lowest when the mixture contains 45% of carbon monoxide. The values of Pier (A., 1910, ii, 1031) for the volumetric heat are low compared with those of the authors (6.32 compared with 6.92, 60% CO, 2066° Abs.; 7.21 compared with 7.32, 60% CO, 2713° Abs.). The agreement is better at higher temperatures. It is assumed that chemical equilibrium is nearly complete at the time of maximum pressure. The amount of dissociation can be calculated from the temperature curve, since two mixtures which give the same temperature must have the same carbon dioxide content at equilibrium. On the rich side, this composition is known, and hence for any dissociated mixture the amount of carbon dioxide formed can be calculated. The values of the equilibrium constants are slightly higher than those found by Bjerrum (A., 1912, ii, 540). The lower limit of inflammability of carbon monoxide and air is raised by increasing the initial pressure. Nitrogen as an inert diluent slows down the flame velocity and subsequent combustion.

R. A. M.

**Rate of Thermal Decomposition of Sulphuryl Chloride. A First-order Homogeneous Gas Reaction.** D. F. SMITH (*J. Amer. Chem. Soc.*, 1925, **47**, 1862—1875).—The decomposition,  $\text{SO}_2\text{Cl}_2 = \text{SO}_2 + \text{Cl}_2$ , at 320° is a reaction of the first order proceeding entirely in the gas phase. At lower temperatures, there appears to be some wall-reaction. It is suggested that the high rates of decomposition of sulphuryl chloride obtained by Hinshelwood and Prichard (T., 1923, **124**, 2725) in presence of glass wool are due to spurious effects. None of the theories of reaction rate as yet put forward has a general application.

J. S. C.

**Theory of Catalysis. I. Kinetics of Mutarotation.** H. VON EULER, A. ÖRLANDER, and E. RUDBERG (*Z. anorg. Chem.*, 1925, **146**, 45—68).—The velocities of mutarotation of  $\alpha$ - and  $\beta$ -dextrose have been determined at 5.2° in solutions of different  $p_{\text{H}}$  value. Both acids and alkalis accelerate the reaction. In acid solution, the mutarotation is not proportional to the hydrogen-ion concentration, but in alkaline solution it is directly proportional to the concentration of hydroxyl ions. Between  $p_{\text{H}}$  2 and  $p_{\text{H}}$  8, the velocity is little affected by the acidity and sinks to a flat minimum at  $p_{\text{H}}$  5, corresponding with the isoelectric point of dextrose, which can act either as an acid or as a base. The velocity constant  $(k_1 + k_2) = 1/t \cdot \log a/(a-x)$ , where  $x$  is the amount transformed after time  $t$ . If  $K_a$  and  $K_b$  are the acidic and basic dissociation constants of dextrose, and  $r_{q_1}$  and  $r_{q_2}$  the specific reactivities of the dextrose anions and cations, the results can be expressed in the form  $(k_1 + k_2) = k_0 + A[\text{H}^+] + B/[\text{H}^+]$ , where  $A = r_{q_2}K_b/K_w = 3.83 \times 10^{-12}$  at 5.2°,  $B = r_{q_1}K_a = 3.78 \times 10^{-2}$ , and  $k_0 = 0.00119$ . At 5.2,  $K_b = 2 \times 10^{-18}$ , and on the assumption that  $r_{q_1} = r_{q_2}$ , the specific reactivity of the dextrose ions is  $r_q = 40$ .

W. H.-R.

**Kinetics of the Thermal Decomposition of the Permanganates.** E. MOLES and M. CRESPI (*Anal. Fis. Quim.*, 1925, **23**, 198—216; cf. A., 1923, ii, 642).—The kinetics of the thermal decomposition of permanganates are discussed, with special reference to the work of Hinshelwood and Bowen (A., 1921, ii, 443), and of Sieverts and Theberath (A., 1922, ii, 360). From their experiments, the authors conclude that these reactions are positive and autocatalytic, and may be represented by the equation  $dx/dt = (k_1 + k_3x/a)(a-x)$ . The decompositions are shown to be made up of two reactions, namely, a simple decomposition and an autocatalytic decomposition which is negligible at first and then passes through a maximum. Comparing the values of the different constants for the decomposition of the permanganates of silver, cadmium, potassium, sodium, caesium, rubidium, barium, and lithium, respectively, it is seen that there is a correlation between the values for total velocity and the heats of formation of the corresponding oxides. G. W. R.

**Velocity of Decomposition of Esters and the Relation to the Hydrogen-ion Concentration.** K. G. KARLSSON (*Z. anorg. Chem.*, 1925, **145**, 1—57).—The velocity constants of the hydrolysis of methyl acetate, ethyl acetate, and monoacetin have been determined at 25° and at various  $p_H$  values, the method used being similar to that previously described (A., 1922, ii, 42). The desired  $p_H$  values were obtained by the addition of hydrochloric acid, acetic acid, or an acetate buffer mixture, and were determined electrometrically at the beginning and end of each experiment; the maximum concentration of sodium acetate in the buffered solutions was 0.05N. Measurements with methyl acetate were also made in the presence of 0.5N concentrations of sodium, calcium, strontium, and barium chlorides, and of sodium sulphate. In the absence of salts the velocity constant for methyl acetate is a minimum at  $p_H$  5.2, and for ethyl acetate and acetin at 5.4 and 5.0, respectively. When the velocity constants are plotted against the  $p_H$  values, the curves are symmetrical about a line vertical to the  $p_H$  axis and passing through the minimum value of the constant, and, except in the neighbourhood of the minimum, the curves are straight lines. The asymmetry of the curves previously obtained at higher temperatures was due to experimental errors unavoidable at such temperatures. In acid solutions the velocity constants are nearly independent of the nature of the ester (cf. A., 1894, ii, 274; 1895, ii, 107), the curves for methyl and ethyl acetates being identical; on the alkaline side of the minimum, there are greater differences. The action of neutral salts is positive, although sodium chloride is practically without influence in the concentration used. The anions of the salts have most influence on the acid side of the minimum and the cations on the alkaline side, and the salt action increases with increasing charge on the ions. In the presence of calcium, strontium, and barium chlorides, the minimum is shifted to a slightly lower  $p_H$ . Comparison with previous results at 85.45° shows that the neutral salt action is much greater at higher temperatures.

It is shown mathematically that the suggestion of von Euler and

Laurin (A., 1921, ii, 498), that carboxylic acid esters are amphoteric electrolytes and that it is only the ions that take part in the hydrolysis, leads to a symmetrical curve of the form found, and that velocity constants calculated on this basis agree approximately with the experimental values. It is also shown that the action of neutral salts can be explained on the assumption that they cause an actual or apparent increase in the dissociation constants, and that the required values of these increases, viz., sodium sulphate, 0.20, strontium and barium chlorides, 0.25, and calcium chloride, 0.40, are close to the values found by Michaelis and Krüger (A., 1922, ii, 157) for the displacement of the dissociation constant of acetic acid, viz., sodium chloride, 0.18, barium chloride, 0.28, and calcium chloride, 0.40.

Similar determinations were also made with ethyl benzenesulphonate, the hydrolysis being, in this case, carried out in the presence of excess of the liquid ester, and separate determinations made of the solubility of the ester in each of the solutions used. The desired  $p_H$  values were obtained by the addition of sodium acetate, sodium hydroxide, or benzenesulphonic acid. The relation between the velocity constant and the  $p_H$  is entirely different from that of the carboxylic esters, in agreement with the fact that it is not an amphoteric electrolyte. The constant remains unchanged in acid solutions, but rises with increasing alkalinity proportionally to the concentration of sodium hydroxide. This is in agreement with the results of Wegscheider and Furcht (A., 1903, i, 342), and Praetorius (A., 1905, i, 186; 1907, i, 835), according to whom the velocity constant for methyl benzenesulphonate is given by the equation:  $dx/dt = kC_{\text{ester}} + k'C_{\text{ester}}C_{\text{NaOH}}$ . The value of the constant  $k$  is nearly the same for the two esters (methyl 7.015, ethyl 6.46), but that of the constant  $k'$  is much lower for the ethyl ester (0.05275 and 0.0070). Sodium chloride increases the velocity constant in acid and alkaline solutions. A. G.

**Velocity of the Reaction  $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$  in the Condensed State.** M. TRAUTZ and W. GERWIG (*Z. anorg. Chem.*, 1925, 146, 1—41).—The solubility of nitric oxide in liquid nitrosyl chloride, pentane, and toluene has been determined at temperatures from  $20^\circ$  to  $-78^\circ$ , and the partial pressures for the solutions in nitrosyl chloride have been calculated on the assumption that the method of Dolezalek can be applied below the critical point. The freezing-point diagram has been determined for mixtures of nitric oxide and chlorine from pure chlorine to the composition corresponding with that of nitrosyl chloride. Mixtures kept for some time show a normal eutectic freezing-point diagram with nitrosyl chloride and chlorine as solid constituents, but freshly-prepared mixtures show a break in the liquidus at the composition of an unstable intermediate compound,  $\text{NOCl}_2$ . The velocity of absorption of nitric oxide by liquid chlorine has been determined at  $-58^\circ$ , whence a complex method permits the calculation of the velocity constants of the reactions involved, which are (1)  $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$ , for which the velocity constant  $k$  is of the order  $10^7$ ,



(2)  $\text{NO} + \text{Cl}_2 \rightarrow \text{NOCl}_2$ , and (3)  $\text{NOCl}_2 + \text{NO} \rightarrow 2\text{NOCl}$ , for which  $k$  (mol./c.c. and secs.) is of the order  $10^2$ . Within the limits of error of the method, the velocities of the pseudo-bimolecular reaction (1) and of the termolecular decomposition of  $\text{NOCl}_2$  (2) are the same if the reaction takes place in the gaseous state or in liquid nitrosyl chloride as solvent, in contradiction to the methods of calculation of van't Hoff.

W. H.-R.

**Reactivity of Silver with Oxygen.** N. PARRAVANO and G. MALQUORI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 622—626).—Silver prepared by precipitation with dextrose and with hydrogen sulphide was heated slowly in a closed vessel in contact with oxygen, originally at 675 mm. pressure. The pressure-temperature curves showed at  $280^\circ$  and  $250^\circ$ , respectively, evidence of reaction extending over a range of about  $50^\circ$ . Crystals of electrolytic silver and massive silver gave no sign of reaction. The above temperatures do not represent equilibrium states, since the vapour pressures of silver oxide at those temperatures are 5.1 and 8.3 atm., respectively. At lower temperatures, the oxygen absorption is greater but slower. The maximum absorption recorded was 0.228% in 5 hrs. by 15 g. of precipitated silver at  $213^\circ$ .

F. G. T.

**Action of Dilute Acid Solutions on Ferrous Metals.** R. GIRARD (*Compt. rend.*, 1925, 181, 215—218).—The action of solutions of sulphuric, hydrochloric, and carbonic acids and of phenol, of concentrations less than 0.1*N*, on polished steel and cast-iron plates is investigated. For a given acid, the two plates are always attacked to equal extents. Below a certain concentration (about 0.001*N*), the acid is the more active the less it is dissociated; above this concentration, the reverse holds. The results for carbonic and hydrochloric acids agree with those of Whitman, Russell, and Altieri (*Ind. Eng. Chem.*, 1924, 16, 665). Sulphuric and hydrochloric acids react similarly to each other. [Cf. *B.*, 1925, 723.]

S. K. T.

**Rapid Corrosion of Metals by Acids within Capillaries.** L. McCULLOCH (*J. Amer. Chem. Soc.*, 1925, 47, 1940—1942).—If a rubber band be wrapped rather tightly round a piece of soft iron and the whole left in dilute hydrochloric acid for some weeks, the iron is found to have been pitted beneath the rubber, the acid acting more rapidly within the capillary spaces between metal and rubber than on the exposed surfaces. An explanation of this is put forward:

J. S. C.

**Induced Oxidation.** W. P. JORISSEN and C. VAN DEN POL (*Rec. trav. chim.*, 1925, 44, 805—809).—Further details of investigations previously described (cf. this vol., ii, 52) are given in support of a criticism of the work of Mitra and Dhar on induced oxidations (this vol., ii, 576). A study of the simultaneous oxidation of sodium sulphate and sodium oxalate or nitrite in aqueous solution is carried out by adding periodically 10 c.c. of the reaction mixture to a standard solution of permanganate and titrating the excess of permanganate with ferrous sulphate or sodium oxalate solutions,

respectively. The end titration of the nitrite or oxalate solutions is uninfluenced by the presence of sodium sulphite, and hence this salt does not induce the oxidation of sodium oxalate or sodium nitrite by atmospheric oxygen under ordinary conditions. The method previously described (*loc. cit.*) for the investigation of the oxidation of sodium antimonite solutions in the presence of sodium sulphite is employed to determine the influence of sodium carbonate on the oxidation of sodium arsenite-sodium sulphite-sodium hydrogen carbonate solutions, the results showing that sodium sulphite does not induce the oxidation of sodium arsenite solution when the alkalinity passes a certain limit (cf. Reinders and Vles, this vol., ii, 567). J. W. B.

**Influence of Water on certain Chemical Reactions. I. Effect of Various Concentrations of Water Vapour on the Reaction between Chlorine and Potassium Iodide or Bromide.** L. B. PARSONS (*J. Amer. Chem. Soc.*, 1925, **47**, 1817—1820).—The minimum partial pressure of water necessary for any appreciable reaction to occur between chlorine and potassium iodide or bromide is approximately the vapour pressure of a saturated aqueous solution of the components present during the reaction. J. S. C.

**Influence of Water on certain Chemical Reactions. II. Reaction between Hydrogen Sulphide and Iodine in Ethereal Solution.** L. B. PARSONS (*J. Amer. Chem. Soc.*, 1925, **47**, 1820—1830).—The reaction between hydrogen sulphide and iodine is complete in absence of water and incomplete in presence of water, the equilibrium point reached depending on the water content of the solvent. In anhydrous ether the reaction proceeds according to the equation  $\text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \text{S}$ . In presence of water, a series of consecutive reactions occurs, which may be formulated into a single equation,  $\text{H}_2\text{S} + 3\text{H}_2\text{O} + 3\text{I}_2 \rightleftharpoons \text{H}_2\text{SO}_3 + 6\text{HI}$ . The changes in the course of the reaction in presence of atmospheric oxygen are ascribed to the formation of ether peroxide which oxidises hydriodic acid to iodine and water, but does not oxidise hydrogen sulphide. J. S. C.

**Influence of Water on certain Chemical Reactions. III. Reactions between certain Metals and Iodine.** L. B. PARSONS (*J. Amer. Chem. Soc.*, 1925, **47**, 1830—1835).—Investigations of systems of various metals with iodine in presence of a number of liquids show that there is a close connexion between the ability of the liquid to bring about reaction and the solubility in the liquid of the metallic iodide. The solvent does not act as a true catalyst, but merely dissolves the thin film of iodide and allows more iodine to come into contact with the metallic surface. J. S. C.

**Sorption of Iodine and Catalytic Decomposition of Hydrogen Peroxide Solution by "Norit" Charcoals.** J. B. FIRTH and F. S. WATSON (*J. Physical Chem.*, 1925, **29**, 987—993).—"Norit" charcoals of grades 1, 2, 3, and 7 shows a very high sorption activity towards iodine in chloroform solution. The percentage of ash does not materially affect the sorption capacity. Charcoals 1 and 2 show feeble catalytic activity towards hydrogen peroxide

solutions, and 3 and 7 show only a moderate activity. A charcoal of high sorptive capacity is not of necessity highly catalytic towards hydrogen peroxide. Results with other active charcoals support this conclusion. J. S. C.

**Catalysis. Active and Inactive Iron Oxide.** O. BAUDISCH and L. A. WELO (*Chem.-Ztg.*, 1925, **49**, 661—662).—When synthetic magnetite is heated in oxygen at 330°, it is converted into a magnetic, catalytically active form of ferric oxide, which has a cubic structure like that of magnetite. When this form of ferric oxide is heated at 550°, it changes to a catalytically inactive, rhombohedral form with the same structure as that of hæmatite. Both active and inactive forms have identical composition and give no blue colour with ferricyanide. Magnetite and the active ferric oxide absorb oxygen, whereas the inactive ferric oxide does not. Both magnetic and catalytic properties depend on the arrangement of atoms in space, and this arrangement plays an important part in catalysis. The catalytic actions studied were (1) the formation of a blue colour in a solution of benzidine hydrochloride and hydrogen peroxide and (2) the growth of *Bacterium leipisepticum*. W. H.-R.

**Effect of Poisonous Substances and Mixed Vapours on Catalytic Activity.** F. H. CONSTABLE (*Proc. Camb. Phil. Soc.*, 1925, **22**, 738—750).—A quantitative study of the dehydrogenation of ethyl and amyl alcohol vapours (alternately or mixed) has been made with copper as catalyst. Both alcohols have the same rate of dehydrogenation. The poisoning of the catalyst by amyl alcohol (from fusel oil) has been followed, and the temperature coefficient of the dehydrogenation of ethyl alcohol has been measured during the poisoning and found to be constant. The temperature coefficient was also unchanged during sintering. The activity of the catalyst poisoned by amyl alcohol decreases in accordance with the logarithmic expression  $\log v = -kt + c$ . An equation is deduced for the rate of poisoning on the assumption that the distribution of the centres of activity is exponential and that the poison attacks the more active centres selectively. The resulting expression cannot usually be distinguished from the simple logarithmic relation. An equation is given showing the reaction velocity as a function of the temperature of the surface and the time. The expression accounts for the heating and cooling curves obtained with "poisonous" alcohols. Except in special circumstances the temperature coefficient remains unaltered after poisoning. R. A. M.

**Catalytic Decomposition of Acetic Acid by Wood Charcoal.** N. V. KULTASHEV and N. A. KUDRJASHEVA (*J. Soc. Phys. Chim. Russe Univ. Leningrad*, 1924, **55**, 383—396).—In contact with wood charcoal, the decomposition of acetic acid proceeds appreciably at 300° and then increases rapidly as the temperature is raised. Under these conditions, the aqueous acid is decomposed to a greater extent than the anhydrous acid at the same temperature. When pure acetic acid is used, about 50% of it undergoes decomposition with formation of methane and acetone, and with dilute solutions of the acid, more than 50% is decomposed according to these reactions.

Under the catalytic influence of the charcoal acetone is decomposed slightly at  $400^{\circ}$ , this decomposition being retarded by dilution of the acetone with water. Messinger's volumetric method for the determination of acetone gives satisfactory results if certain modifications are made in the procedure.

T. H. P.

**Noble Metals as Catalysts of Hydrogenation and Dehydrogenation.** N. D. ZELINSKI and M. B. TUROVA-POLLOK.—(See i, 1052.)

**Electrochemistry of Non-Aqueous Solutions. VI. Electrodeposition of some Metals from Anhydrous Solutions in Amyl Alcohol, Acetonitrile, Aniline, and Quinoline.** R. MÜLLER, E. PINTER, and K. PRETT (*Monatsh.*, 1924, 45, 525—534).—Electrolysis of solutions of lithium nitrate or magnesium bromide in acetonitrile and of calcium nitrate in amyl alcohol with mercury or platinum cathode did not yield the respective metals, decomposition occurring at voltages below those found for the metal against such solutions. On the other hand, crystalline silver was deposited when solutions of silver nitrate in amyl alcohol, acetonitrile, quinoline, or aniline were electrolysed, the potential differences being constant and easily reproducible, so that the reversibility of the silver electrode is proved with these solvents. Values of the potential differences for various current densities in each case are tabulated and represented graphically. The decomposition potential of silver nitrate is 1.0 volt in amyl alcohol, 1.15 volts in acetonitrile, 2.15 volts in quinoline, and 0.5 volt in aniline solution.

G. M. B.

**Production of Antimony Hydride (Stibine) at an Antimony Cathode in Alkaline Solution.** E. J. WEEKS (*Rec. trav. chim.*, 1925, 44, 795—797; cf. A., 1924, ii, 606; this vol., ii, 415).—The yields of stibine obtained when sodium carbonate and sodium sulphate solutions are electrolysed using an antimony cathode are determined. The yield may be calculated approximately from the formula  $\gamma = 12.6h - 8.2$ , where  $\gamma$  is the percentage yield of stibine, and  $h$  the  $p_H$  voltage (cf. Sand and Weeks, A., 1924, ii, 152). The following relationships are also deduced:  $\omega = -0.0282\gamma + C_1$ ,  $\gamma + 20 = C/T$ ,  $\gamma = C_1 - C_2 \log [\text{OH}]$ , where  $\omega$  is the overvoltage,  $[\text{OH}]$  the hydroxyl-ion concentration,  $T$  the absolute temperature, and  $C_1$  and  $C_2$  are constants.

J. W. B.

**Potassium Dichromate as Depolariser.** G. P. VINCENT (*J. Physical Chem.*, 1925, 29, 875—881; cf. Bancroft, *ibid.*, 1924, 28, 831).—The depolarising action of saturated potassium dichromate solution on hydrogen liberated at a smooth platinum electrode has been studied in the presence of varying amounts of sulphuric acid. About 0.28% by volume of concentrated sulphuric acid is necessary before appreciable depolarisation occurs. With a clean mercury cathode, the neutral solution shows 100% depolarisation of the hydrogen set free. Neutral  $M/40$ -potassium permanganate has a distinct depolarising effect on hydrogen at a platinum cathode and also causes appreciable corrosion of zinc, iron, and copper. Corrosion of these metals is only shown by saturated potassium

dichromate solution when acidified, different amounts of acid being required in each case. No corrosion occurs in saturated potassium dichromate solutions when copper is short-circuited with mercury or platinum, or when iron is short-circuited with mercury. Zinc when short-circuited with mercury corrodes slightly and more rapidly in 0.02% acetic acid than in 0.02% sulphuric acid (cf. Bengough and Stuart, *J. Inst. Metals*, 1922, 28, 89). F. G. S.

**Periodic Phenomena in Photochemistry.** J. PLOTNIKOV (*Z. Physik*, 1925, 32, 942—947).—Konigsberger ("Tropismus und Wachstum," 1922) had observed that plants, when allowed to grow at constant temperature and under monochromatic light, increased at a steady rate; when, however, light of two or more different wavelengths was used, the growth was periodic. Other instances of periodicity are the decrease in concentration of chlorine and bromine in carbon tetrachloride solution and the bleaching of dyes. Further work is necessary before any satisfactory explanation can be given. E. B. L.

**Action of Radiation on Gas Mixtures.** H. SENTLEBEN (*Z. Physik*, 1925, 32, 922—932).—Dissociation of a gas is accompanied by a change in conductivity for heat. A wire in one arm of a Wheatstone's bridge was maintained at a constant temperature in a tube the walls of which were kept at a different temperature. The tube was of silica and contained mercury at the ordinary temperature and hydrogen at about 10 mm. pressure. On exposure to the light from the mercury arc, an immediate fall in the resistance of the wire was observed and shown to be due to the increase in thermal conductivity of the gas and hence to the dissociation of the hydrogen, brought about by collisions of the second type with mercury atoms excited by the line 2537 Å. With a mixture of neon and helium or with the aluminium spark, there was no effect. The method can be used for determining the heat of dissociation of a polyatomic gas and also as an indication of the state of excitation of a gas. E. B. L.

**Photochemical Decomposition of Chlorine Monoxide.** M. BODENSTEIN and G. KISTIakovSKI (*Z. physikal. Chem.*, 1925, 116, 371—390; cf. T., 1923, 123, 2328, 2730).—An improved method of preparing chlorine monoxide is described. The decomposition of the gas by light of 405 and of 436 m $\mu$  was investigated; 1 quantum of absorbed light decomposes 2 mols. It is immaterial whether the energy is absorbed by the monoxide or by the chlorine formed during the reaction. The reaction is unaffected by admixed air. The temperature coefficient is 1.09 per 10°. Small amounts of chlorine dioxide are formed during decomposition by light or by gentle warming. L. F. G.

**Mechanism of the Photochemical Reaction between Hydrogen and Chlorine.** A. L. MARSHALL (*J. Physical Chem.*, 1925, 29, 842—852; cf. Bodenstein, A., 1916, ii, 422; Nernst, A., 1919, ii, 208; Chapman and Chapman, T., 1923, 123, 3079; Weigert and Kellermann, A., 1924, ii, 8; Bowen, J., 1924, 125, 1233).—The reaction between hydrogen and chlorine has been studied by intro-

ducing a mixture of atomic and molecular hydrogen into chlorine, and determining the ratio of the concentration of the hydrogen chloride produced to that of atomic hydrogen present. The concentrations of atomic hydrogen and molecular chlorine were approximately constant and that of molecular hydrogen was progressively increased. The ratio of hydrogen chloride to atomic hydrogen increased from unity at a total gas pressure of 0.004 cm., measured on a McLeod gauge, to 7 mols. per atom at a pressure of 0.60 cm. The concentration of atomic hydrogen was determined by control experiments involving admixture of the hydrogen with bromine. One mol. of hydrogen bromide results from 1 atom of hydrogen. It is difficult to interpret the observed increase of the hydrogen chloride formed except by a mechanism involving an excited chlorine molecule (cf. Bodenstein, *loc. cit.*), collision of which with hydrogen before re-radiation of its energy occurs being more probable at higher hydrogen pressures. The Nernst theory is discussed and a number of objections are advanced. F. G. S.

**Light-sensitiveness of Potassium Ferrocyanide.** E. BAUR (*Helv. Chim. Acta*, 1925, 8, 403—405).—The author confirms the observation of Baudisch (A., 1922, i, 993) that alkaline solutions of potassium ferrocyanide become discoloured on exposure to light in absence of oxygen. In addition, he obtains under these conditions a deposit of ferric hydroxide and concludes that the discoloration is due to the latter in colloidal form. Acid solutions are similarly discoloured, giving a precipitate of Prussian blue instead of hydroxide. Failure to detect formaldehyde or ammonia indicates reduction of the cyanide ion, as a counterbalance to the oxidation of the ferrous ion in the ferrocyanide complex. Only free hydrocyanic acid is found.

With potassium ferrocyanide freed from ferricyanide by Treadwell and Chervet's method (A., 1922, ii, 786), the production of ferric hydroxide is almost completely eliminated; hence perfectly pure ferrocyanide solutions, whether acid or alkaline, would be entirely insensitive. The sensitiveness must therefore be ascribed to the establishment of an equilibrium in the ferri- and not the ferro-cyano complex:  $[\text{Fe}(\text{CN})_6]''' \rightleftharpoons \text{Fe}''' + 6\text{CN}'$ . M. J.

**Photosynthesis in Tropical Sunlight.** N. R. DHAR and R. P. SANYAL (*J. Physical Chem.*, 1925, 29, 926—934; cf. Baly and others, T., 1921, 119, 1025; 1922, 121, 1078; 1923, 123, 185).—The statement that the light effective for the formation of formaldehyde has very short wave-length and that no such rays are present in sunlight is held to be incorrect. Experiments carried out in glass vessels in tropical sunlight, the spectrum of which is shown to contain no line of wave-length less than  $290 \mu\mu$ , afford definite proof of the synthesis of formaldehyde from carbon dioxide and water, with or without the use of any catalyst. Experiments on the polymerisation of formaldehyde were not so successful, traces of sugars only being obtained when formaldehyde solutions were exposed to the sunlight in presence of ferric chloride and methyl-orange.

Tropical sunlight is effective in promoting oxidation. Alcohols

are oxidised to the corresponding aldehydes. When air or oxygen is passed into solutions of ammonia, tests for nitrites are obtained. Exposure of ammonia and oxygen results in the formation of nitrogen. The reducing action is considerable; solid iodic acid gives iodine, potassium chlorate shows traces of chloride, and nitrates are converted into nitrites.

Ultra-violet light is more effective in certain photosyntheses, but tropical sunlight contains a number of rays which can effect the synthesis of complex compounds from simple substances. Methylamine, which is formed in about 12 hrs. when ammonia and formaldehyde are exposed to tropical sunlight, passes into a number of complex substances of the alkaloid type. Experiments with ultra-violet light show that nitrogen and oxygen combine to form nitrogen oxides. The difference between the action of sunlight and ultra-violet light in promoting photosynthesis is one of degree rather than of kind. J. S. C.

**Active Hydrogen.** A. BACH (*Ber.*, 1925, 58, [B], 1388—1393).—Recently-melted platinum contains adsorbed sulphur compounds and evolves hydrogen sulphide when heated in hydrogen; according to experimental conditions, this power is more or less rapidly lost. Passage of the evolved hydrogen over powdered sulphur does not increase the amount of hydrogen sulphide produced from the fresh metal and does not cause formation of hydrogen sulphide after the metal has become "tired." Treatment of the "tired" metal with ordinary laboratory air restores its ability to give hydrogen sulphide when heated in hydrogen; under similar conditions, no trace of hydrogen sulphide is produced after treatment with carefully purified air. The phenomenon of "resting" depends therefore on the adsorption of sulphur compounds from the air. Palladium-sponge behaves similarly to platinum. Reduction of nitrate to nitrite, methylene-blue to the leuco-base, or of tungsten trioxide to dioxide by active hydrogen could not be observed. H. W.

**Displacement of Metals from Solutions of their Salts by less Electro-positive Elements. II. Reaction between Amides of the Alkali and Alkaline-earth Metals and Elements more Electro-positive than Tin.** F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1925, 47, 1836—1841; cf. A., 1924, ii, 106, 607).—The initial reaction involves a partial replacement of the more electro-positive metal by the less electro-positive:  $\text{Al} + 3\text{NH}_2\text{K} \rightleftharpoons \text{Al}(\text{NH}_2)_3 + 3\text{K}$ . Equilibrium is displaced by secondary reactions with formation of ammono salts, the mechanism being analogous to that of the reaction between solutions of strong aquo bases (e.g., potassium hydroxide) with zinc or aluminium. Impure specimens of potassium ammonolanthanite,  $\text{La}(\text{NHK})_3 \cdot 2-3\text{NH}_3$ , and potassium ammonocerite,  $\text{Ce}(\text{NHK})_3 \cdot 2-3\text{NH}_3$ , have been prepared by the action of an excess of potassamide on the corresponding metal or metallic halide. Potassamide slowly reacts with gallium to form an extremely soluble ammonogallate. Cadmium, chromium, iron, cobalt, molybdenum, tungsten, and thallium either

fail to react or react extremely slowly. In general, the more electro-positive a metal is, the more readily does it react with potassamide. Solutions of amide react readily with liquid amalgams of magnesium, zinc, and cadmium to form precipitates approximating in composition to the corresponding amides, but contaminated with varying quantities of potassium. Amalgamated aluminium in contact with mercury is less readily, and a dilute iron amalgam very slowly, attacked.

J. S. C.

**Complex Compounds of Beryllium. I.** R. FRICKE and F. RUSCHHAUPT (*Z. anorg. Chem.*, 1925, **146**, 103—120).—By the crystallisation of hot solutions of anhydrous beryllium chloride in dry acetonitrile, benzonitrile, pyridine, or acetone, in the complete absence of water, complex compounds of beryllium are formed of the general type  $\text{BeCl}_2 \cdot 2\text{X}$ , where X is a molecule of the organic solvent. These correspond with a co-ordination number 4, but the number 8 is also found in the compound  $\text{BeCl}_2 \cdot 2\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3 \cdot 4\text{C}_6\text{H}_6$ , which is formed when a solution of beryllium chloride in acetone is treated with benzene and then allowed to crystallise. The compound  $\text{BeCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$  is best prepared by the addition of beryllium chloride to a mixture of benzene and pyridine instead of pyridine alone. All these compounds form colourless crystals and are at once decomposed by water. The compounds  $\text{BeCl}_2 \cdot 2\text{MeCN}$  and  $\text{BeCl}_2 \cdot 2\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$  and the compound  $\text{BeCl}_2 \cdot 2\text{PhCN}$  are described. A compound,  $\text{BeSO}_4 \cdot \text{en} \cdot \text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ , is obtained by the crystallisation of an aqueous solution of beryllium sulphate, ethylenediamine, and sulphuric acid in equimolecular proportions.

W. H.-R.

**Complex Compounds of Beryllium. II.** R. FRICKE and L. HAVESTADT (*Z. anorg. Chem.*, 1925, **146**, 121—131; cf. preceding abstract).—The compounds  $\text{BeCl}_2 \cdot 2\text{Ph} \cdot \text{NO}_2$ ,  $\text{BeCl}_2 \cdot 2\text{Ph} \cdot \text{CHO}$ ,  $\text{BeCl}_2 \cdot 2\text{Ph} \cdot \text{NH}_2$ , and  $\text{BeCl}_2 \cdot 2\text{Et}_2\text{O}$  are formed by the crystallisation of hot solutions of anhydrous beryllium chloride in the dry organic compound, the last named requiring special details for which the original must be consulted. The compound  $\text{BeCl}_2 \cdot 4\text{NH}_2\text{Me}$  and the compound  $\text{BeCl}_2 \cdot 4\text{NH}_3$  are precipitated quantitatively when a dry ethereal solution of beryllium chloride is treated with excess of dry methylamine or ammonia, respectively. The above compounds correspond with a co-ordination number 4, whilst the number 8 is shown in the compound  $\text{BeCl}_2 \cdot 2\text{NH}_3 \cdot 4\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_3$ , prepared by the action of gaseous ammonia on a solution of beryllium chloride in acetone; this compound resembles the benzene-acetone complex previously described (preceding abstract). In addition, the co-ordination number 6 is shown in the compound  $\text{BeCl}_2 \cdot 3\text{Ph} \cdot \text{NH} \cdot \text{NH}_2$ , prepared by the crystallisation of a dry ethereal solution of beryllium chloride and phenylhydrazine. These compounds form white crystals with the exception of  $\text{BeCl}_2 \cdot 2\text{Ph} \cdot \text{NO}_2$ , which is pale yellow. All are decomposed by water, but with  $\text{BeCl}_2 \cdot 2\text{Ph} \cdot \text{NH}_2$  and  $\text{BeCl}_2 \cdot 3\text{Ph} \cdot \text{NH} \cdot \text{NH}_2$  the action is very slow. Beryllium chloride also form a complex of unknown composition with nitromethane, whilst impure beryllium phenoxide is formed when beryllium chloride and phenol are heated to the b. p.

W. H.-R.



**Spectrographic Study of the Formation of Mercury Complexes.** P. JOB (*Compt. rend.*, 1925, **180**, 1932—1933; cf. this vol., ii, 471).—The method developed for the detection of complexes in aqueous solution by spectrographic means has been extended to the systems  $\text{HgCl}_2\text{—KCl}$ ;  $\text{HgCl}_2\text{—KBr}$ ;  $\text{HgCl}_2\text{—KI}$ . Experiments failed to indicate the existence of mercury-chlorine complexes, but the existence of the tetrabromo-mercury complex was established; it is formed by double decomposition from potassium bromide and mercuric chloride. Potassium bromide reacts with mercuric nitrate or sulphate to give mercuric bromide, which then reacts with excess of bromide to give the tetrabromo complex. The tetraiodo complex is similarly formed. Mass action constants are given. R. A. M.

**Origin of Natural Aluminium Hydrosilicates.** R. SCHWARZ and R. WALCKER (*Z. anorg. Chem.*, 1925, **145**, 304—310).—Aluminium hydroxide sol and silicic acid sol in neutral aqueous medium in the proportion  $1\text{Al}_2\text{O}_3 : 6\text{SiO}_2$ , precipitate a substance of the composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , which on keeping becomes similar to kaolin. The theory is advanced that the primary process in the transition of feldspar to kaolin consists in a decomposition of the feldspar into its components:  $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \rightarrow 2\text{KOH} + 2\text{Al}(\text{OH})_3 + 6\text{SiO}_2\text{aq.}$ ; and that then, under special conditions, the products reunite to form kaolin or an intermediate product. The connexion between coagulation and hydrogen-ion concentration is investigated by means of the reaction  $2\text{AlCl}_3 + 6\text{Na}_2\text{SiO}_3 + 6\text{HCl} = \text{Al}_2\text{O}_3 + 6\text{SiO}_2 + 12\text{NaCl} + 3\text{H}_2\text{O}$ . By varying the amount of free acid present, it is found that complete precipitation only takes place in a feebly acid medium,  $p_{\text{H}}$  4.5—5.2. The optimal zone is at  $p_{\text{H}}$  4.8—5.0. In each case, a large excess of silicic acid remains in the sol form, since the ratio  $\text{Al}_2\text{O}_3 : \text{SiO}_2$  in the precipitate is 1 : 2. An investigation of the influence of the anion on the composition of the precipitation product shows that, by using aluminium acetate instead of the chloride, no difference is to be observed. Some experiments with a salt of the composition  $\text{Na}_4\text{Si}_3\text{O}_8$ , instead of sodium metasilicate, give a value somewhat greater than 2 for the molecular ratio of  $\text{SiO}_2$ , whereas with sodium metasilicate, it is somewhat less than 2. Possibly with the acid  $\text{H}_2\text{Si}_2\text{O}_5$  the exact ratio 1 : 2 would be obtained. Experiment appears to confirm the view that the natural formation of kaolin is not due to an ionic reaction, but to the mutual coagulation of aluminium hydroxide sol and silicic acid sol. L. L. B.

**Thermal Analysis of the Systems Thallous Sulphide—Arsenic Trisulphide and Thallous Sulphide—Lead Sulphide.** G. CANNERY and L. FERNANDES (*Atti R. Accad. Lincei*, 1925, [vi], **1**, 671—676).—Thermal analysis of the former system indicates the existence of the compounds  $\text{Tl}_3\text{AsS}_3$ ,  $\text{Tl}_4\text{As}_2\text{S}_5$ ,  $\text{Tl}_6\text{As}_4\text{S}_9$ , and  $\text{TlAsS}_2$ , m. p., respectively, 295°, 278°, 317°, and 300°. The ortho- and pyro-thioarsenites,  $\text{Tl}_3\text{AsS}_3$  and  $\text{Tl}_4\text{As}_2\text{S}_5$ , occur at transition points and decompose on fusion. Thallous sulphide and lead sulphide, completely miscible in the liquid state, are only partly so in the solid state, conjugate solid solutions containing

respectively 3 and 75% of lead sulphide separating at 290°. This system possesses a eutectic mixture, containing 40% of lead sulphide, m. p. 290°. Lead sulphide precipitated from slightly acid solutions containing thallium contains up to 4% of thallos sulphide. The results indicate the probable occurrence of thallium in arsenic minerals as thio-salts in solid solution in the corresponding lead salts, whilst in galena the thallium occurs as sulphide in isomorphous mixture with lead sulphide.

F. G. T.

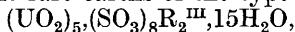
**Combustion of Carbon.** I. H. F. SMITH and W. C. EBAUGH (*Ind. Eng. Chem.*, 1925, 17, 694—695).—From tests conducted in an experimental producer in which the oxidising and reducing zones were clearly defined, it is concluded that at a bright red heat carbon monoxide is the principal, if not the primary, product of combustion, and that the oxidising zone is very thin indeed. [Cf. *B.*, 1925, 657.]

D. G. H.

**Germanium. XI. Germanium Glasses.** L. M. DENNIS and A. W. LAUBENGAYER (*J. Amer. Chem. Soc.*, 1925, 47, 1945—1947).—Germanium glasses of four types have been prepared and compared with the corresponding silicate glasses. Replacement of silicon by germanium raises the refractive index. Owing to their much lower m. p., homogeneous, air-free germanium glasses can be prepared much more easily than the corresponding silicates.

J. S. C.

**Complex Sulphites and Thiosulphites of the Rare-earth Metals.** G. CANNERI and L. FERNANDES (*Gazzetta*, 1925, 55, 440—453).—Metals of the cerium group, by virtue of their high basicity, combine with complex acid radicals to form compounds analogous to those of the alkali and alkaline-earth metals. In these compounds the individuality of the complex is not destroyed by the physical and chemical characteristics of the rare earths. *Uranylsulphites* of the rare earths of the type



where R=La, Ce, Nd, and Pr, were obtained by crystallising in a vacuum at the ordinary temperature, a solution, saturated with sulphur dioxide, containing the rare-earth hydroxide and uranyl sulphate. The products obtained were microcrystalline and of constant composition. By saturating a very concentrated solution of ammonium paramolybdate with sulphur dioxide, and adding a solution of the rare-earth acetate, *molybdosulphites* of the rare earths were obtained as minute prisms. The composition of these crystals varied on fractional crystallisation, the rare-earth content falling. It was not possible to assign rational formulæ to them, and it is suggested that this is due to the partial miscibility in the solid state of ammonium molybdosulphite with the corresponding rare-earth compounds. *Cuprosulphites* of the rare earths were obtained as minute crystals by crystallising under reduced pressure a warm solution of copper carbonate and the rare-earth hydroxide, saturated with sulphur dioxide. These compounds are darker in colour and much less stable than the corresponding alkali metal compounds.

The general formula of these compounds was  $\text{RCu}(\text{SO}_3)_2 \cdot 8\text{H}_2\text{O}$ , where  $\text{R}=\text{Ce}$ ,  $\text{La}$ ,  $\text{Pr}$ , or  $\text{Nd}$ . *Cuprothiosulphates* of the formulae  $\text{RCu}(\text{S}_2\text{O}_3)_2 \cdot 8\text{H}_2\text{O}$  ( $\text{R}=\text{Ce}$ ,  $\text{La}$ ,  $\text{Pr}$ ,  $\text{Nd}$ ,  $\text{Th}$ ) and  $\text{ZrCu}_2(\text{S}_2\text{O}_3)_3 \cdot 30\text{H}_2\text{O}$  were obtained as yellow, microcrystalline precipitates, by mixing solutions of copper sulphate and a soluble rare-earth salt, each previously saturated with sulphur dioxide. In the cases of thorium and zirconium, the solutions must be neutral before the addition of the thiosulphate.

F. G. T.

### Mechanism of the Fixation of Nitrogen as Sodium Cyanide.

E. W. GUERNSEY and M. S. SHERMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 1932—1940).—The formation of sodium cyanide in the system, sodium carbonate-carbon-iron-nitrogen at high temperatures is represented by the reaction scheme:  $\text{Na}_2\text{CO}_3 \rightleftharpoons \text{Na}_2\text{O} + \text{CO}_2$ ;  $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$ ;  $\text{Na}_2\text{O} + \text{C} \rightleftharpoons 2\text{Na} + \text{CO}$ ;  $2\text{Na} + 2\text{C} \rightleftharpoons \text{Na}_2\text{C}_2$ ;  $\text{Na}_2\text{C}_2$  (gaseous) +  $\text{N}_2 \rightleftharpoons 2\text{NaCN}$ . The absorption of nitrogen by sodium carbide is the only one of the series of reactions which is catalysed by iron. The existence of such intermediates as sodium nitride, sodium cyanamide, or cyanogen is improbable.

J. S. C.

### Composition and Stability of Complex Metal-Ammonium Ions.

(MISS) H. J. DE WIJS (*Rec. trav. chim.*, 1925, **44**, 663—674).—The composition of complex metal-ammonium ions was examined by determining the pressure of the gas over a solution of these ions by a dynamic method. The composition of the ion  $\text{M}_m(\text{NH}_3)_n^{++}$  is given by  $n/m = (b - b_1)/a$ , where  $a$  is the concentration of the metallic salt,  $b$  that of ammonia, and  $b_1$  that of free ammonia. This equation can be applied only if the solution contains no free metallic ion or other complex ion. The existence of the ions  $\text{Ag}(\text{NH}_3)_2^+$ ,  $\text{Cu}(\text{NH}_3)_4^{++}$ ,  $\text{Cd}(\text{NH}_3)_4^{++}$ ,  $\text{Zn}(\text{NH}_3)_4^{++}$ , and  $\text{Ni}(\text{NH}_3)_6^{++}$  is indicated. The values of the constants  ${}_2K_c$  and  ${}_4K_c$  for the equilibria  $\text{M}(\text{NH}_3)_2^{++} \rightleftharpoons \text{M}^{++} + 2\text{NH}_3$  and  $\text{M}(\text{NH}_3)_4^{++} \rightleftharpoons \text{M}^{++} + 4\text{NH}_3$  were found to be  $2.7 \times 10^{-5}$  and  $2.5 \times 10^{-7}$ , respectively, for cadmium and  $1.4 \times 10^{-5}$  and  $9.3 \times 10^{-10}$  for zinc. For nickel,  ${}_2K_c = 2.4 \times 10^{-5}$ ,  ${}_4K_c = 4.8 \times 10^{-8}$ ,  ${}_6K_c = 2.1 \times 10^{-8}$ .

L. L. B.

**Action of Phosphorus on Salts containing Oxygen [Nickel Nitrate].** I. W. SCHMOSS (*Bul. Soc. Chim. România*, 1925, **7**, 32—35).—On boiling with yellow phosphorus in an atmosphere of carbon dioxide an alcoholic solution of nickel nitrate, saturated at  $20^\circ$ , for 36 hrs., a pale green precipitate of nickel triphosphate is produced. After washing with benzene and drying at  $20^\circ$ , this compound has the composition  $\text{NiH}_3\text{P}_3\text{O}_{10} \cdot 3\text{H}_2\text{O}$  and  $d_4^{25} 2.159$ . It loses  $3\text{H}_2\text{O}$  at  $100$ — $110^\circ$  and is slightly soluble in water and readily soluble in ammonia and in mineral acids.

A. R. P.

**High-melting Lower Oxides.** E. FRIEDERICH and L. SITTING (*Z. anorg. Chem.*, 1925, **145**, 127—140).—A series of lower oxides has been prepared by reducing the corresponding higher oxides with hydrogen or carbon. From titanium and zirconium dioxides and from tantalum pentoxide no lower oxides of definite composition could be obtained, and it is doubtful whether the previously recorded oxides,  $\text{Ta}_2\text{O}_4$  and  $\text{Ta}_2\text{O}_3$ , exist (cf. this vol., ii, 374). From

vanadium pentoxide a sesquioxide,  $V_2O_3$ , m. p.  $1970^\circ$ , and a tetroxide,  $V_2O_4$ , m. p.  $1640^\circ$ , were obtained by reduction with hydrogen and carbon, respectively; the former was not further reduced by hydrogen, even at  $1700^\circ$ . From niobium pentoxide and cerium dioxide sesquioxides,  $Nb_2O_3$ , m. p.  $1780^\circ$ , and  $Ce_2O_3$ , m. p.  $1690^\circ$ , were prepared by reduction with hydrogen. The oxides  $WO_2$ , m. p.  $1230$ – $1330^\circ$ ,  $W_2O_5$ ,  $MoO_2$ , and  $Mo_2O_5$ , were obtained by reducing the trioxides with carbon or with metallic tungsten and molybdenum, respectively. The oxide,  $U_3O_8$ , formed when uranium trioxide was heated in air, yielded the blue and brown forms of the dioxide,  $UO_2$ , when heated in nitrogen and hydrogen, respectively; both forms melt at  $2230$ – $2330^\circ$ .

These lower oxides differ widely in electrical resistance, but the temperature coefficients are all negative. Tungsten and molybdenum pentoxides have lower resistances than the corresponding dioxides, and the two forms of uranium dioxide differ in specific resistance.

A. G.

**Action of certain Reagents on Ozone.** L. I. SMITH (*J. Amer. Chem. Soc.*, 1925, **47**, 1850–1853).—The destruction of ozone on passing through dilute or concentrated sulphuric acid or acid permanganate solution is so slight as to be negligible. Considerable destruction is produced by 5% sodium hydroxide solution and by ordinary specimens of phosphorus pentoxide. Phosphorus pentoxide after sublimation in a current of oxygen loses its ability to destroy ozone.

J. S. C.

**Sulphur Sesquioxide.** I. VOGEL and J. R. PARTINGTON (*J. Chem. Soc.*, 1925, **127**, 1514–1524).—Sulphur sesquioxide,  $S_2O_3$ , is prepared by adding liquid sulphur trioxide to finely-powdered sulphur in the absence of moisture. After 30 secs. a violent reaction takes place and a bluish-green solid is deposited. The supernatant liquid is poured off and adherent sulphur trioxide removed by warming in a vacuum. Sulphur sesquioxide is at once decomposed by water, a complex reaction taking place in which sulphur is deposited and a mixture of sulphuric, sulphurous, tri-, penta-, and possibly tetra-thionic acids are produced. It reacts violently with ether and alcohol, whilst with sodium ethoxide in alcoholic solution it forms sodium ethyl sulphonylate,  $NaEtSO_2$ , which hydrolyses to form sodium sulphonylate. The sesquioxide soon decomposes at the ordinary temperature with evolution of sulphur dioxide and deposition of sulphur, but it may be preserved unchanged in a completely dry oxygen-free atmosphere at a pressure of less than 1 mm. of mercury. It dissolves in fuming sulphuric acid to form a blue solution which is a true and not a colloidal solution. W. H.-R.

**Additive Products of Selenium Dioxide with the Halogen Acids.** C. W. MUEHLBERGER and V. LENHER (*J. Amer. Chem. Soc.*, 1925, **47**, 1842–1844).—The compounds  $SeO_2 \cdot 2HCl$  and  $SeO_2 \cdot 2HBr$  are identical with the hydrates  $SeOCl_2 \cdot H_2O$  and  $SeOBr_2 \cdot H_2O$ , respectively. The former has  $d^{25}_D$  2.246, a surface tension at  $25^\circ$  of 55 dynes/cm.<sup>2</sup>, an electrical conductivity  $2.7 \times 10^{-2}$

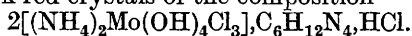
mho, and  $n^{20}$  1.642. The m. p. is below  $-100^\circ$ . Dissociation begins at  $94^\circ$ , the b. p. rising to  $179^\circ$  without indication of any constant-boiling mixture. Metals react to form chlorides and selenites, there being also a simultaneous reduction to selenium monochloride and elementary selenium. The substance readily reacts with sulphur, phosphorus, arsenic, selenium, tellurium, and the halogens.

Selenium oxychloride is conveniently prepared by mixing 4 parts of  $\text{SeO}_2 \cdot 2\text{HCl}$  with 1 part of sulphuric acid ( $d$  1.84). The oxychloride prepared in this way has b. p.  $176^\circ$ , m. p.  $10.9^\circ$ ;  $d^{22}$  2.424.

The compound  $\text{SeO}_2 \cdot 2\text{HBr}$ ,  $d^{22}$  3.077, is prepared as a red-brown oil on passing hydrogen bromide over selenium dioxide. At  $115^\circ$ , it begins to decompose, producing bromine, selenium monobromide, tetrabromide, and oxybromide, selenium dioxide, water, and hydrogen bromide. On cooling to  $-10^\circ$ , crystals of selenium tetrabromide separate. An excess of selenium dioxide causes the separation of yellow needles (m. p.  $40^\circ$ ) of the oxybromide,  $\text{SeOBr}_2$ . The existence of  $\text{SeO}_2 \cdot 4\text{HBr}$  is verified, but no evidence was obtained as to the existence of the compound  $\text{SeO}_2 \cdot 5\text{HBr}$ . J. S. C.

**Dichromates of Ter- and Sexavalent Metals.** G. CALCAGNI (*Gazzetta*, 1925, 55, 396—406).—A highly hygroscopic, amorphous paste of *chromium dichromate*,  $\text{Cr}_2(\text{Cr}_2\text{O}_7)_3$ , was obtained by evaporating a solution of chromium oxide in chromic acid, and the less hygroscopic basic ferric dichromate,  $\text{Fe}_2\text{O}(\text{Cr}_2\text{O}_7)_2$ , from a solution of ferric hydroxide in chromic acid. A *basic aluminium dichromate*,  $\text{Al}_2\text{O}(\text{Cr}_2\text{O}_7)_2$ , and *molybdenum dichromate*,  $\text{Mo}(\text{Cr}_2\text{O}_7)_3$ , were obtained by analogous methods. Attempts to prepare the corresponding compounds of uranium and tungsten were unsuccessful. F. G. T.

**Complex Derivatives of Quinquevalent Molybdenum.** G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1925, [vi], 1, 676—679).—Klason's salt, ammonium molybdenyl chloride,  $(\text{NH}_4)_2\text{MoOCl}_5$  (A., 1901, ii, 162), may act both as a complex and as a double salt. Pyridine acetate precipitates from a cold saturated solution of Klason's salt a brick-red double compound of pyridine and molybdenyl chloride,  $\text{MoOCl}_3 \cdot \text{C}_5\text{H}_5\text{N}$ , whilst from a solution of Klason's salt in aqueous alcohol, hexamethylenetetramine hydrochloride precipitates dark red crystals of the composition



F. G. T.

**Molybdovanadates. II.** G. CANNERI (*Gazzetta*, 1925, 55, 390—396; cf. A., 1924, ii, 118).—The systems  $\text{NH}_4\text{VO}_3\text{--MoO}_3$ ,  $\text{KVO}_3\text{--MoO}_3$ , and  $\text{NaVO}_3\text{--MoO}_3$  have been investigated at  $15^\circ$ . As at  $30^\circ$ , two kinds of crystals are obtained from solutions containing alkali vanadates and molybdic anhydride: red, well-formed, soluble crystals, rich in vanadium, and colourless or yellow, sparingly soluble crystals, rich in molybdenum. The composition of the crystals is generally related to that of the solution, but an apparent anomaly occurs with the red crystals obtained from the system  $\text{KVO}_3\text{--MoO}_3$ . The molybdic oxide content of these crystals

decreases from 14.62% to 0.34% as the ratio  $\text{MoO}_3 : \text{V}_2\text{O}_5$  in the solution increases from 0.5 to 1.125. This apparent contradiction of the hypothesis that the red crystals are isomorphous mixtures is explained by the assumption that the molybdenum is distributed in the solution between a polyvanadate form and that of a complex radical of a heteropoly-anion type, the equilibrium between these being dependent on the amount of molybdenum present and on the temperature. This assumption is supported by the fact that from solutions in which the ratio  $\text{MoO}_3 : \text{V}_2\text{O}_5$  is greater than 1.125, a yellow compound, very rich in molybdenum, separates. Comparison of the behaviour of these systems at 30° and 15° shows that the solubility in the solid state of the polymolybdate compounds in the polyvanadates increases with temperature. On fractionation, the red crystals decrease in molybdenum content, approaching the hexavanadates in composition. On the other hand, increase of the temperature of fractionation results in an augmented molybdenum content. The following are reported as definite compounds:  $2(\text{NH}_4)_2\text{O}, 3\text{MoO}_3, 2\text{V}_2\text{O}_5, 8\text{H}_2\text{O}$ , long, lemon-yellow prisms;  $4(\text{NH}_4)_2\text{O}, 6\text{MoO}_3, 2\text{V}_2\text{O}_5, 6\text{H}_2\text{O}$ , yellow prisms;  $4\text{K}_2\text{O}, 6\text{MoO}_3, 3\text{V}_2\text{O}_5, 10\text{H}_2\text{O}$  and  $5\text{K}_2\text{O}, 10\text{MoO}_3, 4\text{V}_2\text{O}_5, 14\text{H}_2\text{O}$ , both yellow;  $2\text{Na}_2\text{O}, 3\text{MoO}_3, \text{V}_2\text{O}_5, 10\text{H}_2\text{O}$ , yellow micro-crystals.

F. G. T.

**Complex Compounds of Pyrocatechol and Pyrogallol with Acids of the Molybdenum Group.** L. FERNANDES.—(See i, 1061.)

**Supposed Isomorphism of Uranyl Compounds with those of Isomorphogenous Metals of the Magnesium Group.** G. CAROBBI (*Gazzetta*, 1925, 55, 406—410).—Isomorphism of the above type is doubtful as a result of unsuccessful attempts to replace metals of the magnesium group by the uranyl radical in a number of double salts.

F. G. T.

**Hypochlorous Acid and the Alkali Hypochlorites.** R. DIETZEL and F. SCHLEMMER (*Z. anorg. Chem.*, 1925, 145, 381—393).—The reaction  $2\text{NaOH} + \text{Cl}_2 = \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}$  has been quantitatively investigated by titrimetric and absorption spectra methods. If the reaction proceeds as above at low temperatures, a *M*-sodium hypochlorite solution should be formed by passing chlorine into sodium hydroxide solution. Actually, titration with thiosulphate, arsenious acid, or silver nitrate did not give values for the hypochlorite or chloride concentration in accordance with the above equation. At the most, only about 0.5*M*-hypochlorite solutions were obtained. Since the total quantity of chlorine is not recovered, it is assumed that part of the chlorine introduced forms compounds in which the chlorine cannot be determined by usual titrimetric methods. Dilute hypochlorite solutions are fairly stable if prepared and kept under suitable conditions. A slight excess of free chlorine or hypochlorous acid causes a rapid change, according to the equation  $\text{ClO}' + 2\text{HClO} = \text{ClO}_3' + 2\text{H}' + 2\text{Cl}'$ . The Hartley-Baly

absorption method of investigation has been applied to the systems water-chlorine and sodium hydroxide-chlorine. Salt formation completely changes the character of the hypochlorous acid absorption spectrum, a well-marked band taking the place of an essentially linear curve. On account of the great transparency of sodium chlorate, no decision can be reached as to whether part of the chlorine in the reaction  $2\text{NaOH} + \text{Cl}_2 = \text{NaOCl} + \text{NaCl} + \text{H}_2\text{O}$  forms sodium chlorate, or whether by stirring a dilute hypochlorite solution, the free hypochlorous acid (always present on account of hydrolysis) leads to a continuous formation of chlorate.

L. L. B.

**Arsenates of Tervalent Manganese. I.** E. DEISS (*Z. anorg. Chem.*, 1925, **145**, 365—377).—The appearance of a violet colour on oxidation of manganous salts in presence of arsenic acid (Barreswil, *Compt. rend.*, 1857, **44**, 677) is due to the formation of triarsenatomanganic acid,  $[\text{Mn}(\text{AsO}_4)_3]\text{H}_6 \cdot 3\text{H}_2\text{O}$ . Whilst diphosphatomanganic acid is stable and the triphosphato acid unstable (Meyer and Marek, A., 1924, ii, 555), the reverse is the case with the corresponding arsenic compounds. Conditions for the formation of the violet-red crystalline triarsenato-acid are given, and its preparation is described: (i) by dissolving manganic acetate in cold, concentrated arsenic acid solution; (ii) similarly from manganic hydroxide; (iii) by the action of arsenic acid on Christensen's brown "manganic acetate solution" (A., 1884, 398). The brown "manganic acetate" solution of Christensen and crystallised bright red manganic acetate show different behaviour, which is ascribed to their different methods of formation. L. L. B.

**Determination of Equilibria between Stages of Oxidation by Potential Measurements. II. Manganese in Phosphoric Acid Solution.** G. GRUBE and M. STAESCHE (*Z. Elektrochem.*, 1925, **31**, 362—371; cf. Grube and Huberich, A., 1923, ii, 138).—In phosphoric acid solution the reversible reactions  $2\text{Mn}^{\text{III}} \rightleftharpoons \text{Mn}^{\text{II}} + \text{Mn}^{\text{IV}}$  and  $4\text{Mn}^{\text{IV}} \rightleftharpoons 3\text{Mn}^{\text{III}} + \text{Mn}^{\text{VII}}$  take place, the equilibria being slightly affected by the manganese concentration and very markedly by the phosphoric acid concentration. Tervalent manganese phosphate shows a maximum of decomposition in highly concentrated acid and a low minimum in 30—35-N-acid, whereupon decomposition increases slowly as the acidity decreases. With quadrivalent manganese phosphate the equilibrium shifts continuously and rapidly from left to right as the acidity diminishes, so that the salt can be prepared only in highly acid solutions. Quadrivalent manganese phosphate is a better oxidising agent than permanganic acid and a better reducing agent than tervalent manganese phosphate. W. A. C.

**Reactions in the Solid State. V.** D. BALAREV (*Z. anorg. Chem.*, 1925, **145**, 117—121).—A reply to Hedvall and Heuberger's criticism (this vol., ii, 306) of previous papers (cf. A., 1924, ii, 483, 611, 858). Manganese and tin dioxides do not react with calcium oxide at 950°, but they combine rapidly with strontium and barium

oxides. Barium oxide is more hygroscopic than phosphorus pentoxide and much more so than calcium oxide, and is, therefore, very difficult to free from a surface layer of the low-melting hydroxide. Molybdenum and tungsten trioxides react with calcium oxide, but these reactions are conditioned by the fusion of molybdenum trioxide and calcium tungstate, respectively. Barium oxide and calcium carbonate react to the extent of 90% in the presence of a trace of water because barium hydroxide is continuously re-formed by the dehydration of the calcium hydroxide produced. A moist mixture of manganese dioxide and potassium chlorate reacts at a temperature  $12^{\circ}$  lower than when carefully dried. A. G.

**Osmium Tetroxide. II. Compounds of Osmium Tetroxide.** F. KRAUSS and D. WILKEN (*Z. anorg. Chem.*, 1925, **145**, 151—167).—When osmium tetroxide vapour is condensed in a cooled receiver it collects as white needles which are readily soluble and reactive. When heated at  $40^{\circ}$  the needles are converted into a yellow, sparingly soluble, and non-reactive form, which may be re-converted into the white oxide by cooling in liquid air or by sublimation. The white form melts at  $39.5^{\circ}$  and the yellow form at  $41^{\circ}$ , and the former has the higher vapour pressure; the b. p. is  $134^{\circ}$ . Both forms had the calculated osmium content and liberated the calculated weight of iodine from potassium iodide. The compounds of osmium tetroxide with alkali hydroxides described by Tschugaev (A., 1918, ii, 322) could not be obtained by his method, but by adding saturated solutions of the hydroxides to the solid white tetroxide the following compounds were obtained:  $\text{OsO}_4 \cdot 2\text{CsOH}$ ,  $\text{OsO}_4 \cdot 2\text{KOH}$ ;  $\text{OsO}_4 \cdot 2\text{NH}_4\text{OH}$ ;  $\text{OsO}_4 \cdot \text{Ba}(\text{OH})_2$ ;  $\text{OsO}_4 \cdot 2\text{CsF}$ ;  $\text{OsO}_4 \cdot 2\text{RbF}$ ; only the potassium compound has the same composition as Tschugaev's preparation. These compounds form light red-brown or yellow crystals which, however, decompose when separated from the mother-liquor. Complete analysis was, therefore, impossible, but, by washing rapidly with water and then dissolving, solutions were obtained in which the ratio of osmium to alkali metal and to iodine liberated could be determined; the compounds were thus shown to contain octavalent osmium. Similar compounds were not formed with cyanides, thiocyanates, fluorides, or organic bases. A. G.

**Molecular Compounds of Halogen-Metal Acids and Acid Amides.** R. FRICKE and R. RUSCHHAUPT (*Z. anorg. Chem.*, 1925, **146**, 141—148).—The yellow compounds,  $\text{HAuCl}_4 \cdot 2\text{Ph} \cdot \text{CO} \cdot \text{NH}_2$  and  $\text{H}_2\text{PtCl}_6 \cdot 2\text{Ph} \cdot \text{CO} \cdot \text{NH}_2 \cdot 2\text{H}_2\text{O}$ , are prepared by the crystallisation of aqueous solutions of benzamide and chloroauric or chloroplatinic acids, respectively, in the presence of excess of hydrochloric acid. When heated, the compound  $\text{HAuCl}_4 \cdot 2\text{Ph} \cdot \text{CO} \cdot \text{NH}_2$  gradually decomposes even below  $100^{\circ}$  with the formation of metallic gold, whilst the compound  $\text{H}_2\text{PtCl}_6 \cdot 2\text{Ph} \cdot \text{CO} \cdot \text{NH}_2 \cdot 2\text{H}_2\text{O}$  begins to soften at  $100^{\circ}$  and is completely melted at  $130$ — $140^{\circ}$ . The compound  $\text{HAuCl}_4 \cdot 2\text{Me} \cdot \text{CO} \cdot \text{NH}_2$  is obtained in yellow needles by the crystallisation of a concentrated aqueous solution of chloroauric acid and acetamide. The solid must be separated quickly and no free



hydrochloric acid must be present or hydrolysis of the acetamide takes place. On heating, the compound decomposes liberating metallic gold. When concentrated aqueous solutions of acetamide and chloroplatinic acid are mixed and allowed to crystallise in a vacuum in the presence of phosphoric oxide, the yellow-brown compound,  $\text{H}_2\text{PtCl}_6 \cdot 2\text{Me} \cdot \text{CO} \cdot \text{NH}_2 \cdot 2\text{H}_2\text{O}$ , is deposited; it begins to soften at  $65^\circ$  and melts completely at  $83\text{--}84^\circ$ . W. H.-R.

**Degree of Hydration of Calcium Oxalate.** M. AUMÉRAS (*Compt. rend.*, 1925, **181**, 214—215).—Calcium oxalate precipitated from 0.1*N*-oxalic acid and calcium chloride solutions in presence of hydrochloric acid (cf. A., 1924, i, 137) has the composition  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ . S. K. T.

**Preparation of Colloidal Gold Solution by the Mellanby-Anwyl-Davies Technique.** R. L. HADEN (*J. Lab. Clin. Med.*, 1925, **10**, 310—311).—To 1 c.c. of 1% potassium oxalate solution in 100 c.c. of boiling water is added, dropwise, a mixture of 1 c.c. of 1% auric chloride solution and 1.3 c.c. of 1% potassium hydroxide solution. CHEMICAL ABSTRACTS.

**Preparation of Metal Tellurides from Hydrogen Telluride and Solutions of Salts.** A. BRUKL (*Monatsh.*, 1924, **45**, 471—484).—A number of tellurides of the metals have been prepared by precipitation of solutions of salts with hydrogen telluride or, in certain cases, with sodium telluride solution. The compounds  $\text{PdTe}$ ,  $\text{Cu}_2\text{Te}$ ,  $\text{PbTe}$ ,  $\text{BiTe}$ ,  $\text{NiTe}$ ,  $\text{CoTe}$ ,  $\text{As}_2\text{Te}_3$  are described in greater detail than hitherto; the following tellurides have been isolated for the first time: *mercuric*, *auric*, *ferrous*, *stannous*, *stannic*, *antimonious*, *thallous*, and *platinic*. Most of these compounds are unstable in air and tend to reduce solutions of substances such as mercuric or cupric salts. They are soluble in dilute acids with the exception of the lead, nickel, cobalt, gold, platinum, arsenic, and antimony tellurides. There is in all cases a progressive deepening of colour from the sulphide to the selenide and the telluride.

G. M. B.

**Crystal for Wave-length Measurements of Soft X-Rays.** L. PAULING and A. BJÖRKESON (*Proc. Nat. Acad. Sci.*, 1925, **11**, 445—447).—Hexagonal  $\beta$ -alumina possesses an unusually large grating-constant, rendering it very suitable for measurements of soft X-rays. For the line  $\text{CuK}_\alpha$ , the constant is  $11.240 \text{ \AA}$ . and for  $\text{AgL}_\alpha$ ,  $11.225 \text{ \AA}$ . The difference is a real effect. The crystal gives strong reflection. R. A. M.

**Universal X-Ray Spectrograph.** A. MÜLLER (*J. Sci. Instruments*, 1925, **2**, 312—318).—A compact X-ray spectrograph is described, which, by the use of interchangeable parts, permits the employment of the Bragg, Hull, Debye, Laue, and revolving crystal (Schiebold, Polanyi) methods of X-ray and crystal analysis.

F. G. T.

**Potassium as a Mercury-vapour Trap.** A. L. HUGHES and F. E. POINDEXTER (*Phil. Mag.*, 1925, [vi], **50**, 423—439).—The efficiency of a bulb lined with metallic potassium as a mercury trap

in a vacuum system has been investigated. Using the first appearance of mercury lines in the helium spectrum as a criterion, it is found that a potassium-lined trap acts as an efficient barrier until the potassium has absorbed at least 150% of its own weight of mercury. A more complete investigation using an ionisation gauge shows that the potassium-lined bulb is at least as efficient as a liquid air-trap for mercury. Dry air can be passed over the surface of the potassium without affecting its trapping power. The method of making the trap is described in detail. A. B. M.

**Construction of Nernst Filaments.** H. D. GRIFFITH (*Phil. Mag.*, 1925, [vi], 50, 263—265).—A mixture of 80% of zirconium oxide, 10% of thorium oxide, 5% of calcium oxide, 5% of magnesium oxide, with a trace of boric acid is ground to a thick paste with glycerol or with sugar solution, and forced through a press as threads 1.3 mm. in diameter. These are slowly heated until the sugar chars, and fired by passing through a carbon arc. The negative electrode is a loop of platinum wire, 0.1 mm. in diameter, attached by a layer of the above paste, which is allowed to dry in air. The positive seal is made by setting the end of the filament in a twist of several platinum wires, using a luting of equal parts of the oxides of yttrium, thorium, cerium, and zirconium. As a balancing resistance for such a filament 20 mm. long, two 60-watt, 220-volt lamps in parallel are satisfactory. The light from these filaments is somewhat yellower than that from commercial filaments.

F. G. T.

**Filling Mercury Manometers.** P. F. WEATHERILL (*J. Amer. Chem. Soc.*, 1925, 47, 1947; cf. Swan, this vol., ii, 707).—A method of filling mercury manometers is described, mercury being distilled into the apparatus in a high vacuum. Clean mercury surfaces are easily obtained. J. S. C.

**Simple Differential Air Thermometer for Use at Low Temperatures.** W. A. NOYES (*J. Amer. Chem. Soc.*, 1925, 47, 1942—1944).—A simple air thermometer for the approximate determination of temperatures between the b. p. of liquid air and 0° is described. Standard temperatures for calibration are those of melting ice, carbon dioxide snow, and alcohol (−78.5° at 760 mm. with a change of 0.1° for 10 mm.) and of fresh liquid air (−191.62°). J. S. C.

**Laboratory Ozoniser Yielding High Concentrations of Ozone.** L. I. SMITH (*J. Amer. Chem. Soc.*, 1925, 47, 1844—1850).—An ozoniser for general laboratory use is described. The apparatus is capable of producing concentrations of ozone in ozonised oxygen of 15%, or of making 4 g. of ozone per hour. J. S. C.

**Rotating Dialyser.** A. ASTRUC and E. CANALS (*J. Pharm. Chim.*, 1925, [viii], 2, 14—17).—A dialyser is arranged so that it may be mechanically rotated in a vessel containing water, whilst at the same time a stirrer rotates in the opposite direction inside the dialyser. It is shown that the speed of dialysis is increased. The

presence of gum arabic or gum tragacanth in solution, which usually greatly hinders the dialysis of salts, has little or no effect when the dialyser is rotated. B. F.

**Simple Laboratory Apparatus for Electrodialysis.** W. FUCHS and E. HONSIG (*Ber.*, 1925, 58, [B], 1323—1324).—A small glass cylinder is covered at the bottom with a parchment membrane and provided at the side with a small opening which serves for the introduction of the solution or a stirrer. It is fixed by pieces of cork into a Büchner funnel through which water or other liquid can be continuously circulated. The electrodes are placed between the funnel and the cylinder. H. W.

**Simple Apparatus for Extracting Liquids with a Specifically Heavier Solvent.** H. SCHMALFUSS and H. WERNER (*J. pr. Chem.*, 1925, [ii], 110, 37—39).—The solvent (e.g., chloroform) is distilled from a flask, *A*, fitted with a branched delivery tube. The vapour passes through one branch to the condenser, and after condensation streams down a wide connecting tube (into which the two branches are sealed) into a flask, *B*, containing the liquid to be extracted. The second branch bends downward inside the wide tube nearly to the bottom of flask *B*, and serves to return the extract continuously to the flask *A*. Flask *B* may or may not be heated. C. H.

**Apparatus for Preparing Vapour-Air Mixtures of Constant Composition.** W. P. YANT and F. E. FREY (*Ind. Eng. Chem.*, 1925, 17, 692—694).—The liquid to be volatilised is fed into a measured air stream by means of a constant drop of water into one arm of a U-tube containing mercury in the bend, over which, in the other arm, is the reservoir of liquid to be volatilised. This is forced up to the volatiliser by the pressure of the mercury, itself caused to rise by the constantly and evenly increasing head of water over it. The air, which is kept at constant pressure, passes into a flow-meter and out at a rate of 3 litres per minute, giving about 9 air changes an hour in a 20-litre bell jar. The calibration of the apparatus is described. D. G. H.

**Distilling Flask for Corrosive Liquids.** F. E. BROWN (*Ind. Eng. Chem.*, 1925, 17, 706; cf. this vol., ii, 589).—An ordinary distilling flask is adapted by first sealing on to its neck a tube through which the thermometer will pass, and to that another wider tube. The thermometer is kept in place by a small glass tube, too small to allow the ring of the thermometer to pass, which rests on the join of the two sealed-on tubes, and is so arranged that liquid can drain past it. D. G. H.

**Laboratory Apparatus.** H. JOHN and V. FISCHL (*J. pr. Chem.*, 1925, [ii], 110, 279—282).—A description of simple devices for sublimation and distillation. M. J.

**Electrodes for the Measurement of Small Bioelectric Potentials.** E. J. LUND (*Proc. Soc. Exp. Biol. Med.*, 1923, 21, 128—129).—The electrode was made up with a 3% pure lead

amalgam and 0.05—0.01 mol. of lead chloride. The copper leads were dipped into copper amalgam in place of mercury. The drift in potential at constant temperature was slow, and small enough to permit measurements of 1.0—0.05 mv. with an error of about 0.01 mv.

CHEMICAL ABSTRACTS.

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### Mineralogical Chemistry.

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**Presence of the Compound  $K_2Mn_2(SO_4)_3$  among the Products of Activity on Vesuvius.** F. ZAMBONINI and G. CAROBBI (*Gazzetta*, 1925, 55, 414—416).—Minute, faint rose-coloured tetrahedra, intimately mixed with thenardite and alite, have been found by microscopical examination of stalactites in the lava cupola formed in 1922. Their chemical and optical properties identify them with the compound  $K_2Mn_2(SO_4)_3$ , previously synthesised by Carobbi and Caglioti (A., 1924, ii, 685), and the name *mangano-langbeinite* is proposed for them.

F. G. T.

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### Analytical Chemistry.

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**Apparatus for Direct Reading of Conductivity (and Salt Content) of a Salt Solution.** TÖDT (*Chem.-Ztg.*, 1925, 49, 656—657).—An ordinary Wheatstone bridge apparatus is used with a fixed resistance, and the graduations are made to read directly in terms of conductivity or concentration of salts. G. M. B.

**Use of the Cornec-Cottet Pipette in the Measurement of Small Volumes in Micro Analysis.** M. NICLOUX (*Bull. Soc. Chim. biol.*, 1925, 7, 750—752).—The pipette is a capillary tube containing a small bulb and is fused on to a tube of wider bore, the liquid rising to the point where the capillary tube ends. Excellent agreement has been obtained in figures for the density of blood (1.060) with pipettes containing 0.1022—0.1246 g. of water and for urinary nitrogen by the micro-Kjeldahl method.

H. J. C.

**Burette for Gas Analysis in Electrochemical Processes.** W. JOFINOV (*Chem.-Ztg.*, 1925, 49, 657).—The gas burette previously described (A., 1920, ii, 221) is simplified by substituting for the glass tap a pinch-cock on a piece of wide rubber tubing cut off below at an angle. G. M. B.

**Apparatus for Ferrous Oxide Determinations.** F. MEYER (*Chem.-Ztg.*, 1925, 49, 622).—The apparatus, which replaces the Bunsen valve, consists of a narrow glass tube with a glass valve

at the top and having a side siphon tube, the latter dipping into a reservoir containing sodium hydrogen carbonate solution. When the solution flask cools, the valve closes, and the solution siphons over into the acid solution. The carbon dioxide evolved temporarily checks the siphon action, which continues intermittently until the flask is cold.

W. M. C.

**Modification of Duboscq-Pellin Colorimeter for Biocolorimetric Work.** H. WU (*Proc. Soc. Exp. Biol. Med.*, 1923, **21**, 111—114).—An extra cup, movable stage, and vernier are added to one side of the colorimeter; with phenol-red as indicator, the apparatus is specially suitable for  $p_H$  determinations.

CHEMICAL ABSTRACTS.

**Recommended Specifications for Analytical Reagent Chemicals.** W. D. COLLINS, H. V. FARR, J. ROSIN, G. C. SPENCER, and E. WICHES (*Ind. Eng. Chem.*, 1925, **17**, 756—760).—Recommended specifications are given for hydrochloric, nitric, oxalic, and sulphuric acids, ammonium hydroxide, oxalate, and thiocyanate, barium chloride, iodine, potassium dichromate and hydroxide, silver nitrate, sodium hydroxide and oxalate. [Cf. *B.*, 1925, 695.]

D. G. H.

**Explosion Method for Peroxide Fusions.** W. F. MUEHLBERG (*Ind. Eng. Chem.*, 1925, **17**, 690—691).—The finely-divided material is well mixed with sugar carbon and sodium peroxide, and ignited in a nickel crucible. The fused mass readily separates from the crucible, and the acidified solution is clear. It is necessary to use rather larger quantities of peroxide by this method, with a corresponding increase in the volume of solution, and a certain amount of unfused residue is left, which may frequently be disregarded, or its weight subtracted, although it may be necessary to re-fuse it. Results appear to be as accurate as those obtained by peroxide fusion over a free flame or with alkali carbonate in platinum. [Cf. *B.*, 1925, 674.]

D. G. H.

**Potentiometric Hydrogen-ion Measurements with Non-gas Electrodes.** H. C. PARKER (*Ind. Eng. Chem.*, 1925, **17**, 737—740).—A large number of metals and combinations of oxides and metals have been tested by various means for suitability in measuring hydrogen-ion concentrations. Amongst the most promising are tungsten-manganese sesquioxide and platinum-manganese sesquioxide electrodes. [Cf. *B.*, 1925, 696.]

D. G. H.

**Volumetric Determination of the Reaction of a Medium at True Neutrality.** G. CHABOT (*Bull. Soc. chim. Belg.*, 1925, **34**, 202—211).—A mixture of equal proportions of 1% alcoholic solutions of neutral-red and phenol-red which independently show colour changes from red at  $p_H$  6.8 to yellow at  $p_H$  8.0 and from yellow at  $p_H$  6.8 to red at  $p_H$  8.4, respectively, forms an indicator which shows a sharp colour change at the point of real neutrality

( $p_H$  7.07) and is efficient for the titration of very weak acids and bases. If the ordinary method of titration be employed, 1–2 drops of each indicator for each 10 c.c. of liquid are employed, but better results are obtained by using the comparative method of Walpole (cf. A., 1910, ii, 541; 1915, ii, 61), a solution made by adding 50 c.c. of a 0.2*N*-solution of potassium dihydrogen phosphate to 31.51 c.c. of a 0.2*N*-solution of sodium hydroxide and diluting to 200 c.c. ( $p_H$  7.07) being used as the standard. In the latter case 0.25 c.c. of each indicator solution is added to each 10 c.c. of the liquid. The indicator is very sensitive to carbon dioxide, which may be eliminated by any of the usual methods. Full details of technique and examples are given, the results being very satisfactory. J. W. B.

**Determination of Chloride in Animal Tissue.** R. VLĂDESCU.—(See i, 1113.)

**Sodium Arsenite as Reagent for Loosely Combined Reactive Oxygen, Sulphur, and Nitrogen.** A. GUTMANN.—(See i, 1059.)

**Micro Determination of Nitrogen.** A. R. ROSE (*J. Biol. Chem.*, 1925, **64**, 253–256).—The preliminary digestion with sulphuric acid in the micro-Kjeldahl method is hastened by the addition of perchloric acid and hydrogen peroxide; after oxidation is complete the solution is diluted and the nitrogen determined directly by means of Nessler's reagent. C. R. H.

**Micro Determination of Ammonia in Urine.** A. YOVANOVITCH.—(See i, 1114.)

**Colour Reaction for Nitrites.** A. NOVELLI (*Anal. Asoc. Quím. Argentina*, 1925, **13**, 13–22).—The reagent is prepared by dissolving 5 g. of resorcinol in distilled water; 5 drops of 26% ferric chloride solution are added. On warming, the violet coloration gradually disappears and the solution becomes yellow. The solution is boiled for a few minutes and allowed to cool. A few drops of the reagent added to a few c.c. of a solution containing nitrites in the presence of acetic acid give an intense green coloration. It is possible to detect 0.001 g. of nitrite in 10 c.c. of water by this reagent. The reaction is indefinite in the presence of vanadates. G. W. R.

**Determination of Small Quantities of Phosphorus in Proteins.** M. SØRENSEN (*Compt. rend. Trav. Lab. Carlsberg*, 1925, **15**, No. 10, 1–6).—After evaporation, the protein solution is digested with a mixture of sulphuric and nitric acids. It is then diluted and precipitated in the boiling water-bath with ammonium molybdate in presence of ammonium nitrate. After remaining over-night, the precipitate is collected, washed, and dissolved in ammonia. Standard sodium hydroxide is added and ammonia boiled off. Excess of standard sulphuric acid is added, carbon dioxide boiled off, and the excess of acid titrated with standard sodium hydroxide. A control experiment is carried out to allow for traces of impurity in the reagents. C. P. S.

**Determination of Arsenic in Organic Compounds.** G. NEWBERRY (*J. Chem. Soc.*, 1925, **127**, 1751—1752).—The following method gives results correct to 0.2%. The substance is boiled with aqueous ammonium persulphate solution until colourless, oxalic acid is added, and the mixture heated for 2 mins. after carbon dioxide evolution appears to stop. 2*N*-Sulphuric acid and potassium iodide are added, and the whole is vigorously boiled until the solution is of a pale straw colour, which is discharged by the cautious addition of 0.05*N*-sodium thiosulphate. The mixture is at once diluted, sodium hydrogen carbonate added in excess, the mixture is warmed at 35—40°, and titrated with iodine solution. W. H.-R.

**Determination of Small Amounts of Boron in Tungsten.** D. H. BROPHY (*J. Amer. Chem. Soc.*, 1925, **47**, 1856—1861).—0.5 G. of alloy is fused with 0.7 g. of sodium nitrate and 2.5—3.5 g. of sodium chloride in a platinum crucible. The cooled mass is dissolved in 30 c.c. of water in a porcelain, silica, or platinum dish and boiled with 2 g. of barium hydroxide. To the filtered solution a little potassium iodide is added to reduce any nitrites formed during the fusion, and one drop of methyl-orange. Sufficient 1:1-hydrochloric acid is added to make it distinctly acid. After a few minutes free iodine is removed by thiosulphate, and nitrogen oxides are removed by bubbling in air free from carbon dioxide. The solution is neutralised by barium hydroxide free from carbonate and the pink colour just restored with hydrochloric acid. The solution is now filtered, the pink colour just discharged with barium hydroxide, and the solution titrated with barium hydroxide solution in presence of phenolphthalein and glycerol, a blank experiment being also performed. The alloys may alternatively be fused with sodium peroxide and hydroxide. The nitrite difficulty is eliminated, but the manipulations are by no means as easy. J. S. C.

**Volumetric Determination of Carbon and Hydrogen in Elementary Organic Analysis.** J. LINDNER (*Z. anal. Chem.*, 1925, **66**, 305—370).—The substance is heated in the usual way in a current of pure air or oxygen and the gases are passed through a heated tube containing copper gauze, copper oxide coated with lead chromate, and silver gauze in succession; they are then led through a U-tube packed with lead peroxide and heated gently in an air-bath which finally removes any impurities, leaving only water vapour and carbon dioxide. The former is made to react with heated "naphthyloxychlorophosphine,"  $C_{10}H_7 \cdot POCl_2$ , whereby hydrogen chloride equivalent to the hydrogen in the substance being analysed is evolved. The gases are then passed through a special absorption tube containing only 1—2 c.c. of water, which retains completely the hydrogen chloride, into an absorption apparatus containing a measured amount of standard barium hydroxide solution to absorb the carbon dioxide. Titration of the hydrochloric acid with standard alkali gives the hydrogen content and titration of the excess of barium hydroxide with standard acid and phenolphthalein gives the carbon content of the substance. The original paper contains a detailed description of the



absorption apparatus and of the methods of preparing the reagents and of carrying out an analysis. The results are equally as good as those obtained gravimetrically. A. R. P.

**Modification of Laulanié's Apparatus for the Determination of Carbon Dioxide and Oxygen in Air.** L. PLANTEFOL (*Bull. Soc. Chim. biol.*, 1925, 7, 638—651).—Modifications have been made (chiefly in the central tap) to overcome the objections previously described (*ibid.*, 590—605). H. J. C.

**Application of Electrical Conductivity to Quantitative Analysis in Biochemical Practice. I. Titration of Certain Inorganic Salts with Sodium Hydroxide.** S. DEMJANOVSKI.—(See i, 1113.)

**Preparation and Analysis of Constant Mixtures of Air and Carbon Dioxide.** J. JOHNSTON and A. C. WALKER.—(See ii, 851.)

**Modification of the Kramer-Tisdall Method for the Determination of Sodium in Blood.** R. L. HADEN.—(See i, 1112.)

**Perchloric Acid as an Analytical Reagent.** J. H. YOE (*Ann. Chim. Analyt.*, 1925, [ii], 7, 193—197).—For the determination of potassium, the aqueous solution is acidified strongly with hydrochloric acid, sulphates are removed by barium chloride solution (cf. Davis, T., 1915, 107, 1679), and ammonium salts are removed in the usual manner. After conversion into perchlorates, sodium perchlorate is separated by agitation with 97% ethyl alcohol containing 0.2% of perchloric acid and the potassium perchlorate finally washed on the Gooch crucible with 97% ethyl alcohol (cf. Thin and Cumming, T., 1915, 107, 365; Baxter and Kobayashi, A., 1920, ii, 388). The crucible is dried at 130° for 45 mins. Errors do not exceed 0.3%. Methods for the determination of silica in feldspar, limestone, and cement are discussed; that of Willard and Cake (A., 1921, ii, 60) is accurate. Mears and Hussey's modification (A., 1922, ii, 159) of the Kjeldahl method for the determination of nitrogen is also accurate. W. M. C.

**Determination of Small Quantities of Magnesium in Copper-Zinc Alloys.** SCHÜRMANN and SCHOB (*Chem.-Ztg.*, 1925, 49, 625—626).—The alloy is dissolved in nitric acid, the solution evaporated with sulphuric acid, and the copper removed by electrolysis. The electrolyte is then evaporated again until the sulphuric acid is expelled; the residue is dissolved in water and the solution poured into a cold solution of sodium hydroxide. The precipitate is collected, dissolved in the minimum of hydrochloric acid, and the precipitation with sodium hydroxide repeated. The last traces of zinc are removed by hydrogen sulphide from the formic acid solution of the second precipitate and the magnesium is precipitated as magnesium ammonium phosphate. Alternatively, the formic acid solution is evaporated to dryness with a few drops of hydrochloric acid and the magnesium determined colorimetrically with 1 : 2 : 5 : 8-tetrahydroxyanthraquinone. [Cf. Hahn, Wolf, and Jäger, A., 1924, ii, 784, and B., 1925, 724.] A. R. P.

**Co-precipitation of Magnesium Hydroxide with Aluminium Hydroxide in Ammoniacal Solution.** PARISELLE and LAUDE (*Compt. rend.*, 1925, **181**, 116—117).—The precipitation, by four times the necessary amount of ammonia, of the above hydroxides from a 0.005*M*-solution of the mixed sulphates has been investigated, in the presence of varying amounts of ammonium chloride. An excess of the latter is necessary for complete precipitation of aluminium hydroxide alone. The presence of less than an equimolar amount of ammonium chloride is sufficient to prevent the precipitation of magnesium hydroxide alone. In the absence of ammonium chloride, a mixture of the sulphates of magnesium and aluminium is completely precipitated.

Complete co-precipitation is obtained so long as the ammonium chloride is present in amounts not greater than 8 mols. per mol. of each of the sulphates. The co-precipitation diminishes when this value is exceeded, and practically ceases when 100 mols. of ammonium chloride are present per 2 mols. of mixed salts. The co-precipitation may be due to the formation of an insoluble magnesium aluminate. F. G. T.

**Determination of Lead.** C. E. RICHARDS (*Analyst*, 1925, **50**, 398—399).—The lead is precipitated from faintly acid solution by means of sulphur dioxide, with which the liquid must be saturated. The precipitate is rinsed into 0.1*N*-iodine solution and completely dissolved in concentrated hydrochloric acid, the excess of iodine being titrated with thiosulphate solution. D. G. H.

**Determination of Lead in Minute Quantity.** W. W. SCOTT (*Chem. News*, 1925, **131**, 17—20).—To determine minute quantities of lead in baking powder, food, etc., the lead in the material under investigation is generally converted into sulphate, extracted by means of ammonium acetate, converted into sulphide, and the latter determined colorimetrically by comparison with standard solutions. To determine lead in water, aluminium sulphate and sulphuric acid are added, and then ammonia; the lead is occluded in the precipitated aluminium hydroxide, and may be determined as above. [Cf. *B.*, 1925, 654.] B. F.

**Inexpensive Method for Determining Lead.** W. W. SCOTT (*Ind. Eng. Chem.*, 1925, **17**, 678).—The sample is prepared as for the chromate-iodide method and the liberated chromic acid titrated directly by adding excess of ferrous sulphate solution in the presence of diphenylamine, and determining the excess with potassium dichromate or permanganate solution until the green colour is changed to blue. If lead is precipitated the end point will be navy-blue and in the presence of excess of hydrochloric acid, dark green. D. G. H.

**Gravimetric Determination of Copper and its Separation from Cadmium and Zinc.** A. JÍLEK and J. LUKAS (*Chem. Listy*, 1925, **19**, 275—277).—Copper (especially in small quantities) may be determined in the presence of cadmium and zinc by adding to the warm, neutral solution of the cupric salt four times its volume

of a 1.4% alcoholic solution of ethyl acetonedioxalate, when there is precipitated only the brown-yellow substance  $C_{11}H_{12}O_7Cu$ . This precipitate may be weighed as such, or converted into cupric oxide by calcination. B. F.

**Volumetric Determination of Copper with Potassium Iodide.** M. HERSCHKOVITSCH (*Z. anorg. Chem.*, 1925, **146**, 132—140).—In the reaction between cupric sulphate and potassium iodide, cupric iodide is first produced according to the reversible reaction  $CuSO_4 + 2KI \rightleftharpoons CuI_2 + K_2SO_4$ . If free iodine is present copper polyiodides are also formed, but both these and normal cupric iodide react with excess of potassium iodide to form cuprous iodide and potassium polyiodides. To obtain accurate results by titration with thiosulphate, 3 g. of potassium iodide should be taken for each 100 c.c. of solution, which should not contain more than 0.5% of copper. Low results are obtained, especially in dilute solutions, if sufficient potassium iodide is not present, owing to some of the cupric iodide remaining unchanged. W. H.-R.

**Potentiometric Standardisation of Potassium Permanganate Solution with Sodium Oxalate.** C. DEL FRESNO (*Anal. Fis. Quim.*, 1925, **23**, 231—241; cf. this vol., ii, 602).—When potassium permanganate solution is gradually added to an acid solution of sodium oxalate at 70°, the difference of potential between a platinum electrode immersed in the solution and a normal calomel electrode changes gradually until the oxidation of the oxalate approaches completion, when there is a very rapid increase. The critical potential corresponding with the completion of the reaction is +0.74 volt. This rapid increase in potential may be used as the basis for potentiometric standardisation of permanganate solutions. G. W. R.

**Colorimetric Determination of Cobalt in the Presence of Nickel.** B. S. EVANS (*Analyst*, 1925, **50**, 389—393).—Cobalt may be determined by matching the intense rose-pink colour produced on treating the solution with ammonium chloride solution and excess of ammonia, and adding a small quantity of sodium peroxide, with that from a standard solution of cobalt ammonium sulphate. In the presence of nickel, the blue colour given with excess of ammonia may be stabilised by keeping the proportion of ammonia low and adding sodium citrate, and the determination is then carried out using two pairs of tubes, one above the other, in a Walpole colorimeter. Details are also given for the application of the method to steel analysis. D. G. H.

**Use of Liquid Amalgams in Volumetric Analysis. II. Determination of Tungsten etc. by Means of Lead and Bismuth Amalgams.** K. SOMEYA (*Z. anorg. Chem.*, 1925, **145**, 168—180).—Liquid lead amalgam reduces ferric and uranyl salts to ferrous and uranous salts, respectively, and molybdic, titanic, and tungstic acids are reduced to the tervalent state; by titrating the reduced solutions with potassium permanganate the metals may be determined. The reduction is usually carried out in an atmosphere of carbon

dioxide, and the solution is made sufficiently acid with hydrochloric acid to prevent the precipitation of lead chloride; to accelerate reduction, the solution is generally warmed at 50°. When iron is to be determined, less acid must be used or the end-point is not sharp; the precipitated lead chloride does not interfere. Tungstic acid is also reduced to the tervalent state by cadmium and zinc amalgams, but the reactions are inconveniently vigorous; bismuth amalgam at 60—70° reduces only to the quinquivalent state. The liquid lead amalgam can be kept indefinitely without deteriorating and reacts only very slowly with dilute sulphuric or hydrochloric acid. A. G.

**Volumetric Determination of Small Quantities of Ethyl Alcohol.** W. JEROME and F. PEPIN (*Can. Chem. Met.*, 1925, 9, 65—66).—A modification of Nicloux's method for application to blood, urine, etc. The material is distilled with steam in the presence of picric acid, aliquot portions of the distillate being tested by heating with dilute potassium dichromate solution in quantity sufficient to yield a yellowish-green colour, and the results compared with those given by dilute aqueous alcohol of known concentration.

CHEMICAL ABSTRACTS.

**Detection of Benzyl Alcohol as Benzyl Oxalate.** A. S. PFAU (*Perf. Essent. Oil. Rec.*, 1925, 16, 190—191).—Benzyl alcohol is readily converted into benzyl oxalate by warming with ethyl oxalate and anhydrous potassium carbonate. By this means, benzyl alcohol may be detected in mixtures of 25—30% of it with hydrocarbons, alcohols, aldehydes, ketones, etc., unless the mixture contains other primary alcohols, when 50% of it must be present to respond to the test. [Cf. *B.*, 1925, 612.] B. F.

**Micro Determination of Methoxyl.** J. C. SMITH (*J. Chem. Soc.*, 1925, 127, 912).—Low results are obtained with a silver nitrate solution of the concentration recommended in the English translation of Pregl's "Die Quantitative Organische Mikroanalyse" (20 g. in 200 g. of 95% alcohol). The concentration given in the German edition (20 g. in 500 g. of 95% alcohol) gives trustworthy results.

M. J.

**Detection of Plant Phenols by the Use of Nitrites or Nitric Acid.** A. H. WARE.—(See i, 1122.)

**Reactions of Picric Acid and of Cignolin [1 : 8-Dihydroxy-anthranol].** P. TORTI (*Boll. Chim. Farm.*, 1925, 64, 259).—Colour reactions for each of these compounds are given. T. H. P.

**Modifications of the Ferric Citrate Precipitation Test for Tannins.** A. H. WARE (*Analyst*, 1925, 50, 335—336; cf. *A.*, 1924, ii, 789).—The preliminary addition of boiling sodium sulphite solution to the extractive prevents excessive precipitation of dehydrated or oxidised tannin in the form of phlobaphen. A final violet precipitate indicates tannin, but a brownish-black precipitate may be due to phloroglucinol-pyrocatechol flavones or flavonols, or certain phlobatannins. Tannins and phlobaphens are precipitated

if, after boiling with the iron and ammonium citrate solution and filtering, a second boiling with ammonium chloride is carried out. A further addition of ammonium hydroxide solution (in the absence of tannin) will often indicate the presence of anthoxanthins by formation of a deep brown precipitate. D. G. H.

**Determination of Reducing Sugars.** L. PICK (*Z. Zuckerind. Czechoslov.*, 1925, 49, 211—216, 219—225, 235—241, 243—250).—During the reduction of Fehling's solution in the determination of reducing sugars, an error arises from the irregular boiling of the alkaline liquid, differences corresponding with 10 mg. of copper being observed. Superheating may be obviated almost entirely by the addition to the mixture of Fehling's solution and assay liquid of an inert powder to promote regular ebullition, wood charcoal in the gravimetric and talc in the volumetric method being recommended. In gravimetric processes, appreciable errors may be caused by the use of Fehling's solution containing insoluble matter, and also (when dealing with impure products) by the cuprous oxide being formed in colloidal solution, so as to pass the filter, although this latter error would appear generally to be a small one. J. P. O.

**Iodometric Determination of Reducing Sugars.** L. PICK (*Z. Zuckerind. Czechoslov.*, 1925, 49, 251—255, 259—263).—A modification of Shaffer and Hartmann's iodometric method (A., 1921, ii, 417) is proposed, Fehling's solution diluted fourfold being used, and a small quantity of talc added to promote regular ebullition during reduction (cf. preceding abstract). This method gives more accurate results than the permanganate process when organic matter is present in the precipitated cuprous oxide. J. P. O.

**Induced Crystallisation in Micro-chemistry.** G. DENIGÈS (*Mikrochem.*, 1925, 3, 33—37).—0.1—0.2 Mg. of a sugar or polyhydric alcohol to be identified is dissolved in 1 drop of water on a slide, the solvent evaporated by gentle heating, and the glassy residue caused to crystallise throughout by scratching with a glass point, preferably bearing one or two tiny crystals of the substance believed to be that under examination. The mass is treated with 1 drop of a mixture of acetone and acetic acid, the solvent allowed to evaporate, and the residue again treated in the same way. Clear, well-formed crystals suitable for microscopical examination and optical measurement are thus obtained. S. I. L.

**Effect of Sodium Carbonate Concentration in the Determination of Sugar by Benedict's Method.** A. J. QUICK.—(See i, 1115.)

**Chemical Analysis of Cotton. II. Determination of Copper Number.** D. A. CLIBBENS and A. GEAKE (*J. Text. Inst.*, 1924, 15, T, 27—38).—The authors have examined the various methods in use for the determination of copper numbers, and show that Schwalbe's procedure and its modifications, the best of which

is that due to Knecht and Thompson (A., 1920, ii, 712), all fail to fulfil the ideal conditions. These are considered to be: (1) a "blank" as near zero as possible, (2) a very small figure for pure cellulose, (3) high values for slightly modified celluloses, (4) results readily reproducible, and (5) simple technique. The fault in the above methods lies in the use of Fehling's solution, owing to the absorption of copper by the cellulose, the instability of the reagent, and especially to its alteration by auto-reduction. Of other methods described in the literature, the most satisfactory is Braidy's (*Rev. gén. Mat. Col.*, 1921, 25, 35). The solution of copper sulphate is made alkaline with a mixture of sodium carbonate and sodium hydrogen carbonate, and the cuprous oxide formed is determined by the reduction of acidified ferric alum and subsequent titration with permanganate. A critical examination of the method is reported and a procedure is described which meets the above requirements. Pure cotton cellulose gives very low and constant figures and the effects of slight attacks by acids or oxidising agents are revealed by significantly high values. Results obtained with several raw cottons and bleached cloths are described. J. C. W.

**Determination of Pentosans in Wood.** W. GIERISCH.—(See i, 1122.)

**Determination of Acetaldehyde in the Determination of Lactic Acid.** P. LEONE and G. B. TAFURI (*Annali Chim. Appl.*, 1925, 15, 206—208).—This method, which avoids the use of complicated apparatus or of standard solutions liable to deterioration and is applicable to the determination of quite small amounts of lactic acid, is based on the quantitative formation of the oxime when the distillate from a mixture of lactic acid and 50% sulphuric acid is passed into free hydroxylamine. G. L. R.

**Identification of the Alkyl Derivatives of Barbituric Acid.** A. ZAMPARO (*Boll. Chim. Farm.*, 1925, 64, 257—258).—Various reactions are given for distinguishing the different alkyl derivatives of barbituric acid used as hypnotics. [Cf. B., 1925, 651.]

T. H. P.

**Determination of Benzoquinone by Means of Thiosulphate.** J. RZYMKOVSKI (*Z. Elektrochem.*, 1925, 31, 371—372).—When thiosulphate is added to benzoquinone in acid solution, reaction takes place in three stages and finally the quinone is reduced quantitatively to quinol and quinol derivatives, whilst the thiosulphate is oxidised to compounds of the general formula  $R(S_2O_3H)$ . Titration may be carried out by colour-indication or electrometrically. W. A. C.

**Separation of Aliphatic Amines from Ammonia.** P. LEONE (*Gazzetta*, 1925, 55, 246—252).—The presence of ammonia or ammonium salt in the solution of an amine salt may be detected by addition of excess of an aqueous alcoholic solution of sodium cobaltinitrite and sodium nitrite, this giving a turbidity or precipitate with the ammonia. If the volatile alkali is determined both before and after precipitation in this way, the difference between the two

results represents the amine present. A solution of an amine salt may be freed from ammonia by neutralising with acetic acid, treating with sodium cobaltinitrite and nitrite, filtering, adding sodium hydroxide, and distilling. [Cf. *B.*, 1925, 612.] T. H. P.

**Determination of Urea in Dog's Blood.** (MLLE.) E. VARTE-JEANU.—(See i, 1113.)

**Determination of Urea and Sugar in Blood.** B. GRUSKIN.—(See i, 1113.)

**Determination of Urea in Blood and Urine.** T. ADDIS.—(See i, 1113.)

**Use of Acetylene for the Determination of Hæmoglobin.** H. R. MILLER.—(See i, 1112.)

**Iodometric Determination of Methylene-blue.** T. SABA-LITSCHKA and W. ERDMANN (*Chem.-Ztg.*, 1925, 49, 561).—Excess of iodine-potassium iodide solution precipitates a dark-brown solid approximating to a tetraiodomethylene-blue; the excess is titrated with thiosulphate without addition of starch. When the excess of iodine has been removed from the solution, further thiosulphate reacts with the precipitate, liberating methylene-blue, so that the end-point is easily seen. S. I. L.

**Proline and Tryptophan as Factors Influencing the Accuracy of Van Slyke's Method for the Determination of Nitrogen Distribution in Proteins.** R. A. GORTNER and W. M. SANDSTROM (*J. Amer. Chem. Soc.*, 1925, 47, 1663—1671).—Van Slyke's method for the determination of the distribution of nitrogen in proteins (*A.*, 1911, ii, 944) yields accurate results in the absence of tryptophan and of proline if the amino-acids are not boiled previously to analysis. Boiling for 24 hrs. with 20% hydrochloric acid prior to analysis leads to a loss in amino nitrogen of the bases and a gain in the ammonia nitrogen, only 64.5% of the cystine nitrogen being precipitated by phosphotungstic acid. Addition of tryptophan to a similar mixture of 14 amino-acids (containing no proline) leads to appreciable errors in the basic fraction, and in the amino nitrogen and the total nitrogen of the filtrate from the bases, the errors in the basic nitrogen chiefly affecting the arginine fraction. Analysis of the boiled mixture when tryptophan is present shows high results for histidine and low results for cystine (37.9% unprecipitated), and further errors in the ammonia fractions and in the filtrate from the bases. The addition of proline (in the absence of tryptophan) produces errors in the analysis of the unboiled mixture, both in the basic fraction and in the fractions in the filtrates from the bases. Part of the proline appears to be precipitated by phosphotungstic acid with the diamino-acids and distributed between the arginine and histidine fractions. Owing to its entire lack of amino nitrogen, the calculations of Van Slyke's method cause the lysine fraction to show a loss. Analysis of the mixture after 24 hrs.' acid boiling shows that proline produces high results in the basic nitrogen fractions and a corresponding decrease in the filtrate fractions. Ammonia nitrogen is high and only 73.3% of the cystine is precipitated. R. B.

## General, Physical, and Inorganic Chemistry.

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**Structure in the Secondary Hydrogen Spectrum.** O. W. RICHARDSON (*Proc. Roy. Soc.*, 1925, **A**, 108, 553—561; cf. this vol., ii, 469).—Thirty-seven more lines have been arranged in series. Attention is directed to the numerical relations with especial reference to the principle of combination. The causes of the combinations found are discussed. L. F. G.

**Structure in the Secondary Hydrogen Spectrum.** O. W. RICHARDSON (*Proc. Roy. Soc.*, 1925, **A**, 109, 35—56; cf. *A.*, ii, 1924, 217, also preceding abstract).—A continuation of the reduction of this spectrum into groups of related lines, starting from the lines which are selectively weakened in electron discharges, in hydrogen at low pressures. F. G. T.

**Wave-lengths of Additional Lines in the Many-lined Spectrum of Hydrogen.** T. TANAKA (*Proc. Roy. Soc.*, 1925, **A**, 108, 592—606; cf. preceding abstract).—Data for 560 weak lines in the secondary spectrum, not previously recorded, are tabulated. The measurements were made on spectrum plates taken by Merton, as the spectral lines were there better resolved than on plates taken, under different conditions, by the author and Richardson. A list is given of lines recorded by other experimenters, but missing from the plates of both Merton and the author. L. F. G.

**Secondary Spectrum of Hydrogen at Higher Pressures.** I. SANDEMAN (*Proc. Roy. Soc.*, 1925, **A**, 108, 607—616; cf. Kiuti, *Phys. Math. Soc. Japan*, 1922, [iii], 5, No. 2).—The lines of the spectrum given by an arc between tungsten electrodes in an atmosphere of hydrogen have different intensities from those recorded by Merton and Barratt (*A.*, 1922, ii, 461). The method suggests the possibility of detecting regularities among the lines. A band has been found with head at 4582.58 Å., shading towards the violet. The value of the initial moment of inertia of the molecule emitting the band agrees with the value deduced by Allen from a static model of triatomic hydrogen (*A.*, 1923, ii, 679). The lines of the *P*, *Q*, and *R* combination discovered by Richardson and Tanaka (this vol., ii, 11) are also present, and the intensity distribution found for them agrees with that found for the new band. L. F. G.

**Measurement of the Fine Structure of Hydrogen Lines with the Lummer-Gehrcke Plate.** P. H. VAN CITTERT (*Ann. Physik*, 1925, [iv], 77, 372—380).—In measuring intervals between spectral lines with the Lummer-Gehrcke plate errors other than personal ones must be considered. The reflection coefficient is not uniform, but decreases from the centre of the interference



image towards the edges of the plate. As a result, a line near the edge appears enhanced, has a rather flat intensity maximum, and is evaluated as brighter than a similar line lying nearer the centre. A bright symmetrical line is rendered asymmetric, with its intensity maximum somewhat displaced from its centre. The brightening of an outer line makes the interval between two lines appear smaller than it is, and it is very probable that in all measurements with the Lummer-Gehrcke plate the recorded intervals have been too small because the above effects have been disregarded. For this reason, a decision as to the correctness of Sommerfeld's theory is not possible on the basis of such measurements. A further correction is necessary owing to a transformation of the intensity gradation in a line as a result of a difference of phase of the light in the plate. When the values for the separation of the hydrogen lines obtained by Gehrcke and Lau (A., 1921, ii, 565) are subjected to the above corrections, values are obtained which agree with those calculated by Janicki from Shrum's measurements (this vol., ii, 449). Measurements with the Fabry and Perot interferometer are simpler and more accurate because the distortion of the original intensity gradation is less, the reflection coefficient changes less rapidly, and the relation between the intervals in the photograph and the phase difference in the instrument is less complicated than when use is made of the Lummer-Gehrcke plate. The conditions in order to obtain accurate measurements with an interferometer are summarised.

F. G. T.

**Behaviour of Some Spark Lines of Carbon in an Electric Field.** S. NAKAMURA and Y. FUJIOKA (*Sci. Papers Inst. Phys. Res. Tokyo*, 1925, 3, 155—162).—The doublets 4267 and 3921 Å. attributed to singly and positively ionised carbon atoms are enhanced and broadened symmetrically in a high electric field. Transverse observations in a discharge tube containing helium show that the amount of broadening of these lines depends chiefly on the field strength and not on either the pressure of helium or the exposure of the plate. Measurements are also recorded for several ultra-violet lines. Longitudinal observations show that the two lines split into sharply defined "components," but the original lines are totally absent. No definite conclusion is drawn as to whether the broadening is due to an unusual Stark effect or not owing to the intrusion of the Döppler effect.

R. A. M.

**Production of Atomic Nitrogen and its Arc Spectrum.** K. T. COMPTON (*Phil. Mag.*, 1925, [vi], 50, 512—516).—Attempts to dissociate nitrogen thermally into atoms have yielded negative results due to the abnormally high value of the heat of dissociation, 440 kg.-cal./mol. It is suggested that the dissociation might be brought about by inducing collisions of the second kind with excited atoms of helium. The value of the heat of dissociation of the nitrogen molecule corresponds with 19.05 volts, whilst helium has minimum excitation states of 19.73 and 20.56 volts. The conditions for securing the collision of the second kind would then be that the gas mixture should be at a relatively high pressure and

have only a small partial pressure of nitrogen, that a high current density be used in the discharge, and that the gases be very pure. These conditions are those given by Merton and Pilley (this vol., ii, 333) in obtaining a new line spectrum of nitrogen attributed to nitrogen atoms. Failure to produce the spectrum when argon is substituted for helium points to the fact that the heat of dissociation of nitrogen is greater than 280 kg.-cal./mol. and adds support to the value given above. A. E. M.

**Series in the Arc Spectrum of Nitrogen.** C. C. KIESS (*J. Opt. Soc. Amer.*, 1925, **11**, 1—9).—Merton and Pilley (this vol., ii, 333) have recently found conditions under which the arc spectrum of the nitrogen atom can be observed, unobscured by the molecular band spectra. The lines measured by them, with the addition of others, have now been arranged into doublet and quartet series, the existence of which in the arc spectrum of nitrogen was predicted by the displacement law, as the spark spectrum is known to contain series of odd multiplicity. S. B.

**Spectra of Neon and Argon in the Extreme Ultra-violet.** T. LYMAN and F. A. SAUNDERS (*Nature*, 1925, **116**, 358).—The spectrum of argon contains a pair of lines at 1048.28 and 1066.73 ( $\pm 0.2$ ) Å., similar to those observed with neon (*Physical Rev.*, 1925, [ii], **25**, 886) corresponding with Hertz' resonance potential of 11.5 volts, and another pair corresponding with his value of 14.0 volts. The complete argon spectrum is probably like that of neon. The neon line 735 Å. is normally stronger than the line 743 Å., but when a small quantity of neon is present as an impurity in helium the intensities are reversed. It is supposed that the collisions between atoms of neon and helium render the atomic state yielding the line 735 Å. less probable than when neon alone is present. A. A. E.

**Line Breadths and Absorption Probabilities in Sodium Vapour.** G. R. HARRISON and J. C. SLATER (*Physical Rev.*, 1925, [ii], **26**, 176—188; cf. this vol., ii, 734).—From data recorded previously, the theoretical half-breadths of the lines 2 to 8 are calculated, together with the half-breadths in frequency units  $P/2\pi$  which are proportional to the probabilities. The broadening of the first line is 100 times as great as that to be expected from the Stark effect and collision broadening, and the breadths of succeeding lines decrease rapidly with increasing term number at the saturated vapour pressures over the temperature range 450—600°, a result contrary to that found at low vapour pressures. The high pressure broadening is ascribed to diatomic sodium molecules, the perturbation being greater the lower the quantum state. The proportion of diatomic molecules increases with the temperature, suggesting that the energy of dissociation of  $\text{Na}_2$  at absolute zero may be negative. R. A. M.

**Regularities in the Spectra of the Alkaline Earths.** H. N. RUSSELL and F. A. SAUNDERS (*Astrophys. J.*, 1925, **61**, 38—69).—Tabulated data are given of the wave-lengths and wave numbers

of 97 calcium lines, 55 strontium lines, and 95 barium lines, not included in the ordinary series, which have been identified as combinations between known spectroscopic terms and new terms. A number of new lines, mainly of calcium, are also recorded. Calcium affords a new series of five groups of 6 lines each, including the strong groups near 4300 and 3000 Å. and new groups near 2560, 2360, and 2260 Å. There is evidence in favour of other series, and of similar series in the case of strontium and barium. The inner-quantum properties of the new terms are normal; the azimuth-quantum properties are sometimes normal and sometimes correspond with a change of the usual azimuth-quantum number by  $\pm 1$ . Some of the terms have negative values; apparently a neutral atom can contain more than enough energy to ionise it. Bohr's suggestion that the two valency electrons are both displaced to outer orbits is acceptable. The limit of the new calcium series, which differs from that of the ordinary series, corresponds with an ionised and excited atom in the metastable  $1\delta$  state, the normal state being  $1\sigma$ ; apparently all the other new series of calcium, strontium, and barium converge to the  $1\delta$  limit. It is assumed that the angular momenta of the two valency electrons are quantised in space with respect to each other, and their resultant is quantised with respect to that of the residue of the atom. Methods of spectroscopic notation are considered, and a tentative scheme is developed in which the series is denoted by Roman capitals, the system by an index on the left, giving the multiplicity, and the component of a multiple term by a subscript figure on the right, giving the inner quantum number. The index position on the right is reserved for indices denoting the "anomalous" terms, and the serial number is denoted by a prefixed integer; thus, the calcium line 5270.3 Å. is denoted by  $1^3D_3-1^3P_2$ ".

A. A. E.

**Magnetic Resolution of the Scandium Spectrum. I.** S. GOUDSMIT, J. VAN DER MARK, and P. ZEEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 127—141).—The lines of the scandium spectrum are classified, and the classification is confirmed by an examination of the magnetic resolutions of a number of the lines. A concave Rowland grating was used as spectrograph, and a vacuum trembler as source of light. The spark was formed in hydrogen under low pressure between a tungsten electrode and a specially prepared carbon electrode previously soaked in a solution of scandium chloride. A magnetic field of about 41,000 gauss was produced by a Weiss magnet with water cooling. The magnetic resolutions of a number of lines of the Sc I doublet system and the Sc II triplet system are tabulated.

A. B. M.

**Interpretation of Complicated Spectra Particularly of the Elements from Scandium to Nickel.** F. HUND (*Z. Physik*, 1925, **33**, 345—371).—The author extends the methods which have been found applicable to the short periodic groups to the elements from scandium to nickel and assigns to them quantum numbers for the electrons in the normal state of the atom and for the positive

ion. The relationship between the type of spectrum and the position in the periodic table is established. E. B. L.

**Multiplets in the Spectrum of Ionised Vanadium.** W. F. MEGGERS (*Z. Physik*, 1925, **33**, 509—528).—Although the spectrum of vanadium II resembles that of titanium I, in accordance with the displacement law, the ground term is a quintuplet  $f$ -term and not a triplet. Widely separated terms with azimuthal quantum numbers up to six are found. For the vanadium spark spectrum, thirty-three multiplets are ascertained to be combinations of quintuplet and triplet terms. Tables are given containing a list of all the classified lines, their wave-lengths, combinations, and intensities, and the class in which they are placed by King according to their appearance by thermal excitation. E. B. L.

**Arc Spectrum of Nickel.** K. BECHERT and L. A. SOMMER (*Ann. Physik*, 1925, [iv], **77**, 351—371).—The intensities and combinations are tabulated for 354 lines of the arc spectrum of nickel between the wave-lengths 10530.09 and 2244.5 Å. The ground term of this spectrum, which has odd multiplicities, is an  $f$ -term belonging to the triplet series, and has an azimuthal quantum number 4. All the terms are inverted, and the magnetic moment in the ground state has the value 5 Bohr magnetons. Jumps in azimuthal quantum number of 2 units are frequent in the nickel spectrum, and occur in the singlet as well as in the triplet series. F. G. T.

**Order of Appearance of certain Lines in the Spark Spectra of Cadmium and Magnesium.** F. L. BROWN and J. W. BEAMS (*J. Opt. Soc. Amer.*, 1925, **11**, 11—15).—The order in which the various visible lines in the spark spectra of cadmium and magnesium appear after the striking of the spark has been determined. A “shutter” device, consisting of a Kerr cell filled with carbon disulphide, and two suitably disposed Nicol prisms, is placed in the same circuit as the spark, and the light from the latter is observed through the cell. The “shutter” permits the passage of light only when an electric field is applied to the carbon disulphide. By altering the lengths of the leads in the apparatus, the shutter can be “opened” at different intervals, subsequent to the passage of the spark, and the variations in the spectrum observed. The method is being applied to other spectra. Similar observations show that the interval between the appearance of the spark lines of cadmium and that of the arc lines is longer than  $3 \times 10^{-8}$  sec. S. B.

**Series Spectrum of Gold.** J. C. McLENNAN and A. B. McLAY (*Proc. Roy. Soc.*, 1925, **A**, **108**, 571—582; cf. *A.*, 1924, ii, 4).—A method has been developed of obtaining the absorption spectrum of metallic vapours in the Schumann region, and has been applied to the vapours of gold, silver, and copper. The second members of the principal series of doublets in the gold arc spectrum are  $\lambda=1646.71$  and  $\lambda=1665.75$ . The term scheme for the arc series of gold is discussed. Attention is directed to the similarity that exists between the term systems of Au I, Cu I, and Zn II in respect to their inverted  $\delta$  terms, and to the similarity of the term

systems of Au I and Cu I in respect to certain  $\pi$  terms. The ionisation potential of the gold atom is 9.25 volts. L. F. G.

**Absorption Spectrum of Lead Vapour in the Ultra-violet.** R. V. ZUMSTEIN (*Physical Rev.*, 1925, [ii], 26, 189—194; cf. A., 1921, ii, 474; 1924, ii, 455).—In the region 5000—2000 Å. at temperatures up to 1600° a 3 cm. column of lead vapour exhibited absorption of 34 lead lines. The arc spectrum of lead with a current of 100 amperes was photographed. Between 2255 and 2020 Å. all the 15 recorded lines (A., 1923, ii, 672, 710) were reversed; three new lines were measured. The classification of lead lines given by Grotrian (A., 1923, ii, 710) has been extended and confirmed; the  $2p_5$  term, however, is eliminated. Absorption occurs from the normal state  $2p_4$  and the metastable states  $2p_3$  and  $2p_2$ . Most of the 20 new lines lie on the short-wave side of 2400 Å. and the only one unclassified (2393.802) is regarded as  $2p_3-X_3$ , where  $X_3$  is a new term (10232). Values are given for  $3p_2$ ,  $3p_3$ ,  $4p_2$ ,  $4p_3$ ,  $3d_1$ ,  $2x$ ,  $3x$ ,  $4x$ ,  $5x$ . New lead combination lines are calculated, and a new series  $2p_3-mx$  is suggested. R. A. M.

**Effect of Chemical Constitution on the X-Ray Spectrum of Sulphur.** B. RAY (*Phil. Mag.*, 1925, [vi], 50, 505—511).—Measurements of the wave-lengths of the K-lines of sulphur and a large number of sulphur compounds have been made. Within the experimental error, the wave-lengths are the same for sulphur and sulphide compounds, but for sulphite and sulphate compounds the lines  $K\alpha_1$  and  $K\alpha_2$  are shifted to shorter wave-lengths and have their distance apart considerably diminished. For sulphur and sulphides, the distance between  $K\alpha_1$  and  $K\alpha_2$  is  $3X$ -units, whilst for sulphites and sulphates the value is  $2.4X$ -units, the shift of  $K\alpha_1$  being  $3.0X$ -units toward the shorter wave-lengths. No such displacements occur with the lines  $K\alpha_3$  and  $K\alpha_4$ . The results are discussed in connexion with the theory of the origin of doublets. A. E. M.

**New  $K\beta_1$  Doublet of the Elements Manganese and Chromium.** N. SELJAKOV and A. KRASNIKOV (*Z. Physik*, 1925, 33, 601—605).—Photographs were obtained showing the separation of the doublets into  $K\beta_1$  and  $K\beta'$ , the latter having only half the intensity of the former as measured by a Koch microphotometer. The wave-lengths for  $K\beta'$  were : Mn 1910.24, Cr 2085.01 X-units. E. B. L.

**Doublet  $K\alpha_{1,2}$  of the Lighter Elements and the Dependence of the X-Ray Spectra on Chemical Combination.** E. BÄCKLIN (*Z. Physik*, 1925, 33, 547—556).—The distance between the two lines was measured for the elements from aluminium to calcium, using a very large angle of incidence. The lines for aluminium oxide are displaced towards shorter wave-lengths relative to aluminium metal; similarly for sulphur in sulphates as compared with the element, and for phosphorus compared with the pentoxide. The effect is much more pronounced with barium sulphate than with calcium sulphate. E. B. L.

**Energies of Multiple X-Ray Ionisation of Light Atoms.**

L. A. TURNER (*Physical Rev.*, 1925, [ii], 26, 145—149).—Wentzel (A., 1924, ii, 368, 434) considers that the weak lines accompanying the *K* emission lines of some light elements are due to multiply ionised atoms. The author assumes that the removal of a *K* electron exerts the same effect on the energies of the outer electrons as an increase in the nuclear charge of one unit. The energy required for the successive removal of a *K* and an *L* electron is calculated for elements of atomic numbers 11—19 (Na—K) and thence by means of Wentzel's theory multiple ionisation terms are calculated from the ordinary *K* and *L* terms and the  $\alpha_3$ ,  $\alpha_4$ ,  $\alpha_5$ , and  $\alpha_6$  lines. The square roots of the energies for the successive removal of the first, second, and third *L* electrons plotted against atomic numbers give three parallel straight lines, indicating that the screening constant is reduced from 7.27 to 6.65 and then to 6.0. The lines obtained for the two *K* electrons are similar. The results are extended to show that the experimental value for the *K* absorption limit of phosphorus is in error.

R. A. M.

**Quantum Number Relations in Series Spectra.**

R. B. LINDSAY (*J. Opt. Soc. Amer.*, 1925, 11, 17—30).—A theoretical paper in which the effective quantum numbers corresponding with the entire series of stripped atoms in the third group of the periodic system (Bohr's arrangement) are calculated. It is further shown that if a spectrum of a given atom is compared with that of another atom one unit greater in atomic number, but at a higher stage of ionisation (e.g.,  $\text{Mg}^+$  with  $\text{Al}^{++}$ ), the ratio of the quantum defects for corresponding orbits is nearly the same for different pairs of atoms as one passes along a group in the periodic system. This fact, it is suggested, may be used in the prediction of unknown spectral terms.

S. B.

**Fine Structure of Optically Excited Spectrum Lines.**

E. GROSS and A. TEREIN (*Nature*, 1925, 116, 280).—The spectrum lines emitted by mercury vapour illuminated by an intense mercury lamp have a much simpler fine structure than is usual. The absence of some of the satellites suggests that these are not due to isotopy.

A. A. E.

**Measurement of Intensity Ratios of Doublets of Alkali Metals in the Principal Series.**

F. W. OUDT (*Z. Physik*, 1925, 33, 656—657).—The ratio of the lines in the rubidium doublet in the Bunsen flame is 1 : 2. For caesium, the ratio in the arc is 1 : 2, but in the blow-pipe flame the results were not constant, varying from about 1 : 5 to 1 : 2.

E. B. L.

**Intensity Ratios of Some Inter-combination Lines.**

T. BOUMA (*Z. Physik*, 1925, 33, 658—659).—The inter-combination lines show a more rapid decrease in intensity with increasing series number than the diminution found for the singulets.

E. B. L.

**Intensity of Multiple Spectral Lines.** L. S. ORNSTEIN (*Proc. Physical Soc.*, 1925, **37**, 334—347).—A review of the experimental and theoretical investigations of the author and collaborators.

F. G. T.

**$pp'$  Groups in Atoms of the Same Electronic Structure.** I. S. BOWEN and R. A. MILLIKAN (*Physical Rev.*, 1925, [ii], **26**, 150—164).—It is shown that two electrons may simultaneously change their energies within an atom and integrate their joint energy-change into a monochromatic emission. By the methods of hot spark spectroscopy and high dispersion applied to the two series of atoms (*a*) Mg I, Al II, Si III, P IV, S V, Cl VI; (*b*) Be I, B II, C III, N IV, O V, a quintuplet of nearly equally spaced lines has been observed for all these atoms. The group is really a sextuplet, but the two middle lines are not separated. The  $pp'$  group arises from an electron jump from the lowest  $p$  to the lowest  $s$  orbit, combined with a simultaneous jump of the other electron between the  $p_1$ ,  $p_2$ ,  $p_3$  orbits. The frequency differences between the groups of successive atoms obey the irregular doublet law, showing that the jumps are between levels of the same total quantum number. A new quadruplet  $pp'$  group is found in the three-valency electron atoms Al I, Si II, P III, S IV, Cl V, and C II, N III, O IV. The relative intensity increases with the effective nuclear charge from Al I to Cl V. These quadruplet  $pp'$  groups are due to the return of one of the  $s$  electrons after displacement to a  $p$  position combined with the simultaneous interchange of the  $p$  electron between the  $p_1$ ,  $p_2$  orbits. The groups also obey the irregular doublet law.

The earlier work of Wentzel (A., 1924, ii, 434) and of Russell and Saunders (A., 1924, ii, 800) on  $pp'$  groups in calcium led to negative term values. Bohr (*Physikal. Z.*, 1922, **24**, 106) first suggested the simultaneous jump of a second electron as an explanation. The present work supplies a rigorous proof, although the mechanism of the integration of complex vibrations remains unknown. It follows from the work that the ionisation potential must depend on the state in which the ionised atom is left after removal of an  $s$  electron. There will thus be several ionisation potentials differing according as the  $p$  electron is left in the  $p_1$ ,  $p_2$ ,  $p_3$ , or  $P$  orbit.

R. A. M.

**Excitation of Forbidden Spectral Lines.** P. D. FOOTE, T. TAKAMINE, and R. L. CHENAULT (*Physical Rev.*, 1925, [ii], **26**, 165—175).—The following lines which are forbidden on the selection principles of Bohr have been observed in the positive column of a hot-cathode low-gradient discharge at low pressure:  $1S-2p_1$  ( $\Delta j=2$ ) for mercury, cadmium, and zinc at 2270.0, 3141.1, and 3039.8 Å., respectively, and  $1S-2p_3$  for cadmium at 3320.0 Å. A cadmium  $pp'$  multiplet has also been measured. The general applicability of the azimuthal-quantum number rule and the inner-quantum rule is not questioned, but the increasing number of forbidden lines observed makes an investigation of the effects of varying electric and magnetic fields necessary.

R. A. M.

**Joining the Infra-red and Electric-wave Spectra.** E. F. NICHOLS and J. D. TEAR (*Astrophys. J.*, 1925, **61**, 17—37).—The spectrum of a quartz mercury arc, when examined in the long wave region, exhibits radiation at wave-lengths approximately 228, 292, 412, 420, and possibly 685  $\mu$ , as predicted by the quantum theory, when the moment of inertia of the source (HgH molecules) is assumed to be  $5.7 \times 10^{-40}$ . A. A. E.

**Anomalous Electrical Double Refraction of Sodium Vapour.** R. LADENBURG and H. KOPFERMANN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 420—424; cf. this vol., ii, 79).—Electrical double refraction of the  $D_2$ -line of sodium vapour has been observed. Passage of light through a layer of sodium vapour 2.8 cm. thick at a pressure of  $10^{-5}$  mm. causes a phase difference of the components of the  $D_2$ -line, parallel and transverse to the field, of  $6^\circ$  for a field strength of 30,000 volt/cm. No electrical double refraction of the  $D_1$ -line was observed and it is certainly less than one-tenth of that of the  $D_2$ -line. The electrical double refraction causes the  $D_2$ -line to light up under crossed Nicols and a quarter wave-length plate on switching on the field, whilst the  $D_1$ -line remains invisible. The difference in the electrical displacements of the parallel and transverse components of the  $D_2$ -line is evaluated, the parallel component being 10 times as much displaced as the transverse. On the basis of Kramers' theory, the electrical separation of the levels of the  $p$ - and  $s$ -terms of sodium is calculated. F. G. S.

**Intensity of Multiplets and their Zeeman Components.** II. R. DE L. KRONIG (*Z. Physik*, 1925, **33**, 261—272; cf. this vol., ii, 458).—An extension of the former treatment to more complicated cases. The effect of inter-combinations on the spacing of the multiplets is considered, and also the case in which the magnitude of the effect of the core on the outer electrons is comparable with that of mutual action of these electrons. For neon, the calculations agree satisfactorily with experimental data. E. B. L.

**Intensities of the Zeeman Components.** S. GOUDSMIT and R. DE L. KRONIG (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 418—422).—A mathematical paper in which, employing Ornstein and Burger's rule,  $2i_+ + i_0 + 2i_- = C$  (this vol., ii, 340; *Z. Physik*, 1924, **29**, 241), formulæ for the intensities of the Zeeman components for small quantum numbers are deduced corresponding with similar formulæ obtained for large quantum numbers by Sommerfeld and Heisenburg (*ibid.*, 1922, **11**, 131). J. W. B.

**Zeeman Effects Contrary to the Rule for Multiplets of the First Stage.** E. BACK (*Z. Physik*, 1925, **33**, 579—600).—The influence of magnetic fields on the spectrum of calcium has been studied and a relation found to exist between the terms which do and those which do not conform to Landé's rule. The application of the principle of correspondence is considered for magnesium and a modification introduced. A partial Paschen-Back effect was



observed for sodium using a vacuum arc and a field of 38,782 gauss.  
E. B. L.

**Zeeman Effect in Strong Magnetic Fields.** P. KAPITZA and H. W. B. SKINNER (*Proc. Roy. Soc.*, 1925, **A**, **109**, 224-239; cf. *ibid.*, 1924, **A**, **105**, 691; **A**, **106**, 602).—Details are given of a method of utilising for the study of the Zeeman effect transient magnetic fields up to 130,000 gauss, produced by accumulator discharges of about 3000 amp. through a coil. The magnetic constant of the field was determined from the force exerted by it, under standard conditions, on a specially constructed solenoid. The field strength was obtained from oscillograms of the current passing through the magnet coil. As the field was not constant for more than  $1/300$  sec., the spectrum was photographed with a high-dispersion quartz spectrograph, by using a localised spark obtained by the use of a large condenser battery. The method of synchronising the spark with the occurrence of the field is described. The results of photometric measurements of the Zeeman separations indicate that in most cases the splitting is approximately proportional to the field strength, but for the triplet  $p$ - $s$  combinations of zinc and mercury evidence was obtained that the splitting was not strictly proportional to the field strength between fields of 70,000 and 130,000 gauss, being 10% greater than was anticipated for the latter field. The total separations in a field of 120,000 gauss were from 0.3 to 0.15 mm. on the plates, the maximum separation (for Zn 4680) corresponding with 5.8 Å. In most cases, lines in the longitudinal effect split into two components, the intensities of these and of the unaffected line showing that both complex and simple splitting may occur. The splitting in some cases appears not to occur exactly about the position of the unaffected line, but to show a slight shift, non-reproducible, and apparently of secondary origin, towards the red. Reasons are given for attributing this shift to pressure changes. The splitting of the  $s$ - $p$  combinations in doublet and singlet spectra seems to be normal. Three examples of the Paschen-Back effect were observed, namely, the Ca II diffuse doublet (3159, 3179, 3181), the Mg  $pp'$  group (2783.0, 2781.5, 2779.8, 2778.3, 2776.8), and the Be  $pp'$  group (2650.88, 2650.81, 2650.75, 2650.72, 2650.66, 2650.57). In the last case, the splitting is normal, exhibiting the complete Paschen-Back effect. The first example is of an incomplete Paschen-Back effect, and an intermediate stage of the effect is observed in the case of the Mg  $pp'$  group, a field of 120,000 gauss causing the appearance in the longitudinal effect of six components, the positions of which are susceptible to small changes in the field strength.  
F. G. T.

**Ionisation Potential of Ionised Manganese.** D. R. HARTREE (*Nature*, 1925, **116**, 356).—Two independent estimates of terms from some triplets of the spectrum Mn II, one from the position of a line of the triplet and the other from triplet separations, are in satisfactory agreement and indicate that the  $1s$  term of the Mn II septet system lies within the limits  $118,000 \pm 3000$ , whence the ionisation potential corresponding with the removal of the  $4_1$  electron is  $14.5 \pm 0.4$  volts.  
A. A. E.

**Ionisation of Mercury Vapour by Ultra-violet Light.** G. F. ROUSE and G. W. GIDDINGS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 514—516).—The work of Steubing (*Physikal. Z.*, 1909, **10**, 787) has been repeated with an improved technique. The hot mercury arc does not produce ionisation of mercury vapour. With a water-cooled arc and high vapour pressures true ionisation of the vapour is indicated. According to the quantum relation,  $Ve = h\nu$ , there is no single wave-length of sufficient energy to cause ionisation and hence some cumulative action occurs. Various possibilities regarding this cumulative effect are considered. J. S. C.

**Ionisation Produced in Gaseous Reactions.** A. K. BREWER (*Proc. Nat. Acad. Sci.*, 1925, **11**, 512—514; cf. A., 1924, ii, 745).—When ethyl alcohol and oxygen react between gold electrodes below the ignition temperature, the current flowing is proportional to the applied voltage (the mean potential gradient varied between 0 and  $\pm 2400$  volts/cm.) and increases exponentially with the temperature. With aluminium electrodes, the current is almost zero. Glass electrodes give a current for both positive and negative applied potentials; copper electrodes give a current only when the hot outer electrode is negatively charged. No approach to a saturation current is observed. Ions are formed in the gas layer in immediate contact with the conducting surface and not in the gas space between the electrodes. Positive and negative ions are formed in equal amounts on the same surface. The currents observed are due to the ions removed by the field against the attractions in the neighbourhood of the conducting surface. J. S. C.

**Relative Ionisation in Different Gases for Slow-moving Electrons.** W. P. JESSE (*Physical Rev.*, 1925, [ii], **26**, 208—220).—A uniform beam of electrons in a thermionic tube was made to ionise the gas to be studied. Secondary effects were eliminated by low pressures. With increasing electron energies, the ionisation reached a maximum at the following voltages: helium 140, neon 220, argon 100, carbon monoxide 120, nitrogen 100. For 200 volts, the relative ionisations at 1 mm. pressure, taking that of neon as unity, are hydrogen 0.91, helium 0.48, methane 3.5, nitrogen 3.2, carbon monoxide 3.45, argon 4.1. The results, except for argon, are in agreement with those of Hughes and Klein (A., 1924, ii, 375). A second maximum at 350—400 volts appeared in each case, but it is not completely understood. R. A. M.

**Photo-electric Ionisation of Cæsium Vapour.** P. D. FOOTE and F. L. MOHLER (*Physical Rev.*, 1925, [ii], **26**, 195—207).—A sensitive method has been devised for the measurement of photo-electric ionisation in gases. A small cathode is almost enclosed by the anode and the imprisoned ions increase the current in a filament. Changes in thermionic current with unresolved light have been measured as functions of applied voltage, filament temperature, and vapour pressure. The photo-electric effect has been studied as a function of wave-length, using a quartz monochromator. The ionisation increases with increasing wave-length to a sharp maximum

at the limit  $1s=3184 \text{ \AA.}$  of the principal series as required by the Bohr theory. The ionisation decreases to 10% at  $3400 \text{ \AA.}$  The data support the view that radiation on the long-wave side of  $3184 \text{ \AA.}$  produces excited atoms which acquire sufficient energy to become ionised by collisions with other atoms. Hence the photo-ionisation is not sharply discontinuous at the true threshold for direct ionisation as postulated in the simple theory. R. A. M.

**Saha's Ionisation Formula, and the Theoretical Value of the Photo-electric Absorption Coefficient.** E. A. MILNE (*Phil. Mag.*, 1925, [vi], 50, 547—550).—As modified by Fowler, (*ibid.*, 1923, [vi], 45, 21), Saha's formula for the degree of ionisation is correct only when the ionised atom possesses no energy other than translational and requires a factor which is a partition function of the weights of the various stationary states of the ionised atom. The formula for the photo-electric absorption coefficient requires also a similar factor for the weight of the lowest state of the ionised atom in addition to that for the neutral as given by Kramers (*ibid.*, 1923, [vi], 46, 843), Becker (A., 1923, ii, 820), and the author.

A. E. M.

**Passage of Electrons through Photo-electrically Active Crystals.** H. LENZ (*Ann. Physik*, 1925, [iv], 77, 449—476).—Measurements of the Hall effect have been made with diamond and zinc sulphide crystals. In agreement with the theory of the Hall effect developed by the author, the Hall potential was found to be proportional to the strength of the applied magnetic field, and independent of the photo-electric current strength. Calculations of the electron free-path, time of collision, and electron velocity in the case of a diamond, with an electric field of 400 volts, Hall potential 62 volts, and magnetic field of 4000 gauss, gave, respectively,  $3.4 \times 10^{-6} \text{ cm.}$ ,  $10^{-12} \text{ sec.}$ , and  $6.8 \times 10^{-6} \text{ cm./sec.}$  The dependence of the primary photo-electric current on temperature was determined between  $-191^\circ$  and  $80^\circ$ ; with both diamond and zinc sulphide, the temperature coefficient at first increases with temperature, but later becomes constant, with diamond at about  $-90^\circ$ , and with zinc sulphide at about  $-35^\circ$ . Experiments are described showing that the electron stream through unilluminated crystals cannot be attributed to diffuse reflected light, and that no change of diamagnetism through irradiation is detectable.

F. G. T.

**Thermionic Effect from the Point of View of the Phase Rule.** N. VON RASCHEVSKY (*Z. Physik*, 1925, 33, 606—612).—The emission of electrons cannot strictly be regarded as a simple evaporation; the evaporation of molecules and the existence of positive ions must also be considered. A purely thermodynamical formula of the thermionic current is deduced which contains Richardson's formula as a special case. A relation between electron emission, vapour pressure, and specific heat of a body is obtained.

E. B. L.

**Kinetic Theory of the Thermionic Effect.** N. P. RASHEVSKY (*Physical Rev.*, 1925, [ii], 26, 241—246).—Theoretical. Different assumptions are made regarding the behaviour of electrons inside a

solid body and statistical deductions are drawn for the thermionic currents in each case. All the expressions are of the type  $i = AT^a e^{-b/T}$  and differ only in the values of the constants  $A$  and  $a$ . The experimental results are not accurate enough to decide which assumptions are correct.

R. A. M.

**Sodium by Electrolysis through Glass.** R. C. BURT (*J. Opt. Soc. Amer.*, 1925, **11**, 87—91).—It is possible to introduce pure metallic sodium into the high vacuum of an electric light bulb by using the thermionic emission from the filament. The exterior of the bulb is partly immersed in a bath of molten sodium nitrate, between which and the filament a potential difference is maintained, the filament being negative. Currents up to 0.3 amp. may be passed through the glass, and 0.3 g. of sodium per hour deposited in the bulb. Sodium lamps may be prepared in this way, giving a sodium spectrum free from impurity lines, even those of potassium. Ions other than those of sodium will not pass through the glass, and if potassium nitrate or lithium nitrate is substituted in the bath of molten salt, the bulb breaks after passage of a current for a short period.

S. B.

**Apparent Transmission of Low-velocity Electrons through Aluminium Foil.** H. E. HARTIG (*Physical Rev.*, 1925, [ii], **26**, 221—231).—Aluminium foil 0.0003 cm. thick shows apparently a transparent atom effect for slow electrons similar to that observed in rare gases. The effect was reduced to  $10^{-4}$  of the original by a second foil, and was then probably largely photo-electric. A promising method for the determination of critical potentials from the photo-electric effect of soft X-rays from a metal foil is described.

R. A. M.

**Electric Discharge in Gases at Low Pressure.** B. N. BANERJI (*Nature*, 1925, **116**, 429—430).—Polemical and explanatory (cf. McCurdy, A., 1924, ii, 808; Compton, Turner, and McCurdy, this vol., ii, 86). The phenomenon of discharge is intermittent, the conditions at the anode and cathode being of the same kind but different intensity. An alternative explanation of the selective reduction of the oxide  $W_2O_3$  is put forward.

A. A. E.

**Recent Researches in Positive Rays.** W. WIEN (*Proc. Physical Soc.*, 1925, **37**, 324—333).—A lecture, reviewing the author's work on this subject.

F. G. T.

**Isotopic Composition and Atomic Weight of Chlorine in Meteorites.** W. D. HARKINS and S. B. STONE (*Nature*, 1925, **116**, 426).—The atomic weight of meteoric chlorine is identical with that of terrestrial chlorine, e.g., from wernerite, apatite, and commercial hydrochloric acid.

A. A. E.

**Isotopes of Uranium.** O. HAHN (*Z. anorg. Chem.*, 1925, **147**, 16—23).—The possibility of the existence of unknown isotopes of uranium is discussed and the difficulties of extending knowledge on this subject are pointed out.

J. S. C.

**Elements which are "Electron-Isomerides."** R. SWINNE (*Z. Elektrochem.*, 1925, **31**, 417—423; cf. Meyer, this vol., ii, 173).—A discussion of the structure of the rare earths in terms of the Bohr atom. When the inner orbits are fully occupied by electrons, a relation between elements becomes possible to which the name "electron-isomerism" is given, differing from isotopy in that the nuclei remain the same. W. A. C.

**Electric Charge Carried by Thorium-X and Thorium Emanation Recoil Atoms in Gases.** G. H. BRIGGS (*Phil. Mag.*, 1925, [vi], **50**, 600—612).—Two simple, satisfactory methods for obtaining thorium-X by recoil are described. In helium, oxygen, hydrogen, nitrogen, carbon dioxide, nitrous oxide, and acetylene, all the thorium-X recoil atoms are positively charged at the end of their recoil path. In ethyl ether, methyl acetate, ethyl acetate, acetone, methylol, and hexane vapours, and ammonia from 84 to 94% of the recoil atoms were positively charged. It is concluded that in these gases also all the recoil atoms are initially positively charged. Atoms of thorium emanation recoiling from thorium-X in air, oxygen, hydrogen, and carbon dioxide are all neutral. The factors determining the probability of a recoil atom being positively charged or neutral at the end of its recoil path are discussed and a mechanism is suggested. A. E. M.

**Capture and Loss of Electrons by  $\alpha$ -Particles.** G. H. HENDERSON (*Proc. Roy. Soc.*, 1925, **A**, **109**, 157—165; cf. *ibid.*, 1922, **A**, **102**, 496).—The ratio of the number of doubly charged to the number of singly charged  $\alpha$ -particles in equilibrium has been found quantitatively, by an ionisation method, under various conditions. With  $\alpha$ -particles of initial velocities of  $1.922 \times 10^9$ — $0.769 \times 10^9$  cm./sec., it was found that the above ratio at any velocity was independent of the material (gold, mica, aluminium, silver, or copper) through which the  $\alpha$ -particles have passed. The variation of the ratio with the velocity of the  $\alpha$ -particles was determined and is given approximately by  $n=6.4-4.2V/V_0$ , where  $V$  is the velocity of the  $\alpha$ -particle, and  $V_0=1.922 \times 10^9$  cm./sec. F. G. T.

**$\beta$ -Ray Spectra of Thorium Disintegration Products.** D. H. BLACK (*Proc. Roy. Soc.*, 1925, **A**, **109**, 166—176).—An analysis of the  $\beta$ -ray spectra of thorium-B and thorium-C+D has been made by separating the  $\beta$ -rays into a spectrum by a magnetic field, using a focussing method. For thorium-B, 17 lines were measured, that at  $H\beta$  1398 being of extremely high intensity. Of these lines, 4 are ascribed to the conversion of the ordinary  $K$  X-radiation of thorium-B. For thorium-C+D 16 lines were measured, the strongest being at  $H\beta$  541. A group of lines of energies more than  $2.5 \times 10^6$  volts was recorded, probably due to thorium-D, and arising from the conversion of a single  $\gamma$ -ray in the  $K$  and  $L$  levels of the atom. The analysis of these spectra affords strong support for the hypothesis that the lines of the  $\beta$ -ray spectra are due to the conversion of  $\gamma$ -rays in the various absorption levels of the atoms concerned. F. G. T.

**Absorption and Scattering of  $\gamma$ -Rays.** N. AHMAD (*Proc. Roy. Soc.*, 1925, **A**, **109**, 206—223; cf. *A.*, 1924, ii, 440, 582).—Experiments have been made to test the hypothesis suggested by Compton (*Physical Rev.*, 1923, [ii], **21**, 483) and by Debye (*Physikal. Z.*, 1923, **24**, 161) by comparing the theoretical total absorption due to scattering with that given by the general absorption relation characterising each beam. A further test was made by comparing direct measurements, obtained by means of a conical ionisation chamber capable of rotation about the middle of the radiator, of the intensity of rays scattered within a small cone with that given by theory. The results of these experiments were in general agreement with the formulæ obtained by Compton on a classico-quantum basis. The  $\gamma$ -rays from a radium standard were hardened by filters of iron, lead, or mercury, and their absorption by aluminium, copper, tin, and lead investigated by a modified form of balance method. In every case the atomic absorption coefficient,  $\mu_a$ , is closely represented by the expression  $\mu_a = AZ + BZ^4$ , where  $A$  and  $B$  are constants for a particular beam, although decreasing steadily as the rays become harder, and  $Z$  is the atomic number. The right-hand terms represent the scattering and fluorescence absorptions, respectively. The  $\gamma$ -rays, in their absorption by the elements investigated, thus obey the same general law as  $X$ -rays of much lower frequency. By assuming the validity of the  $\lambda^3$  law, the mean effective wavelengths of the beams were calculated, values being obtained only slightly less than those deduced on Compton's theory from the scattering terms. Determinations of the spectral distribution of energy indicate that the homogeneous  $\gamma$ -rays are superimposed on a background of general radiation which contains a considerable fraction of the total  $\gamma$ -ray emission, with a maximum near 0.02 Å. Measurements of the intensities of the rays scattered within a definite cone for two positions of the revolving ionisation chamber gave results one-third to one-fifth of those predicted by classical theory, but only about 10% lower than those calculated from Compton's formula for the angular distribution of the scattered rays.

F. G. T.

**Heating Effects of the  $\gamma$ -Rays of Radium-*B* and Radium-*C*.** C. D. ELLIS and W. A. WOOSTER (*Phil. Mag.*, 1925, [vi], **50**, 521—536).—In an apparatus automatically compensated for the heating due to  $\alpha$ -particles, the heating effect of the total  $\gamma$ -rays emitted by one curie of radium-*B* and radium-*C* has been found to be  $8.6 \pm 0.4$  cal./hour. From the value of the ratio of the  $\gamma$ -ray energies 0.10 determined from the absorption coefficient measurements of Ahmad (*A.*, 1924, ii, 440, 582) 0.86 cal./hour is attributed to radium-*B* and 7.7 cal./hour to radium-*C*, corresponding with  $1.85 \times 10^5$  and  $16.6 \times 10^6$  volt per disintegrating atom, respectively.

A. E. M.

**Atomic Disintegration by  $\alpha$ -Particles.** G. KIRSCH (*Physikal. Z.*, 1925, **26**, 457—465).—In amplification of the "explosion" theory, it is suggested that atomic disintegration by means of  $\alpha$ -particle bombardment occurs in two steps. The first is the

assimilation of the  $\alpha$ -particle into the nucleus, and the second the immediate expulsion of the H-particle. These two processes are nearly simultaneous; the life of the intermediate product, which, in the case of a nitrogen nucleus, is a fluorine isotope, is of the order of  $10^{-10}$  second. The energy with which the H-particle is emitted is regarded as independent of its direction, and the impulse law is assumed to hold in each stage of the process. Calculations are made of the differences of energy content of fluorine isotopes formed by the assimilation into the nitrogen nucleus of  $\alpha$ -particles of various initial velocities. Comparison of these differences with those of the energy contents of H-particles emitted by the disintegration of these fluorine isotopes shows that the emission is accompanied by just as much energy as was contributed by the  $\alpha$ -particle, so that, in all circumstances, the final product has the same energy content. These assumptions are supported by a study of the absorption curves of the H-particles from nitrogen under various conditions of bombardment by  $\alpha$ -particles. The absorption curves of H-particles from aluminium differ markedly from those from nitrogen, in that some particles of very long range are emitted, the energy of which, in some cases, is double that predicted by theory. Several reasons are suggested for this fact, and the conclusion is reached that the emitted H-particles are not derived from protons situated in a single energy level, but that an innermost level, of maximum energy, exists which can receive energy only from those  $\alpha$ -particles which have a maximum velocity and which strike the nucleus centrally. The emission of H-particles from nitrogen, aluminium, and other elements is considered on the basis of the structure of the kernel suggested by the author (A., 1921, ii, 150; 1924, ii, 380), and the existence of the group of four protons and two electrons as a subsidiary unit is supported. It is further suggested that in building up the kernel from such units ("quasi H-particles") and free electrons, levels of energy exist in the nucleus equal in number to the electron shells external to the nucleus, so that the periodicity of the elements is a property directly related to the kernel-structure. In considering the forces which bind the kernel together, it is shown that if the charges in the nucleus are regarded as rotating with an impulse moment  $mvr = \hbar/2\pi$ , the field-energy of negative charges becomes many times greater than that of stationary electrons, and that, in such circumstances, a proton in a one-quantum orbit of  $10^{-12}$  cm. radius may be in equilibrium with an attracting point-charge of magnitude  $2.88e$ .

F. G. T.

**Atomic Weight of the Gold obtained from Mercury by Miethe and Stammreich.** O. HÖNIGSCHMID and E. ZINTL (*Z. anorg. Chem.*, 1925, **147**, 262—264; cf. Miethe and Stammreich, A., 1924, ii, 874; *Naturwiss.*, 1924, **12**, 597, 1211).—The atomic weight of the gold so obtained was determined by the authors' potentiometric method and agrees with that of ordinary gold.

J. S. C.

**Transformation of Mercury into Gold.** A. S. RUSSELL (*Nature*, 1925, **116**, 312).—Theoretical considerations lead to the

suggestion that the transformation of lead into thallium is as possible as that of mercury into gold. If the masses of the thallium isotopes are 203 and 205, and its atomic weight, as recently determined, is 204.4, that element is an exception to the rule whereby, when any element of odd atomic number possesses two isotopes, the heavier is never in excess. Possibly, therefore, the excess of the isotope 205 may be due to a natural process involving absorption of an electron by the nucleus of the lead isotope 205. A. A. E.

**Transmutation of Uranium into Uranium-X.** A. GASCHLER (*Nature*, 1925, **116**, 396—397).—Priority is claimed against Miethe for the transmutation of mercury into other elements. The behaviour of uranium and thorium and their salts in the electric arc and in the glow discharge in evacuated tubes has been examined, but no alteration in the radioactivity or chemical activity could be observed. When, however, strong rushes of momentary high-tension currents are passed, during 30 hrs., between tungsten electrodes in a silica tube containing mercury and uranium oxide, increasing radioactivity was observed, due to the production of uranium-X. A variation of the experimental conditions allows of the production of relatively large quantities of uranium-X in 30 mins. A. A. E.

**Occurrence of Helium and Neon in Vacuum Tubes.** R. W. RIDING and E. C. C. BALY (*Proc. Roy. Soc.*, 1925, **A**, **109**, 186—193).—By bombardment of a hollow anticathode coated with the nitride of magnesium or of aluminium and placed in the focus of a concave cathode in a tube containing oxygen, the nitrogen atoms are disintegrated, helium, hydrogen, and neon being found as products. Previous failures to repeat the results of Collie and Patterson (*T.*, 1913, **103**, 419) are attributed to the strong occlusion of the rare gases in the electrode splash. By heating the powdered discharge tubes, after 60 hrs'. discharge, at 800° in a vacuum a considerable amount of helium was obtained. With a single induction coil giving a 6-inch spark, the rare gases were always obtained, only minor variations in their amounts being observed when the hammer break was replaced by a mercury break and when a condensed discharge was used. Negative results were obtained when a larger coil was used. F. G. T.

**Chemical Activity of Helium.** E. H. BOOMER (*Proc. Roy. Soc.*, 1925, **A**, **109**, 198—205; cf. Manley, this vol., ii, 144).—When helium is subjected to an intense electronic bombardment (1000 volts, 5—10 milliamp.) at low pressures in the presence of a heated tungsten filament, both helium and tungsten disappear and a black deposit is formed. In general, the atomic ratio between the loss in weight of the filament and the loss of helium was 1 : 2, but the proportion of tungsten was increased when a large amount of mercury was present in the discharge tube. In nitric acid or potassium hydroxide, the black deposit was decomposed with the evolution of helium, and the formation of tungstic oxide or a clear solution. If the ratio of tungsten to helium which had disappeared



was greater than 1 : 2, only the amount of tungsten necessary to form  $\text{WHe}_2$  was dissolved from the black deposit in potassium hydroxide, the tungsten in excess of this ratio remaining in the metallic state. The rate of disappearance of helium was greatest in the pressure range 0.1—0.45 mm., reaching a value 4—5 mm.<sup>3</sup> helium at *N.T.P.* per minute. The velocity of the reaction decreased as the discharge voltage was decreased, and was markedly affected by the material composing the leads, or by the presence of mercury vapour. Strong evidence has been obtained for the existence of the distinct and stable compound  $\text{WHe}_2$ , *tungsten helide*, and less certain evidence, by analogous methods, that helium unites with the vapours of mercury, iodine, phosphorus, and sulphur to form compounds which are stable at the temperature of liquid air, and decompose at slightly higher temperatures.

F. G. T.

**Nature of Radiation.** J. C. SLATER (*Nature*, 1925, **116**, 278).—Discussion.

A. A. E.

**Equilibrium between Matter and Radiation.** O. STERN (*Z. Elektrochem.*, 1925, **31**, 448—449).—On the basis of the fundamental relativistic equation  $U=mc^2$  and of Nernst's heat theorem, an expression is developed for the number of atoms per cm.<sup>3</sup> in equilibrium with black radiation at a given temperature.

W. A. C.

**Equilibrium between Radiation and Matter.** W. WESTPHAL (*Z. Physik*, 1925, **33**, 557—562).—The distribution of energy is calculated for an enclosed space containing stationary radiation and molecules of a perfect gas in a stationary state and possessing a single specific frequency.

E. B. L.

**Theory of Atomic Structure.** P. JORDAN (*Z. Physik*, 1925, **33**, 563—570).—Pauli's arrangement (this vol., ii, 339) of the complex terms of the spectrum of an atom in weak and strong magnetic fields and of the multiplicity of states of the atom, leads to more definite grouping of the valency electrons than was previously possible.

E. B. L.

**Equilibrium Principle of G. N. Lewis.** M. LEONTOVICZ (*Z. Physik*, 1925, **33**, 470—474).—Lewis' principle is investigated in connexion with Einstein's derivation of Planck's formula for black body radiation and is found to lead to Wien's formula, unless it is assumed that there is association of quanta.

E. B. L.

**Serious Difficulty in the Determination of the Number of Vibrations Radiated from a Bohr Atom.** R. K. CHATURVEDI (*Z. Physik*, 1925, **33**, 660—663).—The difficulty is to account for the emission of a coherent train of waves in the time allowed by the leap from one Bohr orbit to another.

E. B. L.

**Structure of Zinc.** H. COLLINS (*Chem. News*, 1925, **131**, 145—149).—Speculative. From the laws of relative volume and of heats of formation the structure of zinc is deduced as  $\text{KCN}$ .

A. R. P.

**Absorption Spectra of Mixed Metallic Vapours. II. Spectra of Volatile Compounds of Magnesium and the Alkali Metals.** S. BARRATT (*Proc. Roy. Soc.*, 1925, A, 109, 194—197; cf. A., 1924, ii, 138).—Measurements have been made, at about 1000°, of the absorption of the mixed vapours magnesium-sodium, magnesium-potassium, magnesium-rubidium, and magnesium-caesium. The magnesium-sodium spectrum consists of a single band in the green region, degraded towards the blue, and with a head at 5290.8 Å. Magnesium-potassium vapours of moderate density exhibit two bands, one in the red, degraded towards the long-wave side, with the head at 6549.7 Å., and the other in the blue, degraded towards the short-wave region, with the head at 4611.6 Å. In much denser vapours a third band appears in the green, degraded towards the blue, with the head at 5150.4 Å. The magnesium-rubidium spectrum has a band at 4728.1 Å., degraded towards the blue. Magnesium-caesium vapours show two bands, one shading off on either side of a maximum at 5706 Å., the other, with a head at 4839.2 Å., degraded towards the blue. Reasons are advanced for attributing these bands to the molecules of volatile compounds of magnesium and the alkali metals. F. G. T.

**Absorption of Light by Vapours of Lead, Tin, Bismuth. Antimony, and Magnesium.** A. L. NARAYAN and K. R. RAO (*Phil. Mag.*, [vi], 1925, 50, 645—649).—The absorption spectrum of non-luminous lead vapour shows, in addition to the fundamental line at 2833 Å., a faint banded spectrum, appearing at about 1100°, extending from 3100 to 3400 spaced at intervals of about 32 Å. That of tin vapour showed a faint reversal of the line 2706.6 Å. That of bismuth at 800° showed the typical line at 3067 Å., a banded spectrum extending from 2600 to 2900 with a spacing of 15 Å., and fine lines at 2721.5, 2730, and 2745 Å., and at 1200° a further banded spectrum extending from 6500 to 4500 with the spacing varying from 90 to 35 Å. in passing from the red to the blue. That of antimony shows fine lines at 2312 and 2306 Å., and a banded spectrum extending from 2305 to 2250, with an interval of about 15 Å.; with increasing temperature a band spectrum in the region 2830 to 3000 and a fine line at 2770 Å. appear. That of magnesium at high temperatures shows a line at 4571 Å. corresponding with the change in energy level  $1S-2p_2$ . A. E. M.

**Structure of the Ultra-violet Bands of Water Vapour.** G. H. DIEKE (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, 28, 174—181).—The lines of the water vapour bands at 3064 and 2811 are classified. By making use of Watson's measurements of the band 2811 (this vol., ii, 349) and a modification of Heurlinger's arrangement of the band 3064 ("Untersuchungen über die Struktur der Bandenspektren," Lund, 1918), a complete analysis of the bands is shown to be possible. The question of the origin of the bands, whether due to  $H_2O$  or to OH molecules, is still open. A. B. M.

**Band Spectra Associated with Carbon.** F. BALDET (*Nature*, 1925, 116, 360).—A claim for priority. A. A. E.

**Flame Spectra of Carbon Monoxide and Water-gas. I.**

F. R. WESTON (*Proc. Roy. Soc.*, 1925, A, 109, 176—186).—The flame spectrum of carbon monoxide, and the effect on it of admixture of hydrogen in varying proportions, have been determined. The spectrum of pure undried carbon monoxide consists of a banded radiation extending from 5000 to 2200 Å., on which a continuous spectrum and some steam lines are superimposed. As the carbon monoxide in the burning gas is progressively replaced by hydrogen, both the banded and continuous parts of the spectrum fade away until, at an equimolecular mixture of the gases, they nearly disappear, only steam lines remaining visible. The intensity of these lines increases with the amount of hydrogen, reaching a maximum in the spectrum of pure hydrogen. At the same time, a rapid shortening of the ultra-violet end of the continuous spectrum occurs. The spectrum of carbon monoxide burning in various supporting atmospheres (air, "argon air," dried, undried, and 6% ozonised oxygen, nitrous oxide) was photographed. With undried air, the continuous part of the spectrum is intensified and prolonged. Dried oxygen has the effect of diminishing the intensity of the steam lines. By burning carbon monoxide in oxygen at various pressures it was found that as the pressure is reduced the banded spectrum becomes more distinct and the continuous part less intense, without any alteration of the positions of the bands. Measurements are given of the intensity and distribution of the band spectrum of carbon monoxide burning in air. It is concluded that in the flame of undried carbon monoxide two sets of independent reactions occur simultaneously, (a) direct combination of carbon monoxide and oxygen, exciting radiations which give rise to the continuous and banded parts of the spectrum and to the blue colour of the flame, and (b) reaction between carbon monoxide and oxygen molecules giving rise to steam lines in the spectrum. Addition of hydrogen causes the second reaction to predominate.

F. G. T.

**Red Cyanogen Spectrum in Daniel's Comet (1907).**

F. BALDET (*Compt. rend.*, 1925, 181, 331—333).—Re-examination of plates taken in 1907 shows that the red band of the comet originates in the red group of bands due to cyanogen which are observed in the carbon arc. In the comet the bands are very intense and are superimposed on a fairly intense continuous spectrum. R. A. M.

**Infra-red Absorption Spectra of Organic Derivatives of Ammonia. I. Aniline and some Mono- and Di-alkylanilines.**

F. K. BELL (*J. Amer. Chem. Soc.*, 1925, 47, 2192—2207).—The absorption spectra of aniline, methyl- and dimethyl-, methyl-ethyl-, ethyl- and diethyl-, *n*-propyl- and di-*n*-propyl-, *n*-butyl- and di-*n*-butyl-, and *iso*amyl-anilines between 1.0 and 12.0  $\mu$  have been measured and plotted, the accuracy of the absorption curves being within 0.05  $\mu$ . The main conclusions are as follows: ammonia shows a single deep band at 2.98  $\mu$  (Coblentz, *Carnegie Inst. Pub.*, 1905, 35, 53), whilst in aniline this shifts to 2.8  $\mu$  and the 3.25  $\mu$  band of benzene appears. In the monoalkylanilines, the 2.8  $\mu$  band becomes shallower and the 3.25  $\mu$  band shifts to 3.3  $\mu$  and is con-

sistently deeper than the  $2.8\mu$  band, whilst in the dialkylanilines the latter almost disappears and the  $3.3\mu$  band becomes deeper. Thus with progressive substitution in ammonia the specific influence of tervalent nitrogen on absorption in the region  $2.8\mu$  progressively diminishes. In the region  $2.7-3.4\mu$ , therefore, the absorption permits a pronounced qualitative differentiation between aniline, mono- and di-alkylanilines.

J. W. B.

**Absorption Spectra of Pyruvic Acid. Existence of Tautomeric Forms.** V. HENRI and C. FROMAGEOT (*Bull. Soc. chim.*, 1925, [iv], 37, 845-853).—The study of absorption spectra gives a ready method of proving the presence of tautomeric forms, since the ultra-violet absorption by a molecule with a double bond between two carbon atoms is much stronger than that by a molecule with a double bond between a carbon and an oxygen atom. In concentrated solutions of pyruvic acid the acid is almost entirely in the keto form, but the intensity of absorption increases with dilution, and the presence of a double bond between two carbon atoms is indicated. A formula is given for calculating the growth of the enol form with dilution, from which it appears that the growth of the enol form increases tenfold when the concentration drops from  $0.1N$  to  $0.01N$ , and is only increased one and a half times on dropping from  $0.01N$  to  $0.002N$ . A study of the influence of the  $p_H$  of the medium shows that the amount of the enol form increases with the alkalinity of the solution. The biological significance of these results is pointed out.

L. L. B.

**Ultra-violet Absorption Spectra of Mono- and Di-derivatives of Benzene.** F. W. KLINGSTEDT (*Acta Acad. Aboensis Math. Phys.*, 1924, 3, 1-82; from *Chem. Zentr.*, 1925, i, 2286; cf. A., 1923, ii, 48).—The absorption of ultra-violet radiations up to  $1944 \text{ \AA}$ . has been examined quantitatively for toluene, phenol, aniline, the xylenes, cresols, toluidines, and dihydroxybenzenes. All compounds which show narrow absorption bands in the vapour state give also in indifferent solvents spectra with narrow ( $10-30 \text{ \AA}$ .) bands similar to the spectra of their vapours. The characteristics of the absorption spectra of the compounds mentioned are described, Substitution in the benzene nucleus by methyl, hydroxyl, or amino groups results in a displacement of the selective absorption towards the red, an increased total absorption in the inner ultra-violet, an increase in the molecular absorption coefficient of the strongest inner bands, and a change in the number, form, and distribution of the different bands. Similar effects are observed in substituted toluene derivatives. The selective absorption of para derivatives is distinguished, apart from the nature of the substituent, by a large number of sharply defined narrow bands, begins at longer wavelengths, and is more marked in the extreme ultra-violet than is the case with the other isomerides. Ortho and meta derivatives are similar in the middle ultra-violet and to a certain extent in the outer ultra-violet. The absorption spectra of the hydrocarbons examined have no definite benzene character. The absorption spectra of the phenols, apart from those parts of the spectra of para derivatives

which contain numerous bands, are generally similar. The amines are generally similar in their absorption spectra up to the outer ultra-violet, except that aniline and *p*-toluidine have narrow bands in the inner ultra-violet.

G. W. R.

**General Nature of Band Spectra.** J. W. NICHOLSON (*Phil. Mag.*, 1925, [vi], **50**, 650—662).—A theoretical discussion of band spectra, directing attention to the relationships between line and band spectra. A formula is suggested which contains as a fundamental constant a Rydberg constant only. Some terms arise from ordinary quantum theory as applied to electronic orbits, whilst others arise from the quantising of the degrees of freedom of the nuclei.

A. E. M.

**Complementary Researches on the Structure and Distribution of Band Spectra.** H. DESLANDRES (*Compt. rend.*, 1925, **181**, 265—271; cf. this vol., ii, 736).—The infra-red bands of the simple gases oxygen, carbon monoxide, hydrogen cyanide, ammonia, water, and methane can be expressed by the relation  $\nu=qd_1/rs$ , where  $d_1$  is a universal constant 1062.5 and  $q$ ,  $r$ , and  $s$  are integers. The data for ammonia are examined in detail and are found to agree with the relation very well. Hydrogen fluoride, chloride, and bromide also exhibit bands related to the universal frequency. Although the data are incomplete, a tentative analysis is put forward suggesting that the constant frequency-differences characteristic of sub-groups are also small sub-multiples of the constant. The author agrees with Baly ("Spectroscopy," vol. 1, 1924) that the infra-red region is of primary importance for radiation theories of reaction.

R. A. M.

**Experimental Determination of the Critical Excitation Frequency for the Production of Fluorescent X-Radiation.** S. K. ALLISON and W. DUANE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 485—489; cf. *Physical Rev.*, 1925, [ii], **25**, 581).—Experiments in which the fluorescent radiation was excited in a silver plate by primary radiation from a tungsten target show that to produce a fluorescent line spectrum the primary radiation must contain X-rays of frequency at least as great as that of the corresponding critical absorption, this frequency being the same for all lines in the series. The wave-lengths of the  $K\alpha_1$  and  $K\alpha_2$  lines in the fluorescent silver spectrum are 0.55834 and 0.56266 Å., respectively.

J. S. C.

**Photographic Sensitometry with Fluorescent Oils.** G. R. HARRISON (*J. Opt. Soc. Amer.*, 1925, **11**, 113—123).—The changes in sensitivity and contrast produced in several brands of photographic plates by coatings of fluorescent oils have been studied through the wave-length range 2200—3800 Å. Characteristic curves are given for the coated plates. Some plates show a maximum sensitivity increase with a thick coating of oil, others with a thin coating. Clear paraffin oil gives the maximum sensitivity increase, whilst light lubricating oil has more effect on the contrast. The exposures required may be cut down 400-fold by oil treatment. With some oils, a gain in sensitivity is achieved only when the

intensity of the incident light is above a certain value, below which the sensitivity is diminished. The sensitivity is generally decreased for wave-lengths longer than 2500 Å. Contrast improvement may be obtained even up to 3800 Å. The sensitivity of a plate uniformly oiled is constant over its surface to within 1%. S. B.

**Activating Element in Luminescent Boron Nitride.** E. TIEDE and H. TOMASCHEK (*Z. anorg. Chem.*, 1925, **147**, 111—122; cf. A., 1921, ii, 74; *Z. Elektrochem.*, 1923, **29**, 303).—Experiments are described which show that specimens of boron nitride exhibit luminescence only when small quantities of carbon are present. J. S. C.

**Economy Coefficients of Phosphorescent Substances.** F. SCHMIEDER (*Ann. Physik*, 1925, [iv], **77**, 381—416).—The economy coefficient, defined as the ratio of the energy of the emitted to that of the exciting light, has been measured for three phosphorescent calcium sulphide preparations, employing exciting light of wave-lengths 365 and 435  $\mu$ . A method is described, based on Lenard's differential equation for the light emission of phosphorescent substances, in which the total transmitted and phosphorescent light emerging from a monochromatically illuminated layer of a phosphorescent substance is measured by a photo-electric cell. The transparency of the layer is determined by measuring the transmission of light of the non-exciting wave-length 546  $\mu$ . Measurements were made of the intensity of the phosphorescent bands of the preparations  $\text{CaBiz}$ ,  $\text{ZnCuz}$ ,  $\text{CaCuz}$ , at a series of temperatures. The possible sources of error in the method are investigated in detail, and all assumptions subjected to experimental tests. For the above phosphorescent substances, in the order given, the mean economy coefficients for exciting light of wave-length 435  $\mu$  are 0.97, 0.835, 0.75, and for light of wave-length 365  $\mu$ , 0.82, 0.731, 0.63, respectively. The results confirm Lenard's conclusion that for each quantum of exciting light absorbed, one quantum of emitted light appears. Evidence was obtained that some of the emission centres are able under certain conditions to emit more light energy than they absorb, the excess energy arising possibly from the kinetic energy of the atoms composing the emission centre, or from the thermal energy of the centres. F. G. T.

**Dependence on Temperature of the Internal Friction and Electrical Conductivity of Aqueous Solutions.** M. WIEN (*Ann. Physik*, 1925, [iv], **77**, 560—586; cf. *Physikal. Z.*, 1924, **25**, 559).—A review of data for the effect of temperature on the electrical conductivity of aqueous solutions supports the view that the initial temperature coefficient comprises the two effects of a change of viscosity of the solvent, which occurs in an imperceptibly short time, and of a second effect, which is not instantaneous, and is dependent on the ions in solution. The temperature coefficient of the fluidity of water and of aqueous solutions can be expressed by the formula  $\alpha = 1/(a + bt)$ , where  $a$  and  $b$  are constants. The temperature coefficients of the electrical conductivity of these solu-

tions, plotted against temperature, lie on curves which are parallel to those for the temperature coefficients of the fluidity, so that in the range  $0-100^{\circ}$ , the expression  $\beta = \alpha + \gamma$  holds, where  $\beta$  and  $\alpha$  are the temperature coefficients of the conductivity and the fluidity, respectively. With the exception of sodium carbonate solutions,  $\gamma$  is negative. It has values for neutral salts between  $-0.2$  and  $-0.3$ , for bases between  $-0.5$  and  $-0.7$ , and for acids between  $-0.8$  and  $-1.6$ ; it is a characteristic of a given ion. For most solutions,  $\gamma$  is, within the limits of experiment, independent of temperature, and only slightly, if at all, dependent on the concentration. Except with phosphoric and hypophosphorous acid solutions, the constancy of  $\gamma$  holds over the range  $0.0001-0.05M$ -solutions. The chief deviations from constancy of  $\gamma$  with temperature change are shown with solutions of sulphuric and hydrochloric acids, and of copper sulphate. The significance of  $\gamma$  is discussed, and it is shown that most theories of solution afford simple explanations for it. By integration of the expression  $\beta = \alpha + \gamma$ , the expression  $\lambda_t = \lambda_{\tau} \{1 + q_{\tau}(t - \tau)\}^p e^{\gamma(t - \tau)}$  is obtained for the conductivity of the solution, where  $\{1 + q_{\tau}(t - \tau)\}^p$  represents the dependence of the fluidity of the solution on temperature, and the term  $e^{\gamma(t - \tau)}$  depends on the nature of the ions. This expression accords extremely well with experimental data, for such diverse solutions as  $0.00097M$ -sodium chloride and  $1.014M$ -hypophosphorous acid.

F. G. T.

**Dependence of Dielectric Constant of Aqueous Solutions on Temperature.** L. KOCKEL (*Ann. Physik*, 1925, [iv], **77**, 417—447).—A sensitive apparatus is described by which measurements may be made of the dielectric constants of liquids with conductivities up to  $5 \times 10^{-5}$  mho. Numerous measurements were made with water, and with sucrose solutions containing up to 40% of sucrose at temperatures between  $0^{\circ}$  and  $100^{\circ}$ , and with carbamide solutions containing up to 15% of carbamide between  $-4.3^{\circ}$  and  $63^{\circ}$ . The following values were obtained for the mean temperature coefficients of sucrose solutions between  $0^{\circ}$  and  $100^{\circ}$ : 10%, 0.392%; 20%, 0.395%; 30%, 0.403%; 40%, 0.412%. The values for water between  $0^{\circ}$  and  $100^{\circ}$  may be represented by the expression  $\epsilon = 87.9e^{-0.0047t}$ . A more accurate value of the coefficient in this expression is 0.00481 between  $0^{\circ}$  and  $50^{\circ}$ , and 0.00445 between  $50^{\circ}$  and  $100^{\circ}$ . The behaviour of carbamide is abnormal in that its presence raises the dielectric constant of water, and the alteration of dielectric constant of its solutions on heating above  $35^{\circ}$  is irreversible, although no decomposition can be detected in the solution. The results for water show no agreement with Debye's theory (*Verh. phys. Ges.*, 1913, **15**, 777) and only an approximate one with that of Gans (*Ann. Physik*, 1921, [iv], **64**, 498). The variation of dielectric constant with concentration is in qualitative agreement with the results of other workers.

F. G. T.

**Molecular Fields and their Volumes.** A. BATSCINSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1918, [6], 11—22; from *Chem. Zentr.*, 1925, i, 2528).—The volume of an atom is only accounted for to a small extent

by the nucleus and the electrons, the greater part consisting of electrical fields. Similarly, the volumes of molecules consist largely of interstitial spaces. Molecular volume is thus rather the sum of the volumes of the linkings than of the volumes of constituent atoms. The following mean values in c.c. are given for the molecular volumes of different linkings at the b. p. of compounds in which they occur: C—C and C—H, 7·37; double linkings, twice the value for single linkings; benzene linkings, 51·2; C—Cl, 25·2; C—Br, 31·1; C—I, 41·9. G. W. R.

**Contraction Regularities in the Formation of Solid Chemical Compounds.** I. I. SASLAVSKY (*Z. anorg. Chem.*, 1925, **146**, 315—323).—The molecular volumes  $MV$  of a large number of compounds are compared with the sums of the atomic volumes  $\Sigma AV$ . The quantity  $C = MV/\Sigma AV$ , the "contraction," is calculated in each case. When similar salts are compared, this quantity  $C$  is seen to exhibit regularities which lead to the rule: each metal and each acid radical which enters into a compound has its own specific effect on the contraction. The observed regularities are illustrated graphically. A. B. M.

**Refractive Power of Atoms for X-Rays.** H. MARK and S. TOLKSDORF (*Z. Physik*, 1925, **33**, 681—687).—Anhydrous strontium chloride crystallises in the cubical system of the type of fluorite, the length of the edge of the unit cube being 7·00 Å. The intensities of the interferences indicate that the deflection produced by the ions is not simply proportional to the number of electrons they possess. E. B. L.

**Critical Potentials and the Refractive Indices of Elements and Compounds.** B. DAVIS (*Physical Rev.*, 1925, [ii], **26**, 232—240).—The Lorentz dispersion formula involves terms of the type  $N_1/(\nu_1^2 - \nu^2) + N_2/(\nu_2^2 - \nu^2) + \dots$ , where  $\nu$  is the frequency of the light and  $\nu_1$  and  $\nu_2$  are natural frequencies characteristic of the refracting atom or molecule;  $\nu_1$  and  $\nu_2$  are identified with critical resonance frequencies. For hydrogen, the observed refractive index is obtained if the critical resonance potential is accepted as 16·4 volts. The observed values are 16·0 and 16·9. Unexcited molecular hydrogen should therefore have an absorption band at 760 Å. For the vapours of zinc, cadmium, and mercury the observed refractive indices are reproduced if the following critical resonance potentials at the outer levels are assumed: 4·77, 4·38, and 5·21 volts, respectively. These values in each case lie between values corresponding with two strong absorption lines. For other gases, the potentials observed and those assumed in order to fit the theoretical work are given below:—

	Carbon.	Nitrogen.	Oxygen.	Sulphur.	Chlorine.	Bromine.	Iodine.
Observed :	11·5, 35	17, 29·9	15·5, 52	12·2, 35	13·2, 46	11·3, 32	10, 21
Calculated :	15, 35	17, 29·9	18·5, 52	12·2, 16·2	13·2, 35·3	11·3, 25·8	10, 13·8

The experimental values for carbon, nitrogen, and oxygen cannot all be correct. The values assumed lie on a straight line in a Moseley diagram. For helium, neon, and argon, the observed potentials



cannot be used to calculate the refractive index correctly with the equation of Lorentz and Lorenz.

The calculations are extended to compounds. It is assumed that the heat of formation is associated with an equal energy-change of the valency electrons. For water and ice if the heats of formation are added to the critical potentials of hydrogen, the calculated values of the refractive index are within 0.5% of the observed values. A number of inorganic and organic compounds has been studied in this manner and excellent agreement between observed and calculated values found.

R. A. M.

**Tests on the Accuracy of Measurement with the Rotatory Dispersion Colorimetric Photometer.** K. S. GIBSON (*J. Opt. Soc. Amer.*, 1925, **11**, 75—79).—The rotatory dispersion photometer previously described by Priest (A., 1924, ii, 247) has been subjected to tests of its performance, chiefly in the determination of intensities from incandescence lamps etc. The results are highly satisfactory.

S. B.

**Rotatory Dispersion Power of Organic Compounds. XVI.  $\beta$ - and  $\pi$ -Sulphonic Derivatives of Camphor.** E. M. RICHARDS and T. M. LOWRY (*J. Chem. Soc.*, 1925, **127**, 1503—1514).—The rotatory dispersion and absorption spectra of a series of  $\beta$ - and  $\pi$ -sulphonic derivatives of camphor have been determined in the visible and ultra-violet regions. As in previous cases, there is a discrepancy of nearly 100 Å. between the characteristic frequencies deduced for the low-frequency term by the two series of observations. The rotatory dispersion of these camphor derivatives can be expressed in general by a two-term Drude equation containing a high-frequency and a low-frequency term, the former being identified with the fixed asymmetric atoms and the latter with the induced asymmetry (A., 1924, ii, 373) of the ketonic group. In the  $\pi$ -derivatives the high-frequency term is suppressed or becomes negligible in comparison with the enhanced low-frequency term. In camphor- $\beta$ -sulphonanhydramide the elimination of the ketonic group results in the suppression of the low-frequency term together with the selective absorption with which this term has been correlated. An explanation of these and other related facts is sought in a critical examination of the symmetry of the camphor molecule and of its derivatives. The rotation for light of any wave-length between the limits mentioned can be calculated from the Drude equation  $[\alpha]_{\lambda}^{20} = k_1/(\lambda^2 - \lambda_1^2) + k_2/(\lambda^2 - \lambda_2^2)$ , in which the first term represents the partial rotation due to the low-frequency absorption and the second that due to the high frequency. The numerical values of the constants follow ( $\lambda_1 - \lambda_a$  is the difference between the wave-length of the low-frequency band as determined from the Drude equation and the absorption data respectively, expressed in Å.). Ammonium  $\alpha$ -bromocamphor- $\pi$ -sulphonate in water:  $C = 13.936$ ,  $k_1 = 22.015$ ,  $\lambda_1^2 = 0.09668$ ,  $\lambda_1 - \lambda_a = 90$  Å. ( $\lambda = 6708$  to  $4010$ ); ammonium  $\alpha$ -chlorocamphor- $\pi$ -sulphonate in water:  $C = 20.440$ ,  $k_1 = 17.677$ ,  $\lambda_1^2 = 0.09946$ ,  $\lambda_1 - \lambda_a = 120$  Å. ( $\lambda = 6708$  to  $4055$ );  $\alpha$ -bromocamphor- $\pi$ -sulphonethylchloroamide in chloroform:  $C = 14.287$ ,  $k_1 = 25.889$ ,

$\lambda_1^2=0.09969$  ( $\lambda=6708$  to  $4358$ );  $\alpha$ -bromocamphor- $\pi$ -sulphondichloroamide in chloroform:  $C=10.872$ ,  $k_1=23.897$ ,  $\lambda_1^2=0.10719$  ( $\lambda=6708$  to  $4358$ ); camphor- $\beta$ -sulphonic acid in water:  $C=28.636$ ,  $k_1=22.17$ ,  $\lambda_1^2=0.08515$ ,  $k_2=-18.32$ ,  $\lambda_2^2=0.04945$ ,  $\lambda_1-\lambda_2=70$  Å. ( $\lambda=6708$  to  $3969$ ); potassium  $\alpha$ -chlorocamphor- $\beta$ -sulphonate in water:  $C=12.386$ ,  $k_1=12.060$ ,  $\lambda_1^2=0.09768$ ,  $k_2=5.1354$ ,  $\lambda_2^2=0$ ,  $\lambda_1-\lambda_2=125$  Å. ( $\lambda=6708$  to  $3952$ ); potassium  $\alpha$ -bromocamphor- $\beta$ -sulphonate in water:  $C=16.206$ ,  $k_1=18.78$ ,  $\lambda_1^2=0.09517$ ,  $k_2=5.569$ ,  $\lambda_1-\lambda_2=55$  Å. ( $\lambda=6708$  to  $4041$ ); camphor- $\beta$ -sulphonanhydramide in acetone:  $C=4.941$ ,  $k_1=\lambda_1^2=\lambda_2^2=0$ ,  $k_2=-10.696$  ( $\lambda=6708$  to  $4220$ ).  
E. E. W.

### Calculation of Rotatory Power of a Tetrahedral Molecule.

R. DE MALLEMANN (*Compt. rend.*, 1925, **181**, 298—300).—An expression for the rotatory power of an asymmetric compound is derived. Atoms are assumed to be situated at the apices of a trirectangular tetrahedron.  
J. S. C.

**Production of Optical Activity in Silver by Circularly Polarised Light.** H. ZOCHER and K. COPER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 426—431).—A layer of silver chloride, about  $0.15\mu$  thick, was formed on a glass plate by the action of chlorine on a silver film. The plate was exposed to circularly polarised light for 1 hr. and after this treatment exhibited permanently circular asymmetry. The source of light was a very powerful arc lamp and the light was circularly polarised by Nicol prisms and a Fresnel total reflection epiped. The film not only rotated the plane of linearly polarised light to the extent of  $0.25^\circ$ , but also caused the light to become elliptically polarised. The rotation of the plane of polarisation was unaffected by rotation of the plate through  $90^\circ$ . Circularly polarised light in nature is considered a possible cause of the asymmetry of organic structure.  
F. G. S.

### Thermal Expansion of Crystals and Chemical Constitution.

F. A. HENGLEIN (*Z. Elektrochem.*, 1925, **31**, 424—428).—The expansibilities of alkali halides have been measured in the ranges  $0^\circ$  to  $-79^\circ$  and  $-79^\circ$  to  $-184^\circ$ . All decrease with temperature. For a given cation, the expansibility increases as the atomic weight of the anion rises; for a given anion it diminishes as the atomic weight of the cation rises. Fluorides, however, do not obey this rule.  
W. A. C.

### Chemical Constitution and $K$ Absorption Spectra. II. Investigation of certain Compounds of Phosphorus.

O. STELLING (*Z. physikal. Chem.*, 1925, **117**, 161—174; cf. *A.*, 1924, ii, 139).—The X-ray  $K$  absorption spectra of a number of quinquevalent and tervalent compounds of phosphorus and also of additive compounds of tervalent phosphorus compounds were studied. A systematic connexion between constitution and the positions of absorption bands is shown to hold in most cases.  
L. F. G.

### Chemical Constitution and $K$ Absorption Spectra. III.

O. STELLING (*Z. physikal. Chem.*, 1925, **117**, 175—193; cf. preceding abstract).—Lindh's data of the X-ray  $K$  absorption spectra of

elements and compounds are correlated with chemical constitution (cf. *Z. Physik*, 1925, **31**, 210). The wave-lengths of the absorption bands of elements are higher than those of their compounds; sulphur is an exception. With the same element, the absorption bands become shorter-waved as the valency rises, provided that the successively attached atoms or radicals are the same. With constant valency, the position of the absorption bands of an atom depends on the atoms or radicals directly combined with it. The results are discussed from the point of view of the deformation theory (Fajans, *Z. Kryst.*, 1925, **61**, 18), and the use of X-ray absorption spectra in the solution of problems in chemical constitution is considered. The experimental methods of Lindh and of the author are compared.

L. F. G.

#### Chemical Constitution and *K* Absorption Spectra. IV. Constitution of Phosphorous Acid and Some Derivatives.

O. STELLING (*Z. physikal. Chem.*, 1925, **117**, 194—208; cf. preceding abstracts).—Previous investigations of the constitution of the phosphorous acids are reviewed, and it is shown that the hypothesis of Rosenheim, Schapiro, and Italiener (A., 1924, ii, 51) that these acids exist in double molecules in aqueous solution is based on an incorrect interpretation of their results. A study of the X-ray *K* absorption spectra leads to the conclusion that structural formulæ may be ascribed to derivatives of phosphorous acid as follows:  $(RO)_2PH:O$  for phosphorous acid, its diesters, triphenylmethylphosphorous acid, and ferric monopropyl phosphite (cf. A., 1918, i, 479);  $(EtO)_2PNa:O$  for sodium diethyl phosphite;  $(EtO)_2P:OAg$  for silver diethyl phosphite;  $(HO)_2Pac:O$  for monoacetylphosphorous acid. It is probable that the diesters and metal esters form tautomeric mixtures in solution.

L. F. G.

#### The Parachor and Chemical Constitution. I. Polar and Non-polar Valencies in Unsaturated Compounds. S. SUGDEN, J. B. READ, and H. WILKINS (*J. Chem. Soc.*, 1925, **127**, 1525—1540).

—The parachor (A., 1924, ii, 662) is calculated from the orthobaric densities and the surface tension and affords a means of comparing molecular volumes under equal surface tensions. The parachor is an additive function of certain atomic and structural constants. It has been found that there are two values for the double bond; the one contributes 23.2 (mean value) to the molecular parachor and the other reduces this quantity by 1.6 (mean value) units. The former is characteristic of the groups  $>C=C<$  and  $>C=O$ , and the latter of the groups  $\geq P=O$ ,  $\geq S=O$ ,  $\geq S \begin{smallmatrix} \nearrow O \\ \searrow O \end{smallmatrix}$ , in which  $\rightleftharpoons$  represents what the authors call a semi-polar bond (Lowry's "mixed" or "ionised" double bonds, cf. A., 1923, ii, 480). The nature of the double linking in a number of compounds containing carbon, nitrogen, phosphorus, and sulphur has been investigated. In all the cases examined by the authors, semi-polar bonds (as detected by the parachor) are formed only when each atom, except hydrogen, has attained a complete octet. The octet is never exceeded and semi-polar bonds are not found when their existence would necessitate the presence of a

sextet around one or other of the atoms concerned. New measurements of the surface tension and density of sixteen substances have been made, using for the former the method of maximum bubble pressure (cf. Sugden, A., 1924, ii, 154). E. E. W.

**The Parachor and Chemical Constitution. II. Geometrical Isomerides.** S. SUGDEN and H. WHITTAKER (*J. Chem. Soc.*, 1925, 127, 1868—1874).—By means of the parachor, a distinction can be drawn between the non-polar and semi-polar double bond (cf. A., 1924, ii, 662, and preceding abstract). To determine the type of linking in geometrical isomerides, measurements have been made of the surface tension and density of methyl cinnamate, methyl *allocinnamate*, methyl  $\alpha$ -bromocinnamate, methyl  $\alpha$ -bromo-*allocinnamate*, methyl  $\beta$ -bromocinnamate, methyl  $\beta$ -bromo-*allocinnamate*, methyl mesaconate, methyl citraconate, methyl fumarate, and methyl maleate. All the substances examined contain a non-polar double bond, adding 23.2 units to the molecular parachor. In each case, the *cis*-compounds, in which two bulky groups are adjacent, give values for the parachor closely approximating to the theoretical figure, whilst the *trans*-compounds give values which are lower by from one to four units. L. L. B.

**Theories of Polar and Non-polar Free Affinities. Reply to some Recent Criticisms and Comparisons.** G. N. BURKHARDT and A. LAPWORTH (*J. Chem. Soc.*, 1925, 127, 1742—1750).—The contention of Ingold and his co-workers (A., 1924, i, 322, 323, 1116), that the results of their recent studies of certain reactions of nitrosobenzene provide evidence in favour of the Thiele-Flürscheim non-polar theories of valency, and against the polarity theories, is freely criticised. It is contended that Ingold and Weaver have given a ring formula to the product of the interaction of nitrosobenzene and ethyl methylenemalonate without sufficient evidence. The same compound has now been prepared from ethyl hydroxymethylenemalonate and  $\beta$ -phenylhydroxylamine in cold methyl alcohol. The compound is thus dicarbethoxymethyl-*N*-phenylnitrone,  $\text{O}:\text{NPh}:\text{CH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , or the enolic form of this compound. It is claimed that the formation of this substance is in accordance with the prediction of the polarity theories of Lapworth and Robinson, but quite contrary to the predictions of the Werner-Flürscheim theory. E. E. W.

**Valency Relations of Boron, Carbon, and Nitrogen from the Standpoint of the Bohr Atomic Model.** W. A. WAHL (*Z. anorg. Chem.*, 1925, 146, 201—224).—The valency relations of boron, carbon, and nitrogen are explained by a development of the Bohr theory. It is assumed that different arrangements of the orbits of the electrons outside the stable inert gas kernel can exist, corresponding with the different possible valencies of the atoms, that the atom can pass from one of these arrangements to another under suitable conditions, and that in some cases two such arrangements can exist together in dynamic equilibrium; *e.g.*, the orbits of trivalent nitrogen are arranged thus: two  $1_1$ , two  $2_1$ , three  $2_2$ . This

arrangement is shown to be in accordance with the spectroscopic evidence. In quinquivalent nitrogen, the orbits become two  $1_1$ , one  $2_1$ , four  $2_2$ . Both nitrogen and boron tend to form the especially stable electron configuration of carbon, and this tendency is shown to lead to the formation of the stable complex ions of quinquivalent boron and quinquivalent nitrogen. Thus the addition of KF to  $\text{BF}_3$  is explained by the boron atom taking up a fourth electron with the consequent production of the complex ion  $[\text{BF}_4]^-$ . Nitrogen, on the contrary, forming a stable four-electron arrangement, forces the fifth electron to move in an eccentric outer orbit similar to that of the outer electron in the atoms of the alkali group, so that a positive quinquivalent ion is readily produced. The theory is applied to other valency phenomena of these three elements. A. B. M.

**Problems of Boron Chemistry.** W. A. WAHL (*Z. anorg. Chem.*, 1925, **146**, 230—238).—The quadrivalency of boron cannot be assumed from the existence of such compounds as  $\text{B}_2\text{H}_6$  and  $\text{B}_4\text{H}_{10}$ . These compounds are more closely related in their chemical behaviour to the hydrides of nitrogen than to those of carbon. This comparison leads to a suggested structure for these compounds, which does not need the assumption of quadrivalent boron, but to substantiate which requires further experimental evidence.

A. B. M.

**Regularity in the Rare Earth and Titanium Groups.** G. VON HEVESY (*Z. anorg. Chem.*, 1925, **147**, 217—232).—The properties of the rare earth elements are considered from the point of view of the quantum theory of atomic structure. The molecular volumes of the isomorphous octahydrated sulphates of praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, holmium, erbium, ytterbium, and lutecium decrease with increasing atomic number, from which it is concluded that the binding forces of the valency electrons increase as the series is ascended.

J. S. C.

**Distribution of Intensity in the X-Ray Spectra of certain Long-chain Organic Compounds.** G. SHEARER (*Proc. Roy. Soc.*, 1925, **A**, **108**, 655—666).—The carbon chain with its attached hydrogens is regarded as a uniform distribution of scattering material for X-rays. A methyl group at the end of the chain will result in a low scattering power at the end of the molecule on account of the small mass of the hydrogen atoms. A carboxyl group will have a scattering power in excess of the average scattering power of the chain. In esters and ketones the ketonic oxygen attached to one of the carbons of the chain will result in an increase in scattering power at this point. On the basis of the above assumptions and of ideas previously developed regarding the spacing of molecules (this vol., ii, 366, 367), the theoretical distribution of intensities in the spectra of a number of organic compounds is calculated; the calculated values agree fairly well with those observed. Attention is directed to the possibility of using such methods to elucidate problems in chemical constitution.

L. F. G.

**Dimensions of the Molecule and Molecular Weight of Crystalline Egg-albumin.** P. L. DU NOÛY (*J. Biol. Chem.*, 1925, **64**, 595—613).—The author's surface tension method (this vol., ii, 109) for the study of molecular dimensions has been applied to crystalline egg-albumin; the two most prominent groups of surface tension minima were observed at concentrations of 1/140,000 and 1/190,000; from these, the dimensions of the "phantom shape" of the molecule are calculated as  $41.7 \times 10^{-8}$  cm. and  $30.8 \times 10^{-8}$  cm., which, assuming the shape to be that of a parallelepiped with a square base and the specific gravity to be a property of all the space occupied by the molecule, gives for the volume occupied by a molecule  $39.6 \times 10^{-21}$  c.c. and for its weight  $51.3 \times 10^{-21}$  g. Taking the constant of Avogadro,  $N$ , to be  $6.004 \times 10^{23}$  this leads to a molecular weight of 30,800, which agrees well with the figure (31,406) obtained by doubling the minimal molecular weight as determined by analysis. The figures receive further support from the fact that the volume occupied by one carbon atom (vol. of molecule  $\div$  number of carbon atoms) calculated from them is  $28.45 \times 10^{-24}$  c.c., which is in close agreement with the mean value obtained similarly from eight compounds of which the molecular dimensions have been determined by Langmuir (A., 1917, ii, 525).  
C. R. H.

**Two New Elements of the Manganese Group.** W. NODDACK, I. TACKE, and O. BERG (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 400—409).—From theoretical considerations, it was concluded that the missing elements of the manganese group, of atomic numbers 43 and 75, respectively, occur in platinum ores and in the mineral earths. Examination of platinum ores led to the separation of a volatile oxide, probably the highest oxide of element 75. Its identity was established by examination of its X-ray spectrum. Both elements occur in columbite, and a product was obtained containing 5% of element 75 and 0.5% of element 43. The sublimate from this product gave the lines of the new elements. Small amounts of element 43 occur in sperryolith, gadolinite, fergusonite, and zircon, and traces of element 75 in tantalite and tungstite. The following lines have been measured in the X-ray spectrum of element 43:  $K\alpha_1 = 0.672$ ,  $K\alpha_2 = 0.675$ ,  $K\beta_1 = 0.601$  Å.; those measured for element 75 are  $L\beta_2 = 1.2048$ ,  $L\beta_3 = 1.216$ ,  $L\beta_1 = 1.2352$ ,  $L\alpha_1 = 1.4299$ ,  $L\alpha_2 = 1.4407$  Å. The positions of these lines agree well with the calculated values, and their relative intensities are as expected from those of the neighbouring elements.

The names "masurium" (Ma) for element 43 and "rhenium" (Re) for element 75, have been chosen. Their estimated total amount is between  $10^{-12}$  and  $10^{-13}$  of the earth's crust. F. G. S.

**X-Ray Investigation of the Structure of Alloys.** A. SACKLOVSKI (*Ann. Physik*, 1925, [iv], **77**, 241—272; cf. A., 1923, ii, 519; 1924, ii, 110).—The Bohlin-Seeman method (A., 1920, ii, 214) of investigating powdered materials using a cylinder has been employed with alloys. The technique is described and its advantages and disadvantages fully discussed. The crystallographic results for the

following sets of alloys, silver-copper, lead-magnesium, tin-magnesium, copper-nickel, fully confirm the conclusions based on phase diagrams, and in particular the non-existence of the compounds  $\text{Ag}_3\text{Cu}_2$  and  $\text{NiCu}$  is reaffirmed.

The rule given by Vegard (A., 1916, ii, 405) that the lattice constants in mixed crystals are purely additive is found to be valid for the silver-copper and copper-nickel systems. Bain has advanced the view that the lattices of inter-metallic compounds exhibit lower symmetry than those of their components. Becker and Ebert have already denied the validity of this generalisation, and the author shows that the compounds  $\text{PbMg}_2$  and  $\text{SnMg}_2$  are also in conflict with Bain's rule. These compounds both exhibit a regular face-centred structure,  $a_{\text{PbMg}_2}=6.76$ ,  $a_{\text{SnMg}_2}=6.75$  Å. From the densities ( $\text{PbMg}_2$  5.542,  $\text{SnMg}_2$  3.591) the calculated values are 6.75 and 6.77 Å., respectively.

R. A. M.

**Application of X-Rays to the Study of Alloys.** H. WEISS (*Proc. Roy. Soc.*, 1925, A, 108, 643—654).—The  $\alpha$ -bronzes and the silver-gold alloys were examined by the powder-photograph method. The spectra of the  $\alpha$ -bronzes follow the same laws of position and intensity as the spectrum of pure copper, the side of the cell increasing, however, with increase of tin until the limiting solid solution is reached (about 10% Sn). The results suggest that one atom of tin takes the place of several atoms of copper. With the silver-gold alloys all the results are again in accordance with a face-centred cubic lattice. From silver to gold the size of the cell varies continuously, the sudden increases recorded by McKeehan (A., 1923, ii, 428) not being observed.

L. F. G.

**Determination of Intensity Ratios in Systems of Debye-Scherrer Rings. Application to the Investigation of the Photographic Process.** R. BLUNCK and P. P. KOCH (*Ann. Physik*, 1925, [iv], 77, 477—494).—An X-ray camera of the Debye-Scherrer type is described, with a photometer device consisting of a sectional cylinder rotating against the lower half of the film, so that the illumination of that portion of the film may be proportionately reduced, compared with that of the upper half. A series of measurements with X-rays of wave-length 0.71 Å. showed that the density of the image was proportional to the intensity of the X-rays. X-Ray analysis of the silver in a photographic plate which had been developed in artificial daylight indicated a face-centred cubic lattice with an elementary cell of edge 0.403 Å., agreeing with the value for massive silver. Measurement of the intensity-distribution in individual rings of the X-ray photograph gave values, by Scherrer's method (A., 1919, ii, 274), of  $1-2\mu$  for the diameter of individual silver crystals in the exposed photographic film. Comparison was made of the measured intensity-distribution in single rings with that calculated from the geometry of the instrument. The measured intensities were slightly higher than the calculated. X-Ray absorption measurements of an exposed photographic film corresponded with a silver content of 0.00065 g./cm.<sup>2</sup>

F. G. T.

**Separation of Silver from Silver Halides through Intense Irradiation.** P. P. KOCH and H. VÖGLER (*Ann. Physik*, 1925, [iv], **77**, 495—502).—The assumption that the formation of the latent photographic image, if due to the passage of an electron from the bromine ion to the silver ion, and the separation of free silver, should be associated with a derangement of the crystal lattice of silver bromide has been investigated by the photometric X-ray analysis method of Blunck and Koch (cf. preceding abstract). Measurements with silver bromide prepared in red light from a dry plate or by precipitation, indicated a cubic lattice, with lattice-constant  $a = 2.89 \times 10^{-8}$  cm., agreeing with previous measurements. Slight but definite differences in the intensity-distributions were found in the Debye-Scherrer rings for these two preparations. The ratio of the intensity of the innermost (001), to that of the second (011) ring was 0.99 for the technical silver bromide and 1.16 for the gelatin-free product. With specimens of silver bromide exposed to sunlight for a day, or under 5% sodium nitrite for  $1\frac{1}{2}$  hrs., a second series of rings, corresponding with the silver lattice, was superimposed on the silver bromide rings in the X-ray photograph.

An X-ray photograph of a dry plate, exposed in sunlight, undeveloped, but fixed in an acid fixing bath, showed the rings corresponding with the silver lattice with great clearness. Measurements of the absorption of X-rays by a plate so treated, corrected for the absorption by the gelatin, gave a free silver content in the plate of 0.00024 g./cm.<sup>2</sup> Similar results were obtained with silver chloride, but no development of the rings of the silver lattice was observed with silver iodide, even after 4 months' daily exposure to sunlight.

F. G. T.

**Compton's Theory of X-Ray Scattering.** H. FRICKE (*Nature*, 1925, **116**, 430—431).—Two methods are briefly described whereby, for very hard X-rays ( $\lambda < 0.15$  Å.), Compton's theory of scattering has been verified within an experimental error of about 10%.

A. A. E.

**Crystal Structure of Thallium Chloride and Thallium Bromide.** G. LUNDE (*Z. physikal. Chem.*, 1925, **117**, 51—56).—Debye-Scherrer diagrams for these substances were obtained. The data for thallium chloride obtained by Davey and Wick (*Physical Rev.*, 1921, [ii], **17**, 403) are corroborated. The thallium bromide unit cell contains about 1 mol.; the side is 3.968 Å.; the structure is cubic body-centred, as found by Niggli (A., 1922, ii, 36).

L. F. G.

**Permutoid Structure.** H. KAUTSKY and G. HERZBERG (*Z. anorg. Chem.*, 1925, **147**, 81—90).—The concept of permutoid structure is considered in relation to the siloxen derivatives (A., 1924, ii, 674), graphitic acid (Kohlschütter and Haenni, A., 1919, ii, 152), and silicic acid from biotite. These substances behave as if the molecules are arranged in a series of surfaces. They all show the same structure and consist of a series of lamellæ of thickness of the order of molecular magnitudes. In the several cases, the original



substances for the preparation of these compounds possess a structure of this type. The reaction between calcium silicide and hydrochloric acid takes place exclusively along the basal surfaces, the side surfaces being unattacked. Rapid diffusion occurs only within the spaces between the lamellæ. J. S. C.

**The Molecule in Crystals.** R. O. HERZOG and K. WEISENBERG (*Kolloid-Z.*, 1925, **37**, 23—24).—The name "dynad" is given to a unit within which each atom is held by forces stronger than those between the atom and any atom outside the unit. Two broad groups are recognised: microdynes, which are never larger than the elementary cell, and macrodynes, which may be of the order of a whole crystal. Determination of the dynads should replace at present attempts to define the molecule in crystals. E. M. C.

**Crystallography of Methylphenylmethyldichloroamine.** D. J. FISHER (*Amer. J. Sci.*, 1925, [v], **10**, 201—203).—The crystals (from light petroleum and from alcohol) are monoclinic-prismatic,  $a : b : c = 0.402 : 1 : 0.365$ ;  $\beta = 67^\circ 16'$ . They are acicular along the  $c$ -axis and have a strong cleavage along (010). They are optically positive, with refractive indices approximately  $\alpha = 1.64$ ,  $\beta = 1.68$ , and  $\gamma = 1.74$ . W. A. C.

**Dissolution Velocity and Etched Figures on Crystals.** G. TAMMANN (*Z. anorg. Chem.*, 1925, **146**, 413—419).—The kinetics of the dissolution of a crystal is considered in relation to the figures produced by etching. A theory of the phenomena observed is briefly outlined. A. B. M.

**Orientation of Etched Figures and the Distribution of the Atoms in the Space Lattice.** G. TAMMANN and W. KRINGS (*Z. anorg. Chem.*, 1925, **146**, 420—432; cf. preceding abstract).—The etched figures produced on a number of crystals are compared in the light of our knowledge of the structure of the crystals. It is shown that the crystal surface is first attacked along the lines of the crystal lattice in which the atoms entering into the reaction are most closely packed. On continued etching, figures appear the outlines of which are parallel to the primary grooves. A. B. M.

**Theory of Metallic Conductivity.** H. CASSEL (*Z. Physik*, 1925, **33**, 477—478).—The specific conductivities of the elements are multiplied by the atomic volume raised to the power  $\frac{2}{3}$  and the results exhibited in connexion with the periodic table of elements. E. B. L.

**Theory of Electrical Conduction in Metals.** A. WOLF (*Physical Rev.*, 1925, [ii], **26**, 256—260; cf. Frenkel, this vol., ii, 479; Højendahl, A., 1924, ii, 647).—The electrons are assumed to have kinetic energy corresponding with the thermionic work function  $W$  and to move in orbits which form a space lattice with a constant  $\delta$  of the same order as that of the positive ions  $\delta_1$ . At each critical point of an orbit, each of the six directions is taken as equally probable. It is then deduced that  $\sigma$ , the specific conductivity, is

given approximately by  $0.6Ne^2(\delta^2/h)eW/E^1$ , where  $E^1$  is the mean heat content of one degree of freedom of the metal. Fair agreement between observed and calculated values is obtained. R. A. M.

**Electron Conduction in Crystals.** B. GUDDEN and R. POHL (*Physikal. Z.*, 1925, 26, 481—483).—Lenz (*ibid.*, 365) found that the stationary photo-electric current in zinc sulphide crystals or the diamond was very much less at the temperature of liquid air than at the ordinary temperature. From the contrast with ordinary metallic conduction in which falling temperature increased the conductivity up to super-conductivity, Lenz concluded that the so-called photo-electric current was not caused solely by illumination, but that thermal effects also occurred. The present authors have examined the photo-electric current per unit of light-intensity of various wave-lengths falling on a crystal of sodium chloride at (a) 20° and (b) -180°. Over the range 410—490 $\mu$ , the current is larger at -180° than at 20°, but over the ranges 340—410 $\mu$  and 410—600 $\mu$  it is smaller. Lenz takes little account of the wave-length of the light used, so that whilst his observations are doubtless correct, they by no means justify his generalisation. Photo-electric currents were also observed with zinc sulphide and diamond at -180°. The work is discussed theoretically and a mechanism in harmony with the results is put forward.

R. A. M.

**Photo-resistance Effect for Metals at Low Temperatures.** R. S. BARTLETT (*Physical Rev.*, 1925, [ii], 26, 247—255).—Thin films of metals were prepared by means of electrode splashing, and after ageing were exposed to ultra-violet radiation at the temperature of liquid air. The resistances of gold and silver were unchanged, that of platinum decreased to a very small extent, and those of bismuth, palladium, and copper decreased by 16, 14, and 1.6 parts in a million, respectively. The effect increased with time and the original value was slowly regained in the dark. Tellurium, which was sensitive at the ordinary temperature, showed a 70% greater effect at -185°. For bismuth, the temperature coefficient of resistance decreased from 0.0014 at 0° to approximately zero at -185°. The results are in accord with the predictions of Waterman's equilibrium theory of resistance (*ibid.*, 1923, 22, 259).

R. A. M.

**Magneton Numbers of Iron in Some Complex Salts.** L. A. WELO (*Nature*, 1925, 116, 359—360).—Preliminary data indicate that the magneton numbers for ferrous iron can have the values 0 and 10 as well as 26, 26.5, 27, and 27.5 (cf. Jackson, this vol., ii, 732, and following abstract), and that the values for ferric iron are 0 and 10 as well as 29. The magnetic moment of iron is thus extremely variable, and is not uniquely defined by a statement of its valency. The iron in iron carbonyl is diamagnetic. Thus the electron system of the iron atom may have at least seven main configurations.

A. A. E.

**[Magneton Numbers of Iron in Some Complex Salts.]** L. C. JACKSON (*Nature*, 1925, **116**, 360; cf. preceding abstract).—Paramagnetic substances do not obey Curie's law,  $KT = C$ , but the more general law  $K(T + \Delta) = C$ ; hence Welo's magneton numbers need correction. Further, Welo's method of calculating the Bohr magneton numbers is not permissible. A. A. E.

**Magnetisation Numbers of the Rare Earth Elements.** S. MEYER (*Physikal. Z.*, 1925, **26**, 478—479).—The magnetisation numbers previously reported (this vol., ii, 173) in some cases require correction, owing to the discovery of impurities in the specimens examined. The corrected values of  $k \times 10^6$  are about 9.3 for ytterbium and about 4.2 for europium, instead of 8.8 and 5.6, respectively. F. G. T.

**Simple Characteristic Relationships among the Ferromagnetics.** J. R. ASHWORTH (*Nature*, 1925, **116**, 397).—The ratio of the critical temperature ( $\theta^\circ \text{Abs.}$ ) to the maximum intensity of magnetisation ( $I_0$ ) for iron, cobalt, nickel, and magnetite is, respectively, 0.58, 0.95, 1.19, and 1.83, or  $2 \times \frac{\pi}{\sqrt{2}}$ ,  $3 \times \frac{\pi}{\sqrt{2}}$ ,  $4 \times \frac{\pi}{\sqrt{2}}$ , and  $6 \times \frac{\pi}{\sqrt{2}}$ . Heusler's alloy fits this scale, the ratio  $\theta/I_0$  being 1.50 or  $5 \times \frac{\pi}{\sqrt{2}}$ . The numbers 2 to 6 are exactly integral within the accuracy with which  $\theta$  and  $I_0$  are known. The ratio of  $I_0$  for iron to  $I_0$  for nickel, and that of the values for cobalt and magnetite, are both 3.3, the respective ratios of the critical temperatures being 1.60 and 1.67. A. A. E.

**Theory of Ferromagnetism.** L. W. MCKEEHAN (*Physical Rev.*, 1925, [ii], **26**, 274—279; cf. ii, 945).—In ferromagnetic materials magnetisation involves (a) intra-atomic quantised changes and (b) intra-atomic stresses and strains. The interdependence of (a) and (b) is described as atomic magnetostriction. Hysteresis loss and magnetic hardness are then due to the energy required to produce successively the local deformations associated with changes in the magnetisation of single atoms or small groups of atoms. The high initial permeability and low hysteresis loss in "permalloy" result from locally compensatory atomic magnetostrictions of the nickel and iron atoms in small groups. Differing atomic magnetostrictions account for the differences in the magnetic behaviours of iron, nickel, and cobalt. Mechanical properties account for other differences by altering the energy expended when atomic magnetostriction occurs. R. A. M.

**Artificial and Natural Ferromagnetic Ferric Oxide.** R. B. SOSMAN and E. POSNJAK (*J. Washington Acad. Sci.*, 1925, **15**, 329—342).—Natural ferromagnetic ferric oxide has the same X-ray pattern and nearly the same magnetic susceptibility as magnetite and artificial ferric oxide. It gives a hysteresis curve differing from those of the other two oxides. Other minor differences are recorded. Ferric oxide loses its ferromagnetic property reversibly at a little above  $500^\circ$  and irreversibly at  $650^\circ$ , or lower if heated for some time. Lepidocrocite and goethite,  $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , yield ferromagnetic and paramagnetic ferric oxides, respectively, on dehydration. S. K. T.

**Paramagnetism of "Odd Molecules."** N. W. TAYLOR and G. N. LEWIS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 456—457).—Magnetochemical theory predicts that substances with an odd number of electrons will exhibit paramagnetism. In support of this prediction, preliminary experiments with solutions of chlorine dioxide in carbon tetrachloride,  $\alpha$ -naphthyldiphenylmethyl in benzene, sodium in liquid ammonia, and thallium in mercury indicate the existence of paramagnetic substances in solution. J. S. C.

**Paramagnetic Salts.** (MME.) E. COTTON-FEYTS (*Ann. Chim.*, 1925, [x], **4**, 9—78).—A more detailed, collected account of previously published work (cf. A., 1911, ii, 367, 1058; 1913, ii, 381). S. K. T.

**Optical Properties of Mixed Crystals.** M. W. PORTER (*Proc. Roy. Soc.*, 1925, **A**, **109**, 78—98).—The optical properties of mixed crystals of the pairs ammonium magnesium sulphate-ammonium magnesium chromate, and ammonium magnesium chromate-rubidium magnesium chromate have been examined. No proportionality was found between the refractive indices and the composition of the mixed crystals of the former pair, possibly owing to inhomogeneity of the crystals. For mixed crystals of the latter pair, the variation of the principal refractive index for vibrations along the symmetry axis is directly proportional to the composition, expressed as volume or molecular percentage. The other two principal indices are also continuous functions of the composition, but the variation is not linear, the curve for the  $\beta$ -axis being concave, and that for the  $\gamma$ -axis convex, to the composition axis. F. G. T.

**Effect of Tension upon Magnetisation and Magnetic Hysteresis in "Permalloy."** O. E. BUCKLEY and L. W. MCKEEHAN (*Physical Rev.*, 1925, [ii], **26**, 261—273).—The effect of tension on magnetisation and hysteresis was determined in wires of five nickel-iron alloys (permalloys) containing (a), 45, (b), 65, (c), 78.5, (d), 81, and (e), 84% of nickel. Alloy (d) is nearly indifferent to tension; (a), (b), and (c) are more easily magnetised and have less hysteresis under tension; the reverse is true for (e). In (c), an abnormally low saturation is observed and the low hysteresis is regarded as due to slight inhomogeneity. The crystals are shown by the X-ray method to exhibit random orientation. Alloy (e) contracts like nickel; (a), (b), and (c) expand like iron. Thus the magnetostriction change of sign is confirmed (Honda and Kido, *Sci. Rep. Tôhoku Imp. Univ.*, 1920, **9**, 221). The demagnetisation factor for a wire of length 600 times the diameter varies from a maximum of  $1.6 \times 10^{-4}$  to a low value (cf. Benedicks, *Ann. Physik*, 1901, [iv], **6**, 726). R. A. M.

**Orientation of Crystals in Metal Test-pieces Subjected to Small Strains Followed by Heat Treatment.** C. F. ELAM (*Phil. Mag.*, 1925, [vi], **50**, 517—520).—Examination of the orientations of the crystal axes of sixty-four crystals of aluminium, iron, and an aluminium-zinc alloy containing 18% of zinc, produced by a

process of straining followed by heat treatment, show that the variety of orientation is great. For aluminium, most of the crystals favour the (110), but not the (100) axis, and several of the iron and alloy crystals are oriented in the latter direction. Possibly the rate of growth is more rapid in some directions than in others, so that the majority of the largest crystals produced may favour one orientation. There appears, however, to be no relation between crystals in the same test-piece, and the direction of straining has little influence on the orientation of the crystals.

A. E. M.

**Orientation of Crystals Produced by Heating Strained Iron.** C. F. ELAM (*J. Iron and Steel Inst.*, Sept. 1925, advance copy, 2 pp.).—The crystal axes relative to the direction of straining have been determined by X-ray analyses and the results show that the orientation is very varied. Two out of ten crystals showed cubic etching pits, and in both of these the surface of the strip was parallel to a cubic (100) plane in the crystal. Crystals of other orientations only showed pitting on prolonged etching; it should therefore be possible to pick out those crystals in which a (100) plane lies in or near the plane of section. [Cf. *B.*, 1925, 806.]

M. E. N.

**Tensile Properties of Single Iron Crystals and the Influence of Crystal Size upon the Tensile Properties of Iron.** C. A. EDWARDS and L. B. PFEIL (*J. Iron and Steel Inst.*, Sept. 1925, advance copy, 32 pp.).—The values for the tensile strength and the limit of proportionality given by single iron crystals were generally very low. Smaller single crystals gave more variable results for tensile strength than larger ones. Elongations were very variable, generally increasing with the tensile strength. Some of the types of fracture encountered in the work are described. Tensile tests made on iron of varying crystal sizes revealed a discontinuity in properties with change in crystal size. [Cf. *B.*, 1925, 806.]

M. E. N.

**Electrical Conductivity of Some Dilute Amalgams.** E. J. WILLIAMS (*Phil. Mag.*, 1925, [vi], 50, 589—599).—Values obtained for the resistivity of mercury over the temperature range 0—300° are represented by the formula

$$\rho_t = \rho_0(1 + 0.8879 \times 10^{-3}t + 0.975 \times 10^{-6}t^2 + 0.20 \times 10^{-9}t^3),$$

which gives a value at 100° in accordance with that of Jaeger and Steinwehr (*Ann. Physik*, 1914, [iv], 43, 1165). For cadmium amalgams containing less than 2% of cadmium, the conductivity is a quadratic function of the concentration. For indium amalgams it is approximately a linear function of the concentration. At 14°, the rates of variation of the relative increase of conductivity with concentration at infinite dilution are 7.2, 50.7, and 7.8 for indium, magnesium, and cadmium amalgams, respectively. The effects of these metals atom for atom on the conductivity of pure mercury are sensibly the same, a result in agreement with that of Skaupy. The change of relative conductivity with the temperature is small.

A. E. M.

**Change of Resistance of Platinum and Iron Wires in a High Vacuum Due to Absorbed Gas.** H. KLEINE (*Z. Physik*, 1925, 33, 391—407).—In the preliminary experiments with iron, the resistance decreased as the pressure decreased and increased again on admitting air. In the main experiment with platinum, it was necessary to heat the platinum in a high vacuum and get rid of gas from the walls of the vessel. When the platinum was kept glowing for 20 hrs., the fall in resistance amounted to 12%.

E. B. L.

**Influence of the Gas Content on the Photo-electric Behaviour and Electrical Conductivity of Platinum.** K. HERRMANN (*Ann. Physik*, 1925, [iv], 77, 503—536).—Methods are described for the measurement of the photo-electric effect and electrical conductivity of platinum foil under conditions such that the occluded gas could be removed by repeated electrical heatings of 10 sec. duration at 50 sec. intervals, or replaced by any desired gas. As the gas content is reduced by heating in a vacuum, the photo-electric effect diminishes. For effective outgassing the temperature of the foil must be near the m. p. After 1500 such heatings, the photo-electric effect was reduced to about one-seventh, and, by subsequent exposure for  $3\frac{1}{2}$  days to a pressure less than  $10^{-6}$  mm., to about one-twentieth its original value. At the same time, the resistance of the foil increased. Both these results are in agreement with the view that these properties are due to the free electron content of the foil, the number of such electrons decreasing with diminishing gas-content. The admission of oxygen to the outgassed foil, followed by repeated heatings at  $1700^{\circ}$ , and further evacuation, resulted in an additional fall of the photo-electric effect to a constant value.

Hydrogen was then admitted at 30 mm. pressure, and the foil reheated 800 times at  $1700^{\circ}$ , a sharp rise of photo-electric effect occurring. The oxygen treatment caused a rise in the electrical resistance. This was attributed to a dual cause, the formation of pores through the heat treatment, which facilitated the escape of occluded gas, and the oxidation of occluded hydrogen by the oxygen, followed by the removal of the less easily occluded water vapour. Microscopical examination of the foil after heating supported the above suggestion. The rise of photo-electric effect on the admission of hydrogen was accompanied by a marked fall in resistance, both effects being attributable to the increase of free electrons in the foil as a result of occlusion of hydrogen.

The experiments of Velo were repeated, and it was shown that complete outgassing of the foil could not have been attained by his method, and that his interpretation of his results is thus invalid. The photo-electric effect measured by Velo is not a purely metallic effect, but is due mainly to the presence of dissolved gas, the removal of which reduces the photo-electric current.

The minimum in the photo-electric sensitiveness observed between  $300^{\circ}$  and  $400^{\circ}$  is now shown to be due to mercury vapour adsorbed on the foil.

F. G. T.

**Electrical Resistance of Thin Films of Organic Liquids on Paper.** S. S. BHATNAGAR, M. PRASAD, N. G. MITRA, and D. L. SHRIVASTAVA (*Z. physikal. Chem.*, 1925, **117**, 88—96; cf. Reinold and Rücker, *Phil. Trans.*, 1893, **A**, **184**, 505).—Measurements were made of the resistances of thin films and of the specific resistances of thick films of methyl acetate, propyl, isopropyl, butyl, and isobutyl alcohols, and of mixtures of acetone with acetic and propionic acids, respectively. The resistances of thin films of other substances investigated were too high to be measured conveniently. The resistances of thin films are roughly inversely proportional to their thicknesses. The observed resistances of thin films were greater than those calculated from the data for thick films.

L. F. G.

**Physical Properties of Aniline and its Aqueous Solutions.** M. P. APPLEBEY and P. G. DAVIES (*J. Chem. Soc.*, 1925, **127**, 1836—1840).—Pure aniline has f. p.  $-5.98^{\circ}$ , b. p.  $184^{\circ}$  (approx.),  $d_{20}^{20}$  1.02315,  $n_D^{20}$  1.58685. These values are compared with those of Timmermans (*A.*, 1910, i, 533), Knowles (*A.*, 1920, i, 834), Schweser (*J. Chim. physique*, 1911, **9**, 15), and Tyrer (*T.*, 1912, **101**, 84). The lower values obtained by other workers for the f. p. are ascribed to the presence of traces of moisture. Freezing-point curves are given for aniline-water solutions (eutectic at 2.575% water), and evidence is given for the association of water in aniline solution and of aniline in aqueous solution. Water has little effect on the density, that of a saturated solution of water in aniline at  $20^{\circ}$  being 1.02393. Measurements of the refractive indices of aqueous solutions of aniline show that this property is a linear function of the percentage composition. The viscosity of aniline decreases with time, that of a freshly distilled sample being 1% higher than that of a week-old sample.

L. L. B.

**Pseudo-symmetry of Racemic Potassium Chlorosulphoacetate.** F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 423—425).—Detailed crystallographic data for racemic potassium chlorosulphoacetate,  $\text{CHCl}(\text{SO}_3\text{K})\text{CO}_2\text{K}$ , are given. The symmetry is apparently rhombic-bipyramidal with a close approximation to tetragonal, the parameters being 0.9973 : 1 : 2.7650, but examination by polarised light shows that it is really a twin produced by almost perpendicular crossing of monoclinic lamellæ, suggesting that the salt is not a true racemate, but a pseudo-racemic inter-growth of equal proportions of the *d* and *l* antipodes.

J. W. B.

**Approximate Calculation of Atomic Frequencies of the Inert Gases.** J. NARBUTT (*Physikal. Z.*, 1925, **26**, 470—471).—Theoretical. In calculating the ratio of the atomic frequencies of an element in the solid and liquid states more terms must be considered than are included in Ratnowsky's equation (*Verh. Phys. Ges.*, 1914, **16**, 1033) when, as in the case of the inert gases, the absolute m. p. of the element is not very considerably

greater than the product  $4.77 \times 10^{-11}v$ . The above ratio, for monatomic elements, is usually not constant, and shows marked variations even in adjacent groups of the periodic table. The values of the ratio are about  $\frac{4}{3}$  for the alkali metals, and about  $\frac{7}{4}$  for the inert gases.

F. G. T.

**Buffer Method in High-temperature Calorimetry.** W. A. ROTH (*Z. Elektrochem.*, 1925, **31**, 456).—In determining the specific heats of solids at high temperatures, the calorimeter is charged with a stable salt or mixture of salts melting at a suitable temperature, which is partly melted when the test-piece is dropped in. The temperature of the calorimeter cannot rise above the m. p. of the salt. Hence liquids such as paraffin can be used in the calorimeter; also the allowance for heat-exchange with the atmosphere can be calculated more accurately.

W. A. C.

**Atomic Heat Capacities of Iron and Nickel at Low Temperatures.** W. H. RODEBUSH and J. C. MICHALEK (*J. Amer. Chem. Soc.*, 1925, **47**, 2117—2121).—The specific heats of iron and nickel at liquid-air temperatures were determined with the apparatus previously described (A., 1923, ii, 532). The results for nickel differ only slightly from those for iron; the latter agree almost exactly with the figures of Griffiths and Griffiths (A., 1913, ii, 753), but not with those of Günther (*Ann. Physik*, 1917, [iv], **51**, 828). The calculated entropies at 25° are 6.87 units for iron and 7.24 for nickel. At higher temperatures, the atomic heat curves deviate from the theoretical Debye curve (A., 1918, ii, 149; 1924, ii, 666), possibly due to crystal structure.

S. K. T.

**Thermal Data on Organic Compounds. II. Heat Capacities of Five Organic Compounds. Entropies and Free Energies of some Homologous Series of Aliphatic Compounds.** G. S. PARKS and K. K. KELLEY (*J. Amer. Chem. Soc.* 1925, **47**, 2089—2097).—The specific heats over the approximate temperature range 70° to 290° Abs., m. p., and latent heats of fusion per gram ( $\lambda$ ) of the following compounds have been determined by the method previously described (this vol., ii, 491): isopropyl alcohol ( $\lambda=21.08$ ), acetone ( $\lambda=23.42$ ), ethylene glycol ( $\lambda=44.76$ ), acetic acid ( $\lambda=46.68$ ), and palmitic acid. The entropies and free energies are calculated and it is suggested that, in organic compounds, these quantities are related to the constitution. In an homologous series of liquids there is an average entropy increase of  $9 \pm 1$  units for each additional  $\text{CH}_2$  group, though in the fatty acid series the free energies remain approximately constant. In each case formic acid is an exception. In the series ethylene glycol, glycerol, etc., each additional  $\text{CH}\cdot\text{OH}$  group causes an entropy increase of 7 units for the solid state. In the change:  $\cdot\text{CH}_2\cdot\text{OH}_{(\text{liq.})} \rightarrow \cdot\text{CO}_2\text{H}_{(\text{solid})}$  there is an entropy decrease of 6.4 units. Substitution of H by OH in a liquid involves a free energy decrease of about 35,500 cal. The free energy of *n*-propyl alcohol is predicted to be —44,200 cal.

S. K. T.



**Metastability of the Elements and Chemical Compounds as a Consequence of Enantiotropy or Monotropy.** E. COHEN and A. L. T. MOESVELD (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 347—354; cf. A., 1924, ii, 234, 382, 383, 449, 450, 521, 603).—A criticism of the determinations of the specific heats of white and grey tin by Wigand (A., 1914, ii, 99), Brönsted (A., 1915, ii, 221), and Lange (this vol., ii, 96). It is pointed out that in no case was the physical purity determined, and that probably the materials used were mixtures of two modifications. S. I. L.

**Thermal Expansion of Alkali Halides at Low Temperatures.** II. F. A. HENGLEIN (*Z. physikal. Chem.*, 1925, **117**, 285—292; cf. this vol., ii, 375).—The densities of the fluorides of lithium, sodium, and potassium, and of the chlorides, bromides, and iodides of lithium and rubidium were determined at 0°, -79°, and -184°; from these measurements the coefficients of expansion between 0° and -79° and between -79° and -184° were calculated. As the lithium and rubidium salts were not quite pure, Baxter's data for the densities at 0° were used in conjunction with the above coefficients of expansion (which were not appreciably affected by the impurities) to calculate the true densities of these salts (except lithium fluoride) at -79° and -184°. L. F. G.

**Thermal Expansion of Fused Salts.** R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1925, **147**, 135—141).—The values of the product  $\alpha T$ , where  $\alpha$  is the coefficient of expansion in the neighbourhood of the m. p. and  $T$  the m. p. on the absolute scale, have been calculated for a number of fused salts from existing data. For an ideal substance this product has the value 0.077 and for "ordinary" substances the value 0.230. The calculated values of  $\alpha T$  range from 0.103 (silver nitrate) to 0.934 (aluminium chloride).

J. S. C.

**Critical Constants and Vapour Pressures of Hydrogen Cyanide.** G. BREDIG and L. TEICHMANN (*Z. Elektrochem.*, 1925, **31**, 449—453).—Determinations of critical data by the usual methods on carefully purified materials give the following results:  $T_c = 183.5^\circ \pm 0.1^\circ$ ,  $P_c = 53.2 \pm 0.5$  atm.,  $d_c = 0.195$ . Vapour pressures have been determined from -15° to 180°; they are given by the formula  $\log p = -\lambda_0/4.571T \pm 1.75 \log T - \epsilon T/4.571 + C$  satisfactorily if  $\lambda_0 = 7790$ ,  $\epsilon = 0.021675$ , and  $C = 2.789$ . From the data at hand, the molecular latent heat of evaporation is calculated to be 6.76 kg.-cal. at 25.6° (b. p.) and 7.22 kg.-cal. at -13.4° (m. p.). The calculated gaseous specific heats agree with the experimental values of Partington and Carroll (this vol., ii, 373). The degree of association of the liquid varies according to the method of calculation from 2.0 to 2.4. W. A. C.

**Simple Formula for Determining the Critical Temperature from the Coefficient of Expansion of the Liquid Phase, and the Cause of its Non-applicability for many Molten Salts.** J. J. VAN LAAR (*Z. anorg. Chem.*, 1925, **146**, 263—280).—From the straight-line law connecting the mean density of a liquid and its

saturated vapour with the temperature, a formula for determining the critical temperature from the coefficient of expansion of the liquid phase is deduced. This fails with the alkali halides because the straight line law fails. This failure is shown to be related to the very considerable volume contraction in the liquid phase in comparison with the sum of the atomic volumes. Other methods of arriving at the critical temperature are suggested. These require the value of  $D_0$ , i.e., the density of the liquid extrapolated to  $T=0$ . These values are calculated for the alkali halides from Jaeger's results, and their bearing on the abnormal behaviour of these substances is discussed. The theory is to be developed further in later papers.

A. B. M.

**Theory of State of Matter. I. Internal Pressure, Vapour Pressure, and Critical Data.** F. SCHUSTER (*Z. anorg. Chem.*, 1925, 146, 299—304).—An expression for the internal pressure in terms of the critical pressure and temperature is deduced:  $B=41.04T_cT \cdot \log(p_c/p)/V(T_c-T)$ . The internal pressures are calculated for a large number of compounds. In general, associated compounds possess higher internal pressures than non-associated, but there are exceptions to this rule. A distinction between the two classes of substances, however, is shown clearly in the temperature coefficient of the internal pressure. For non-associated liquids the temperature coefficient amounts to 2 to 3 atm.; for the others it is much higher, thus for ethyl alcohol it is 5.9 and for water 8 to 10.

A. B. M.

**Vapour Pressures of Organic Crystals by an Effusion Method.** T. H. SWAN and E. MACK (*J. Amer. Chem. Soc.*, 1925, 47, 2112—2116).—The following vapour pressures of the crystalline solids over the range  $10^\circ$  to  $30^\circ$  were obtained by a modified Knudsen method (*Ann. Physik*, 1910, [iv], 32, 809): naphthalene,  $\log p(\text{mm.}) = -29,820/T - 200.682 \log T + 595.642$ ; *p*-chloroaniline,  $\log p = -22,332/T - 138.475 \log T + 416.007$ ; *p*-chloronitrobenzene,  $\log p = -4339.2/T + 12.918$ ; *p*-bromonitrobenzene,  $\log p = 35,611/T + 305.935 \log T - 879.254$ . The calculated molar heats of evaporation at  $20^\circ$  are 19600, 21600, 19900, and 21200 (at  $30^\circ$ ) cal., respectively.

S. K. T.

**Statistical Definition of Entropy of an Ideal Gas.** E. SCHRÖDINGER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 434—441).—Theoretical. Various definitions of entropy and Planck's recent work (this vol., ii, 495) are discussed. It is shown that by making Planck's assumption that the interchange of energy types is negligible, a form of gas statistics results which is similar to that evolved by Einstein (this vol., ii, 495).

F. G. S.

**Statistical Definition of Entropy.** M. PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 442—451; cf. preceding abstract).—Mathematical. An extension of previous work (this vol., ii, 495) on the energy content and the free energy of gases.

F. G. S.

**Entropy of Supercooled Liquids at the Absolute Zero.**

L. PAULING and R. C. TOLMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 2148—2156).—Theoretical. It is shown that the entropy of a glass exceeds that of the corresponding crystal by a term  $R \log a$ , where  $a$  is a small number, mathematically defined, which increases with the complexity of the molecule. Different crystalline forms of a substance have the same entropy at the absolute zero, irrespective of the number of atoms in the crystal unit (cf. Eastman, A., 1924, ii, 143).  
S. K. T.

**Capillary and Photo-electric Properties of Mercury.**

J. G. POPESCO (*Ann. Physique*, 1925, [x], **3**, 402—464).—The surface tension of mercury has been found to be 436.3 dynes/cm. when the drop of mercury is formed and kept in a vacuum. Exposure of the drop formed in a vacuum to various common gases leads to a diminution of the surface tension. When the surface is formed in a gas, the surface tension is greater than when the surface is formed in a vacuum, but decreases within twenty-four hours to the same lower value. These effects have been investigated with different gases and at different temperatures and pressures. They are ascribed partly to adsorption and partly to a change in the orientation of the surface molecules of the mercury (cf. Langmuir, A., 1917, ii, 525; Frenkel, *ibid.*, 191). The initial velocity of photo-electrons from mercury is similarly modified when the drop formed in a vacuum is exposed to a gas. There is a close parallelism between surface tension effects and photo-electric phenomena.

A. S. R.

**Scattering of Light by Liquid Boundaries and its Relation to Surface Tension. II.**

C. V. RAMAN and L. A. RAMDAS (*Proc. Roy. Soc.*, 1925, A, **109**, 150—157).—Strong evidence of the molecular origin of the surface scattering of incident light at a liquid boundary and of its relation to the surface tension of the liquid has been obtained by a comparative study of some 64 organic liquids. Surface scattering is observed most conveniently with liquids such as the lighter paraffins, ether, and the alcohols, which show a small internal scattering. In liquids of approximately equal internal scattering powers, the surface opalescence varies inversely with the surface tension. Transparent liquids show an effect 30—50 times more intense than that of mercury. The intensity and state of polarisation of the scattered light depend on the angle of incidence of the primary beam and on the direction of observation. When the light is incident from above, the surface opalescence is seen most conspicuously from below. The scattered light has a maximum intensity and a sudden complete polarisation, with the electric vector parallel to the liquid surface, when viewed from below from a direction inclined to the vertical at the critical angle of the liquid. When the light is incident from above, the light scattered upwards exhibits a polarisation, partial for small angles of incidence, but complete, for practically all angles of observation, when the incidence is at the polarising angle.  
F. G. T.

**Influence of Chemical Constitution on the Thermal Properties of Binary Mixtures. Triazine and Benzene Derivatives.** P. PASCAL (*Bull. Soc. chim.*, 1925, [iv], **37**, 836—840).—Binary mixtures of triphenylbenzene, triphenyltriazine, methyl 1 : 3-diphenyl-5-methyltriazine, ethyl 1 : 3 : 5-benzenetricarboxylate, and ethyl 1 : 3 : 5-triazinetricarboxylate have been studied. The m. p. curves are said to indicate that the interatomic bonds in the benzene and triazine nuclei are identical. Complete isomorphism is still found to exist when the nature of the substituted radical is slightly altered (*e.g.*, diphenylmethyltriazine and triphenylbenzene); but if the difference between the substituted radicals becomes too great, isomorphism gives place to isodimorphism, as with the mixture triphenyltriazine and ethyl triazine-tricarboxylate.  
L. L. B.

**Calculation of Points in the Ethyl Alcohol-Water Distillation Curve.** E. ÖMAN and A. GUNNELIUS (*Tekn. Tidsk.*, 1925, **55**, 33; *Ind. Eng. Chem.*, 1925, **17**, 964).—If the composition of a water-alcohol mixture is known, the composition of any vapour obtained by its distillation may be calculated as follows. The b. p. of the mixture is obtained by reference to a table (given in the original), and the partial pressure of water vapour above the mixture at the b. p. is calculated from the known molar percentage of water in the liquid and the vapour pressure of water at this temperature. From this, the partial pressure of the alcohol is found by difference and the product of the partial pressure and molecular weight of the vapour of each substance gives the relative proportions of the two in the vapour. The molecular weight of the vapour above an aqueous solution containing 10% of alcohol is 43.15, and above one containing 70% of alcohol 26.05, the variation for each 1% of alcohol being 0.285.  
A. R. P.

**Critical Miscibility and Elevation of B. P.** C. DRUCKER and H. WEISSBACH (*Z. physikal. Chem.*, 1925, **117**, 209—241; cf. Timmermans, A., 1907, ii, 229; Drucker and Wagner, A., 1923, ii, 612).—The change in the b. p. of mixtures of carbon disulphide and methyl alcohol on the addition of sodium iodide, carbamide, succinic acid, water, diphenylamine, naphthalene, azobenzene, and acetanilide has been measured. The initial molecular composition of the solvent varied from 36.8 (critical composition) to about 100% methyl alcohol in most cases. The results obtained are not explicable by Nernst's theory (*Z. physikal. Chem.*, 1893, **11**, 1), the deviations from this being especially great in the case of mixtures with high alcohol concentrations. To elucidate this point the following determinations were made. The heats of mixture and the specific heats of a wide range of mixtures of carbon disulphide and methyl alcohol were measured at 20° and 36°. The data of Büchner and Prins for the total vapour pressure of such mixtures were supplemented by additional measurements. The partial vapour pressures of the components were calculated from the total vapour pressures with the aid of data for the composition of the vapour phases, for which a method of determination is described. It is shown that the

inapplicability of Nernst's theory is not due to his neglect of the comparatively small heats of mixture, but to the fact that the composition of the vapour is not independent of the nature and concentration of the solute, as required by the theory. The "salting-out" phenomena which result are quantitatively interpreted by the use of a new equation, derived theoretically. The shifting of the temperatures of critical miscibility is shown to be related to the salting-out effect.

L. F. G.

**Colloidal Separations in Alloys.** J. H. ANDREW and R. HAY (*J. Inst. Metals*, Sept. 1925, advance copy, 3 pp.).—Passage of an alternating current through  $\beta$ -brass at a temperature just below the transformation point causes the gradual appearance of an eutectoidal structure, presumably owing to the neutralisation of the charge on the colloidal particles present after normal cooling. The ageing of "duralumin" after quenching is somewhat accelerated by an alternating current, suggesting that the phase the separation of which is suppressed during cooling is present in a colloidal form. [Cf. *B.*, 1925, 809.]

A. R. P.

**Tensile Tests of an Aluminium-Zinc Alloy.** C. F. ELAM (*Proc. Roy. Soc.*, 1925, **A**, 109, 143—149).—Tensile tests have been made on large crystals of an alloy containing 18.6% Zn, representing a solid solution near the limit of solubility of zinc in aluminium. X-Ray examination indicated a structure of cubic symmetry, similar to pure aluminium, but with a larger lattice, 4.18 Å.<sup>3</sup> The appearance of slip bands on the surface, and a study of the movement of the axis of the test piece relative to the crystal axes indicate the probability of a slip occurring normally on an octahedral (111) plane in the (110) direction as in aluminium. There was a variation of from 16 to 21 tons/in.<sup>2</sup> in the breaking loads for different crystals, but all values for single crystals were higher than for a polycrystalline test-piece. The elongation during test was 10—15%. Compared with aluminium, this alloy has a very much greater hardness, and the amount of slip that can occur before fracture is much reduced. The orientation of the crystal relative to the axis of the test-piece affects the breaking stress and type of fracture. Fracture occurs on planes at approximately 45° to the axis, on the plane of maximum shear. In some cases, however, fracture occurs along the slip plane.

F. G. T.

**Effect of Composition on the Viscosity of Glass. III. Some Four-component Glasses.** S. ENGLISH (*J. Soc. Glass Tech.*, 1925, **11**, 83—98).—In continuation of viscosity determinations between 750° and 1400° with a series of glasses, the successive replacement of lime in the parent glass 1.2Na<sub>2</sub>O, 0.8CaO, 6SiO<sub>2</sub> by 0.2, 0.3, 0.4, 0.5, and 0.6 mol. of magnesia, respectively, was found to render the rate of increase of viscosity with falling temperature more uniform, all the glasses having a viscosity lower than that of the lime glass at the upper and lower temperature limits, but approximately the same value between 1100° and 1200°. A series in which

part of the lime of the glass  $1.1\text{Na}_2\text{O}, 0.9\text{CaO}, 6\text{SiO}_2$  was replaced equimolecularly by 0.1, 0.2, and 0.3 mol. of alumina gave glasses which all set more slowly than the parent glass. [Cf. *B.*, 1925, 715.]  
A. C.

**Solubility of Carbamide in Water.** L. A. PINCK and M. A. KELLY (*J. Amer. Chem. Soc.*, 1925, 47, 2170—2173).—The solubility of carbamide in water is redetermined over the range  $0^\circ$  to  $70^\circ$ . The results agree more or less with those of Speyers (*A.*, 1902, ii, 388) up to  $10^\circ$ , but get consistently higher as the temperature increases.  
S. K. T.

**Solubility of Proteins and Proteoses in Aldehydes and Other Organic Solvents.** E. A. COOPER and S. D. NICHOLAS (*Biochem. J.*, 1925, 19, 533—537).—Benzaldehyde dissolves hydrolytic products of proteins, but not the proteins themselves. Proteoses are only soluble in aldehydes of the aromatic type, but not in the aliphatic and heterocyclic aldehydes. Acetophenone, but not acetone or benzophenone, dissolves proteoses. Previous treatment of proteoses with formaldehyde and nitrous acid destroys their solubility in benzaldehyde. Although proteoses are insoluble in chloral, they are soluble in fused chloral hydrate and butylchloral hydrate. They are insoluble in the alkoxides. Gelatin, albumin, gliadin, and lecithin are also soluble in chloral hydrate, from which they can be precipitated by paraldehyde, but not by alcohol. Lecithin is precipitated from an ethereal solution by anisaldehyde, acetophenone, acetaldehyde, paraldehyde, phenylacetaldehyde, and cinnamaldehyde, but not by benzaldehyde, *m*-tolualdehyde, salicaldehyde, and *n*-heptaldehyde. Acetaldehyde reacts much less readily than formaldehyde with glycine and alanine, whilst acetone has no chemical action on them. Below and above a certain critical range of acetone concentration there is no evidence of any absorption of acetone by the protein. From experiments on the solubility of gelatin and egg-albumin in molten phenols and cresols, the following facts are deduced: The solvent action of the phenols diminishes as the homologous series is progressively ascended. The introduction of a chlorine atom into phenol diminishes the solvent power, but to a less degree than a methyl group. The solvent action is diminished by introduction of the  $\cdot\text{CO}_2\text{Me}$  group and inhibited by that of  $\cdot\text{CO}_2\text{C}_5\text{H}_{11}$ ,  $\text{CO}_2\text{Ph}$ , nitro, and methoxy groups, and by hydrogenation of the benzene nucleus.  $\alpha$ -Naphthol and benzyl alcohol have no solvent action on proteoses and gelatin. With amines and their derivatives the following results were obtained. Aniline, *o*-toluidine, *m*-xylylidine, methylaniline, chloroaniline, anisidine, and phenylhydrazine dissolve proteoses on warming, but not at the ordinary temperature. Dimethylaniline and ethylaniline, however, dissolve proteoses at the ordinary temperature, but not on warming. Proteoses are slightly soluble in formamide, but insoluble in benzylamine, dichloroaniline, phenylethylamine, diphenylamine,  $\alpha$ -naphthylamine, azobenzene, urethane, pyridine, and camphylamine.  
S. S. Z.

**Absorption of Carbon Dioxide by Salt Solutions under Pressure.** W. IPATIEV and A. ANDRUSCHTSCHENKO (*Bull. Acad. Sci. St. Pétersbourg*, 1917, [6], 851—862; from *Chem. Zentr.*, 1925, i, 2525—2526).—Carbon dioxide is more soluble in a solution of nickel acetate than in water, the difference decreasing with the pressure (5 to 26 atmospheres). No precipitation of nickel carbonate occurs.  
G. W. R.

**Salts of certain Aromatic Carboxylic Acids and their Solubility.** F. EPHRAIM and A. PFISTER.—(See i, 1148.)

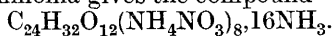
**Distribution of Surface-active Substances between Water and Organic Solvents.** R. G. SCHULZ (*Koll.-Chem. Beihefte*, 1925, 21, 37—54).—In the distribution of a solute at a liquid-liquid boundary the relationships between the surface activity and distribution are similar to those at a liquid-solid boundary. The distribution is said to be determined by the relative surface activities of the solute in the two solvents.  
E. M. C.

**Beryllium Compounds as Adsorption Media.** J. KLEEGER (*Kolloid-Z.*, 1925, 37, 17—18).—Beryllium hydroxide adsorbs Congo-red and pancreas amylase more strongly and yeast invertase less strongly than does aluminium hydroxide. Dextrose, tributyrin, and acetic acid are not adsorbed, but eosin and methylene-blue are adsorbed slightly. The adsorption is greatly increased when the substance to be adsorbed is added before the beryllium hydroxide is precipitated, and the sedimentation of the precipitate is accelerated. In 14 days, a beryllium hydroxide precipitate completely loses its adsorptive power.  
E. M. C.

**Influence of Salt Content on the Adsorptive Power of an Active Charcoal and a Review of the Chief Properties of the More Important Technical Active Charcoals.** H. HERBST (*Koll.-Chem. Beihefte*, 1925, 21, 1—36).—The true static adsorptive power of active charcoal is reduced on impregnation with water, dry salts, or solutions of salts and alkalis to an extent which is approximately proportional to the amount added and becomes zero for additions of 50—60%. The adsorption velocity falls off more rapidly. A comparison is made of the density and adsorptive powers towards carbon dioxide, sulphur dioxide, and succinic acid solutions for a number of active charcoals of different origins. [Cf. B., 1925, 697.]  
E. M. C.

**Absorptive Power of Cellulose Nitrate for Gases.** D. COSTA (*Gazzetta*, 1925, 55, 540—548; cf. A., 1920, i, 16; 1924, i, 714).—Dry cellulose nitrate containing 12.95% of nitrogen corresponding with the formula  $C_{24}H_{48}O_8(OH)_2(O\cdot NO_2)_{10}$  was used in the experiments made at 18—24° at atm. pressure. The results indicate that each nitro group fixes 1 mol. of ammonia, forming a true ammonium salt. Denitration and dehydration of the cellulose nitrate complex follow, and each molecule of ammonium nitrate set free takes up 2 mols. of ammonia. After careful washing with boiling

water, the product contains no nitrogen. Both volumetric and gravimetric measurements point to the formation of the compound  $C_{24}H_{20}O_{10}(NH_4NO_3)_{10} \cdot 20NH_3$ ; titration of the absorption product shows that the free ammonia is not more than two-thirds of the total ammonia absorbed. In order to prove that the absorption of ammonia depends on the nitro groups present, similar experiments were made with a cotton collodion containing 11.31% of nitrogen, corresponding with the formula  $C_{24}H_{32}O_{12}(O \cdot NO_2)_8$ . In this case saturation with ammonia gives the compound



When cellulose nitrate is saturated with hydrogen chloride, all the nitro groups are replaced and the product, soluble in water, reduces Fehling's solution and is optically active. The results obtained in the absorption of sulphur dioxide and carbon dioxide are tabulated; oxygen and hydrogen are not appreciably absorbed. The absorptive powers of cellulose and cellulose nitrate for different gases are compared.

W. E. E.

**Adsorption [of Alkali from Alcoholic Solutions by Cellulose].** II. S. LIEPATOV (*Kolloid-Z.*, 1925, **37**, 112—116).—Some of the experiments previously described (this vol., ii, 385) are repeated in 40% and 90% aqueous-alcoholic solutions. The velocity of adsorption by cellulose of sodium hydroxide in 40% alcohol follows the equation  $kt = \log_e a / (a - \gamma x)$ , where  $\gamma$  is a constant. In the stronger solution, the velocity is greater and approximates to that for an aqueous solution. The character of the adsorption curve is unaltered by duration of time. The adsorption of sodium and barium hydroxides from alcoholic solutions is much greater than from pure water and increases with the alcohol content. Adsorption from such solutions is an irreversible chemical process, the presence of the alcohol hindering the hydrolysis.

S. K. T.

**Adsorption of Acids by Filter-paper.** S. G. MOKRUSCHIN (*Kolloid-Z.*, 1925, **37**, 144—146).—A theoretical explanation of the constants  $K$  in Holmgren's equation (A., 1909, ii, 25), and  $z$  in Schmidt's equation (*Kolloid-Z.*, 1913, **13**, 146) is given in which a unimolecular layer of acid on the capillary walls of the filter-paper is assumed in agreement with Langmuir's adsorption theory. Since the constants are independent of the degree of dissociation of the acid, adsorption of the molecules is indicated, and this finds support in the work of Schulov and Lepin [*Ann. d. Lomonosoff. phys.-chem. Ges.* (Moscow), 1919, **1**, 56—65, 66, 67]. The theoretical conclusions are borne out by experiments with hydrochloric, nitric, sulphuric, oxalic, and tartaric acids in 1/4 to 1/1024 molar solutions.

N. H. H.

**Mechanism of the Adsorption of Sugar by Colloidal Solutions and Precipitates.** M. PRASAD, D. L. SHRIVASTAVA, and R. S. GUPTA (*Kolloid-Z.*, 1925, **37**, 101—104).—The adsorption of certain sugars from solution by sulphide sols and precipitates is investigated (cf. A., 1924, i, 942). Except in the case of xylose and



arsenic trisulphide and of lævulose and antimony trisulphide, Freundlich's adsorption equation is not followed. The amount of sugar adsorbed always decreases with diminishing concentration of the adsorbent. Practically no adsorption occurs in presence of powdered substances, such as magnesium oxide, zinc oleate, etc.  
S. K. T.

**Adsorption. XI. Life Period of Organisms and its Dependence on the Concentration and Volume of the Toxic Medium and on the Concentration of the Organisms.** P. N. PAVLOV (*Kolloid-Z.*, 1925, **37**, 105—111).—The toxic effect of a medium on the life period,  $T$ , of an organism is expressed by the "life period depression"  $(T_0 - T)/T$ ,  $T_0$  being the value of  $T$  in the natural medium, and not by  $1/T$  (cf. Ostwald, A., 1910, ii, 592). Combining this with the adsorption formula, equations are derived connecting the life period with the concentration of the toxic substance, the volume of the medium, and the number of organisms in unit volume. According to the nature of the relations involved the toxic effect is said to be chemical or physical. Experiments carried out with *Gammarus* (at high salt concentrations) and *Artemia salina* in common salt solutions support the chemical explanation of toxicity. At lower salt concentrations (16—19%) the results with *Gammarus* support a physical explanation. Some of the equations deduced are numerically confirmed.

S. K. T.

**Adsorption and Surface Energy at the Boundary of Different Phases.** B. ILIN (*Physikal. Z.*, 1925, **14**, 497—501).—Szyszkowski's equation (A., 1908, ii, 1018) leads to the relation  $Q = b \log_{10}(ac + 1)$ , in which  $Q$  is the heat of adsorption,  $C$  the concentration of the capillary-active substance, and  $a$  and  $b$  are constants. This has been tested by reference to the data of Titoff (A., 1910, ii, 1041) on nitrogen, carbon dioxide, and ammonia, and by Lamb and Coolidge (A., 1920, ii, 471) on carbon disulphide with excellent agreement between observed and calculated values of  $Q$ . The theoretical treatment is also supported by the results of Reh-binder (A., 1924, ii, 662) for solutions of valeric acid, butyric acid, and tetrapropylammonium chlorate.  
R. A. M.

**Electrical Theory of Adsorption.** B. ILIN (*Z. Physik*, 1925, **33**, 435—469).—On the assumption that adsorption forces are purely electrical a formula is developed connecting the heat of adsorption and adsorptive capacity with the dielectric constant and surface energy of the adsorbent. The electrical moment of the polarisation is found to be about  $10^{-19}$ , and the thickness of the film about  $10^{-8}$  cm. From the formula for the adsorptive capacity the value 2 is obtained for the gas constant,  $R$ . A relationship is established between the critical temperature of the adsorbed gas, the van der Waals attraction constant, and the adsorption constant. The effective surface of 1 g. of charcoal is found to be about  $10^5$  cm.<sup>2</sup> In the case of charcoal and mica, for gases of about the

same heat of absorption, the amount of adsorption is much the same, from which it is concluded that adsorption is not a specific property.

E. B. L.

**Derivation of Adsorption Isotherms.** A. GORBATSCHEV (*Z. physikal. Chem.*, 1925, **117**, 129—142).—It is assumed that lines of force originate from the surface of an adsorbent, adsorbed molecules being thereby attracted and held. The effective radius of attraction is less than the diameter of a molecule. On this assumption equations are derived which correspond with adsorption isotherms obtained by Langmuir, Freundlich, and co-workers, Reichinstein (A., 1924, ii, 22), Schmidt (A., 1911, ii, 969), Williams (A., 1919, ii, 496), Lockemann and Paucke (A., 1911, ii, 720), and with extended forms of Henry's law (cf. Williams, A., 1919, ii, 392; Abderhalden and Fodor, A., 1921, ii, 21; Fodor and Schönfeld, A., 1922, ii, 688).

L. F. G.

**Theories of Liesegang Ring Formation.** N. R. DHAR and A. C. CHATTERJI (*Kolloid-Z.*, 1925, **37**, 89—97; cf. this vol., ii, 865).—Criticism of previous work is continued. The coagulation of silver chromate sol is brought about by potassium chromate within certain concentration limits; outside these limits a yellow sol is produced. This phenomenon, it is shown, offers a complete explanation of Liesegang ring formation. No rings are formed when the protective colloid has a very small or a very large peptising effect on a sparingly soluble substance, provided, in the latter case, that a peptised sol of the substance is not coagulated by either of the reactants from which it is formed. Rings are only formed when the peptising action is of medium strength.

S. K. T.

**Precipitates with Stratified Structures.** I. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **37**, 78—88).—From a consideration of the dispersion curves for some precipitates with stratified structures it is shown that Liesegang rings result from the periodic variations in the concentrations of the dispersed and dispersing phases caused by the mixing of the appropriate precipitating agents; these are tracks indicating the places of contact of the vessel and the surface skin of the precipitate. The points of contact move downwards as evaporation proceeds.

S. K. T.

**Structure of Films of Water on Salt Solutions. I. Surface Tension and Adsorption for Aqueous Sodium Chloride Solutions.** W. D. HARKINS and H. M. McLAUGHLIN (*J. Amer. Chem. Soc.*, 1925, **47**, 2083—2089).—The surface tensions of 0.1 to 5*N*-sodium chloride solutions have been measured by the drop method, and by an application of the Gibbs adsorption equation, modified by the introduction of the activity coefficient, the thickness of the water film on the solutions is shown to decrease from 4.00 to 2.30 Å. as the concentration rises. The thickness is of the order of a linear dimension of a water molecule, but some molecules of the type (H<sub>2</sub>O)<sub>2</sub> may be involved. As the concentration increases

diffusion pressure forces the ions closer and closer to the surface and the surface tension rises. A small departure of the water molecule from perfect symmetry is sufficient to account for the observed variation in the thickness of the water film, but probably other factors are also effective.

S. K. T.

**Composition of Soap Films.** M. E. LAING (*Proc. Roy. Soc.*, 1925, **A**, 109, 28—34).—The nature of the material which accumulates in soap films has been investigated by determining the concentration changes in a sodium oleate solution as a result of foam formation. The concentration changes were followed by conductivity measurements, and by analysis of the condensed foams and of the residual soap solutions. In every case, the foam is more concentrated than the bulk of the solution. The analytical data show that an acid sodium soap, and not free oleic acid, collects in the interfacial film. From neutral or acid soap solutions, the material adsorbed has the composition 1 mol. sodium oleate + 0.61 mol. oleic acid. Excess of alkali in the solution converts this material into neutral sodium oleate. The absolute amount of substance adsorbed is least from neutral solution, and increases with addition of either oleic acid or alkali. These results are in accord with the suggestion of Bragg that the black spot in soap films is due to the actual contact of the two adsorbed layers, except that it consists of an acid sodium soap, instead of free fatty acid. The presence of this colloidal material is suggested as the cause of the stability of soap films. F. G. T.

**Kinetic Theory of Surface Films. I. Surfaces of Solutions.** R. K. SCHOFIELD and E. K. RIDEAL (*Proc. Roy. Soc.*, 1925, **A**, 109, 57—77).—When Gibbs' equation, modified by the introduction of the activity in place of the mole fraction of the solute, is applied to the surface tension-concentration curves for aqueous solutions of capillary-active organic substances, evidence is obtained that the adsorbed film is unimolecular in the case of dilute solutions. The analogy between  $F$ , the lowering of surface tension, and a three-dimensional gas or osmotic pressure as postulated by Traube has been critically examined and it is shown that whilst existing theories account for the proportionality between  $F$  and the mole fraction of the solute for low values of  $F$ , the lack of proportionality for large values of  $F$  is unexplained. It is possible that the latter anomaly is due to the same causes which render the gas laws inapplicable to compressed gases. Weak solutions, for which  $F$  exceeds about 10 dynes/cm., and in which the surface phase is relatively highly condensed, conform to the equation  $F(A - B) = xRT$ , where  $A$  is the area occupied by a g.-mol. as surface excess,  $B$  the limiting area of a g.-mol. under high compression, and  $1/x$  a measure of the lateral molecular cohesion of the film. This relation has been tested at three interfaces: for a number of the lower fatty acids at a water-air interface, for *n*-butyric acid at a water-benzene interface, and for tertiary butyl and amyl alcohols, sucrose, and pyridine at a water-mercury interface. The above equation, which fits existing data within the limits of experimental error, yields values for the limiting areas of the adsorbed molecules in close agreement with those

anticipated from measurements of molecular dimensions. At water-air and water-benzene interfaces the common value of  $B$ , 24—25 Å., found for normal fatty acids, supports Langmuir's orientation hypothesis. The values of  $x$  for a series of fatty acids show that at a water-air interface the lateral molecular cohesion increases with the length of the hydrocarbon chain. The *iso*-acids have a slightly larger value of  $x$  than the corresponding normal acids, indicating an apparently smaller cohesion between branched chains than between normal chains with the same number of carbon atoms. At a water-benzene interface the value of  $x$  for butyric acid is almost unity, indicating that there is little or no cohesion between such molecules at that interface. The similar value of  $x$  for sucrose shows that sucrose molecules do not cohere at a water-mercury interface. Strong support is found for the view that the molecules of the capillary-active substances examined are adsorbed from a weak solution in a unimolecular layer, and that the effect they produce on the surface tension is due to their thermal agitation alone. At a given temperature their activity depends solely on the surface concentration, the interfacial area occupied, and on the lateral cohesion.

F. G. T.

**Capillary Chemical Phenomena.** R. DUBRISAY (*Bull. Soc. chim.*, 1925, [iv], **37**, 996—1008).—An account of work previously abstracted (*A.*, 1918, ii, 368; 1923, ii, 741; 1924, ii, 154, 731).

S. K. T.

**Effect of Capillary-active Substances on the Surface Tension of Salt Solutions. Its Relation to Ionic Hydration.**

W. SEITH (*Z. physikal. Chem.*, 1925, **117**, 257—284).—Measurements were made by Stocker's method (*A.*, 1920, ii, 593) to ascertain the effect of different capillary-active substances (methyl, ethyl, *iso*-propyl, *isobutyl*, and *isoamyl* alcohols, and aniline) on the surface tension of pure water and of aqueous solutions of salts (lithium, sodium, potassium, magnesium, and barium chlorides and magnesium sulphate) and carbamide. The lowering of surface tension increases with concentration of salt. When surface tension is plotted against concentration of capillary-active substance, the curves obtained for different concentrations of the same salt cut each other at a point. The concentrations of the capillary-active substances in the surface films are calculated. A method of calculating the hydration of the salt ions from the lowering of surface tension is described. The degrees of hydration thus obtained agree with those calculated from the effect of the salts on the solubilities of non-electrolytes in water (see Armstrong and others, *A.*, 1907, ii, 848).

L. F. G.

**Surface Tension of Aqueous Phenol Solutions. II. Activity and Surface Tension.** A. K. GOARD and E. K. RIDEAL (*J. Chem. Soc.*, 1925, **127**, 1668—1676).—Measurements of the surface tensions of mixtures of water, sodium chloride, and phenol in various proportions have been made by the drop weight method (cf. this vol., ii, 510), and of the partition of phenol between paraffin

oil and water or aqueous sodium chloride solution. From the latter and freezing-point data the activities of phenol in water and aqueous sodium chloride solution have been deduced. Using the differential equation of Gibbs determining the surface adsorption of substances in solution and taking into account the activity of the phenol, the surface adsorption has been calculated. The maximum surface adsorption is found to be independent of the concentration of the sodium chloride and equal to  $69.2(\pm 1) \times 10^{-11}$  g.-mol./cm.<sup>2</sup> Assuming that the surface layer consists of a unimolecular film of phenol molecules, the cross-sectional area and length of the phenol molecule are calculated to be 23.8 and 6.4 Å., respectively. These values are in good agreement with those determined by Adam (A., 1923, ii, 539). The fact that the dissolved sodium chloride exerts a marked effect on the surface tension through this unimolecular film indicates that the surface tension is affected by the presence of molecules below the surface layer, although the opposite has been assumed by Langmuir and some other workers. E. E. W.

**Influence of Density and Geometrical Dimensions of a Molecular Stream on the Formation of Deposits.** J. ESTERMANN (*Z. Physik*, 1925, **33**, 320—324).—The relation between the critical temperature of condensation of metallic vapours and their concentration has been determined for different surfaces, and the heat of adsorption and the adsorption pressure calculated. The edge of the deposit has a lower temperature of condensation than the centre, owing to the density being lower at the edge. E. B. L.

**Angles of Contact and Polarity of Solid Surfaces.** N. K. ADAM and G. JESSOP (*J. Chem. Soc.*, 1925, **127**, 1863—1868).—The equation  $W = T_{LV}(1 + \cos \theta)$ , in which  $W$  represents the adhesion of a liquid for a solid surface on which it rests at an angle  $\theta$ , and  $2T_{LV}$  the cohesion of the liquid, has been examined with reference to the polarity of solid surfaces. For solid long-chain aliphatic compounds in contact with water,  $\theta$  should be low if many polar groups are at the free surface, whilst if the hydrocarbon ends of the chains are all turned outwards,  $\theta$  should be approximately the same as for paraffin wax. Of the nine solids investigated, paraffin wax and octadecyl iodide (no groups with a strong affinity for water) give practically the same angle at a surface cut from the interior as at the natural surface. Acids and alcohols give varying results for surfaces cut from the interior, according as the cut surface runs parallel or perpendicular to the direction of the crystal flakes. Crystalline flakes (from alcohol or benzene) give a lower angle than the mass solidified after fusion. Alternative explanations for this are suggested. The chief difficulty in measuring the angle of contact (the "dragging" effect or "hysteresis") is attributed to friction of the liquid on the solid. L. L. B.

**Action of Silica on Electrolytes.** J. MUKHERJEE (*Nature*, 1925, **116**, 313—314).—Joseph's failure (cf. this vol., ii, 383) to confirm the author's results is ascribed to the use of silica heated at 180°; a suitable method for the preparation of the silica is described.

Three types of adsorption are distinguished : (a) primary, resulting from the chemical affinity of the atoms on the surface, (b) electrical, and (c) adsorption of solutions resulting from the capacity of the substance to adsorb water.

A. A. E.

**Electric Charge on Sparingly Soluble Substances.** L. MICHAELIS and S. DOKAN (*Kolloid-Z.*, 1925, 37, 67—72).—Two new classes of colloids are described : “obligatory” and “facultative.” The former can exist in the medium only in the colloid state (e.g., mastic in water), whilst the latter are sparingly soluble and exist suspended in their saturated solutions (e.g., silver iodide). One of the ions is responsible for the colloid state in the former group, but neither is separately responsible in the latter. The influence of dissolved electrolytes on “facultative” colloids is investigated, especially in the case of barium sulphate. Univalent ions have no perceptible influence on the charge of the colloid, but bivalent ions, excepting such cations as form easily soluble sulphates, exhibit marked effects. Tervalent ions have a still stronger influence (cf. Umetsu, A., 1923, ii, 299).

S. K. T.

**Contraction, Refractivity, and Absorption of Light in Solutions of Lithium Salts.** F. HÜTTIG and M. KELLER (*Z. Elektrochem.*, 1925, 31, 390—403).—The densities and refractive indices of aqueous solutions of lithium chloride, bromide, and iodide have been measured from saturation down to 0.1*N*, and the coefficients of extinction between  $\lambda 230$  and  $\lambda 410$  down to *N*. The resulting curves show discontinuities at  $n=6$  and near  $n=30$  and  $n=75$ , when  $n$  is the number of mols. of water per mol. of salt, for all three salts. It is suggested, on the basis of Werner's co-ordination theory, that the lithium ion requires 6 mols. of water for complete envelopment, and that when there are fewer, the partly unprotected ion exerts an attraction on the surrounding halogen ions which causes a corresponding contraction. A second complete envelope will consist of 30 mols. of water, and a third of 76 mols.

W. A. C.

**Refractive Indices of Perchlorates in Aqueous Solution.** A. MAZZUCHELLI and A. VERCILLO (*Gazzetta*, 1925, 55, 498—501).—The refractive powers of ammonium and sodium perchlorates and of perchloric acid calculated by Landolt's formula from observations on aqueous solutions are found to be almost independent of the concentration. For perchloric acid, however, the refractive power increases slightly with dilution. The compounds studied are found to obey the law of Le Blanc and Rohland (A., 1896, ii, 345).

W. E. E.

**Cause of the Colour Change in Cobalt Chloride Solutions.** J. GRÓH (*Z. anorg. Chem.*, 1925, 146, 305—314).—The molecular extinction coefficients for solutions of cobalt chloride in propyl alcohol, ethyl alcohol, methyl alcohol, and water have been measured and plotted against wave-length of light. The effect of addition of lithium chloride to some of the solutions has been observed. The results are in complete accordance with the assumption of an

equilibrium  $\text{CoCl}_2 + 2\text{Cl}' \rightleftharpoons \text{CoCl}_4''$ , the blue colour of the solutions being due to the complex ion  $\text{CoCl}_4''$ . A. B. M.

**Variation in the Rotatory Power of Tartaric Acid as a Function of  $p_{\text{H}}$ .** F. VLÈS and E. VELLINGER (*Bull. Soc. chim.*, 1925, [iv], **37**, 841—845).—The rotatory power of *d*-tartaric acid in  $M/2$ ,  $M/4$ , and  $M/10$  solution has been examined in its dependence on  $p_{\text{H}}$ . The curve  $\alpha=f(p_{\text{H}})$  shows a rapid rise of rotatory power between  $p_{\text{H}} 2$  and  $p_{\text{H}} 5$ . From  $p_{\text{H}} 5$  up to  $p_{\text{H}} 13$ , the rotatory power is practically independent of the acidity of the solution, but above  $p_{\text{H}} 13$  it decreases. Below  $p_{\text{H}} 2$  the value is almost constant. The experimental values agree with the assumption that the rotatory power is the sum of the effects due to the two anions and the undissociated acid molecule. The mechanism of the removal of a hydrogen ion from the tartaric acid molecule, and the consequent change in space arrangement, is briefly discussed. L. L. B.

**Viscosity and Surface Tension during Esterification.** (MLLE.) G. CAUQUIL (*Compt. rend.*, 1925, **181**, 114—116).—Measurements have been made of the viscosity and surface tension during esterification of equimolecular mixtures of acetic acid and the following alcohols: *cyclohexanol*, *o*-methyl*cyclohexanol*, *o*-ethyl*cyclohexanol*, *m*-methyl*cyclohexanol*, *p*-methyl*cyclohexanol*, 1:3-dimethyl*cyclohexan-4-ol*. Esterification was carried out at  $95^\circ$ , portions of the reaction mixture being cooled to  $20^\circ$  for purposes of measurement. The viscosity and surface tension may be represented by formulæ of the type  $\eta_t = \eta_0 + Bx$ , where  $x$  is the percentage of acid esterified. The coefficient  $B$  is negative in the case of the viscosity, and positive in that of the surface tension measurements. F. G. T.

**Dielectric Constants of Solutions of Electrolytes.** H. Ulich (*Z. Elektrochem.*, 1925, **31**, 413—417).—The dielectric constants of solutions of amine halides and tetra-alkylammonium salts in organic solvents show in general, first, a decrease proportional to the concentration, then a minimum, and lastly a steady increase with concentration to values which in some cases exceed those of the pure solvents. The incidence of the minimum is found, applying Walden's rule, at  $v = (13.4/\epsilon_0)^3$ , where  $v$  is the molecular dilution and  $\epsilon_0$  the dielectric constant of the solvent. W. A. C.

**Osmotic Pressure by the Solubility Method in Concentrated Solutions.** M. P. APPELBEY and P. G. DAVIES (*J. Chem. Soc.*, 1925, **127**, 1840—1846).—Solutions of sucrose of known concentration are shaken with aniline at  $20^\circ$ , and the solubility of water in the aniline layer determined. From the data of Berkeley and Hartley (A., 1907, ii, 234), the connexion between osmotic pressure and lowering of solubility is obtained. In dilute solutions, this may be calculated by the equation of Nernst, whilst in more concentrated solutions a new combination of the equations of Van Laar and of Berkeley and Burton (*Phil. Mag.*, 1909, **17**, 598) leads to a relation which is in good agreement with experiment up to concentrations of 420 g. per 1000 g. of solution. By finding the

percentage of water in the aniline phase in equilibrium with a solution of unknown osmotic pressure, and reading off from the present results the concentration of the sucrose solution in equilibrium with the same aniline solution, the osmotic pressure of the unknown solution can be equated with that of the sucrose solution.

W. H.-R.

**Method for Investigating Diffusion in Gels.** R. FRICKE (*Z. Elektrochem.*, 1925, **31**, 430—435).—A microtome is described by means of which gels of elongated shape may be cut transversely into slices down to  $\frac{1}{2}$  mm. thickness.

W. A. C.

**Dialysis of Easily Decomposable Colloidal Systems.** A. GUTBIER (*Z. anorg. Chem.*, 1925, **146**, 411—412).—Easily decomposed colloidal solutions are protected from the air during dialysis by covering them, as well as the outer liquid in the dialyser, with a layer of paraffin or other suitable pure oil.

A. B. M.

**Direct Method of Measuring the Osmotic Pressure of Hæmoglobin.** G. S. ADAIR (*Proc. Roy. Soc.*, 1925, **A**, **108**, 627—637).—The difficulties in measuring the osmotic pressure of hæmoglobin, due to alteration of the state of aggregation in the colloidal system, and to chemical change, have been overcome by a method involving the use of an osmometer in which equilibrium is reached rapidly, and by making all measurements at 0°. The osmotic pressures of solutions of various hæmoglobins are tabulated.

L. F. G.

**Physico-chemical Study of U.S.P. Agar.** E. H. HARVEY (*Amer. J. Pharm.*, 1925, **97**, 447—456; cf. B., 1925, 296).—The heat of combustion of U.S.P. agar ( $d_{20}^{20}$  0.7190) is 4870 cal./g. Boiling hydrolyses the agar, lowering the viscosity and destroying the ability to gel. Hot agar sols show no optical activity. Imbibition of water is comparatively rapid at first and becomes gradually slower. The heat of imbibition is 2.7 cal./g. of dry agar. Adsorption of acetic acid is relatively greater from dilute solutions than from more concentrated solutions. Quantitative experiments have been carried out on the rate of adsorption of water vapour, and on the rate of dehydration of agar gels.

C. P. S.

**Effect of Low Temperatures on Liquid Colloidal Systems.** F. BOTTAZZI and G. BERGAMI (*Arch. Sci. biol.*, 1924, **6**, 74—93; from *Chem. Zentr.*, 1925, i, 2539).—At 0°, protein solutions rich in electrolytes are not coagulated, although removal of the electrolytes by dialysis produces a partial coagulation (turbidity). This coagulation is reversible. Differences exist, however, between different proteins. For example, even after removal of electrolytes, octopus blood and, probably, hæmoglobin remain clear at -4°. Neutral electrolytes stabilise dialysed protein in respect of coagulation at low temperatures. Denaturing scarcely takes place even at -25° or by freezing. Native blood-serum and plasma are very stable against the effect of low temperatures. The less stable colloids



are rendered coagulable by removals or additions which modify their reaction in the direction of their isoelectric points.

G. W. R.

**Spontaneous Structure-formation in Sols. (New Type of Anisotropic Liquid Media).** H. ZOCHER (*Z. anorg. Chem.*, 1925, **147**, 91—109; cf. A., 1922, ii, 102).—When hot aqueous solutions of benzopurpurin and chrysophenin are cooled, sols with an orderly, parallel arrangement of oblong colloid particles are obtained. A similar parallel orientation of particles is observed in old vanadium pentoxide and ferric hydroxide sols. The particles of vanadium pentoxide are rod-shaped with a tendency to form twin-particles, whilst those of ferric hydroxide are disc-shaped.

J. S. C.

**Photographic Gelatin.** S. E. SHEPPARD (*Phot. J.*, 1925, **65**, 380—387).—The very high speed of photographic emulsions is primarily due to the presence of small amounts of foreign substances in the gelatin. The sensitising properties of certain gelatins are due to the presence of traces of organic thiocarbimides and thiocarbamides, viz. allylthiocarbimide and allylthiocarbamide. The sensitiser can be extracted from gelatin deliming liquors by precipitating alumina in the solution, drying the precipitate, and then extracting with alcohol, ether, or light petroleum; also from mustard seeds, and the seeds and hulls of beans, peas, and cereals, and from lucerne. The sensitiser is carried over with the cholesterol. Photographically active gelatins contain 1 part in a million to 1 part in 300,000 of the sensitiser, which is probably present as both thiocarbimide and thiocarbamide. Under fixed conditions the sensitising effect reaches a maximum for a definite amount of sensitiser, further addition resulting in a decrease of sensitivity and an increase in fog. The formation of "sensitivity centres" is due to conversion of the thiocarbimide into thiocarbamide in presence of ammonia, and the reaction of the thiocarbamide with the silver halides to form nuclei of silver sulphide, which is the material of the "sensitivity centres." Silver selenide and silver telluride behave in the same way. The results are in harmony with the author's "orientation" theory of photographic sensitivity. [Cf. B., 1925, 785.]

W. C.

**Effect of Water on Dried and Pressed Silica Gel.** I. S. S. BHATNAGAR, M. PRASAD, and D. D. OHRI (*Kolloid-Z.*, 1925, **37**, 97—101).—The decrepitation of pressed anhydrous silica gels on wetting with water, salt solutions (*e.g.*, sodium chloride and silicate), and organic liquids (*e.g.*, ether, benzene) is accompanied by practically no temperature change, indicating that the phenomenon cannot be due to chemical action or to solution. It must therefore be due to the pressures set up on the walls of the capillaries of the gel caused by adsorption of liquid. A blue opalescence accompanies the adsorption of water by the powdered gel. The effect is quite different from the Pouillet effect since the latter is accompanied by a temperature rise (cf. Bhatnagar and Mathur, *ibid.*, 1922, **33**, 368).

S. K. T.

**Temperature of Swelling of Starch Granules.** W. ARZICHOWSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1918, [6], 349—368; from *Chem. Zentr.*, 1925, i, 2543).—The swelling of starch granules was studied microscopically, using a statistical method. Swelling begins at 55°; at 67·5° it is practically complete. The mean temperature of complete swelling of individual granules is  $60\cdot97 \pm 0\cdot10^\circ$ . The distribution about this mean value only follows Gauss' law of error as a first approximation. The frequency curve is asymmetrical, but there is no indication of the occurrence of two kinds of granules.

G. W. R.

**Liquefaction of Starch Paste.** P. PETIT (*Compt. rend.*, 1925, **181**, 259—260).—Soluble starch is readily obtained by adding to a 2% starch paste (150 g.) 10 c.c. of a solution containing sodium chloride (7 mg.), potassium hydrogen phosphate (5 mg.), and lactic acid (2 mg.). The reaction may be carried out in presence of toluene or ether. The product does not reduce Fehling's solution and has a specific rotation of 195°. Very slight alterations in the amount of lactic acid may retard or stop the reaction. With slow reactions a flocculent deposit is formed, containing silica and alumina. This deposit is not obtained when the operation is conducted in pyrex glass, or in the absence of mechanical agitation. The deposition and clarification can be accelerated by the addition of traces of alkali or lactic acid, or of sodium silicate and lactic acid. R. B.

**Action of Alkalis on Konyaku Colloid.** S. DOKAN (*Kolloid-Z.*, 1925, **37**, 73—78).—Barium and calcium hydroxides depress the viscosities of Konyaku sols to a much greater extent than the hydroxides of sodium and potassium. The same applies to the action of the chlorides of these metals on slightly alkaline sols; the effect in the case of the alkaline-earth chlorides increases with time. Cataphoresis experiments indicate practically no charge on the colloid in acid and neutral solutions and only a weak negative charge in alkaline solution. These conflicting results are explained on the assumption that the calcium, for example, in the colloid, which cannot be obtained ash-free, reacts with the carbonate in the alkali to form calcium carbonate, which then forms a layer over the colloid particles. In acid solutions, this layer is not formed, so that, indirectly, the observed effects are attributable to hydroxide ions. Measurements of the adsorption of Konyaku by crystalline barium carbonate, prepared *in situ* and added externally, support this explanation.

S. K. T.

**Kinetics of the Sol-Gel Transformation of Concentrated Ferric Oxide Sols.** H. FREUNDLICH and A. ROSENTHAL (*Kolloid-Z.*, 1925, **37**, 129—131).—By reducing the velocity of the sol-gel transformation of concentrated iron oxide sols (cf. Schalek and Szegvary, A., 1923, ii, 423) by the addition of glycine, alanine, and similar substances it has been possible to study the kinetics of the process and to show that it resembles that of coagulation. The glycine etc. do not act as protective colloids in the ordinary sense, but increase the charge on the particles.

N. H. H.

**Kinetics of the Swelling and Shrinking of Gels. II.** S. LIEPATOV (*Kolloid-Z.*, 1925, **37**, 146—150).—The influence of various factors on the velocity of swelling of glue in water has been studied. The velocity is a function of the thickness of the gel; surface and weight play a secondary part. Van Bemmelen's view of the enormous mobility of water in colloids is supported. The swelling can be regarded as the first stage of solution, *i.e.*, peptisation. Temperature and electrolytes have a great influence on the swelling velocity. N. H. H.

**Emulsifying Power of Sodium Stearate and Sodium Palmitate.** N. A. YAJNIK and B. ILAHI (*Kolloid-Z.*, 1925, **37**, 139—144).—The emulsifying power of sodium stearate and sodium palmitate towards cotton-seed, poppy-seed, mustard, coconut, sesamé, and olive oils has been measured at 80°. The curves connecting oil concentration with the concentration of soap just required for emulsification are of the same type. With increasing oil concentration the soap concentration increases, at first rapidly and then more slowly, until an oil concentration of 20—40% (by volume), depending on the oil, is reached, when a more rapid increase suddenly occurs for which no explanation can be offered. This effect is most marked with cotton-seed and poppy-seed oils. In all cases, the concentration of sodium palmitate required for emulsification is less than that of sodium stearate, in agreement with the fact that soap solutions have a greater emulsifying power, the lower the surface tension. The results show that emulsifying power has an important influence in determining cleansing properties. N. H. H.

**Action of Protective Colloids.** J. TRAUBE and E. RACKWITZ (*Kolloid-Z.*, 1925, **37**, 131—138).—Traube's concept of "clinging intensity" between a solvent and dissolved substance is extended to colloids and in particular to coagulation and protective action. The magnitude of this quantity is large for lyophile and small for lyophobic colloids. In considering protective action, three clinging intensities come into question, namely, that between the protected substance and water, that between the protecting substance and water, and that between the protected and protecting substances. Since surface-active substances have a smaller clinging intensity towards water than surface-inactive substances, it is to be expected that the former would exert a smaller protective effect on a lyophobic colloid than would the latter. To test this theory the "protection numbers" of gelatin, gum arabic, egg-albumin, dextrin, soap, sodium stearate, saponin, and sodium cholate with reference to the sols of gold, silver, carbon, ferric hydroxide, Prussian-blue, sulphur, and arsenious sulphide have been determined by the Zsigmondy gold number method. With gold, silver, and carbon sols the order of the protection numbers is the same. Surface-inactive colloids such as gelatin are much more effective protectors than surface-active substances such as saponin. Ferric hydroxide sol gives almost the same order of protection numbers. Prussian-blue, sulphur, and

arsenious sulphide, which have small clinging intensities towards water, are on the other hand very differently affected. Here the surface-inactive colloids fall, in general, into the same order as with the gold etc. sols, but the surface-active substances are in many cases as good or better protectors. These observations are generally in accord with the theory.

A new method for the study of protective action is described, which differentiates sharply between surface-active and inactive substances. It depends on the fact that if a gold hydrosol containing a suitable quantity of a surface-inactive substance such as gelatin be shaken with chloroform, the latter forms an emulsion, containing the whole of the gold, under the water layer. If a surface-active colloid such as saponin be used, an emulsion is formed, but no gold is withdrawn from the hydrosol. In the first case, the gelatin, being a good protector for gold, surrounds the gold particles which are carried to the chloroform when the emulsion is formed. In the second case, the saponin, having a low clinging intensity towards gold, surrounds the chloroform drops only, leaving the gold in the hydrosol.

N. H. H.

#### **Influence of Added Substances on the Life of Dispersoids.**

I. P. P. VON WEIMARN (*Kolloid-Z.*, 1925, 37, 151—158).—A general theoretical treatment. Curves are drawn showing the dependence of the life period on the concentration of added substance and some experimental evidence is brought forward in support of them. The treatment is based on the author's views relative to the part played by electrical energy, the existence of free ions, and the nature of adsorptive power, which are: (i) that electrical energy plays no outstanding part in determining the life of dispersoids: it is only one of the many variables which influence this; (ii) that completely free ions do not exist, but that the ions adsorbed by the colloid particles are strongly solvated molecules with greatly weakened linkings between the atoms or atom groups; (iii) that the difference between adsorptive power and chemical affinity is one of intensity only.

N. H. H.

**Joule Effect in Rubber.** L. HOCK (*Z. Elektrochem.*, 1925, 31, 404—409; cf. Freundlich and Hauser, *B.*, 1925, 514).—Against the view that the heating which takes place when rubber is stretched is due to heat of compression of a liquid phase, it is pointed out that stretched raw rubber retains its extension permanently at 20° and under, which it could scarcely do in presence of a compressed liquid. The heat of extension is ascribed to the enforced orientation of the rubber particles into crystalline fibres, with accompanying disengagement of the heat of crystallisation. It is shown that frozen stretched rubber actually breaks up into fibres under the hammer, whereas if frozen before stretching it breaks up like glass.

W. A. C.

**Cause of Characteristic Extensibility of Rubber. II. Joule Effect and Formation during Stretching of a Three-dimensional Structure.** J. R. KATZ (*Kolloid-Z.*, 1925, 37, 19—22; cf. *B.*, 1925, 557).—Further observations on the X-ray

spectrogram of stretched rubber make it highly probable that the crystalline substance is formed during the stretching and is not present in unstretched rubber. In stretched and twisted rubber the X-ray spectrogram corresponds with a spiral arrangement of crystallites as in cotton and other cellulose fibres. The stretching involves the formation of a three-dimensional lattice and not simply the arrangement of molecules in the same direction. The heating of rubber on stretching is regarded as strictly analogous with the liberation of heat on the crystallisation of an amorphous substance. Joule's data are shown to be in harmony with the author's interpretation of the X-ray spectrograms. The relationships between extension and tension and between extension and optical anisotropy are also explained.

E. M. C.

**Kinetic Theory of Compressibility of Solutions and Binary Liquid Mixtures.** K. C. KAR (*Physikal. Z.*, 1925, 26, 465—467).—Theoretical. By a statistical method equations are derived giving the connexion between the compressibility of solutions and liquid mixtures and their composition. For solutions, the equation  $\beta_x(1+x)^2=\beta_0$  holds, where  $\beta_x$  and  $\beta_0$  are the compressibilities of the solution and the solvent, respectively, and  $x$  is the concentration. For both solutions and liquid mixtures, the compressibility curves have the same form as the corresponding vapour-pressure curves. The calculated values of the compressibilities agree approximately with the experimental values.

F. G. T.

**Inter-ionic Attraction Theory of Ionised Solutes. III. Testing of the Theory in Alcoholic Solvents.** A. A. NOYES and W. P. BAXTER (*J. Amer. Chem. Soc.*, 1925, 47, 2122—2129).—The activities of ionised solutes, calculated from the *E.M.F.* of certain cells involving alcoholic solutions of lithium and hydrogen chlorides and sodium ethoxide, are shown to be in agreement with the inter-ionic attraction theory. The results show that the logarithm of the activation is inversely proportional to  $\kappa^{3/2}$ , where  $\kappa$  is the dielectric constant of the solution, as is required by theory. The numerical coefficients expressing the relationship between activation and its parameters have values 30% to 25% lower than the theoretical values, even at concentrations as low as 0.01*N*, but as the concentration decreases they tend towards the theoretical limiting value.

S. K. T.

**Inter-ionic Attraction Theory of Ionised Solutes. IV. Influence of Variation of Dielectric Constant on the Limiting Law for Small Concentrations.** P. DEBYE and L. PAULING (*J. Amer. Chem. Soc.*, 1925, 47, 2129—2134).—Consideration of Debye and Hückel's theory indicates that the variations in the dielectric constant of the solution,  $\kappa$ , in the immediate neighbourhood of an ion do not affect the limiting equation for zero concentration. Correct values for the coefficient in this equation are obtained by substituting for  $\kappa$  the value for the pure solvent. The smaller numerical coefficients sometimes found can only be attributed to

variations in  $\kappa$  if it is assumed that the solutions are still too concentrated for the applicability of the limiting equation.

S. K. T.

**Activity of Strong Electrolytes. IV. Application of the Debye-Hückel Equation to Alcoholic Solutions.** G. SCATCHARD (*J. Amer. Chem. Soc.*, 1925, **47**, 2098—2111).—The Debye-Hückel equation for the activities of ions of strong electrolytes is shown to fit the data for the observed *E.M.F.* of the cell  $\text{Pt}(\text{H}_2)|\text{HCl}, \text{AgCl}|\text{Ag}$  in water, alcohol, and 50 mol. % alcohol, up to at least *N*-concentrations. Further confirmation is found in *E.M.F.* measurements on lithium chloride solutions in ethyl and methyl alcohols and in water and also in the solubilities of sodium chloride in aqueous ethyl alcohol. The variation in the activities of the ions of hydrochloric acid in ideally dilute solutions in different solvents indicates the formation of the ion  $\text{H}_3\text{O}^+$  in water. In dilute alcoholic solutions (negligible hydration) the activity change is more than twice as great for potassium chloride as for hydrogen chloride: this makes it improbable that equal changes in activity for the potassium and chloride ions occur with changing salt concentration in a single solvent. Data and methods are given for calculating the activities of the ions of hydrogen and sodium chlorides in any mixture of alcohol and water.

S. K. T.

**Freezing Points of Glycerol and its Aqueous Solutions.** L. B. LANE (*Ind. Eng. Chem.*, 1925, **17**, 924).—The f. p. of mixtures of glycerol and water have been determined. The lowest temperature,  $-46.5^\circ$ , corresponds with a mixture containing approximately 33% of water. [Cf. *B.*, 1925, 826.]

D. G. H.

**Solubility and Freezing-point Curves of Hydrated and Anhydrous Orthophosphoric Acid.** W. H. ROSS and R. M. JONES (*J. Amer. Chem. Soc.*, 1925, **47**, 2165—2170).—The solubility and f. p. curves of aqueous phosphoric acid solutions offer no evidence of the existence of a decahydrate (Smith and Menzies, *A.*, 1909, ii, 998). The eutectic points of ice and the hemihydrate (m. p.  $29.32^\circ$ ) and of the hemihydrate and anhydrous acid (m. p.  $42.35^\circ$ ) correspond with  $-85.0^\circ$  and  $23.50^\circ$  and with concentrations of 62.5 and 94.75 g. of anhydrous acid per 100 g. of saturated solution, respectively. The anhydrous acid crystallises 13 times as fast as the hydrated form at  $20^\circ$ .

S. K. T.

**Freezing-point Curve of Aqueous Sodium Nitrite Solutions.** H. HELBERG (*Ann. Chim.*, 1925, [x], **4**, 121—125).—Oswald's determination of the f. p. of sodium nitrite solutions, which fall on an uneven curve, are criticised and repeated. A smooth curve is obtained corresponding with lower freezing temperatures than those found by Oswald. The cryohydric point is  $-26^\circ$ , the corresponding nitrite concentration being 38%. The present results give normal figures for the molecular f. p. depression of the solutions (cf. Oswald, *A.*, 1914, ii, 197; Sidgwick and Ewbank, this vol., ii, 38).

S. K. T.

**Stability of Additive Compounds between Esters and Acids.** J. KENDALL and J. E. BOOGE (*J. Chem. Soc.*, 1925, 127, 1768—1777).—From the depression of the f. p. of the additive compounds produced by benzene, water, and by one of the constituent compounds, the degrees of dissociation of three ester-acid additive compounds at their m. p. have been derived: For ethyl acetate-trichloroacetic acid (m. p.  $-26.8^{\circ}$ ) the dissociation is 12%, for benzyl benzoate-trichloroacetic acid (m. p.  $13.6^{\circ}$ ) 35%, and for methyl succinate-trichloroacetic acid (m. p.  $8.3^{\circ}$ ) 4—6%. The molecular heats of fusion of the three compounds are 5170, 5660, and 9600 cal., respectively. The f. p. depression curves given by water and benzene are almost identical owing to internal pressure differences masking the greater decomposition produced by the water. In dilute benzene solution at temperatures slightly above  $0^{\circ}$ , the compound ethyl acetate-trichloroacetic acid is still markedly stable, and even the weak complex ethyl acetate-acetic acid is not entirely decomposed. W. H.-R.

**Additive Compounds in the Ternary System : Ester-Acid-Water.** J. KENDALL and C. V. KING (*J. Chem. Soc.*, 1925, 127, 1778—1791; cf. preceding abstract).—Measurements of f. p., conductivity, and velocities of hydrolysis have been made for the binary systems acid-water, ester-water, and also for the ternary systems water, ethyl acetate, and hydrochloric, trichloroacetic, chloroacetic, or acetic acids, respectively. Ethyl acetate gives a "pseudo ideal" f. p. depression curve in aqueous solution, indicating that extensive hydration occurs, but the effect of this is marked by internal pressure differences. No appreciable quantity of ester-acid complexes remains undecomposed in aqueous solution. The conductivities of both neutral salts and acids are lowered by the addition of ethyl acetate owing to diminished ionic mobility. The solubility of ethyl acetate in water at  $0^{\circ}$  varies very greatly when electrolytes are also present. The rate of hydrolysis of ethyl acetate in the presence of hydrochloric acid in equivalent quantity increases more rapidly than the molecular concentration of the acid, but with weaker acids the increase is less rapid, and with acetic acid a maximum rate exists near the saturation point. W. H.-R.

**Formation of Martensite in Carbon Steels.** K. HONDA (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, 14, 165—172).—During the cooling of austenite through the A1 point, the atomic configuration of the iron changes from the face-centred  $\gamma$  form to the body-centred  $\alpha$  form, and as this form of iron has only a very small power of dissolving carbon the carbon separates from the interspace of the lattice as cementite. If this separation is suppressed by quenching, martensite is produced at temperatures below  $300^{\circ}$ , but the further change to pearlite does not occur owing to the great viscosity of the metal at these low temperatures. As martensite is harder than austenite or pearlite, maximum hardness of the specimen will be obtained only when the quenching is so conducted that all the austenite has changed to martensite, whilst the further change to pearlite is completely arrested. It is suggested that the hardness

of martensite is due to the bracing action of the carbon atoms distributed in the faces of the elementary lattice cubes of  $\alpha$ -iron. [Cf. *B.*, 1925, 722.] A. R. P.

### Equilibrium Diagram of the Iron-Carbon-Nickel System.

T. KASE (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, 14, 173—217).—The iron-nickel binary system consists of a continuous series of solid solutions with a break between 15% and 30% Ni; the A3 point in iron is lowered continuously by the addition of nickel and coincides with the A2 point at about 5% Ni on cooling and 10% Ni on heating. Nickel dissolves 0.55% C at 1300°, but only 0.25% C at 20°, and this solid solution forms a eutectic with carbon which contains 2.22% C and melts at 1318°. The ternary system iron-carbon-nickel contains no ternary eutectic, but a binary eutectic of iron-nickel solid solution and carbon, the carbon content of which decreases as the nickel content increases. The sum of the combined and total carbon in iron-nickel alloys decreases with increasing quantities of nickel to a constant value of 0.3% C with 30% or more Ni, whilst the A1 point of iron is lowered by nickel, eventually disappearing with 10% Ni. [Cf. *B.*, 1925, 724.] A. R. P.

$\beta$ -Transformations in Copper-Zinc Alloys. J. L. HAUGHTON and W. T. GRIFFITHS (*J. Inst. Metals*, Sept. 1925, advance copy, 9 pp.).—A sudden and marked decrease in the temperature coefficient of the electrical resistance of copper-zinc alloys takes place at the transformation temperature. As this varies from 453° to 470° between 55% and 51% Cu, the authors consider that this transformation is not eutectoidal (cf. Andrew and Hay, ii, 954). Electrical resistance measurements confirm Genders and Bailey's delineation of the  $\beta$ -phase boundaries (this vol., ii, 297). A. R. P.

$\alpha$ -Phase Boundary in the Copper-Tin System. D. STOCKDALE (*J. Inst. Metals*, Sept. 1925, advance copy, 9 pp.).—The  $\alpha$ -phase in the copper-tin system is bounded by the solidus, which is a smooth curve connecting the m. p. of copper to the triple point at 799° (13.3% Sn), by a straight line connecting this point to the triple point at 518° (16.0% Sn) and then by a line parallel to the temperature axis. The  $\beta$ -phase undergoes a polymorphic transformation at 590°. [Cf. *B.*, 1925, 809.] A. R. P.

Equilibrium at High Temperatures in the Iron-Carbon-Silicon Systems. M. L. BECKER (*J. Iron and Steel Inst.*, Sept., 1925, advance copy, 13 pp.).—As the silicon content of iron-carbon-silicon alloys increases up to 4.0%, the solubility of carbon at any constant temperature between 1100° and 940° decreases, whilst the effect of temperature in raising the solubility becomes less marked. Below 940° the solubility drops rapidly to zero, probably in the neighbourhood of 920°. [Cf. *B.*, 1925, 806.]

M. E. N.

### Iron-Nickel and Iron-Cobalt Equilibrium Diagrams.

L. GRENET (*J. Iron and Steel Inst.*, Sept. 1925, advance copy, 9 pp.).—The author postulates the existence of "limited states" between the



$\alpha$ - and  $\gamma$ -phases and shows how a diagram based on this idea may be used to relate the  $\alpha$ - $\gamma$  transformation and the magnetic transformation and also to explain anomalies of dilatation and density at different temperatures. [Cf. *B.*, 1925, 808.] M. E. N.

**Constitution of Alloys of Aluminium, Copper, and Zinc.** D. HANSON and M. L. V. GAYLER (*J. Inst. Metals*, Sept. 1925, advance copy, 45 pp.).—The five invariant points found by Jares (*Z. Metallk.*, 1919, **10**, 1) in the aluminium-copper-zinc system are confirmed, but the reaction at  $406^\circ$  is found to be  $\text{liq.} + (\text{CuAl}) \rightleftharpoons \beta + (\text{CuZn}_4)$ . In addition, two new invariant points have been found due to reactions taking place in the solid state. These occur at  $265^\circ$  and  $270^\circ$  and are due to the invariant reactions,  $\beta + [\text{CuZn}_4] \rightleftharpoons [\text{CuAl}] + [\text{Zn}]$  and  $\beta + [\text{CuAl}_2] \rightleftharpoons [\text{CuAl}] + [\text{Al}]$ , respectively. Copper depresses the temperature of the  $\beta$ -transformation in aluminium-zinc alloys until the presence of CuAl causes it to take place at a constant temperature,  $245^\circ$ . [Cf. *B.*, 809.]

A. R. P.

**Equilibrium of the System Cryolite-Alumina.** G. A. ROUSH and M. MIYAKE (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 99—103).—The eutectic temperature is  $935^\circ$ , corresponding with 18.5% of alumina. The solubility of alumina in cryolite in solid solution extends to about 12% and that of cryolite in alumina to about 77.5%. These results were confirmed by metallographic observations. Pure cryolite melts at  $995^\circ$  (cf. Pascal and Jouniaux, A., 1913, ii, 508). S. K. T.

**Equilibria in Molten Salts. (Reactions between Molten Alloys of the Alkalis and Alkaline-earths and their Molten Chlorides.)** K. JELLINEK and J. WOLFF (*Z. anorg. Chem.*, 1925, **146**, 329—387).—The equilibria between molten binary mixtures of alkali or alkaline-earth chlorides and molten alloys of the corresponding metals with a third metal have been investigated (cf. A., 1924, ii, 658; this vol., ii, 123, 124). The alloy was formed by electrolysis, using the third metal as cathode and a carbon anode. The temperature being maintained between  $900^\circ$  and  $1200^\circ$ , the mixture was electrolysed until an alloy of suitable concentration was obtained (0.5 to 2.5 hrs. with 6 to 14 amp.). The current was then discontinued, the crucible allowed to cool, and the mass of mixed salts and the alloy analysed. Results which show that the variation of the equilibrium with the temperature is negligible have been obtained for the following equilibria: in lead:  $\text{Ba} + \text{CaCl}_2 \rightleftharpoons \text{BaCl}_2 + \text{Ca}$ ; in tin:  $\text{Ba} + 2\text{KCl} \rightleftharpoons \text{BaCl}_2 + 2\text{K}$ ;  $\text{Ba} + 2\text{NaCl} \rightleftharpoons \text{BaCl}_2 + 2\text{Na}$ ; in antimony:  $\text{Ba} + 2\text{KCl} \rightleftharpoons \text{BaCl}_2 + 2\text{K}$ ;  $\text{Ba} + 2\text{NaCl} \rightleftharpoons \text{BaCl}_2 + 2\text{Na}$ ;  $\text{Sr} + 2\text{NaCl} \rightleftharpoons \text{SrCl}_2 + 2\text{Na}$ ;  $\text{Ca} + 2\text{NaCl} \rightleftharpoons \text{CaCl}_2 + 2\text{Na}$ ; in bismuth:  $\text{Ba} + 2\text{KCl} \rightleftharpoons \text{BaCl}_2 + 2\text{K}$ ;  $\text{Ba} + 2\text{NaCl} \rightleftharpoons \text{BaCl}_2 + 2\text{Na}$ ;  $\text{Ca} + 2\text{NaCl} \rightleftharpoons \text{CaCl}_2 + 2\text{Na}$ .

The equilibria are to a large extent independent of the cathode metal employed. Taking the alkali metals as diatomic, the alkali chlorides as double molecules, the alkaline-earth metals as mon-

atomic, and their chlorides as simple molecules, it is shown that the law of mass action and Nernst's partition theorem lead to a value for the equilibrium constant which expresses the results at least to a first approximation. Thus in the equilibrium  $\text{Ba} + 2\text{NaCl} \rightleftharpoons \text{BaCl}_2 + 2\text{Na}$ , the constant is given by  $(\text{At.}\% \text{Na} \cdot \text{Mol.}\% \text{BaCl}_2) / (\text{At.}\% \text{Ba} \cdot \text{Mol.}\% \text{NaCl})$ , and the values obtained, with antimony as the cathode metal, are 0.20, 0.13, 0.12, and 0.15. The same equilibrium with bismuth as cathode metal gives values 0.22 and 0.23. The results are compared and shown to be in accord with those of G. McP. Smith on equilibria between amalgams of sodium, potassium, and strontium and aqueous solutions of their chlorides. The effect of association and dissociation of the molten salts as well as of the metals in the alloys is discussed. A more rigid theory of the equilibria is developed (cf. Lorenz, A., 1924, ii, 484), but cannot be fully tested owing to lack of numerical data. The equilibria can be calculated approximately from thermodynamical considerations based on the difference of the heats of formation of the solid chlorides. The normal potentials between the alloys and the molten salts are calculated and the theory of the electrolysis of ternary metallic alloys is discussed. A. B. M.

**In-, Uni-, and Multi-variant Equilibria. XXIX. Influence of One or More New Substances on an Equilibrium in which a Phase Reaction may Occur.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 252—261).—A mathematical treatment of various cases which may arise from the addition of new components to a system in equilibrium. S. I. L.

**Equilibria in Systems with Phases Separated by a Semi-permeable Membrane. VI and VII.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 231—242, 243—251).—VI. The osmotic water attractions of various systems separated by a membrane from a second system are derived mathematically from the changes in the thermodynamic potentials which accompany the passage of small quantities of liquid through the membrane. From a discussion of cases in which one of the systems consists only of solids, it is deduced that all solutions, which can exist in equilibrium with a system of solid substances in which a phase-reaction may occur by the addition or removal of the diffusing substance, have the same osmotic water attraction and are isotonic. Special cases dealt with in preceding papers are discussed in the light of the general treatment.

VII. When two systems are in osmotic equilibrium with respect to  $d$  diffusing substances, the osmotic solvent attractions of the two for each such substance are equal. Since the phase law is valid for each system separately, it follows that the number of degrees of freedom is the sum of the freedoms of each, less  $d$ , i.e., if  $n_1, n_2$  be the components, and  $v_1, v_2$  the phases for the two systems, respectively, the freedom of the two in osmotic equilibrium is  $n_1 + n_2 - (v_1 + v_2) + 2 - d$ ; this constitutes the membrane-phase-rule. A number of special cases are considered. S. I. L.

**Heats of Solution of Enantiotropic Modifications (of Ammonium Nitrate) at the Transition Point.** E. COHEN and H. L. BREDÉE (*Z. physikal. Chem.*, 1925, **117**, 143—155; cf. this vol., ii, 23).—Further determinations have been made of the solubility of ammonium nitrate III and IV between 33° and 48° and 0° and 32°, respectively, and of the specific volumes of solutions saturated with ammonium nitrate III at 50°. The results obtained are not in agreement with those of Mondain-Monval (*A.*, 1923, ii, 635; this vol., ii, 654), and his proof of Le Chatelier's tangent law is therefore invalid. L. F. G.

**Heats of Solution and Dilution of Salts.** J. WÜST and E. LANGE (*Z. physikal. Chem.*, 1925, **117**, 336).—Amendments to a previous paper (this vol., ii, 791). The correctness of Richards and Rowe's method of calculating heats of dilution is now upheld. L. F. G.

**Measurement of Very High Electrolyte Resistances by Kohlrausch's Method.** H. ÜLICH (*Z. physikal. Chem.*, 1925, **117**, 156).—An amplification of the statements made in a previous paper (this vol., ii, 671) concerning the method of Lorenz and Klauer. L. F. G.

**Conductivity of Acids of Medium Strength in Methyl Alcohol, and their Catalytic Action.** H. GOLDSCHMIDT and H. AARFLOT (*Z. physikal. Chem.*, 1925, **117**, 312—333; cf. *A.*, 1924, ii, 825; this vol., ii, 128).—A detailed investigation of the conductivities, degrees of ionisation, affinity constants, and activity constants of trichloroacetic, trichlorobutyric, and picric acids in absolute and in aqueous methyl alcohol solutions. On the assumption that catalytic activity is proportional to hydrogen-ion concentration, theoretical values based on Bjerrum's theory are obtained for the effect of these acids on the velocity of various esterifications in methyl alcohol solutions. These values agree with those actually observed. This, however, is not the case when ethyl alcohol is the solvent. L. F. G.

**Conductance by Metallic Colloids and its Electro-technical Applications.** H. ANDRÉ (*Compt. rend.*, 1925, **181**, 243—244).—When concentrated sulphuric acid is electrolysed by alternating current between silver electrodes, the resistance of the liquid decreases progressively with the electrolysis, and a colloidal solution of silver, showing Brownian movement, is produced. Similar results are obtained with orthophosphoric acid and also by the use of graphite in place of silver. Used in conjunction with a non-oxidisable metal cathode, the electrode of colloidal silver is a convenient depolarising agent. With a current density of 1—2 amp./cm.<sup>2</sup> at 40—60°, the following effective potentials are attained: copper, 8 volts; nickel, 16; ferronickel (50%), 18; soft iron, 25; ferrosilicon, 35; silicon, 80 volts. A thermal effect is observed on drying the colloids. The current is established at 300—400°, but ceases on cooling. R. B.

**Separation of Rare Earths by the Ionic Migration Method.** J. KENDALL and B. L. CLARKE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 393—400).—The technique devised in the attempted separation of isotopes by the ionic migration method has been developed and applied to the separation of mixtures of rare earths. A 2% agar-agar gel containing a given mixture (0.5*N*) is placed in a long glass tube, between similar gels containing a faster cation ( $K^+$ ), nearer the cathode and a slower cation ( $Cr^{++}$ ) nearer the anode. On electrolysis, the more mobile rare earth cation accumulates in the forward portion of the sample. The gel is cut into slices and analysed. Three typical pairs of binary mixtures were studied: yttrium-erbium, neodymium-praseodymium, gadolinium-samarium. In the first pair, a mixture containing 27.5% of yttrium yielded in 14 days extreme samples of 97.1% and 21.2%. In 21 days, with a longer tube, the purest fraction contained 99% of yttrium. In all three mixtures a very considerable degree of separation was effected.

The experiments could be followed by direct-vision absorption spectra, or by conductivity and refractivity measurements. The technique is being applied to hafnium-zirconium and rubidium-potassium mixtures.

R. A. M.

**Migration of Ions in Solid Electrolytes.** M. LE BLANC and M. KRÖGER (*Z. Elektrochem.*, 1925, **31**, 359—360).—Controversial in reply to Tubandt (*ibid.*, 1924, **30**, 253).

W. A. C.

**Hydrogen and Oxygen Electrode Titrations of Some Dibasic Acids and of Dextrose.** H. T. S. BRITTON (*J. Chem. Soc.*, 1925, **127**, 1896—1917).—Approximately 0.025*M*-solutions of oxalic, tartaric, succinic, and malonic acids were titrated electrometrically at 18° with 0.1*N*-sodium hydroxide solution, the  $p_H$  values being determined with a hydrogen electrode. New formulæ are derived for the calculation of dissociation constants of dibasic acids from any two points on the titration curve. These are more accurate than the formulæ given by Auerbach and Smolczyk (this vol. ii, 118), and the relation  $K_1K_2=h^2$ , where  $h$  is the hydrogen ion concentration at the mid point of the titration curve, is inconsistent with the author's data. The following dissociation constants are recorded: oxalic acid,  $K_1=0.17$ ,  $K_2=1.34 \times 10^{-4}$ ; tartaric acid,  $K_1=1.27 \times 10^{-3}$ ,  $K_2=9.65 \times 10^{-5}$ ; succinic acid,  $K_1=9.21 \times 10^{-5}$ ,  $K_2=5.30 \times 10^{-6}$ ; malonic acid,  $K_1=2.02 \times 10^{-3}$ ,  $K_2=4.41 \times 10^{-6}$ . A solution of dextrose, similarly titrated with sodium hydroxide, gave for the first dissociation constant  $K=[H^+][C_6H_{11}O_6]/[C_6H_{12}O_6]=5.77 \times 10^{-13}$ . Attempts made to use an oxygen electrode for similar titrations show that the results are complex and not reproducible with different electrodes.

W. H.-R.

**Thermodynamics of Solutions of Simple Electrolytes.** H. S. HARNED (*Z. physikal. Chem.*, 1925, **117**, 1—50; cf. A., 1916, ii, 597; 1920, ii, 664; 1922, ii, 255; 1923, ii, 115).—The thermodynamics of the activity function is discussed. An apparatus for

measuring the *E.M.F.* of cells having streaming alkali-amalgams as liquid junctions is described (cf. Knobel, A., 1923, ii, 116); it was employed with the following systems at 25°:  $\text{H}_2|\text{NaOH}(c_2)|\text{Na}_x\text{Hg}|\text{NaOH}(c_1)|\text{H}_2$ ,  $\text{H}_2|\text{NaOH}(c_1), \text{NaCl}(c)|\text{Na}_x\text{Hg}|\text{NaOH}(c_1)|\text{H}_2$ ,  $\text{H}_2|\text{KOH}(c_1), \text{KCl}(c)|\text{K}_x\text{Hg}|\text{KOH}(c_1)|\text{H}_2$ . From the data obtained in this and earlier work, the activity coefficients of sodium hydroxide in sodium chloride solutions, of potassium hydroxide in potassium chloride solutions, and of water in potassium chloride and sodium chloride solutions were calculated. Further calculations give the degree of ionisation of water in sodium chloride and in potassium chloride solutions. With increasing salt concentration, the degree of ionisation of water at first increases rapidly, but soon attains a maximum, after which it decreases (cf. Schreiner, this vol., ii, 96). The individual properties of simple ions in concentrated solutions are discussed in the light of these results and of the theory of Debye and Hückel. L. F. G.

**Thermodynamics of Quinhydrone Electrodes. Chemical Constants of Hydrogen.** E. SCHREINER (*Z. physikal. Chem.*, 1925, 117, 57—87).—The total and free heat contents of benzoquinone, quinol, quinhydrone, and hydrogen, between 10° and 300° Abs., are calculated from published data for the molecular heats of these substances. The electromotive forces of the cells quinol–quinhydrone|hydrogen and benzoquinone–quinhydrone|hydrogen, using *M*-sulphuric acid as the common electrolyte, were measured at different temperatures. Corrections are made for neutral substance effect. Measurements were made of the solubilities and heats of solution of benzoquinone and quinol and the heats of combustion of benzoquinone, quinol, and quinhydrone. From the above data the affinities and heats of the reactions involved were determined. The heats of reaction calculated from calorimetric data agree, within the limits of error, with those calculated from electrometric data. The quinhydrone electrode is regarded as an unsaturated benzoquinone–quinol electrode and its constants are determined on that basis. Values for the true and the normal chemical constants of hydrogen were obtained agreeing approximately with those put forward by other investigators. L. F. G.

**Electrode Vessel for Liquids Heavier and Lighter than the Liquid Junction Potential Eliminator.** L. E. DAWSON (*J. Amer. Chem. Soc.*, 1925, 47, 2172—2173).—A form of apparatus is described which facilitates the use of solutions of different densities in potential measurements. S. K. T.

**Turgoelectricity.** W. KOPACZEWSKI (*Compt. rend.*, 1925, 181, 244—246).—The addition of water to a number of powders, hydrosols, and hydrogels under defined conditions produces displacements in a capillary electrometer. With emulsoid hydrosols such as inulin, dextrin, fibrin, glycogen, and with fine powders such as animal charcoal, kaolin, flowers of sulphur, there is little or no displacement, whereas the swelling of gels such as mucin, gelatin,

gum arabic, etc., or the process of jellification, *e.g.*, the addition of water to ethyl salicylate, or of acetic acid to aluminium hydroxide, gives rise to pronounced displacements in the electrometer. These movements are regarded as the manifestation of a new kind of electricity, turgoelectricity, produced by the rupture of the external layer of the molecules of water, causing the fall of potential observed. The hydrogel lattice acquires a negative charge, the dispersed liquid becomes positively charged (*cf.* this vol., ii, 529). R. B.

### Passage of an Alternating Current through Sulphuric Acid.

R. T. LATTEY (*Phil. Mag.*, 1925, [vi], **50**, 444—453).—The effective resistance and the capacity of a pair of platinum electrodes immersed in a solution of sulphuric acid of maximum conductivity have been measured for alternating currents of periodicity varying from 25 to 500. The resistance is regarded as made up of  $r$ , the resistance of the electrolyte, and  $S$ , the resistance in the surface layers of the electrodes. The variation of the capacity and of  $S$  with periodicity has been investigated for electrodes platinised in different ways and for bright electrodes. The most consistent results were obtained with electrodes coated with pure platinum, electrodes otherwise treated behaving more or less erratically. The relation between capacity  $C$  and periodicity  $p$  is expressed by  $pC = A + pB$ , and that between  $S$  and  $p$  by  $pS = D$ , where  $A$ ,  $B$ , and  $D$  are constants depending on the condition of the electrode surfaces.

A. B. M.

### Electrolytic Polarisation. III. The Diffusion Layer. S.

GLASSTONE (*J. Chem. Soc.*, 1925, **127**, 1824—1831; *cf.* this vol., ii, 43, 133).—The rate of fall of back-*E.M.F.* of polarised mercury and lead cathodes in different electrolytes has been examined, and indicates that the thickness of the diffusion layer at an electrode, from which gas is being freely liberated, decreases with rise of current density owing to the stirring effect of the bubbles. With mercury cathodes in sulphuric acid containing alkali sulphates, the back-*E.M.F.* first decreases gradually when the polarising current is stopped, and then shows a sudden decrease after a period of time which diminishes with rise of temperature and of current density, since these factors diminish the thickness of the diffusion layer. Owing to the diffusion of anodic chlorine, abnormal results are obtained in hydrochloric acid unless the electrodes are separated by a porous pot.

W. H.-R.

**Apparatus for Anodic Processes** [Dichromates, Per-Salts, Chloroform]. I. STSCHERBAKOV (*Z. Elektrochem.*, 1925, **31**, 360—362).—When a porous pot is used as diaphragm, there are losses of yield owing to diffusion of cathodically formed alkali into the electrolyte. This is avoided by filling the porous pot with mercury acting as cathode; the catholyte floating on this becomes progressively alkaline and may be run off continuously. The mercury, on the upper surface of which a layer of alkali-amalgam is formed, may also be continuously replenished. Sodium chromate is thus converted into dichromate with a current efficiency

of 92—95% at the ordinary temperature; persulphates are obtained at 7—8 volts with an efficiency of 80—90%. In the chlorination of alcohol in presence of sodium chloride solution, the requisite alkali is supplied to the anolyte by means of a suitably adjusted auxiliary cathode of iron, and chloroform is produced with almost theoretical current efficiencies.

W. A. C.

**Effect of Infra-red Radiation on the Rate of Combustion of Inflammable Gaseous Mixtures.** W. T. DAVID (*Proc. Roy. Soc.*, 1925, **A**, **108**, 617—627).—The effect of infra-red radiation on the rate of combustion of mixtures of air with hydrogen, carbon monoxide, and methane, respectively, was measured. An increased rate of combustion was found in all cases when the superimposed radiation, or the radiation emitted by the burning gases, was of a type which could be absorbed by the combustible gas. [Cf. *B.*, 1925, 793.]

L. F. G.

**Influence of Curvature on Air Saturation of Water and its Relation to the Air-binding of Filters.** J. R. BAYLIS (*Ind. Eng. Chem.*, 1925, **17**, 974—979).—A concave water surface increases and a convex surface decreases the solubility of air and other gases in water. The rate of solution of air from a very small bubble decreases with the age of the bubble. When two air-water surfaces come violently into contact with each other the minute bubbles so formed dissolve rapidly when the water is in equilibrium with a plane surface but increase in size if the equilibrium is greater than that for the diameter of the bubble. This is the case if the water is more than 100% supersaturated. These facts are considered in relation to the air-binding of sand filters. [Cf. *B.*, 1925, 824.]

A. R. P.

**Corrosion Effect of Naphtha Solutions of Sulphur and Sulphur Compounds.** A. E. WOOD, C. SHEELY, and A. W. TRUSTY (*Ind. Eng. Chem.*, 1925, **17**, 798—802).—A study of the action on metals of naphtha solutions of sulphur, mercaptans, hydrogen sulphide, alkyl sulphates, sulphonic acids, and other sulphur compounds shows a general increase in corrosion in presence of water. In some cases, this is due to ionisation, but in other cases, as with free sulphur, apparently to the formation of anodic and cathodic areas. A mercaptan solution yields a mercaptide with most metals which is decomposed on heating, yielding sulphide. [Cf. *B.*, 1925, 745.]

C. I.

**Hydration of Anhydrite.** M. FARNSWORTH (*Ind. Eng. Chem.*, 1925, **17**, 967—970).—Anhydrite ( $\text{CuSO}_4$ ) cannot be hydrated by heating it with water under a pressure of 19 atm. ( $210^\circ$ ) and no hydration takes place in a sealed tube containing excess of water between  $100^\circ$  and  $210^\circ$ ; in fact under these conditions gypsum is converted into the hemihydrate at  $107^\circ$  and into anhydrite at  $160^\circ$ . When, however, anhydrite is ground extremely finely in a colloid mill hydration takes place slowly at the ordinary temperature, particles of  $7\mu$  size being completely converted into gypsum in

3 weeks and coarser particles taking correspondingly longer. [Cf. *B.*, 1925, 804.] A. R. P.

### Reduction of Ferric Oxide and Iron Ores by Hydrogen.

H. KAMURA (*J. Iron and Steel Inst.*, Sept. 1925, advance copy).—The reduction velocity of pure ferric oxide and iron ores by hydrogen at 500°, 600°, and 700° was determined. The higher the temperature of reduction, the less was the volume of hydrogen required; also the velocity of reduction increased with the temperature. At 600°, the velocity of reduction increased rapidly and the volume of hydrogen required decreased to a marked extent; this was probably due to the appearance of the solid phase FeO, which cannot exist below 570°. Thus below 570° the reduction takes place according to the equation  $\text{Fe}_3\text{O}_4 + 4\text{H}_2 = 3\text{Fe} + 4\text{H}_2\text{O}$ , whilst above 570° it takes place in two stages: (i)  $\text{Fe}_3\text{O}_4 + \text{H}_2 = 3\text{FeO} + \text{H}_2\text{O}$ ; (ii)  $\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$ . M. E. N.

**Kinetics of the Oxidation-Reduction Reaction of Formaldehyde.** H. VON EULER and T. LÖVGREN (*Z. anorg. Chem.*, 1925, 147, 123—134).—Investigation of the kinetics of the reaction whereby formaldehyde is converted into methyl alcohol and formic acid (Cannizzaro reaction) at 50° over the  $p_{\text{H}}$  range 11—13, shows that the process is bimolecular and that it occurs between formaldehyde anions. The value of  $k_a$  for formaldehyde at 50° is found to be  $3.3 \times 10^{-13}$ . J. S. C.

**Relation of Homogeneous to Catalysed Reactions. Catalytic Decomposition of Hydrogen Iodide on the Surface of Gold.** C. N. HINSHELWOOD and C. R. PRICHARD (*J. Chem. Soc.*, 1925, 127, 1552—1559).—The decomposition of hydrogen iodide on the surface of a heated gold wire is a catalytic reaction of zero order. The temperature coefficients of such reactions are not affected by the changing degree of adsorption of the reactant. Therefore the “heat of activation” calculated from the temperature coefficient may be expected to have, without correction, the direct physical significance which it possesses in the case of homogeneous reactions. The “heats of activation” found for the homogeneous thermal decomposition of nitrous oxide, hydrogen iodide, and ammonia, and the heterogeneous decomposition of nitrous oxide on platinum and gold, of hydrogen iodide on gold, and of ammonium on tungsten are compared and it is shown that the surface reactions have heats of activation only about half as great as those of the bimolecular homogeneous changes. Probably all (and certainly some) surface reactions of this type involve only one molecule. Thus the function of the surfaces in these reactions is to permit the occurrence of a unimolecular process instead of a bimolecular process requiring an energy of activation about twice as great. E. E. W.

**Catalytic Decomposition of Hydrogen Peroxide in Acid Chlorine-Chloride Solution.** R. S. LIVINGSTON and W. C. BRAY (*J. Amer. Chem. Soc.*, 1925, 47, 2069—2082).—The catalytic influence of mixtures of hydrochloric acid with sodium chloride



and with perchloric acid on the decomposition of hydrogen peroxide solutions at 25° and 40° is investigated. The previous work of Maass and Hiebert (A., 1924, ii, 326) is criticised. The reaction is of the first order with respect to the peroxide, within concentrations 0.22 to 0.02*N* of the latter. The velocity constant is increased 3.60 times for a 10° temperature rise with hydrochloric acid alone between the concentrations 0.244*N* and 0.498*N*. At the steady state, in solutions of ionic strength below unity, the rate of decomposition is given by:  $d[\text{H}_2\text{O}_2]/dt = -(0.000101 \pm 0.000005)[\text{H}_2\text{O}_2][\text{H}^+][\text{Cl}']^2\gamma_{\text{HCl}}$ ,  $\gamma$  being the activity coefficient; in more concentrated solutions a negative deviation occurs. Assuming Brönsted's theory (A., 1922, ii, 699), this deviation indicates that the activity coefficient of the neutral "reaction complex" is greater than that of the hydrogen peroxide. In the steady state, with hydrochloric acid concentrations between 4.55*N* and 5.86*N*, the relation  $[\text{Cl}_2]/[\text{H}']^2[\text{Cl}']^2\gamma_{\text{HCl}} = 1.5 \times 10^{-8}$  holds. A method of calculating the time required for the chlorine concentration to reach a given fraction of its steady state is given, based on the calculations of Abel (A., 1921, ii, 35). The suggested mechanism of the reaction is similar to that outlined by Maass and Hiebert. The reaction between hydrogen peroxide and hypochlorous acid has a large reaction rate, of the same order of magnitude as with hypobromous acid.

S. K. T.

**Reduction of Carbon Monoxide to Methane with Metal Catalysts.** F. FISCHER, H. TROPSCH, and P. DILTNEY (*Brennstoff-Chem.*, 1925, 6, 265—271).—The metals catalysing the reduction of carbon monoxide to methane in order of decreasing efficiency, are ruthenium, iridium, rhodium, nickel, cobalt, osmium, platinum, iron, molybdenum, palladium, and silver. Copper, gold, tungsten, antimony, manganous oxide, and chromic oxide are without influence. Since no carbonyls of osmium, iridium, palladium, or rhodium are known, it cannot be definitely stated that the formation of a metal carbonyl is a stage in the reaction. Similarly, no relation can be traced between the affinity of the metal for hydrogen and its efficiency as a catalyst. No intermediate products likely to be formed, such as formaldehyde etc., could be isolated, but unsaturated hydrocarbons were observed with ruthenium and platinum which cannot be accounted for. Ruthenium is also active in the reduction of carbon dioxide to methane; although poisoned by sulphur compounds, it is reactivated by heating at 600—700° in a current of air. Oxides such as aluminium oxide in conjunction with nickel have a beneficial catalytic influence.

B. W. C.

**Catalytic Decomposition of Nitroamide. II. Catalysis by Simple Amino-bases.** J. N. BRÖNSTED and H. C. DUUS (*Z. physikal. Chem.*, 1925, 117, 299—311; cf. A., 1924, ii, 331).—The basic dissociation constants of aniline, *o*-, *m*-, and *p*-toluidine, and *o*-, *m*-, and *p*-chloroaniline were determined by an electrometric and by a kinetic method, the latter depending on the rate of decomposition of ethyl diazoacetate. The catalytic decomposition of

nitroamide by these bases was found to follow very nearly, but not exactly, the same quantitative law as that previously found for anions of carboxylic acids used in this connexion. L. F. G.

**Effect of Diluents on the Initial Stages of Catalytic Action.** F. H. CONSTABLE (*Nature*, 1925, **116**, 278—279).—The depressant action on the reaction velocity at a catalytic surface of diluent vapours in the reactants is considered from a quantitative point of view, and the expressions deduced have been verified experimentally, within the limits of experimental error, in the case of the effect of water vapour on the initial stages of the dehydrogenation of ethyl alcohol by copper. A. A. E.

**Interaction of Carbon Dioxide and Hydrogen on the Surface of Tungsten.** C. N. HINSHELWOOD and C. R. PRICHARD (*J. Chem. Soc.*, 1925, **127**, 1546—1552).—The kinetics of the interaction of hydrogen and carbon dioxide on the surface of a heated tungsten filament have been investigated between 953° and 1303°. Above a certain pressure the surface becomes saturated with the gases, the rate of reaction becoming independent of the initial pressure. The adsorption of the one gas is almost independent of the pressure of the other, and the rate of reaction is proportional to  $\sigma_{H_2} \cdot \sigma_{CO_2}$ , where  $\sigma_{H_2}$  and  $\sigma_{CO_2}$  are the fractions of certain active portions of the surface which are covered with adsorbed hydrogen and carbon dioxide, respectively. The portions of the surface which adsorb and render active the one gas are different from those parts which adsorb the other gas. Interaction is supposed to take place when the two gases are adsorbed on adjacent centres of appropriate kinds. The value of the apparent heat of activation calculated by means of the Arrhenius formula is 30,000 cal. E. E. W.

**Catalytic Oxidation of Hydrogen Cyanide.** R. HARA and H. SINOZAKI (*Tech. Repts. Tôhoku*, 1925, **5**, 71—113).—The oxidation of mixtures of hydrogen cyanide and air in presence of fine platinum gauze according to the equation  $2HCN + 5O = 2NO + 2CO + H_2O$  appears to occur at the first point of contact with the catalyst. The reaction starts abruptly at 450°, independently of the velocity of flow. High yields (80%) of nitric oxide are obtained between about 600° and 800°, this range widening with increasing velocity of flow. At higher temperatures, combustion to nitrogen occurs before the gases reach the catalyst, and the yield is then greatly influenced by the rate of flow; the reaction  $2NO + 2CO = N_2 + 2CO_2$  also occurs. Maximum yields are obtained with a rapidly flowing inlet gas containing 8% of hydrogen cyanide; with just above 15% of the latter explosions occur and at higher concentrations (30%) cyanuric acid and cyamelide are formed. The intermediate stage of the oxidation is probably the immediate formation of cyanic acid, which either polymerises or decomposes into water, carbon monoxide, and nitric oxide, according to the conditions. The mass action constants,  $K_p$ , for the oxidation are comparable in magnitude with those for ammonia oxidation. Contrary to Wehrheim's observation, hydrogen cyanide decomposes slowly in acid potassium permanganate solution. S. K. T.

**Electrolysis of Equimolar Mixtures.** R. SAXON (*Chem. News*, 1925, **131**, 129—131).—When solutions containing metallic sulphates in equimolecular proportions are electrolysed the hydroxide of the more electronegative metal is deposited around the cathode when the two metals are widely separated in the electrochemical table, *e.g.*, copper and zinc, whereas a mixture of hydroxides is deposited when the metals are near one another in the table, *e.g.*, cobalt and nickel, the hydroxide of the less electropositive element tending to concentrate in the first fractions.

A. R. P.

**Electrolytic Separation of Alkali and Alkaline-earth Metals.** R. SAXON (*Chem. Trade J.*, 1925, **77**, 236).—With an anode of Meldrum's acid-resisting metal and a porous cathode compartment containing mercury, electrolysis of a paste of sodium hydroxide and water yields an amalgam containing 3.4% of sodium. The mercury is preferably covered with a little petroleum. Lithium, rubidium, barium, and calcium have been obtained by a similar method, using for the last a mixture of the chloride, nitrate, and iodide.

S. I. L.

**Quantum Laws in Photochemistry.** E. WARBURG (*Naturwiss.*, 1924, **47**, 1058—1063).—A summary of the investigations carried out to test Einstein's law of photochemical equivalence. Provided that certain assumptions are made as to the nature of the specific photochemical reaction and the secondary reactions, the law has been proved to apply when the quantum absorbed is greater than the energy of dissociation, but in certain cases the molecule may dissipate part of the energy absorbed by collision with other molecules and the law is not fulfilled. When the quantum absorbed is smaller than the energy of dissociation, the reaction is probably the result of collisions between excited molecules, but here again the dissipation of energy absorbed prevents more than a fraction of the excited molecules from reacting. The photodecomposition of ozone in presence of chlorine is an example of a sensitised photochemical reaction which obeys Einstein's law.

E. B. L.

**Photochemical Formation of Hydrogen Chloride.** G. KORNFIELD and H. MÜLLER (*Z. physikal. Chem.*, 1925, **117**, 242—256).—Experimental evidence is given that the rate of photochemical formation of hydrogen chloride is proportional to the intensity of the activating light; this is not in agreement with Baly and Barker (*T.*, 1921, **119**, 653). With the most sensitive mixture that could be employed it was found that  $1.10 \times 10^5$  molecules of hydrogen chloride were formed per quantum of absorbed energy.

L. F. G.

**Condensation Nuclei Produced by the Illumination of Air-Halogen Mixtures.** I. JONES (*Proc. Physical Soc.*, 1925, **37**, 287—296).—When dust-free air, saturated with iodine or bromine vapour, or mixed with small amounts of chlorine, is illuminated and subjected at atmospheric pressure to a pressure fall of

about 20 cm., dense clouds are formed. With iodine or bromine, illumination for 1 sec., and with chlorine for 2 secs. is necessary to produce clouds of maximum density. By keeping gas mixtures, activated by illumination, in darkness before expansion, it was shown that all the nuclei persist for 5 secs., and that some are still present after 30 secs. in darkness. By experiments on the production of clouds under various conditions, it was shown that in addition to illumination, the presence of a trace of moisture and of some oxidisable impurity on the walls of the apparatus is necessary for the production of nuclei. Oxygen is unnecessary. The conditions for the formation of nuclei in air-halogen mixtures resemble in several respects those for the occurrence of an induction period in the photochemical combination of hydrogen and chlorine, and it is suggested that the induction period is due to the consumption of the available light energy in the formation of nuclei before the activation of the chlorine-hydrogen mixture occurs.

F. G. T.

**Combination of Bromine with Unsaturated Hydrocarbons under the Influence of Light.** J. PLOTNIKOV (*Bull. Acad. Sci. St. Pétersbourg*, 1916, 1083—1114, 1563—1594; from *Chem. Zentr.*, 1925, i, 2535).—The author derives equations, on the assumption of Beer's law and the proportionality between light absorption and the amount of decomposition, for the velocity of reaction in the case of a photosensitive compound, a sensitive compound and a non-sensitive compound, and two sensitive compounds, respectively, for receptacles of different shape, with transparent or reflecting walls. Formulæ are given for photochemical balanced actions and for the reaction between bromine and  $\alpha$ -phenylcinnamionitrile.

G. W. R.

**Photochemical Potential Changes.** K. SCHAUM and W. SCHLEUSSNER (*Z. wiss. Phot.*, 1925, 23, 319—324).—The criteria for the recognition of a true Becquerel effect, and in particular the influence of other reactions and of the presence of a foreign substance, are discussed. Investigation of vanadium salts of different valencies showed that pure solutions of a single salt generally give a bad adjustment, and uncertain and scarcely reproducible effects. Mixtures of two salts of different valencies, or the addition of foreign substances capable of reacting, often give very clear results. The reaction between ferric ions and iodine provides an example of a case where the reversible photochemical reaction predominates over the Becquerel effect.

W. C.

**Silver in Photography.** LÜPPO-CRAMER (*Z. wiss. Phot.*, 1925, 23, 294—302).—The author summarises the published work on the forms and colours of silver produced by electrolysis and by reduction of silver salts, colloidal silver, dichroic fog, and the silver of the "print-out" image. The adsorption of thiosulphate by silver with particular reference to persulphate reduction is considered.

W. C.

**[Photographic] Ripening Process.** V. LÜPPO-CRAMER (*Z. wiss. Phot.*, 1925, **23**, 286—293; cf. *B.*, 1925, 150, 477).—The influence of excess of bromide used in preparing emulsions on the rate of ripening, the grain size, and fog formation is considered. The influence of potassium bromide is generally less marked than that of the equivalent amount of ammonium bromide, although with some emulsions the potassium salt and with others the ammonium salt is preferred. The difference is probably due to inclusion of the salts in the silver bromide lattice, precipitated under different conditions. Observations are also made on the effect of rate of stirring, rate of mixing, etc. on the properties of an emulsion. [Cf. *B.*, 1925, 829.] W. C.

**Solarisation of the Photographic Plate.** J. M. EDER (*Z. physikal. Chem.*, 1925, **117**, 293—298).—Experimental evidence is adduced to show the incorrectness of Arens' view that the direct photochemical blackening of a silver bromide-gelatin plate impregnated with sodium nitrite is so intense that solarisation is masked (see this vol., ii, 313). Arens' consequential inferences are therefore not valid. L. F. G.

**Potassium Chloroiminodisulphonate.** F. RASCHIG (*Z. anorg. Chem.*, 1925, **147**, 1—4).—Potassium chloroiminodisulphonate,  $\text{NCl}(\text{SO}_3\text{K})_2$ , is obtained as colourless, anhydrous crystals when a hot solution of sodium hypochlorite and potassium iminodisulphonate,  $\text{NH}(\text{SO}_3\text{K})_2$ , is allowed to cool slowly to the ordinary temperature. The substance is unstable and decomposes into nitrogen trichloride and potassium nitrilotrisulphonate,  $\text{N}(\text{SO}_3\text{K})_3$ . J. S. C.

**Systematic Doctrine of Affinity. XXXI. Thiohydrates.** W. BILTZ and E. KEUNECKE (*Z. anorg. Chem.*, 1925, **147**, 171—187).—The existence of the following *thiohydrates* is demonstrated:  $\text{BeBr}_2 \cdot 2\text{H}_2\text{S}$ ;  $\text{BeI}_2 \cdot 2\text{H}_2\text{S}$ ;  $\text{AlCl}_3 \cdot \text{H}_2\text{S}$ ;  $\text{AlBr}_3 \cdot \text{H}_2\text{S}$ ;  $\text{AlI}_3 \cdot 2\text{H}_2\text{S}$ ;  $\text{AlI}_3 \cdot 4\text{H}_2\text{S}$ ;  $\text{TiCl}_3 \cdot \text{H}_2\text{S}$ ;  $\text{TiCl}_4 \cdot 2\text{H}_2\text{S}$ ;  $\text{TiBr}_4 \cdot \text{H}_2\text{S}$ ;  $\text{TiBr}_4 \cdot 2\text{H}_2\text{S}$ ;  $\text{SnCl}_4 \cdot 2\text{H}_2\text{S}$ ;  $\text{SnCl}_4 \cdot 4\text{H}_2\text{S}$ . The formation and stability of thiohydrates are discussed. J. S. C.

**Action of Hydrogen Sulphide on Mercuric Salts.** H. PÉLABON (*Bull. Soc. chim.*, 1925, [iv], **37**, 854—856).—The action of hydrogen sulphide at the ordinary temperature on a solution of mercuric chloride containing hydrochloric acid causes an immediate precipitation of the white chlorosulphide, with liberation of hydrogen chloride. If this, together with the acid initially in the mixture, brings the concentration of acid up to that demanded by the formula  $\text{HCl} \cdot 6\text{H}_2\text{O}$ , the precipitate remains white, however long the gas is passed. If this concentration limit is not reached, the precipitate blackens, partly or completely, owing to the formation of mercuric sulphide (cf. Jolibois and Bouvier, *A.*, 1920, ii, 494). L. L. B.

**Aluminium Sulphide.** W. BILTZ (*Z. anorg. Chem.*, 1925, **146**, 289—290; cf. *A.*, 1911, ii, 804).—Colourless crystals obtained

when a preparation of aluminium sulphide was sublimed in a vacuum and described as aluminium sulphide itself are now shown to be silicon disulphide.

A. B. M.

**Combustion of Carbon.** II. F. G. KEENEN, L. W. PRINE, and W. C. EBAUGH (*Ind. Eng. Chem.*, 1925, **17**, 804—805).—The gases resulting from the combustion of the carbons of an electric arc in oxygen contain increasing proportions of carbon monoxide with increase of temperature, indicating that at high temperatures this gas is the primary product of the combustion. [Cf. *B.*, 1925, 744.]

C. I.

**Thermal Decomposition of Carbonyl Chloride.** A. STOCK and W. WUSTROW (*Z. anorg. Chem.*, 1925, **147**, 245—255).—Carbonyl chloride not only decomposes into carbon monoxide and chlorine, but also to a slight extent into carbon dioxide and carbon tetrachloride. The rate of the latter decomposition, which is very small in the temperature region 400—500°, is accelerated in presence of certain catalysts (silica, blood charcoal, etc.). Although the thermodynamical treatment of the problem predicts that the major portion of the carbonyl chloride should be decomposed in this way, only about 1% of carbon tetrachloride is observed even after several hours.

J. S. C.

**Formation of Mullite from Cyanite, Andalusite, and Sillimanite.** J. W. GREIG (*J. Amer. Ceram. Soc.*, 1925, **8**, 465—484).—When heated, cyanite, andalusite, and sillimanite are decomposed into mullite and silica, or into mullite and a silicious liquid, the silica being probably cristobalite. No definite point of temperature is observed at which the minerals decompose sharply, or below which they remain unaffected for indefinitely long periods. Cyanite requires the lowest, and sillimanite the highest temperature. Decomposition is accompanied by an expansion in all three cases; with cyanite it is very pronounced. In the case of cyanite and andalusite, the alteration commences on the surfaces of the grains and advances inward, whereas with sillimanite it appears to take place throughout the grain. The rate of decomposition increases rapidly with a rise in temperature in all three minerals. The mullite crystals newly formed from andalusite and sillimanite are oriented parallel to the original crystals, whereas with cyanite this orientation is determined by the surfaces from which the mullite grows. An absorption of heat is observed when cyanite and andalusite decompose.

F. S.

**Phenomena in the Electric Arc Process of Nitrogen Fixation.** S. KARRER (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 25—32).—The author discusses the factors which may possibly affect the efficiency of the arc method of nitrogen fixation, more particularly with regard to those phenomena, other than purely thermal, which occur in the arc core. The following points are dealt with: dissociation of oxygen and nitrogen molecules into neutral atoms; ionisation within the arc; excitation; radiation; energy transfer.

N. H. H.

**Attempt to Prepare Nitro-nitrogen Trichloride. III. Failure to Obtain a Compound containing only Nitrogen and Chlorine from Oxides of Nitrogen.** W. A. NOYES (*J. Amer. Chem. Soc.*, 1925, 47, 2159—2164).—An account of unsuccessful experiments carried out to prepare a new compound containing only nitrogen and chlorine. (Cf. A., 1921, ii, 42.)

S. K. T.

**New Oxide of Nitrogen, Nitroso-nitrogen Trioxide, and its Bearing on the Oxidation of Nitric Oxide.** R. L. HASCHE (*J. Amer. Chem. Soc.*, 1925, 47, 2143—2148).—*Nitrosanitrogen trioxide*,  $(\text{N}_3\text{O}_4)_x$ , is prepared as a green solid by bubbling nitric oxide through liquid oxygen or by the action of air on solid nitric oxide kept at the temperature of liquid air. It decomposes just above the b. p. of oxygen to the blue oxide,  $\text{N}_2\text{O}_3$  (Helbig, A., 1903, ii, 361); Raschig's formula for this compound (A., 1911, ii, 346) could not be substantiated. Assuming, because of its instability and its instantaneous formation, that the green oxide is a peroxide of polymerised nitric oxide, its formation may be explained as follows:



The phenomena observed in the oxidation of nitric oxide may be explained by the assumption of similar intermediate compounds, viz. at higher temperatures,  $\text{O}\cdot\text{N}\cdot\text{NO}\cdot\text{O}\cdot\text{O}\cdot\text{NO}\cdot\text{N}\cdot\text{O}$ , formed by the oxidation of  $(\text{NO})_2$ , and, in the gaseous state,  $\text{O}\cdot\text{N}\cdot\text{O}\cdot\text{O}\cdot\text{N}\cdot\text{O}$ , formed by the oxidation of NO.

S. K. T.

**Amphoteric Hydroxides, their Alkaline Solutions and Alkali Salts. III. Alkali Antimonates from Aqueous, Alkaline Solutions.** G. JANDER and L. BRANDT (*Z. anorg. Chem.*, 1925, 147, 5—15).—The hydrated crystalline precipitates of sodium and lithium antimonates obtained by oxidising alkaline solutions of antimony trisulphide with hydrogen peroxide, are not of fixed composition, the alkali content varying with the alkalinity of the mother-liquor and the temperature of precipitation. Potassium antimonate obtained by the oxidation of alkaline solutions of antimony trioxide with hydrogen peroxide is difficult to obtain in a crystalline form. The value of the ratio  $[\text{K}_2\text{O}]:[\text{Sb}_2\text{O}_5]$  usually approximates fairly closely to unity.

J. S. C.

**Bismuth Dihydride.** E. J. WEEKS and J. G. F. DRUCE (*J. Chem. Soc.*, 1925, 127, 1799—1800).—Bismuth dihydride,  $\text{Bi}_2\text{H}_2$ , is obtained as a grey, flocculent precipitate by the addition of bismuth chloride to a mixture of zinc and concentrated hydrochloric acid. It deposits metallic bismuth when heated, and is rapidly oxidised by fused potassium nitrate.

S. I. L.

**Action of Ozone on Aqueous Colloidal Solutions of Inorganic Substances.** E. H. RIESENFELD and W. HAASE (*Z. anorg. Chem.*, 1925, 147, 188—195).—Silver sols are converted into solutions of silver hydroxide. Mercurous oxide is precipitated from mercury sols. Gold sols are only partly dissolved, the red

colour changing to blue. Whereas lead oxide sols are easily oxidised, cuprous oxide sols are quite stable. Arsenic and antimony trisulphide sols are decomposed with formation of sulphur, sulphuric acid, and the corresponding pentoxides. Silver, mercury, and copper sulphide sols are converted into solutions of the corresponding sulphates. J. S. C.

**Formation of Ozone in Incandescent Capillaries.** E. H. RIESENFELD (*Z. Elektrochem.*, 1925, **31**, 435—440).—When pure dry oxygen is passed rapidly through quartz capillaries heated at 1000—1500° Abs., ozone is found in the issuing gas to the amount of several millionths of an atmosphere partial pressure. Presence of moisture reduces the yield; nitrogen (1%) does not affect it. There is more than 1000 times as much ozone as would be expected by calculation from Nernst's theorem. It is suggested that particles from the quartz adsorption layer, in which the equilibrium leans towards ozone, are carried over by the rapid current in the quartz capillary, thus giving rise to a false equilibrium. W. A. C.

**Decomposition of Sulphur Monochloride by Water.** E. NOACK (*Z. anorg. Chem.*, 1925, **146**, 239—262).—The course and the end products of the reaction between sulphur monochloride and water have been shown to agree qualitatively and quantitatively with those of the reaction between sulphur dioxide and hydrogen sulphide in the presence of water. A slight difference in the amount of sulphuric acid produced, even when rigid precautions are taken to exclude air, is probably due to the oxidising action of a small quantity of a higher chloride produced by dissociation of the monochloride. In one experiment sufficient of the latter was dissolved in water to give 0.2 g.-at. of sulphur per litre, an atmosphere of carbon dioxide being maintained, and the following end-products were obtained (expressed as percentage of total sulphur): sulphur as sulphuric acid, 3.2%, as polythionic acids, 35.7%, as sulphurous acid, 0.7%, and elementary sulphur, 60.4%. The results support the assumption that the first stages of the reaction can be represented by the schemes:  $S_2Cl_2 + H_2O \rightarrow S_2(OH)_2 + 2HCl$ ;  $S_2(OH)_2 \rightleftharpoons H_2S + SO_2$ . The existence of hydrogen sulphide and sulphur dioxide as intermediate products is demonstrated, and the change of their concentration with time shown to confirm the assumption made. Attempts to prepare the assumed intermediate compound  $H_2S_2O_2$ , however, by the action of hydrogen sulphide on sulphur dioxide in the absence of water, e.g., in alcoholic solution, or by passing hydrogen sulphide into liquid sulphur dioxide, failed. The reaction under such conditions proceeds thus:  $2H_2S + SO_2 \rightarrow 2H_2O + 3S$ . The reaction between a thiosulphate and hydrogen sulphide is shown to admit of a simple interpretation on the assumption of the formation of  $H_2S_2O_2$  as an intermediate product. A. B. M.

**Amidopersulphuric Acid [Hydroxylamineisomonosulphonic Acid].** F. SOMMER, O. F. SCHULZ, and M. NASSAU (*Z. anorg. Chem.*, 1925, **147**, 142—155; cf. A., 1914, ii, 458).—Amidopersulphuric acid,  $NH_2O \cdot SO_2 \cdot OH$ , prepared by the interaction of



chlorosulphonic acid and hydroxylamine sulphate, may be obtained pure as colourless prisms by dissolving in cold dry methyl alcohol and precipitating with dry chloroform. Alcohols react to form compounds of the type  $\text{RO}\cdot\text{SO}_2\cdot\text{OH}\cdot\text{NH}_2\cdot\text{OH}$ . Aldehydes and ketones in alkaline solution react to form salts of oxime acids, e.g.,  $\text{CR}_1\text{R}_2\cdot\text{NO}\cdot\text{SO}_2\cdot\text{OK}$ . On boiling with alkali, the acid is decomposed according to the equation  $3\text{NH}_2\text{O}\cdot\text{SO}_2\cdot\text{OH} + 6\text{KOH} = 3\text{K}_2\text{SO}_4 + 6\text{H}_2\text{O} + \text{NH}_3 + \text{N}_2$ . The salts are very unstable and liable to explode. Many of the reactions of the acid suggest that it possesses the alternative structural formula  $\text{HN}:\text{O}:\text{S}(\text{OH})_2$ . On boiling aqueous solutions of the acid with a considerable excess of ammonia yields of hydrazine of the order of 50% are obtained. Amino compounds yield the corresponding hydrazine derivatives. Alkaline solutions of ethylenediamine react to form  $\alpha$ -hydrazino- $\beta$ -aminoethane (dioxalate, needles, m. p.  $204^\circ$ ; dipicrate, yellow crystals, m. p.  $166^\circ$  [decomp.]; dihydrochloride, colourless crystals, sintering at  $165$ – $166^\circ$ , and decomposing at  $200$ – $205^\circ$ );  $\alpha$ -Benzylidenehydrazino- $\beta$ -aminoethane oxalate, needles, m. p.  $150$ – $152^\circ$  (decomp.), and  $\alpha$ -o-hydroxybenzylidenehydrazino- $\beta$ -aminoethane oxalate were also prepared. J. S. C.

**Bivalent Chromium.** W. TRAUBE, E. BURMEISTER, and R. STAHN (*Z. anorg. Chem.*, 1925, **147**, 50–67; cf. A., 1916, ii, 625).—Concentrated solutions of pure chromous chloride are obtained by the prolonged electrolytic reduction of aqueous solutions of green chromic chloride, using lead plates as electrodes and employing a current density of  $0.175$  amp./dm.<sup>2</sup> Electrolysis of chromous chloride solutions using an iron cathode results in the formation of a cathodic deposit of metallic chromium mixed with chromium oxides. The autoxidation of chromous salts in acid solution with evolution of hydrogen is considerably accelerated in presence of catalysts such as palladium chloride. Precipitation of solutions of chromous salts by alkali yields a mixture of hydrated chromous oxide and chromium sesquioxide in varying proportions.

Chromous formate exists also as a violet salt. The following double salts have been prepared: *chromous pyridine formate*,  $[\text{Cr}(\text{C}_5\text{H}_5\text{N})](\text{CO}_2\text{H})_2$ , *chromous pyridine chloride*,  $[\text{Cr}(\text{C}_5\text{H}_5\text{N})_2]\text{Cl}_2\cdot 2\text{H}_2\text{O}$ , *chromous formate ammonium chloride*,  $\text{Cr}(\text{CO}_2\text{H})_2\cdot\text{NH}_4\text{Cl}$ , *chromous ammonium fluoride*,  $\text{CrF}_2\cdot\text{NH}_4\text{F}\cdot 2\text{H}_2\text{O}$ , *chromous potassium fluoride*,  $\text{CrF}_2\cdot\text{KF}$ . J. S. C.

**Complex Uranyl Carbonates.** J. A. HEDVALL (*Z. anorg. Chem.*, 1925, **146**, 225–229).—A large number of metallic ions give a precipitate with solutions of the alkali uranyl carbonates, but analytical results, the visible evolution of carbon dioxide, and the gradual colour change due to hydrolysis show that most of these products even shortly after precipitation cannot be regarded as definite compounds. Least hydrolysis occurs when the potassium uranyl carbonate in not too dilute a solution is precipitated in the cold by addition of excess of the metallic salt solution; the pre-

citrate is rapidly washed with water and allowed to dry in the air. *Silver uranyl carbonate*,  $\text{Ag}_4\text{UO}_2(\text{CO}_3)_3$ , forms yellow flocks which turn to a crystalline powder. It darkens in colour even when kept in the dark, owing to the uranium radiation. The dry salt begins to evolve its carbon dioxide at  $165^\circ$ . *Barium uranyl carbonate*,  $\text{Ba}_2\text{UO}_2(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ , yellow, microscopic plates, loses water slowly at the ordinary temperature, more quickly at  $50^\circ$ , changing in colour from bright yellow to lemon-yellow. Above  $350^\circ$ , considerable quantities of carbon dioxide are given off and the colour becomes orange-yellow. A. B. M.

**Chlorine Hexoxide.** M. BODENSTEIN, P. HARTECK, and E. PADEL (Z. anorg. Chem., 1925, **147**, 233—244).—Analysis and measurements of f. p. depression in carbon tetrachloride solution show that the dark-red oil obtained by exposure to light of chlorine dioxide is chlorine hexoxide,  $\text{Cl}_2\text{O}_6$ . The substance has a very low vapour pressure, 1 mm. at  $20^\circ$ ,  $d^{20}_4$  1.65, and m. p.  $-1^\circ$ . When in an impure condition it is readily explosive, but at the ordinary temperature in the pure state it is much more stable. Contact with organic substances, however, brings about violent decomposition. At high temperatures, chlorine hexoxide decomposes into chlorine and oxygen. The substance reacts with water as a mixed anhydride, forming chloric and perchloric acids. Chlorine hexoxide is also formed on illumination of a mixture of ozone and chlorine, rays in the red portion of the spectrum being active and not those in the blue. J. S. C.

### Mechanism of Reduction of Iron Oxides in a Current of Gas.

II. K. HOFMANN (Z. angew. Chem., 1925, **38**, 715—721).—Samples of ferric and ferrosferric oxide powder were reduced by heating them in a current of hydrogen, the degree of reduction being taken as the percentage of the total oxygen reduced. The reduction of ferric oxide is practically complete at  $550^\circ$  and  $1000^\circ$ , but between these temperatures the degree of reduction shows minima due to adhesion of the solid particles and to the process of  $\beta$ - $\gamma$  transformation. It is most complete when the diameter of the oxide particles is 0.02—0.05 mm. Similar minima occur in the reduction of ferrosferric oxide, which, however, is less easily reduced than ferric oxide. Adhesion phenomena can be eliminated by admixture of basic oxides, e.g., magnesia. In other cases, reduction is hindered by the diminished diffusive power of the water produced through the shell of metallic iron formed round the oxide particles. The reduction of ferric oxide in a current of hydrogen does not progress in the anticipated stages, and the oxide  $\text{Fe}_3\text{O}_4$  is not produced, although in a static system the case is otherwise. The mechanism of reduction cannot be explained from the equilibrium diagram, but account should rather be taken of surface phenomena, e.g., adhesion, sintering. Further light may be expected from a study of the spatial configuration of the iron oxides and of the rearrangements of the oxygen atoms during the reduction process. W. T. K. B.

**Ageing of Ferrous Carbonate and Ferrous Hydroxide. Ageing of Natural Mineral Waters.** O. BAUDISCH and L. A. WELO (*J. Biol. Chem.*, 1925, **64**, 753—770, 771—779).—Ferrous hydroxide and ferrous carbonate, precipitated and stored in the absence of air, although apparently stable even to boiling, gradually lose their power of reducing nitrates to nitrites or of catalysing the oxidation of organic compounds such as uracil and lactic acid, although on exposure to air they still absorb oxygen. It is suggested that the ageing process consists in a gradual passage from the amorphous to the crystalline state.

The loss of therapeutic efficacy, undergone by certain mineral waters through keeping, has been correlated with a precipitation and consequent inactivation of ferrous salts analogous to the ageing process described above; it was found that the ageing of the mineral waters was accelerated by exposure to light.

C. R. H.

**Cobaltammines with more than Six Molecules of Ammonia.** F. EPHRAIM (*Z. anorg. Chem.*, 1925, **147**, 24—41).—Hexaminecobaltic chloride, bromide, and iodide, chloropentamminecobaltic iodide, aquopentamminecobaltic chloride, bromide, and iodide, *cis*-dinitritotetramminecobaltic bromide and iodide, *trans*-dinitritotetramminecobaltic bromide, and potassium tetranitritodiamminocobaltate can take up ammonia at temperatures in the region of  $-20^{\circ}$  to form more complex compounds. The number of molecules of ammonia added per mol. of salt varies between 2 and 10. On raising the temperature, ammonia is evolved and less complex compounds result. Generally speaking, these complexes are completely decomposed to the original cobaltamine when the ordinary temperature is reached.

J. S. C.

**Fractional Precipitation. I. Dependence on Solubility Products, Dissociation Constants, Constitution of the Precipitate, etc.** O. RUFF and B. HIRSCH (*Z. anorg. Chem.*, 1925, **146**, 388—410).—The possibility of separating a mixture of metals in solution by fractional precipitation as hydroxides, carbonates, or sulphides has been studied. The method is exemplified by the separation of iron and nickel by sodium hydroxide, which depends on the reaction  $\text{FeCl}_3 + 3\text{Ni}(\text{OH})_2 \rightleftharpoons \text{Fe}(\text{OH})_3 + 3\text{NiCl}_2$ . If one equivalent of ferric chloride is added to two equivalents of nickelous hydroxide, the reaction proceeds completely in the direction from left to right. The same occurs if one equivalent of ferric chloride is added to 0.5 equivalent of nickelous hydroxide. In the first case, all the iron is precipitated; in the second, all the nickel passes into solution. Thus the two metals can be completely separated. The result is confirmed by the actual separation of a mixture of iron and nickel salts by the gradual addition of sodium hydroxide, the precipitate being separated in stages and analysed. Experiments have been carried out with a large number of metallic salt mixtures and with hydroxyl, carbonate, and sulphide as precipitating ions. The mixtures that can be successfully separated are tabulated. The theory of the process is briefly outlined, and

it is shown that in cases where the solubility products are known the results are in accordance with the theory provided that no mixed crystals or adsorption phenomena occur and no other compounds are formed. These exceptions, however, are infrequent.

A. B. M.

**Concentration of Praseodymium Material and the Preparation and Properties of Metallic Praseodymium.** J. WIERDA and H. C. KREMERS (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 65—74, advance copy).—High-grade praseodymium material with a probable purity of 99.7% has been prepared from cerium earth residues. The impurities known to be present in the final product were 0.02% of neodymium and less than 0.01% of lanthanum. In the course of the investigation the following methods of separation were tried: fractional crystallisation of the double magnesium nitrates, the double manganese nitrates, and the double ammonium nitrates; fractional decomposition of the nitrates by heat; fractional precipitation with ammonia in the presence of ammonium salts; fractional precipitation by magnesium oxide. As a result, the authors recommend a procedure which involves fractional crystallisation of the double magnesium or, at certain stages, manganese nitrates, cerium being removed at an intermediate point. The average magnetic susceptibility of the product was  $13.28 \times 10^{-6}$ .

Preparation of the metal was effected by electrolysis of the fused chloride, using a low current density. The metal is silvery white, corrodes rapidly in air, is slightly attacked by hot water, and vigorously attacked by mineral acids and free halogens. The kindling temperature is  $290^{\circ}$ . The metal is not pyrophoric. The Brinell hardness (500 kg. weight) is 25,  $d^{25}$  6.60. Alloys with most common metals are readily formed.

N. H. H.

**Preparation of Mixed Iodides and Sulphides.** T. KARANTASSIS (*Bull. Soc. chim.*, 1925, [iv], **37**, 854).—The compound  $PI_3.3S_8$  may be obtained by dissolving phosphorus tri-iodide and a slight excess of sulphur in carbon disulphide. On cooling and evaporating in a slow stream of dry carbon dioxide, reddish-brown prismatic crystals are obtained, which change rapidly in air. An attempt to prepare the substance  $PI_5.5S_8$ , gave, on proceeding as above and evaporating at  $-10^{\circ}$  or  $-15^{\circ}$ , deep red crystals, which on analysis proved to be  $PI_3.3S_8$ . The mother-liquor contained free iodine.

L. L. B.

**Preparation of Nitric Oxide from Sodium Nitrite.** W. A. NOYES (*J. Amer. Chem. Soc.*, 1925, **47**, 2170).—Nearly pure nitric oxide is rapidly generated by dropping concentrated sulphuric acid on to sodium nitrite covered with two or three times its weight of water:  $3HNO_2 = HNO_3 + 2NO + H_2O$ . By washing the gas with concentrated sulphuric acid or water the trace of nitrogen dioxide present is removed.

S. K. T.

**Nitrogen Tetrasulphide and Nitrogen Tetraselenide.** H. B. VAN VALKENBURGH and J. C. BAILAR, jun. (*J. Amer. Chem. Soc.*, 1925, **47**, 2134—2137).—Good yields of nitrogen tetrasulphide

are obtained by passing dry ammonia at the rate of 1 litre/min. through 150 c.c. of ether containing 5 c.c. of sulphur monochloride. On keeping, orange crystals separate, ether extraction of which yields the tetrasulphide. Hydrolysis of the latter with a large excess of boiling water yields a neutral solution in which 21.3% of the sulphur is present as pentathionic acid, 40.6% as sulphurous acid, 38.1% as free sulphur, and all the nitrogen as ammonia. Prolonged passage of ammonia through an ethereal solution of sulphur monochloride yields, after evaporation, a viscous *liquid* of offensive odour which does not lose ammonia on heating. A similar compound was obtained with selenium. Liquid ammonia gives a black solid when mixed with sulphur monochloride. Nitrogen tetraselenide is prepared as above, using, however, more dilute solutions of selenium monochloride in carbon disulphide. The molecular weight, determined by a cryoscopic method, corresponds with the formula  $N_4Se_4$ . S. K. T.

**Preparation of Phosphorus Trichloride and Tribromide from Red Phosphorus.** V. REKSCHINSKI (*Trans. Inst. Pure Chem. Reagents Moscow*, 1924, [3], 46—49).—Dry red phosphorus is treated with dry chlorine or bromine in an atmosphere of carbon dioxide, the formation of higher halides being prevented by suitably regulating the temperature and admission of halogen. The procedure is described in detail; the yields are more than 60% for the chloride and 80% for the bromide. G. A. R. K.

**Preparation of Arsenic Di-iodide.** T. KARANTASSIS (*Bull. Soc. chim.*, 1925, [iv], 37, 853).—One part of finely powdered arsenic and 2 parts of iodine are introduced into a retort-shaped tube. After repeated evacuation and filling with pure, dry hydrogen, the tube is sealed and the mixture heated to the b. p. for 2 hrs. On careful distillation, pure arsenic di-iodide is obtained. The undistilled product melts at 117—120°, the distilled compound at 130°, the change in m. p. proving the solubility of arsenic in the crude product. In an atmosphere of hydrogen or carbon dioxide, the compound boils at 375—380°. L. L. B.

**Factors Affecting the Physical Condition of Bismuth Carbonate.** A. J. JONES (*Pharm. J.*, 1925, 115, 143—144).—Bismuth carbonate, prepared by adding bismuth nitrate solution to sodium carbonate solution, varies in density as follows: at constant concentration of sodium carbonate, precipitation at 45° yields the lightest powders, increase or decrease of temperature increasing the density. When the basic solution consists of a mixture of sodium carbonate and hydrogen carbonate, increase in the ratio carbonate/hydrogen carbonate seems to increase the density of the precipitate. There seems to be one particular set of values of all variables yielding bismuth carbonate of least density, increase or decrease of any of the values leading to a denser form. B. F.

**Application to Chromium of a General Method for Synthesis of Fluorides and Silicates.** A. DUBOIN (*Compt. rend.*, 1925, 181, 336—337; cf. A., 1892, 1161).—Small quantities of the

precipitated oxide or fluoride of chromium are added to molten potassium hydrogen fluoride. The mixture is heated to redness and silica is then added. When the mass is cooled and treated with water, silica in the form of tridymite ( $d$  2.32) and the double fluoride of chromium and potassium ( $\text{CrF}_3 \cdot 3\text{KF}$ ) can be isolated. The double salt consists of well-formed green crystals which are quite white when powdered. The material dissolves readily in hydrochloric and nitric acids;  $d^{20}$  2.93. Analytical details are given. R. A. M.

**Lithium Arc Spectrum for Polarimetric Use.** P. C. AUSTIN (*J. Chem. Soc.*, 1925, **127**, 1752—1753).—A method of producing a lithium spectrum by introducing lithium carbonate into the arc produced between carbon, copper, or silver electrodes is described. The value of the lithium lines in polarimetry is pointed out.

E. E. W.

**Spiral Springs of Quartz.** H. D. H. DRANE (*Nature*, 1925, **116**, 315).—A method is described for the production of spiral springs of silica fibres having a diameter of about  $10^{-3}$  cm. (cf. this vol., ii, 818).

A. A. E.

**Flow Calorimeter for Specific Heats of Gases.** N. S. OSBORNE, H. F. STIMSON, and T. S. SLIGH, jun. (*U.S. Bur. Standards*, 1925, **20**, [503], 119—151).—The paper describes the design, construction, and operation of a calorimeter for the measurement of  $C_p$  at pressures below 100 atm. and temperatures below  $150^\circ$ . The application of the instrument to superheated ammonia vapour has already been described. [Cf. *B.*, 1925, 497.]

N. H. H.

**Calorimetric Bomb with Platinum Lining.** C. MOUREU and P. LANDRIEU (*Bull. Soc. chim.*, 1925, [iv], **37**, 986—996).—Details are given of the calorimetric bomb built to replace that of Berthelot (cf. this vol., ii, 427).

S. K. T.

**Theory and Construction of Lever Manometers.** O. FRANK (*Z. Biol.*, 1925, **83**, 1—15).—The theory and construction of lever manometers is discussed and an equation obtained from the roots of which the system is calculable. If the volume elasticity coefficient is made equal to infinity, a system results having two degrees of freedom and possessing the essential properties of a lever manometer. The chief data are calculable to within 1%.

P. W. C.

**Sensitive Glass Manometer for Gases which Attack Mercury.** A. KLEMENC (*J. Amer. Chem. Soc.*, 1925, **47**, 2173—2175).—The manometer consists of an inverted funnel-shaped capillary tube with a very thin glass diaphragm over the end, which is nearly filled with a light paraffin oil and sealed into a thick-walled vessel. The latter, which is sealed up at the temperature at which the vapour-pressure measurement is to be made, contains a sample of the substance being investigated sealed up in a bulb and also a piece of iron, so arranged that the latter can be made to break the bulb by the application of a magnet. The top end of the capillary

tube is connected to a differential mercury manometer, the reservoir of which is raised during an experiment so as to keep the level of the oil in the capillary constant. The pressure is then read in the usual way.

S. K. T.

**Apparatus for the Extraction of Solids.** R. STRUENSEE (*Chem.-Ztg.*, 1925, **49**, 647).—A modified form of the Soxhlet apparatus has a small glass cup with a bottom plate of sintered glass instead of the usual asbestos or paper thimble. The apparatus is useful for the extraction of sulphur from gas purification residues, using carbon disulphide or tetrachloride.

A. R. P.

**Device for Estimating Corrosion.** W. R. FETZER (*Ind. Eng. Chem.*, 1925, **17**, 788).—A device for making comparative corrosion tests of metals in which the samples, consisting of small pieces of sheet metal, are partly immersed in the corrosive liquid in bent glass tubes and rocked uniformly. [Cf. *B.*, 1925, 765.]

C. I.

**Electrolytic Gas Explosions.** W. NORMANN (*Chem.-Ztg.*, 1925, **49**, 757).—A discussion of the Fresenius safety-tube and other safety-devices.

R. A. M.

**Glass Filter Apparatus.** P. H. PRAUSNITZ (*Analyst*, 1925, **50**, 440—444).—Glass filter apparatus is made by a process of grinding and sieving suitable glasses, and fusing particles of equal size to form filter discs with pores of approximately equal diameter. These discs may be fused together with the same type of glass in various pieces of apparatus, many of which are described.

D. G. H.

**Prevention of Bumping when Boiling Liquids.** J. W. REBBECK (*Canadian Chem. Met.*, 1925, **9**, 177—178).—Small glass tubes closed at one end and having a small opening with sharp edges at the other are laid on the bottom of the container.

S. I. L.

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### Mineralogical Chemistry.

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**Distribution of the Chemical Elements in the Earth's Crust.**  
W. VERNADSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1916, [6], 1323—1342; from *Chem. Zentr.*, 1925, i, 2545).—Most of the bismuth minerals occur in the weathering zone of the earth's crust and are thus exposed to atmospheric influences. It is characteristic of the less numerous primary bismuth minerals that they generally occur in the presence of larger amounts of copper, cobalt, nickel, gold, lead, silver, or tin. The most important of the primary minerals have been deposited by steam. The natural concentration of bismuth is very slow and incomplete. G. W. R.



**Occurrence of Hydrogen Sulphide in Limestone and Dolomite.** W. NENADKEVITSCH (*Bull. Acad. Sci. St. Pétersbourg*, 1917, [6], 1037—1040; from *Chem. Zentr.*, 1925, i, 2545).—Many limestones and dolomites yield hydrogen sulphide when pulverised. From 0.006% to 0.012% of hydrogen sulphide has been found to be present.  
G. W. R.

**Hydrogen Sulphide in Limestone and Dolomite.** W. VERNADSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1917, [6], 1379—1388; from *Chem. Zentr.*, 1925, i, 2545; cf. preceding abstract).—The amount of hydrogen sulphide in different limestones and dolomites approximates closely to an average figure of 0.01%. This is regarded as not fortuitous, but it is not known whether it represents an equilibrium or a stable condition. Gypsum or natural gas may be the source of hydrogen sulphide. If the former be the case, the limestones and dolomites in question must have originated by the metamorphosis of clays or marls rich in gypsum.  
G. W. R.

**Leverrierite as a Schist-forming Mineral.** C. S. CORBETT (*Amer. J. Sci.*, 1925, [v], 10, 247—268).—A number of schists from localities in the United States, especially those associated with quartzite, show a defect of potash by analysis, and some of them are found by a microchemical test to be free from potash. The micaceous schist-forming mineral in these cases is considered to consist wholly or partly of leverrierite. X-Ray powder photographs, compared with those of pure specimens of leverrierite, also gave clear indications of its presence.  
W. A. C.

**Crystalline Modifications of  $\text{NaAlSiO}_4$ .** N. L. BOWEN and J. W. GREIG (*Amer. J. Sci.*, 1925, [v], 10, 204—212).—Whereas the hexagonal form, nephelite, is stable up to 1248°, the highly-twinned, possibly triclinic, form known as carnegieite or sodium anorthite undergoes a transition from a birefringent to an isotropic form at temperatures between 650° and 690°, varying with the specimen. The inversion, as followed under the microscope, is sharp in both directions. Another inversion at 226.5° is indicated by the heat-curves and also by a change of birefringency, which is sharp on heating but gradual on cooling.  
W. A. C.

**Amphibolites from Austria.** A. MARCHET (*Tsch. Min. Mitt.*, 1924, 36, 170—211; 1925, 36, 229—320).—Detailed petrographical descriptions with 25 chemical analyses are given of amphibolites, granulites, eclogites, and other rocks from the Waldviertel in Lower Austria.  
L. J. S.

**Rhine Water.** F. HABER and J. JAENICKE (*Z. anorg. Chem.*, 1925, 147, 156—170).—Twenty-three samples of Rhine water showed the presence of gold in amounts up to  $10.3 \times 10^{-9}$  g./litre. The silver content varied between the limits  $0$ — $65 \times 10^{-9}$  g./litre.  
J. S. C.

**Measurement of the Altitude of the Layer of Ozone in the Atmosphere.** J. CABANNES and J. DUFAY (*Compt. rend.*, 1925, **181**, 302—304).—Optical measurements lead to the conclusion that the altitude of the layer of ozone is of the order of 50 km.  
J. S. C.

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## Analytical Chemistry.

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**Quartz Apparatus with Filtering Bottoms.** G. F. HÜTTIG and H. KÜKENTHAL (*Chem.-Ztg.*, 1925, 49, 716).—Silica crucibles with porous filtering bottoms of transparent or translucent, sintered quartz particles have been prepared in a manner similar to the porcelain crucibles previously described (Hüttig and Nette, this vol., ii, 431). The crucibles have the same resistance to attack by chemicals as the ordinary silica crucible, do not flake on heating or cooling, and are superior to ordinary Gooch crucibles.

A. R. P.

**Oxycalorimeter.** F. G. BENEDICT and E. L. FOX (*Ind. Eng. Chem.*, 1925, 17, 912—918).—The principle involved is the accurate measurement of the contraction in volume produced when the substance under examination is burnt in a known volume of nearly pure oxygen, provision being made for the rapid absorption of the carbon dioxide produced. The calorific value is then found by application of a factor representing the calorific value of oxygen. The most accurate apparatus suitable for fuels is described in detail, whilst a simpler form may be used for substances with a greater error in sampling, such as foods and excreta.

D. G. H.

**Simplified Method of Micro-combustion; the Micro-Dennstedt Method.** C. FUNK and S. KON (*J. Chem. Soc.*, 1925, 127, 1754—1755).—The apparatus consists of a "pyrex" glass tube of the Pregl pattern fitted with an inner tube reaching about one-third the length of the outer and a diffusion stopper providing a double supply of oxygen. The combustion tube contains a platinum contact star and three boats filled respectively with molecular silver, lead peroxide, and red lead. The substance to be burnt is placed in a small boat in the inner tube and the combustion is carried out as described by Dennstedt, the temperature of the absorbents being maintained at 320°. In the determination of nitrogen by Pregl's method, high results are obtained unless the layer of reduced copper is placed at the end of the tube, as in the Dubsky process.

A. R. P.

**Preparation of Standard Solutions.** F. PREGL (*Z. anal. Chem.*, 1925, 67, 23—27).—A 12-litre cylinder is calibrated as nearly as possible by weighing and then filled with water to the 10-litre mark. A slight excess over the theoretical amount of substance the standard solution of which is required is added and, after

mixing, 40 c.c. are titrated with an approximately standard solution. The extra amount of water required to bring the desired solution to standard is calculated, but only 90% of this is added. Titration is repeated as before, and again 90% of the necessary water is added. A third titration is made against a weighed quantity of the standard substance, using the burette that is to be employed when working with the solution that is being prepared, and from the result of this the correct amount of water to be added to the solution to bring it exactly to standard strength is calculated and added. Finally, the solution is again titrated against a weighed amount of standard. In this manner, errors in the calibration of the measuring instruments are nullified. To prepare sodium hydroxide solution free from carbonate the hydroxide is dissolved in its own weight of water and the solution is kept at nearly 100° for several hours, then cooled slowly over-night. The clear liquor can be siphoned off and diluted as required; the residue contains all the sodium carbonate.

A. R. P.

**Differential Electro-titration.** D. C. Cox (*J. Amer. Chem. Soc.*, 1925, **47**, 2138—2143).—The solution to be titrated (0.1 to 0.05*N*) is divided into two equal parts. Platinum wires are immersed in each and connected to a millivoltmeter. The two solutions, which are connected with a strip of filter paper, are now simultaneously titrated, one burette being always kept 0.2 c.c. ahead of the other. As the end-point is passed, the voltmeter readings suddenly pass from zero through a sharp maximum (end-point) and then rapidly decrease to nearly zero. Curves are not necessary for finding the maximum. Two maxima are obtained with soluble carbonates, one almost corresponding with the phenolphthalein, and the other with the methyl-orange, end-points.

S. K. T.

**Spectrophotometric Determination of Hydrogen-ion Concentrations and of the Apparent Dissociation Constants of Indicators.** IV. Sodium  $\alpha$ -Naphthol-2-sulphonate Indophenol. W. C. HOLMES and E. F. SNYDER (*J. Amer. Chem. Soc.*, 1925, **47**, 2232—2236).—The ratio  $R_2$ , the relative intensity of the two absorption bands at 520 $\mu$  and 600 $\mu$  (cf. Holmes, A., 1924, ii, 346), at various  $p_H$  values is determined for sodium  $\alpha$ -naphthol-2-sulphonate indophenol. The indicator is relatively unstable in aqueous solution, but is stable in absolute alcohol. The dissociation of the dye follows the normal course of a monobasic acid, the apparent dissociation constant in 5% aqueous alcoholic solution being 8.63. In the spectrophotometric determination of hydrogen-ion concentration, the measurements must be made immediately after the preparation of the solutions. Data for the use of the indicator in the drop-ratio method (cf. Gillespie, A., 1920, ii, 282) are as follows: drop ratio, 1 : 9, 2 : 8, 3 : 7, 4 : 6, 5 : 5, 6 : 4, 7 : 3, 8 : 2, 9 : 1,  $p_H$  values, 7.68, 8.03, 8.26, 8.45, 8.63, 8.81, 9.00, 9.23, and 9.58, respectively.

J. W. B.

**Micro-determination of Hydroxyl Groups.** B. FLASCHENTRÄGER (*Z. physiol. Chem.*, 1925, **146**, 219—226).—By means of

a special apparatus and particular care in the preparation of the reagents, the method of Tschugaev and Zerewitinov (A., 1907, ii, 509) for the determination of hydroxyl groups, by measurement of the methane evolved on treatment with magnesium methyl iodide, has been adapted for use with 3—10 mg. of material. The best solvent in most cases is pyridine. C. R. H.

**Determination of Chlorine in Benzaldehyde.** J. D. BUKSCHNEWSKI (*Z. angew. Chem.*, 1925, **38**, 723—724).—The sample (2 g.) is burnt in oxygen under pressure in a bomb calorimeter, which is then cooled with water. In releasing the pressure the gases are passed through 0.01*N*-silver nitrate, to which are added the washings from the calorimeter. Nitrous acid is removed by adding nitric acid and ferric alum and evaporating the whole to about half bulk. When cold, the unchanged silver nitrate is determined by titration with 0.02*N*-ammonium thiocyanate. The error is  $\pm 0.0018\%$ . W. T. K. B.

**Determination of Chlorine in Benzaldehyde and Cinnamaldehyde.** T. H. FAUST and T. SPÄGLER (*Chem.-Ztg.*, 1925, **49**, 724—725).—Small quantities (*e.g.*, 0.02%) of chlorine in benzaldehyde and cinnamaldehyde are rapidly and accurately determined by gradually adding 25 g. of the sample, from a dropping funnel, to a mixture of 5 c.c. of fuming nitric acid and 25 c.c. of concentrated sulphuric acid. The resulting hydrogen chloride and sulphur dioxide are passed into a solution of silver nitrate. Heat is applied to complete the reaction, the silver nitrate solution is acidified with nitric acid, and the silver chloride determined gravimetrically. W. T. K. B.

**Titration of Iodides with Iodate.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1925, **62**, 878—882).—Lang's method of titration in presence of cyanide is rendered even more delicate by using carbon tetrachloride in place of starch as an indicator. Mere traces of combined iodine in presence of large excess of bromides or chlorides can be determined, 0.1 mg. being titrated by means of a microburette and an *M*/60,000 solution of potassium iodate with an error not exceeding 1% in presence of 1 g. of potassium bromide. S. I. L.

**Microchemical Determination of Sulphur. I. Determination of Sulphur in Easily Soluble Sulphides.** W. GEILMANN (*Z. anorg. Chem.*, 1925, **146**, 324—328).—Sulphur in easily soluble sulphides can be determined microchemically by titration with 0.05*N*-iodine and thiosulphate with an accuracy equal to that of the macrochemical determination. One to 2 c.c. of 2*N*-hydrochloric acid and 3—5 c.c. of the iodine solution are introduced into a stoppered Erlenmeyer flask. The sulphide solution is added from a pipette, or a solid sulphide weighed on the micro-balance and added from the weighing bottle as quickly as possible and the flask at once re-stoppered. The contents are shaken and after 10 mins. titrated back with thiosulphate. A blank experiment is carried out under the same conditions. Loss of iodine by evapor-

ation must be prevented, and the concentration of acid in the solution must be kept as low as possible. A. B. M.

**Action of Some Oxidising Agents on Sulphite.** II. W. S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1925, **47**, 2156—2159; cf. this vol., ii, 712).—Sulphites may be determined accurately by titration with iodate solution, with free bromine, or with bromate, permanganate, or dichromate solutions containing half their equivalent of iodide. In the case of bromate, one-sixth of an equivalent of iodide suffices. It is recommended that titrations in which the action of air or escape of gas is to be guarded against should be carried out in a vacuum flask, which is described.

S. K. T.

**Action of Sodium Carbonate on Phosphates.** A. COLANI (*Bull. Soc. chim.*, 1925, [iv], **37**, 937—940).—An investigation of the accuracy of the method frequently adopted in qualitative analysis for the separation of metals of the iron group in presence of phosphates. The action of sodium carbonate on phosphates of iron, chromium, manganese, barium, calcium, strontium, and magnesium was studied by adding to a solution of sodium phosphate four-thirds of the quantity of metallic salt necessary to form the tribasic phosphate, redissolving the precipitate in acid, precipitating with ammonium chloride and ammonia, and heating this precipitate with sodium carbonate. The phosphates of manganese and calcium are scarcely attacked by sodium carbonate, whilst those of chromium, strontium, and magnesium lose about half their phosphorus by this treatment. The method is completely successful only in the case of iron and barium. The addition of a little sodium hydroxide to the sodium carbonate gives identical results.

L. L. B.

**Determination of Small Quantities of Carbon Dioxide.** S. NISHI (*Act. Schol. Med. Univ. Imp. Kyōto*, 1925, **7**, 263—270).—In Warburg's method of determination of carbon dioxide (A., 1909, ii, 830) an error is introduced and the end-point of the titration rendered uncertain by the slow decomposition of barium carbonate. An apparatus has been devised whereby the barium carbonate is removed by filtration before titration. By this means the experimental error is reduced to less than 1% in determining 1.0 to 2.5 mg. of carbon dioxide.

L. F. H.

**Determination of Small Amounts of Carbon Dioxide.** S. NISHI (*J. Biochem.*, 1925, **4**, 473—480; cf. preceding abstract).—To avoid the error involved in Warburg's method (*loc. cit.*) and the cumbersome filtration described in the preceding abstract, the carbon dioxide is absorbed in sodium hydroxide and the solution is titrated using thymolphthalein as indicator. Both systematic and casual errors are reported as being obtained by this method.

L. F. H.

**Separation of the Alkalis in Silicate Analysis.** O. CANTONI (*Z. anal. Chem.*, 1925, **67**, 33—34).—In the method of Berzelius for decomposing silicates by hydrofluoric and sulphuric acids time

may be saved and a preliminary separation of the iron, alumina, and alkaline earths effected by evaporation of the sulphuric acid completely to dryness followed by ignition of the crucible to a dull red heat. The cold mass, when extracted with water, leaves a residue free from alkalis and the solution may be treated immediately with barium chloride to remove sulphuric acid and convert the alkalis into chlorides. The analysis is finished as usual.

A. R. P.

**Critical Studies on Methods of Analysis. XVI. Zinc.** L. A. CONGDON, A. B. GUSS, and F. A. WINTER (*Chem. News*, 1925, **131**, 65—68, 81—84, 97—100, 113—117).—Comparative analyses of pure zinc nitrate were made by various modifications of the phosphate, sulphide, sulphate, oxide, and volumetric ferrocyanide methods and by several other less known methods. Practically all the results were within 0.2% of the theoretical. In using the phosphate method, the precipitate must be washed with dilute ammonium nitrate solution and not with hot water, which has a slight solvent action on the precipitate. For the determination of zinc in solutions containing alkali or magnesium salts, precipitation of the zinc with thiocyanate and pyridine followed by ignition to oxide gives satisfactory results.

A. R. P.

**Gravimetric Determination of Zinc by Means of Cyanamide.** W. MARCKWALD and H. GEBHARDT (*Z. anorg. Chem.*, 1925, **147**, 42—49).—To a neutral solution of zinc salt 1—2 g. of ammonium acetate are added for each 0.1 g. of zinc. Dilute ammonia is added until the precipitate formed redissolves and the solution is faintly alkaline. Excess of ammonia must be avoided. A considerable excess of cyanamide is now added and the precipitate of zinc cyanamide allowed to settle on the steam-bath, filtered, washed with very dilute ammonia, and finally ignited and weighed as zinc oxide. In presence of nickel, for each 0.1 g. of metal 0.5—1 g. of ammonium thiocyanate or acetate is added and then an excess of cyanamide solution. Dilute ammonia is added dropwise until the solution just turns red litmus paper blue. The solution should have a green and not a blue colour. The zinc cyanamide precipitate is converted into oxide and weighed as such. Zinc can be determined in presence of magnesium by precipitation as cyanamide in presence of ammonium chloride and ammonia.

Cadmium may be precipitated as cyanamide in presence of ammonium chloride and ammonia. The washed precipitate is dissolved in dilute hydrochloric acid and the solution evaporated to dryness. The residue is then evaporated to fuming with sulphuric acid and weighed as sulphate.

The cyanamide solution is prepared by treating a mixture of calcium cyanamide with twice its weight of water with carbon dioxide at 40—70° until no more gas is absorbed. The filtered solution is treated with air to precipitate calcium hydrogen carbonate and again filtered. If a solution of cyanamide free from any traces of impurity is desired, the solution is evaporated in a vacuum

with a little acetic acid. The residue is extracted with ether and pure cyanamide obtained after evaporating the ethereal solution to dryness. In presence of a little acetic acid, cyanamide solutions undergo very small changes in concentration on long keeping.

J. S. C.

**Determination of Very Small Quantities of Lead in Animal Tissues and the Ageing of Very Dilute Solutions of Lead Nitrate.** H. BERNHARDT (*Z. anal. Chem.*, 1925, **67**, 97—105).—

After destruction of the organic matter by any suitable process, the solution is treated with ammonium citrate and saturated with hydrogen sulphide. The precipitate is collected and dissolved in nitric acid and the solution is electrolysed at 2·8—3·2 volts for 1·5—2 hrs., using a rotating platinum gauze anode on which the lead is deposited as peroxide. The deposit is dissolved in 5% potassium iodide solution containing acetic acid, and ammonium acetate is added until the lead iodide dissolves. The liberated iodine is titrated with 0·001N-thiosulphate. Very dilute solutions of lead nitrate appear to undergo hydrolysis on keeping, the lead content segregating towards the bottom or top layers according as to whether the water used was boiled or not. In addition, there appears to be a considerable action on the glass involving the formation of a silicate of lead.

A. R. P.

**Detection of Copper.** G. SPACU (*Z. anal. Chem.*, 1925, **67**, 31—32).—The neutral solution is treated with a little ammonium thiocyanate and then with two drops of a 2% alcoholic tolidine solution. A flocculent precipitate of  $\text{CuC}_{14}\text{H}_{16}\text{N}_2(\text{CNS})_2$  having a Prussian-blue colour indicates the presence of copper. A similar precipitate is obtained by the use of potassium iodide and alcoholic benzidine. The tolidine compound is readily soluble in alcohol, whilst the benzidine compound is only slightly soluble.

A. R. P.

**Standardisation of Titanous Chloride Solutions, and Potentiometric Titration of Copper.** E. ZINTL and A. RAUCH (*Z. anorg. Chem.*, 1925, **146**, 281—288).—

Methods of standardising titanous chloride solutions, using the potentiometric method, have been investigated. The author recommends a standard copper sulphate solution for the purpose. The titration proceeds more smoothly, the potential reaching its equilibrium value more rapidly, than with potassium dichromate or ferric alum. The copper solution must be free from iron. Its strength is accurately determined by electrolytic deposition. The titration by titanous chloride is carried out in the presence of 4—8% hydrochloric acid with complete exclusion of air. Several determinations can be carried out with one and the same solution by re-oxidising after reduction with a few drops of concentrated bromate or dichromate solution. The method can be applied to the determination of copper in the presence of mercury, lead, cadmium, zinc, and arsenic.

A. B. M.



**Separation of Copper and Mercury.** G. SPACU (*Z. anal. Chem.*, 1925, 67, 27—31).—The hot dilute solution of the chlorides of copper and mercury is treated with pyridine until it becomes blue, then with eight to ten times the weight of the combined metals in ammonium thiocyanate. After cooling, the green flocculent copper pyridine thiocyanate (cf. Spacu, A., 1923, ii, 40) is collected, washed with water containing pyridine and ammonium thiocyanate, and ignited very slowly to copper oxide for weighing. Mercury is recovered from the filtrate by acidifying with hydrochloric acid and passing a stream of hydrogen sulphide. A. R. P.

**Direct Determination of Tervalent Iron in Silicates Insoluble in Acids. Use of the Method in Determining the Ratio of Ferric to Ferrous Iron after Decomposition of the Mineral with Sulphuric and Hydrofluoric Acids.** O. HACKL (*Z. anal. Chem.*, 1925, 66, 401—430).—Ferric iron may be determined directly in silicates by dissolving the minerals in the minimum quantity of sulphuric and hydrofluoric acids in an atmosphere of carbon dioxide, and, after cooling, pouring the solution into a saturated solution of boric acid sufficient to combine with all the hydrofluoric acid; the liquid is then titrated with 0.1N-titanous chloride solution using potassium thiocyanate as indicator. The results agree closely with those obtained by the indirect method (determination of total and ferrous iron and calculation of the ferric iron by difference), but are always 2 mg. too high due to slight oxidation during decomposition of the mineral. The process is useful in determining the ratio of ferric to ferrous iron in substances containing organic matter which would interfere in the permanganate titration. [Cf. B., 1925, 711.] A. R. P.

**Application of Liquid Amalgams to Volumetric Analysis. I. Determination of Molybdenum, Titanium, and Iron.** T. NAKAZONO (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, 14, 109—117).—See A., 1921, ii, 596.

**Electro-analytical Precipitation of Antimony.** A. SCHLEICHER and L. TOUSSAINT (*Chem.-Ztg.*, 1925, 49, 645—646).—Complete precipitation of antimony in an adherent and dense form may be obtained from a chloride solution to which tartaric acid and hydrazine sulphate have been added if the temperature is maintained at 60° and the voltage at 0.6 volt throughout the electrolysis, and a small amount of ammonium persulphate is added towards the end of the analysis. [Cf. B., 1925, 740.] A. R. P.

**Potentiometric Titration of Bismuth in Presence of Other Metals.** E. ZINTL and A. RAUCH (*Z. anorg. Chem.*, 1925, 146, 291—298).—The method previously described for the potentiometric titration of bismuth with titanous chloride (this vol., ii, 442) can be used for the determination of bismuth in the presence of other metals. Ferric iron is first reduced to ferrous, then the bismuth is precipitated. The solution is made slightly acid with hydrochloric acid (in acetic acid solution the method fails) and is

titrated hot. The beginning and the end of the reduction of the bismuth salt are shown by a well-marked fall in potential. The presence of a small quantity of an iron salt simplifies the titration of bismuth, obviating the necessity of first boiling out the air from the solution. Bismuth can be determined also in presence of lead (in a solution acidified by hydrochloric or acetic acid), tin (only in acetic acid solution), cadmium (in dilute hydrochloric acid solution), and arsenic (as arsenic acid in hydrochloric acid solution), but not in the presence of antimony. A. B. M.

#### **Precipitation of Bismuth Sulphide from Acid Medium.**

S. RAMACHANDRAN (*Chem. News*, 1925, **131**, 135).—Precipitation of bismuth sulphide from hydrochloric acid solutions by hydrogen sulphide begins to take place when the proportion of concentrated acid to water is 1 : 3 and is complete when the ratio is 1 : 5. Conversely, precipitated bismuth sulphide is completely soluble at 30° in 1 : 3 hydrochloric acid. A. R. P.

#### **Potentiometric Titration of Gold.**

E. ZINTL and A. RAUCH (*Z. anorg. Chem.*, 1925, **147**, 256—261).—Solutions of gold, free from nitric acid, after first being boiled in an atmosphere of carbon dioxide for 10 mins. to expel dissolved air, followed by addition of a drop of bromate solution, are titrated potentiometrically with titanous chloride. The first fall of potential corresponds with the complete reduction of bromate and the commencement of the  $\text{Au}^{+++} \rightarrow \text{Au}$  reduction. The solutions should contain 4—10% of hydrochloric acid. In this way, gold can be determined in presence of mercury, tin, lead, and copper. In the case of copper, both metals may be determined in one operation. In presence of iron, a considerable amount of phosphoric acid should be added. J. S. C.

#### **Separation of Palladium from Platinum.**

F. KRAUSS and H. DENEKE (*Z. anal. Chem.*, 1925, **67**, 86—96).—A review of the methods of separating palladium from platinum by precipitation with  $\alpha$ -nitroso- $\beta$ -naphthol, acetylene,  $\alpha$ -dimethylglyoxime, and mercuric cyanide shows that all these methods yield bulky precipitates which retain small quantities of platinum when the proportion of palladium present is high. The following method is recommended: the chloride solution is evaporated to dryness with a slight excess of ammonium chloride, the residue is dissolved in water, and the solution saturated with ammonium chloride. The precipitated ammonium chloroplatinate is collected, washed with saturated ammonium chloride solution, and dissolved in hot water. The platinum in this solution and the palladium in the filtrate are each precipitated by boiling with sodium formate. A. R. P.

#### **"Höchst Test" for the Determination of Anthracene.**

F. H. RHODES, M. L. NICHOLS, and C. W. MORSE (*Ind. Eng. Chem.*, 1925, **17**, 839—842).—The Höchst test (*Z. anal. Chem.*, 1877, **16**, VOL. CXXVIII. ii.

61) has been critically investigated. Loss may arise if an excess of chromic acid is present (as happens with rich samples of crude anthracene) because anthraquinone itself is oxidised by the hot chromic-acetic acid mixture. Very little loss takes place in the precipitation of the acetic acid solution by dilution, the separation being almost quantitative, and no loss by sulphonation occurs in the purification by solution in fuming sulphuric acid. In drying the anthraquinone a slight loss by volatilisation may occur. Filtering loss is prevented by using hardened filter paper in a Gooch crucible and is eliminated in the second filtration by using an asbestos mat, from which the anthraquinone is directly sublimed, preferably in a special oven at 350°. At that temperature sublimation is complete in  $\frac{1}{2}$  hr. Revised directions are given. [Cf. *B.*, 1925, 838,] W. A. S.

**Determination of Methyl and Ethyl Alcohol.** J. WIMMER (*Z. angew. Chem.*, 1925, 38, 721—723).—Methyl and ethyl alcohol in aqueous solutions, the former also in the presence of acetone or formaldehyde, are determined by esterifying with a large excess of formic acid, with a small quantity of sulphuric acid as catalyst, and removing the ester as fast as formed by fractional distillation. The ester is distilled into sodium hydroxide, whereby it is quantitatively saponified, the last traces of ester being swept out of the apparatus with nitrogen, and the unchanged alkali is titrated. When formaldehyde is present, the sodium hydroxide should be cooled with ice. W. T. K. B.

**Colour Reaction of *tert.*-Amyl Alcohol.** L. EKKERT (*Pharm. Zentr.*, 1925, 66, 599).—A strong alcoholic solution (0.5 c.c.) of *tert.*-amyl alcohol is mixed with 5 c.c. of concentrated sulphuric acid and strong tartaric acid solution is added. A rose-red colour appears first in the surface of contact and then throughout the supernatant layer. Guaiacol, resorcinol, or potassium guaiacol-sulphonate can replace the tartaric acid, but the last named gives the most rapid reaction. A definite coloration is obtained with 3 mg. of *tert.*-amyl alcohol. R. B.

**Comparison of the Polarimeter and Copper Reduction Values of Dextrose Solutions.** H. L. WHITE (*Amer. J. Physiol.*, 1924, 68, 116).—In the presence of 0.1M-phosphate solution, neither the copper value nor the polarimeter value of dextrose solution is changed in the presence of insulin and liver extract. Consistently lower figures are, however, obtained with the polarimeter than by copper reduction. A. A. E.

**Influence of Nitrogenous Substances on Dextrose Determinations.** L. ROSENTHALER (*Pharm. Zentr.*, 1925, 66, 517—520). Determinations of dextrose by six well-known methods, involving reduction of copper solutions or of iodine, have been made in presence of small quantities of added ammonium chloride, asparagine, glycine, carbamide, uric acid, peptone, or urine, and the influence of the added substances is shown in tabular form.

Urine causes large errors in all cases and uric acid in most. The Rupp-Lehmann and Willstätter-Auerbach methods are in general least affected.

G. M. B.

**Analysis of Acetic Anhydride.** W. S. CALCOTT, F. L. ENGLISH, and O. C. WILBUR (*Ind. Eng. Chem.*, 1925, 17, 942—944).—Orton's method of determining small amounts of acetic anhydride in glacial acetic acid (T., 1911, 99, 1181) has been adapted to the determination of acetic anhydride by acetylation of 2:4-dichloroaniline in glacial acetic acid. The 2:4-dichloroacetanilide is separated from the excess of dichloroaniline by extraction and washing with 10% hydrochloric acid and is hydrolysed by refluxing with 19% hydrochloric acid, and the resulting 2:4-dichloroaniline titrated with 0.1N-sodium nitrite solution. The dichloroacetanilide does not interfere, however, if the temperature is kept below 26° and the titration completed within 1 hr. of the time of dilution of the acetylated mass. [Cf. B., 1925, 826.]

D. G. H.

**Colour Reaction for Lactic Acid.** L. EKKERT (*Pharm. Zentr.*, 1925, 66, 552—553).—If a dilute solution of lactic acid is poured on to a 1% solution of pyrocatechol in concentrated sulphuric acid, a blood-red coloration is produced at the surface of contact of the liquids. Alternatively, the dilute lactic acid solution, mixed with sulphuric acid, may be poured on to a 1% aqueous or alcoholic solution of pyrocatechol. The coloration is visible with 0.02% solutions of lactic acid. Resorcinol, quinol, and  $\alpha$ -naphthol yield with lactic acid only greenish-yellow colorations.

W. T. K. B.

**Detection of Small Quantities of Lactic Acid in Fruit [Tomato] Juice as Calcium Lactate.** A. BORNTÄGER (*Z. anal. Chem.*, 1925, 66, 430—460).—The detection of lactic acid in fruit juices containing citric, malic, and succinic acids is based on the solubility of calcium lactate in 75% alcohol and the insolubility of the calcium salts of the other acids in this solvent. After dilution of the alcoholic extract with water so that the alcohol content is about 93 vol.-%, addition of an equal volume of ether precipitates the calcium lactate as a syrup which crystallises in small bunches of needles after keeping for some hours. The fruit juice is treated with calcium chloride and milk of lime until slightly alkaline, evaporated to a syrupy consistency, and extracted with 95% alcohol, the extract being evaporated to dryness and the residue extracted with 93 vol.-% alcohol; the clear filtrate is then treated with ether as above. An alternative method consists in shaking the acidified juice with several small portions of ether, evaporating the ether extracts to dryness, and continuing the process as in the first method after neutralisation with calcium hydroxide. [Cf. B., 1925, 734.]

A. R. P.

**Oxidimetric Determination of Tartaric Acid and Other Organic Substances.** K. TÄUFEL and C. WAGNER (*Z. anal. Chem.*, 1925, 67, 16—20).—Tartaric acid, sucrose,  $\beta$ -naphthol,

salicylic acid, and phthalic acid may be determined by heating the substance with twice the theoretical quantity of potassium dichromate and a large excess of 85% sulphuric acid for 15 mins. on the water-bath. After cooling and diluting the solution the excess of dichromate is determined iodometrically. A. R. P.

**Precipitation of Oxalic Acid with Basic Bismuth Nitrate in Qualitative Analysis.** A. KESCHAN (*Z. anal. Chem.*, 1925, **67**, 81—86).—Oxalic acid may be removed from the solution before precipitation of the group III metals by boiling the liquid with nitric acid until the bulk of the hydrochloric acid is expelled, adding basic bismuth nitrate and boiling for some time. Iron must be reduced to the ferrous condition and a little phosphoric acid added if chromium is present. The procedure is the same as that used for the separation of phosphoric acid (cf. Keshan, this vol., ii, 328). A. R. P.

**Tests for Ethyl Phthalate.** H. LEFFMANN and M. TRUMPER (*Amer. J. Pharm.*, 1925, **97**, 507—510).—The conditions suitable for the detection of small quantities of ethyl phthalate in alcohols by condensation with phenol or resorcinol are discussed. S. I. L.

**Detection of Ethyl Phthalate.** S. LEVINSON (*Ind. Eng. Chem.*, 1925, **17**, 929).—Ethyl phthalate, phthalic acid, or its salts may be detected by adding dry boric acid to the nearly evaporated sample and resorcinol to the dry residue. After further heating the mass is dissolved in water, and on rendering alkaline with sodium hydroxide a fluorescence indicates a positive reaction. [Cf. *B.*, 1925, 821.] D. G. H.

**Detection of Ethyl Phthalate in Essential Oils.** H. THOMS (*Apoth.-Ztg.*, 1925, **40**, 196; from *Chem. Zentr.*, 1925, i, 2475).—An adulteration of 10% of ethyl phthalate may be detected in certain essential oils as follows. The oil is evaporated to dryness on a water-bath with ethyl alcohol and sodium hydroxide solution. If a resinous residue is obtained, this is extracted with water and the aqueous extract evaporated to dryness. The residue is treated with cold sulphuric acid and resorcinol and heated at 80—85°. Some of this mixture is then added to ammonia solution. Freedom from ethyl phthalate is shown by the absence of any greenish-yellow fluorescence after 15 mins. Certain phenols such as eugenol interfere with the test since they also yield fluorescent condensation products with resorcinol. G. W. R.

**Winkler's Bromine Method of Determining the Iodine Value of Fats.** K. SCHEFFLER (*Pharm. Zentr.*, 1925, **66**, 533—538).—Winkler's bromine method of determining the iodine value of fats and oils gives equally good results as the Hübl iodine method in a much shorter time if the work is carried out in a flask or bottle of brown glass and the iodine value does not exceed 120. The results with fats having a higher value than

this do not agree very well with those obtained by the iodine method. The determination is carried out by shaking a solution of the fat in carbon tetrachloride with potassium bromide and bromate and a little hydrochloric acid; after 15 to 20 mins. for fats having an iodine value below 100, or 40 to 60 mins. for fats with a higher value, an excess of standard arsenite solution is added and the excess is determined by titration with potassium bromate. [Cf. *B.*, 1925, 728.] A. R. P.

**Preparation of Bromine-Acetic Acid Solution for Determination of Iodine-Bromine Number [of Fats and Oils].** L. W. WINKLER (*Pharm. Zentr.*, 1925, **66**, 581—583; cf. *ibid.*, 571).—Commercial glacial acetic acid is distilled, rejecting the first and last fractions; the distillate is adjusted by addition of water to 96—97% strength, 0.3% by volume of bromine added, and the product distilled after one day. Further bromine is added, the solution standardised against castor oil, and adjusted to 0.1N. S. I. L.

**Determination of Formaldehyde.** G. ROMEO (*Annali Chim. Appl.*, 1925, **15**, 300—304).—With potassium hydrogen sulphite, especially in presence of the normal sulphite, formaldehyde reacts readily with formation of the neutral sulphonate,  $\text{OH}\cdot\text{CH}_2\cdot\text{SO}_3\text{K}$ . The excess of the hydrogen sulphite may be determined by titration with standard alkali hydroxide free from carbonate. [Cf. *B.*, Oct. 30th.] T. H. P.

**Determination of Camphor in Plants, and Industrial and Pharmaceutical Products.** G. GORI (*Annali Chim. Appl.*, 1925, **15**, 283—300).—Giglioli's method for the determination of camphor in plants, based on extraction of the distillate with ether and removal of the essential oil by means of filter-cloth and filter-paper, is tedious and results in considerable loss of camphor. Better results are obtained by using carbon tetrachloride in place of ether, and by eliminating the oil of camphor by oxidation with permanganate. Details of the procedure are given for plants, celluloid, spirit of camphor, camphorated oil, etc. [Cf., *B.*, Oct. 30th.] T. H. P.

**Iodometric Determination of Cyanogen Compounds.** R. LANG (*Z. anal. Chem.*, 1925, **67**, 1—15).—Cyanide or thiocyanate may be determined in a solution by addition of bromine and phosphoric or acetic acid followed by removal of the excess of bromine with ferrous ammonium sulphate or hydrazine sulphate, addition of potassium iodide, and titration of the liberated iodine with thio-sulphate (cf. Schulek, A., 1923, ii, 591). When both cyanide and thiocyanate are present together the sum is obtained by the above process; in a second portion the cyanide is destroyed by the addition of formaldehyde and sodium or ammonium hydroxides and the thiocyanate is determined as above. In the presence of mercury salts, sufficient formaldehyde must be added to reduce the mercury to metal and sufficient bromine to effect its solution. If the solution contains also ferrocyanide, zinc sulphate is added before carrying out the foregoing operations and the ferrocyanide is determined

in a third portion by oxidation with permanganate in hydrochloric acid solution followed by destruction of the excess of permanganate with a little sodium nitrite and carbamide and titration of the iodine liberated by the ferricyanide on addition of potassium iodide. Details are given of the procedures employed in determining the above acids and the halogen acids in admixture.

A. R. P.

**Determination of Cyanides and the Use of Benzene as an Indicator in Iodometry.** N. KANÔ (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 101—107).—In the iodometric determination of cyanides a mixture of equal volumes of dilute solutions of boric acid and borax may be used for acidifying the solution before titration or by adding a solution of carbonic acid obtained by mixing the stoicheiometrical quantities of sodium hydrogen carbonate solution and dilute hydrochloric acid; in either case benzene is a better indicator than starch, as it has no action on the cyanogen iodide formed in the titration. More exact observations of the end point in the iodometric determination of chromates may also be made if the starch indicator is replaced by benzene. Ferricyanides may be determined iodometrically by the addition of potassium iodide followed by zinc sulphate to remove the ferrocyanide ions and subsequent titration of the iodine with thio-sulphate, using benzene as indicator.

A. R. P.

**Determination of Allantoin in Presence of Uric Acid, Creatinine, and Amino-acids.** E. LANGFELDT and J. HOLMSEN (*Biochem. J.*, 1925, **19**, 715—716).—In the determination of allantoin by precipitation with mercuric acetate, figures are obtained for the amount of allantoin in aqueous solution not more than 10% below the real amount. In presence of amino-acids in small quantities, and of creatinine and uric acid in quantities such as are present in normal urine, figures for allantoin obtained by the above method are higher and approximate to the real amount of allantoin. This is most probably due to the precipitation of other nitrogenous constituents. When amino-acids are present in larger amounts (0.2%), the figures for allantoin are too high. S. S. Z.

**Reactions of Some Opium Alkaloids.** L. DAVID (*Pharm. Ztg.*, 1925, **70**, 969—972).—The substance is dissolved in glacial acetic acid to which has been added a little "magnol" powder (commercial basic magnesium hypochlorite) and the solution carefully poured on to the surface of concentrated sulphuric acid. The various colour changes observed for thirteen opium alkaloids are tabulated, the colours being described by comparison with those of synthetic dyes of specified commercial origin.

G. M. B.

**Identification of Secale Cornutum Preparations. [Detection of Ergotinine].** W. P. H. VAN DEN DRIESSEN MAREEUW (*Pharm. Weekblad*, 1925, **62**, 789—793).—The various methods of

identifying ergotinine by means of colour reactions are recapitulated. A more delicate test is the addition of an ethereal solution to 50% nitric acid, an intense blue ring developing at the surface of separation, and remaining for two days. The ether plays a part in the reaction, since only a faint yellow-brown colour appears if light petroleum be used. The reaction is attributed to the presence of nitrous acid.

S. I. L.

**Determination of Morphine by Conductometric Titration with Silicotungstic Acid.** F.-E. RAURICH SAS (*Anal. Fis. Quim.*, 1925, 23, 277—289).—Morphine in tincture of opium may be titrated with silicotungstic acid by a conductometric method. Narcotine and codeine may be similarly determined. Mixtures of these alkaloids give curves showing points of inflexion corresponding with successive precipitation of the alkaloids.

G. W. R.

**Physico-chemical Studies on Proteins. II. Alkali Binding. Comparison of the Electrometric Titration of Proteins and of Phosphoric Acid with Sodium and Calcium Hydroxides.** W. F. HOFFMAN and R. A. GORTNER (*J. Physical Chem.*, 1925, 29, 769—781).—The electrometric titration of phosphoric acid by sodium and by calcium hydroxides (cf. Wendt and Clarke, A., 1924, ii, 417) shows that dicalcium phosphate and tricalcium phosphate are formed at the same hydrogen-ion concentration as is disodium phosphate, in spite of the much smaller tertiary ionisation constant of phosphoric acid. It is supposed that dicalcium phosphate consists of 2 mols. of phosphoric acid, one of which has all its hydrogen atoms replaced by calcium, whilst the other has its secondary and tertiary hydrogen atoms free. The presence of a secondary hydrogen atom in dicalcium phosphate is also indicated by its reaction with sodium hydroxide at  $p_H$  7.5. If the tertiary hydrogen atoms only of phosphoric acid were present, no combination would have occurred below  $p_H$  12.0. The stability of tricalcium phosphate in relatively acid solutions and its bearing on physiological and biochemical problems are discussed.

Sodium and calcium hydroxides behave similarly towards the proteins, casein, durumini, teozin, and fibrin, which have been titrated electrometrically with these alkalis over the  $p_H$  range 4.7 to 11.0 and titrated back with hydrochloric acid. The titration curves of casein and fibrin show binding of alkali at  $p_H$  5.5 and that of durumini at  $p_H$  11.0, and are similar to the titration curves of weak acids.

F. G. S.

**Quantitative Colour Test for the Grignard Reagent.** H. GILMAN and F. SCHULZE (*J. Amer. Chem. Soc.*, 1925, 47, 2002—2005).—The solution to be tested (0.5—1 c.c.) is treated with an equal volume of a 1% solution of Michler's ketone in dry benzene. Water (1 c.c.) is then added slowly with agitation, and finally several drops of a 0.2% solution of iodine in glacial acetic acid. The presence of Grignard reagent is indicated by the development



of a characteristic greenish-blue colour. Positive results were obtained for 25 Grignard reagents examined. Calcium and barium phenyl iodides, and sodium ethyl and sodium *p*-tolyl, also gave colorations. No coloration was given by compounds in which the magnesium atom was attached to any element other than carbon. Zinc ethyl iodide, zinc diethyl, mercury diethyl, mercury di-*p*-tolyl, mercuric *p*-tolyl iodide, and lead tetraethyl also gave negative results, as well as normal and basic halides of magnesium. Magnesium ethyl bromide gave a positive test in 0.037*M* solution, whilst magnesium phenyl bromide gave a strong coloration in 0.02*M* solution. Metallic magnesium may give rise to a blue or purple colour on the addition of acetic acid in the test, and should be removed by prior filtration.

F. G. W.

### New Principle for Testing Organotherapeutic Powders.

JAVILLIER, H. ALLAIRE, and [MLLE.] M. GROG (*J. Pharm. Chim.*, 1925, [viii], 1, 513—525).—Dried materials from horse, pig, ox, calf, and sheep contain total lipoids: nervous tissue, 40—80% or more; suprarenal gland, liver, pancreas, and testicle, 25—40%; and lung, heart, kidney, muscle, spleen, thyroid, and ovary, less than 25%; total phosphorus: thymus, nervous tissue, pancreas, suprarenal gland, and testicle, 1.3—2% or more; spleen, kidney, liver, and lung, 1—1.3%; and heart, ovary, muscle, and thyroid, less than 1%; lipid phosphorus: nervous tissue, pituitary, and suprarenal glands, 0.6—1.4%; testicle, liver, pancreas, lung, heart, kidney, and ovary, 0.35—0.6%; and placenta, spleen, thymus, thyroid, breast, and muscle, less than 0.35%; nucleic phosphorus: thymus gland, more than 1%; pancreas, spleen, placenta, lung, and testicle, 0.3—0.6%; prostate, liver, kidney, and ovary, 0.1—0.3%; and nervous tissue, heart, and muscle, less than 0.1%. Tables are also given of the percentage of total phosphorus which is lipid: nervous tissue, 60—90%; pituitary, testicle, kidney, liver, heart, lung, suprarenal gland, and ovary, 35—55%; and pancreas, muscle, and spleen, 10—25%; the percentage of total phosphorus which is nucleic: calf thymus, 60%; pituitary, pancreas, spleen, thyroid, gastric mucous membrane, breast, placenta, ovary, lung, and prostate, 20—40%; testicle, liver, and kidney, 10—20%; nervous and muscular tissue, less than 10%. The figures differ so much from organ to organ as to be indexes to their respective organs, and this method may therefore be used for the characterisation and testing of organotherapeutic powders.

B. F.

## General, Physical, and Inorganic Chemistry.

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**Structure in the Secondary Hydrogen Spectrum. III.** O. W. RICHARDSON (*Proc. Roy. Soc.*, 1925, **A**, 109, 239—266; cf. this vol., ii, 909).—In a previous paper (cf. this vol., ii, 11), it has been shown that many of the lines of the secondary hydrogen spectrum which are weakened in electron discharges can be arranged in series. Regularities have now been found among the lines not selectively affected by the discharge; 132 additional lines have been classified. Up to the present, 20 combinations have been found, leading to 40 sets of term numbers, of which 22 are of half-quantum type. The changes of intensity in the spectrum produced by varying the temperature (from liquid air to the ordinary temperatures) are discussed, and it is held that they cannot decide between the translational and rotational origin of the lines, a point which is still under discussion. S. B.

**Spark Spectrum of Lithium.** S. WERNER (*Nature*, 1925, **116**, 574).—With an apparatus including a very intense source of light, and so arranged that fluorite windows are not introduced in the path of light, the classification of the spectrum denoted by Schüler as the doublet system of the Li II spectrum has been extended, and the conclusions already reached (this vol., ii, 165) have been confirmed. A. A. E.

**Structure of the Red Lithium Line 6708 Å.** J. B. GREEN (*J. Opt. Soc. Amer.*, 1925, **11**, 213—216).—Light from the negative electrode of a vacuum arc was focussed on the slit of a spectrometer and a Lummer plate placed between the collimator and prism. The Lummer pattern was found to be that of a simple doublet for low vapour densities. Changes in appearance with increased vapour density are ascribed to self-reversal. With increased current, a wide quadruplet pattern is formed which is attributed to Stark effects due to interatomic fields. E. B. L.

**Series Spectra of Two-valency-electron Atoms of Boron (B II) and Carbon (C III).** I. S. BOWEN and R. A. MILLIKAN (*Physical Rev.*, 1925, [ii], **26**, 310—318).—Thirteen lines additional to the *pp'* group of B II have been identified, and the identification has been completed of all the known boron lines of appreciable intensity; the classification into series of all the lines due to B II and B III is also completed. Term values assigned to the series lines for B II are tabulated. For C III, eight lines additional to the *pp'* group are recorded, and term values assigned. The progression of frequency separations and of screening constants for regular doublets from lithium to oxygen for 1 to 6 valency electrons is also tabulated. A. A. E.

**Spectra of Silicon and Aluminium.** W. C. MCQUARRIE (*Phil. Mag.*, 1925, [vi], **50**, 819—821).—The spectra of the under-water spark and arc between electrodes of an alloy of 23% silicon

and 77% aluminium have been observed. In addition to the known aluminium absorption lines, the under-water spark showed those of the silicon multiplet 2507—2529 and the first member of the silicon sharp series 2882. Attempts to photograph the silicon multiplet 1977—1988 gave only a continuous spectrum over that region. The under-water arc gave no silicon absorptions, but twelve aluminium absorptions in addition to those observed in the spark.

A. B. M.

**Arc Spectrum of Phosphorus.** N. K. SUR (*Nature*, 1925, **116**, 542).—Series relations arising from Saltmarsh's observations (A., 1924, ii, 436) are pointed out.

A. A. E.

**$K\beta$  Lines in the X-Ray Emission Spectra of Phosphorus and Potassium.** O. LUNDQUIST (*Z. Physik*, 1925, **33**, 901—915).—The  $K\beta$  line of phosphorus is dependent on the state of chemical combination of the element and also on the material of which the anticathode is composed. The chemical combination of the potassium does not affect the wave-length of its  $K\beta$  line.

E. B. L.

**Spectrum of Potassium at Low Voltages.** F. H. NEWMAN (*Phil. Mag.*, 1925, [vi], **50**, 796—803; cf. this vol., ii, 723).—The radiation emitted by potassium vapour when bombarded by electrons depends on the energy of the electrons. Potassium vapour in a suitable discharge tube was bombarded by electrons which had been accelerated through a measured potential difference, and the radiation produced with gradually increasing *P.D.* was examined spectroscopically. The first doublet of the principal series appeared at 1.9 volts, and then other lines in the order corresponding with the energy levels calculated from the applied voltage.

A. B. M.

**Structure of the Nickel Spectrum. II.** K. BECHERT (*Ann. Physik*, 1925, [iv], **77**, 537—559; cf. this vol., ii, 913).—The previous analysis is extended so that, in all, the intensities and combinations of 568 lines are tabulated. Two quintuplet and three triplet systems are described, the combinations being, respectively,  $\varphi_1\delta_1$ ,  $\varphi_1\gamma_1$ ,  $g_1f_1$ ,  $d_1g_1$ , and  $f_2g_1$ . Several intercombinations of the singlet-triplet, singlet-quintuplet, and triplet-quintuplet types are recognised. Many of the latter type occur with lines of the high-temperature class, the quintuplet term  $\varphi_1$  combining with  $d_1$ ,  $d_2$ ,  $\bar{f}_1$ ,  $\bar{f}_{1a}$ ,  $\bar{f}_2$ , and  $g_1$ . Of the singlet-quintuplet type, which usually is weak, the most easily excited is the  $\bar{D}_1\delta_1$  combination. A comparison of the suggested energy levels of the iron, nickel, and cobalt atoms emphasises the spectroscopic regularities shown by this triad. Heisenberg's selection rule applies successfully to the intercombinations in the nickel spectrum.

F. G. T.

**Analysis of the Arc Spectrum of Copper.** A. G. SHENSTONE (*Nature*, 1925, **116**, 467).—The copper spectrum is even more complex than was previously supposed. About 125 lines are accounted for by the new terms, which can be divided into two

sets, (a) all positive and combining with one or both of the known abnormally high *d*-terms, (b) negative, each combining with three or more of the first positive set. An explanation of the abnormally large inverted *d*-terms, due to Turner, is given. A. A. E.

**Experimental Determination of the Relative Intensities of Some of the Molybdenum and Copper *K* Lines and the Tungsten *L* Lines.** S. K. ALLISON and A. H. ARMSTRONG (*Proc. Nat. Acad. Sci.*, 1925, **11**, 563—566).—By means of an ionisation method, the relative intensities of the strong *L* lines of tungsten, the *K* lines of molybdenum, some of the *K* lines of copper, and the weaker *L* lines of tungsten have been evaluated. The numbers are considered in relation to the extension to X-ray spectra by Sommerfeld and by Coster and Goudsmit of Burger and Dorgelo's rules (*Z. Physik*, 1924, **23**, 258) for relative intensities in the optical region. J. S. C.

**Arc Spectrum of Palladium, its Zeeman Effect, and Spectral Type.** C. S. BEALS (*Proc. Roy. Soc.*, 1925, **A**, **109**, 369—384).—New observations have been made on the Zeeman effects in the palladium spectrum. Most of the Zeeman resolutions show marked dissymmetries. The results have been used in analysing the spectrum, and it has been found that the arc lines consist of singlets, triplets, and intercombinations between singlet and triplet terms. The discovery of odd multiplicities in this spectrum suggests a rearrangement of the eighth group of the periodic table into three sub-groups corresponding with the three vertical columns. S. B.

**Fine Structure, Absorption, and Zeeman Effect of the 2536 Mercury Line.** R. W. WOOD (*Phil. Mag.*, 1925, [vi], **50**, 761—774).—The fine structure of the 2536 mercury line has been studied by using two crossed Lummer-Gehrke plates of quartz. A magnetic field was used to press the discharge in the mercury arc against the wall of the lamp and so prevent reversal of the components of the line. The technique of the method is fully described. The line has five components of very nearly equal intensity, the separations being 0.014, 0.010, 0.011, and 0.011 Å., respectively. The apparent structure of seven elements observed by Nagaoka is shown to be due to absorption by the column of unexcited vapour in the type of lamp he used. The absorption of the light by mercury vapour is abnormally increased by the presence of nitrogen. Some qualitative observations on the Zeeman effect of the 2536 line were made. The interference dots were widened by the application of a sufficiently strong magnetic field, but only in one case were they split into distinct components. A. B. M.

**Optical Excitation of the Mercury Spectrum, with Controlled Orbital Transfers of Electrons.** R. W. WOOD (*Phil. Mag.*, 1925, [vi], **50**, 774—796; cf. this vol., ii, 3).—The spectrum emitted by mercury vapour when excited by the radiation from a mercury arc has been studied with the view of testing Bohr's theory of the absorption and emission of light by metallic vapours.

A water-cooled quartz-mercury arc of the vertical type with tungsten anode was mounted close to a vertical quartz tube containing mercury vapour in a vacuum at the ordinary temperature. A magnetic field was used to deflect the discharge in the arc against the wall of the tube and so prevent reversal of the lines by absorption (cf. preceding abstract). The light emitted by the vapour was examined by a quartz spectrograph. By the use of suitable filters between the tubes, the vapour can be illuminated with two or more monochromatic mercury radiations. The lines emitted by the excited vapour are shown to conform with the possible orbital transfers of electrons on Bohr's theory. The effect of introducing nitrogen and other gases into the resonance tube is remarkable, certain frequencies being strongly enhanced and others decreased in intensity. Yet others appear which cannot be accounted for by the orbital transfers previously considered, but are due apparently to intermediate excitation of the nitrogen. A. B. M.

**Screening-doublets of the Bowen-Millikan Ultra-violet Spectra.** A. UNSÖLD (*Z. Physik*, 1925, **33**, 843—848).—A formula is obtained relating separation between the doublets and the effective charge of the core of the atom which is in satisfactory agreement with experiment. E. B. L.

**Multiple Electron Transitions and Primed Spectral Terms.** A. E. RUARK (*J. Opt. Soc. Amer.*, 1925, **11**, 199—211).—Low-voltage arcs were produced in heated silica tubes containing metallic magnesium and cadmium. The stronger lines of  $Mg^+$  appeared at the expected potential above the ionisation potential of the metal. A single electron impinging on an atom can, therefore, ionise the atom and simultaneously raise another electron to a higher orbit. Photographs of the space between the grid and anode showed the lines  $Mg\ pp'$  (2776—2783 Å.), which are produced by the jump of two electrons as the result of a single impact. In cadmium, the similar group appears at its quantum voltage, but is too faint to be detected unless the current density is increased beyond the point which excludes the possibility of excitation by successive impacts. A number of new lines of cadmium were found, belonging to the singlet and triplet subordinate series. The cadmium lines were found to appear at the voltage to be expected. E. B. L.

**Intensities of Zeeman Components of Multiplets.** W. C. VAN GEEL (*Z. Physik*, 1925, **33**, 836—842).—Höhl's theory of the intensities was found to be in satisfactory agreement with experimental results for manganese (octuplets) and chromium (septuplets and quintuplets). E. B. L.

**Diamagnetism and the Anomalous Zeeman Effect.** P. TARTAKOVSKI (*Z. Physik*, 1925, **34**, 216—226).—Anomalous Zeeman effect is presumed to be caused by anomalous precession of the electron orbits and, as diamagnetism is a phenomenon the explanation of which involves precession of the orbits, a relationship may be expected to exist between the magnetic properties and the

anomalous Zeeman effect. A formula is obtained and applied to the cases of helium, lithium, sodium, potassium, and caesium.

E. B. L.

**Electrically Exploded Wires.** S. SMITH (*Astrophys. J.*, 1925, **61**, 186—203).—By the use of a rotating mirror spectrograph, the order of appearance of lines in the spectra of exploded wires of various elements can be recorded photographically. Data are tabulated for lines between 3000 and 5000 Å. in the spectra of lead, tin, aluminium, copper, cadmium, and magnesium. Values representing the relative resistances of the vapours of copper, silver, gold, nickel, tungsten, zinc, aluminium, lead, tin, lithium, and iron are also given. In the case of certain elements, small areas of the surface of the vapour produced by the explosion were very opaque for wave-lengths in the region studied; the phenomenon is possibly due to anomalous dispersion.

A. A. E.

**Persistence of the Radiation excited in Mercury Vapour.** L. J. HAYNER (*Physical Rev.*, 1925, [ii], **26**, 364—375).—The decay of radiation excited in a quartz cell containing mercury vapour at 40—100° by an intermittent mercury arc is shown by a photographic method to be exponential, and independent of the vapour pressure within the limits investigated. No persistence is observed if the cell does not contain liquid mercury, or if the cell is sealed off; thus the presence of fresh distilling mercury appears necessary, as well as the absence of air or water vapour which might be introduced during sealing.

A. A. E.

**Ionisation of Hydrogen Chloride by Electron Impacts.** E. F. BARKER and O. S. DUFFENDACK (*Physical Rev.*, 1925, [ii], **26**, 339—345).—Earlier determinations of the ionisation potential of hydrogen chloride as 14 volts are confirmed by plotting current-voltage curves obtained with a two-electrode hot-cathode discharge tube, whether the gas was stationary or flowing. In the latter case, no hydrogen lines or bands whatever appeared with accelerating potentials up to 120 volts, and it is therefore considered that ionisation takes place without dissociation, as was postulated by Mackay. In the former case, faint hydrogen lines and bands are attributed to dissociation products arising from the thermal action of the filament. The fact that no critical potentials have been detected below that of ionisation indicates that when a hydrogen chloride ion is neutralised the electron is probably bound in a single operation. Exposure of the tungsten filament to hydrogen chloride increased its conductivity; Langmuir suggests that the chloride  $WCl_6$  is formed and subsequently decomposed.

A. A. E.

**Critical Potentials in Secondary Electron Emission from Iron, Nickel, and Molybdenum.** R. L. PETRY (*Physical Rev.*, 1925, [ii], **26**, 346—359).—Precision experiments were carried out in order to determine whether the number of secondary electrons emitted per primary electron changes gradually as the velocity of the primaries is increased, or whether at certain critical velocities

this number changes abruptly. All three metals after heat treatment gave similar results, the curves representing the ratio of the secondary emission to the primary current exhibiting maxima at 348, 455, and 356 volts for iron, nickel, and molybdenum, respectively. The ratio varied only slightly with the primary current, and neutralisation of the earth's magnetic field was also without influence. Up to 40 volts, good agreement was obtained between the critical potentials (about 60 in all) located by slight changes of slope of the curves, and soft X-ray levels determined by Thomas, suggesting that a common phenomenon is involved in the origin of the two effects. With high voltages, however, different phenomena have apparently been studied in the two investigations, photo-electric emission due to X-radiation being here masked by larger effects.

A. A. E.

**Electron Affinity of the Halogens.** E. B. LUDLAM (*Trans. Faraday Soc.*, October 1925, advance proof).—Methods of determining the electron affinity of the halogens are considered. It is still doubtful whether the band of shorter wave-length observed in the spectra of the halogens originates in the atom and can be used for calculating the electron affinity.

A. B. M.

**Chemical Statics of Electronic Phenomena.** L. ROLLA and G. PICCARDI (*Atti R. Accad. Lincei*, 1925, [vi], 2, 29—31).—A thin metallic wire heated in a flame tends to emit electrons, and if the flame contains atoms  $A$  which give ions  $A^+$  and electrons, these ions, on approaching or impinging on the metal, will be transformed into neutral atoms by the electrons of the metal. The electrons will remain free in the flame and, if collected and led back to the incandescent wire through a conductor, will give rise to a continuous electronic current, the intensity of which will be  $15.84 \times 10^{-20}$  amp. for each electron passing per second. The number of electrons per second is equal to the number of ions per second given by the reaction  $A \rightleftharpoons A^+ + \ominus$  and, since the concentration  $[A]$  is readily calculable from the weight of substance volatilised in unit time and from Avogadro's number, the dissociation coefficient and the equilibrium constant of the reaction may be determined at once.

Preliminary experiments show that fine wire gauze is a suitable generator of electrons, and a piece of foil, placed above the gauze, a suitable collector.

T. H. P.

**Chemical Statics of Electronic Phenomena. Mass-action Law applied to Electronic Equilibrium.** L. ROLLA and G. PICCARDI (*Atti R. Accad. Lincei*, 1925, [vi], 2, 128—132).—The applicability of the law of mass-action to the thermal ionisation of salts according to the expression  $A = A^+ + \ominus$ , has been investigated. A bead of the salt to be examined is introduced into the flame, and the current through the flame, at a known potential-difference, is measured by a galvanometer. The concentration of the salt is varied by varying the number and size of the beads and the nature of the salt of any single metal. By this means

the law in question is shown to hold over a wide range of concentration for the thermal decomposition of salts of lithium, sodium, and barium. If  $x$  is the percentage dissociation of the salt and  $C$  the concentration of its vapour,  $x^2C$  is constant. The ionisation potential of a salt is obtained from the equation  $\log K_2 - \log K_1 = U(1/T_1 - 1/T_2)/R$ , the equilibrium constant being measured at two different temperatures. Experiments on lithium, sodium, potassium, rubidium, calcium, barium, thallium, copper, boron, and phosphorus show that, at the flame temperature used, only those elements with decomposition-potentials less than 8 volts are appreciably ionised. Since all elements of acid radicals exceed this limit, the observed current is entirely due to the ionisation products of the metallic atoms, which agrees with Arrhenius' observation that the conductivity of the flame is independent of the nature of the acid radical of the vaporised salt (A., 1891, i, 515).

W. E. E.

### Refraction and Electron Constraint in Ions and Molecules.

C. P. SMYTH (*Phil. Mag.*, 1925, [vi], **50**, 715; cf. this vol., ii, 843).—Attention is directed to the work of Fajans and Knorr (*Chem.-Ztg.*, 1924, **48**, 403) on the same subject as the author's recent paper.

A. B. M.

**Electronic Conduction in Crystals.** H. LENZ (*Physikal. Z.*, 1925, **26**, 642—643; cf. *ibid.*, 1925, **26**, 36; this vol., ii, 920).—A reply to a criticism by Gudden and Pohl (this vol., ii, 943).

M. S. B.

**Attachment of Electrons to Gas Molecules.** V. A. BAILEY (*Phil. Mag.*, 1925, [vi], **50**, 825—843).—A method is described for measuring the rate at which ions are formed when a stream of electrons moves through a gas. The electrons, generated by the incidence of ultra-violet light on a zinc plate, and the ions formed by collision with gas molecules move under a uniform potential gradient through equal apertures in three parallel metal plates, and finally impinge on a fourth plate. The stream of electrons and ions diverges between the plates, only part of it passing through the next aperture. The currents received by the plates, and therefore the ratio of the number of electrons and ions passing any particular aperture to the number impinging on that plate, are determined for varying gas pressures and potential gradients. From these it is shown possible to calculate  $k$ , the factor by which the mean energy of agitation of the electrons exceeds that of the molecules, and  $h$ , the factor giving the fraction of the number of collisions between electrons and molecules which produce ions. The apparatus is tested by using hydrogen, for which values of  $k$  are known. Results are given for dry air at pressures  $p$  of 8, 11.3, 16, and 22.6 mm. and gradients  $Z$  of 5, 7.07, 10, and 20 volts/cm. For values of  $Z/p$ , 0.5, 1, and 2, those of  $h$  are  $3.3 \times 10^{-6}$ ,  $2 \times 10^{-6}$ , and  $0.7 \times 10^{-6}$ , respectively.

A. B. M.



**Absorption Coefficient for Slow Electrons in Vapours of Mercury, Cadmium, and Zinc.** R. B. BRODE (*Proc. Roy. Soc.*, 1925, **A**, **109**, 397—405).—The absorption coefficient, or the effective area of a molecule within which an electron is deflected, has been measured for electrons of from 0.4 volt to 50 volts velocity, in the vapours of these metals. With a few minor deviations the curves approximate to hyperbolas of the same size. No indications of long free paths at low velocities were found. S. B.

**Negative Ion Emission from Oxide-coated Filaments.** H. A. BARTON (*Physical Rev.*, 1925, [ii], **26**, 360—363).—Platinum, coated with barium oxide or strontium oxide, emits when heated negative ions (having a value for  $e/m$  of about 33) as well as electrons, but no positive ions. The ions are oxygen molecules which are probably detached from the filament in the already ionised condition. A. A. E.

**Passage of Slow Canal Rays through Hydrogen.** A. J. DEMPSTER (*Proc. Nat. Acad. Sci.*, 1925, **11**, 552—554).—Experiments are described which show that protons with a velocity of  $4.16 \times 10^7$  cm./sec., corresponding with a fall through 900 volts, will pass through a great many hydrogen molecules without being neutralised. J. S. C.

**Isotope Effect in Band Spectra. IV. Silicon Nitride.** R. S. MULLIKEN (*Physical Rev.*, 1925, [ii], **26**, 319—338; cf. this vol., ii, 833).—The band spectrum between 3800 and 5300 Å., shaded towards the red, obtained by Jevons (A., 1913, ii, 813) by the introduction of silicon tetrachloride vapour into active nitrogen, and ascribed by him to a nitride of silicon, has been reinvestigated. The measurements have been repeated and extended to all possible heads; the intensity minimum observed by Jevons must represent the region of the null-line, the unusual prominence of which is ascribed to the low temperature of active nitrogen. That author's data must refer to  $\text{Si}^{28}\text{N}$  heads; new photographs clearly show that these heads are accompanied, at theoretically anticipated positions, by satellites corresponding with  $\text{Si}^{29}\text{N}$  and  $\text{Si}^{30}\text{N}$ , the former isotope being slightly more abundant than the latter, a result confirmed by Aston. Hence  $\text{SiO}$  or any compound other than  $\text{SiN}$  is definitely excluded as the emitter of the bands. Further, the results yield definite, but not conclusive, evidence against the existence of half-quantum numbers for  $\text{SiN}$ ; such existence, however, would be expected in view of the close analogy between  $\text{SiN}$  and  $\text{BO}$ . Jevons' arrangement is revised, and correct initial ( $n'$ ) and final ( $n''$ ) vibrational quantum numbers are assigned. The following wave-number equation is developed for the null-lines of the  $\text{Si}^{28}\text{N}$  bands:  $\nu = 24234.17 + 1016.30n' - 17.773n'^2 + 0.410n'^3 - 0.00487n'^4 - 1145.00n'' + 6.570n''^2$ . The internuclear distance for the vibrationless  $\text{SiN}$  molecule is computed to be  $1.56 \times 10^{-8}$  cm. In addition to these  $\text{SiN}$  bands, herein called *A* bands, an extensive new system of weaker bands, shaded towards the red, and presumed also to be due to  $\text{SiN}$ , has been observed; they are quenched in the same manner as the *A* bands by small

amounts of oxygen. The heads (for which an equation is given) are in pairs of about equal intensity; numerical values of the coefficients and the spacing of the structure lines are of the same order of magnitude as for the *A* bands. The intensity distribution of both systems of bands has been examined. A. A. E.

**Determination of Mass of H-Particles.** G. STETTER (*Z. Physik*, 1925, **34**, 158—177).—The mass of the hydrogen particle emitted by paraffin on bombardment by an  $\alpha$ -particle was determined by a method similar in principle to Aston's mass-spectrograph, but the high velocity of the particles made it necessary to use much stronger electrical and magnetic fields to deflect the particles. The deflection was measured by observing the scintillations on a zinc sulphide screen with a microscope. The apparatus was calibrated by using  $\alpha$ -particles from polonium, of known velocity. The result obtained was within 1% of the theoretical value for the hydrogen nucleus. E. B. L.

**Mass Spectra of Light Elements.** J. L. COSTA (*Ann. Physique*, 1925, [x], **4**, 425—456; cf. this vol., ii, 619).—The following results were obtained by the bracketing method, with a new modification of the mass-spectrograph, giving results correct to 0.03%, using the mass 4.000 of helium as standard of comparison: the masses of the atom and of the molecule of hydrogen are in the ratio of 1:2, the value for the neutral atom being  $1.0079 \pm 0.0005$ ; the values 6.009 and 12.000 are found for the lithium isotope 6 and the carbon atom, respectively; by comparison with the doubly ionised nitrogen atom, the lithium isotope 7 has a mass between 7.010 and 7.013 if the atomic weight of nitrogen be 14.008.

W. H.-R.

**Fundamental Atomic Weights.** E. MOLES (*Z. physikal. Chem.*, 1925, **117**, 157—158).—A previous paper (this vol., ii, 346) is slightly amended. L. F. G.

**Determination of the Variation of the Mass of the Electron with Velocity, using Homogeneous  $\beta$ -Rays.** R. A. R. TRICKER (*Proc. Roy. Soc.*, 1925, **A**, **109**, 384—396).—A method of determining the variation in the mass of the electron is described, using the homogeneous  $\beta$ -rays from thin layers of radium-*B* with velocities up to 0.8 of the velocity of light. In previous investigations, less homogeneous rays have been employed, with corresponding loss of accuracy. The rays are sent first through an accelerating and then through a retarding electric field, in a special magnetic focussing apparatus, and the deflections produced are measured. The results obtained agree better with the theory of relativity than with Abraham's theory of the rigid electron. The maximum error in the observed deflections is about 2%, whilst the theories differ by about 5%. The published measurements are preliminary only. S. B.

**Transformation of Atoms into Radiation.** O. STERN (*Trans. Faraday Soc.*, October 1925, advance proof).—Eddington's theory implies the transformation of mass into radiation. If this

is true the reverse process, radiation into matter, must be conceivable. In another paper (unpublished) the author deduced the conditions of equilibrium between the two processes by means of semipermeable membranes. A new deduction has now been made substituting the assumption that the energy and the entropy of a hollow space containing black radiation and an ideal gas in equilibrium represent the sum of the values that these quantities would possess if gas and radiation were each alone present. R. A. M.

**"Meta-stationary" Atomic and Molecular States.** A. SMEKAL (*Z. Physik*, 1925, **34**, 81—93).—Meta-stationary states may exist for a very short time as a result of absorption of radiation or of collisions. In these states the energy of the atom or molecule is not quantised and Ehrenfest's adiabatic principle is not applicable; they may be of fundamental importance in the scattering of radiation and in regard to dispersion. E. B. L.

**Action of Atoms in Collision.** N. BOHR (*Z. Physik*, 1925, **34**, 142—157).—Interactions between atomic systems are characterised as those which exhibit "reciprocity" and those which do not. The former class can be accounted for adequately by the quantum theory without sacrificing the conservation of energy as hitherto understood. In the latter class, the interactions can only be related by probability laws and the conservation of energy be taken as true in a statistical sense. Reference is made to the work of Bothe and Geiger (*ibid.*, 1925, **33**, 639) on the scattering of X-rays as indicating that the above treatment does not lead to a satisfactory solution of the problem. E. B. L.

**Law of Photochemical Equivalents and the Place of the Quantum Theory in Relation to the Atomic Theory and Energetics.** D. BERTHELOT (*Trans. Faraday Soc.*, October 1925, advance proof).—A *résumé* of the author's work (A., 1911, ii, 86; 1914, ii, 402; 1915, ii, 329; 1924, ii, 320). There are two factors of radiant energy, the capacity factor (radiant energy or action) and the tension factor (frequency or photochemical potential). Einstein's law is a special case of the law of equivalent capacity, which applies to every form of energy; Planck's constant is analogous to Faraday's electrochemical constant. The discontinuity of matter imposes discontinuity on the capacity factors by which the diverse forms of energy manifest themselves; thus there are three fundamental invariants of capacity, the electron, thermon, and radion. All verifications of the law of photochemical equivalents have hitherto been mere approximations. These views are developed by considering the kinetics of electrochemical, thermochemical, and photochemical reactions. R. A. M.

**Derivation of Planck's Law from Einstein's Equation.** A. S. EDDINGTON (*Phil. Mag.*, 1925, [vi], **50**, 803—808).—A deduction of Planck's law is given which does not involve the assumption of Boltzmann's formula. The latter is derived in the course of the argument. A. B. M.

**Distribution of Electrons in Atoms.** J. D. M. SMITH (*Phil. Mag.*, 1925, [vi], 50, 878—879).—A claim for priority addressed to citers of the work of Stoner (cf. this vol., ii, 85). A. B. M.

**Quantitative Apprehension of the Principle of Correspondence and the Calculation of the Intensities of Spectral Lines.** I. I. TAMM (*Z. Physik*, 1925, 34, 59—80).—The principle of correspondence was originally merely qualitative. If the magnitudes calculated according to the quantum theory are equated to those calculated from classical theory, the formulæ can be tested and the principle made precise. This has been done. The equations obtained enable the relative intensities of the Zeeman components of any spectral line to be calculated. The addition rule of Ornstein, Burger, and Dorgelo (A., 1924, ii, 361, 433; this vol., ii, 251, 340) is a simple corollary. The Bohr frequency condition is a necessary consequence. E. B. L.

**Structure of Magnesium.** H. COLLINS (*Chem. News*, 1925, 131, 212—215).—Speculative.

**Origin of Band Spectra.** M. DUFFIEUX (*Ann. Physique*, 1925, [x], 4, 249—318).—Owing to the Döppler-Fizeau effect, the thermal agitation of radiating atoms or molecules produces a slight widening of the emitted rays, the extent of which, under suitable conditions, depends only on the temperature and the mass of the particle emitting the radiation. The following deductions are made from measurements of the width of rays by an interference method. The 102 lines examined in the second spectrum of hydrogen are all emitted by the  $H_2$  molecule. The first positive group of the nitrogen spectrum is emitted by the  $N_2$  molecule, whilst the second positive group and the negative group of nitrogen, as well as the 3883 and 4212 bands of the cyanogen spectrum, are due to the nitrogen atom. In the spectrum of carbon monoxide, the bands 6079, 5610, 5198, 4835, 4511, and 4393 are due to the oxygen atom, and the band 4123 is due to either the oxygen or carbon atom and not to the molecule of the compound. The negative bands of nitrogen, and those of cyanogen and carbon monoxide agree well with the laws of succession deduced from Schwarzschild's theory, in spite of its dependence on the assumption that the bands are produced by molecules. The second positive and the negative groups of nitrogen are probably due to the neutral and ionised atom, respectively, whilst for the cyanogen bands the nitrogen atom is probably in a different state of ionisation. W. H.-R.

**Structure and Distribution of Band Spectra.** M. H. DESLANDRES (*Compt. rend.*, 1925, 181, 387—392).—The formula  $\nu = qd_1/rs \pm q'd_1/r's'$  is tested by means of Coblenz's measurements of the infra-red absorption bands of methane, acetylene, ethylene, chloroform, carbon tetrachloride, ethane, carbon dioxide, carbon monoxide, hydrogen sulphide, sulphur dioxide, carbon disulphide, and crystalline sulphur. The agreement is satisfactory. The bands for which  $r$  has the value 1 are the strongest. E. B. L.

**Intensities of Band Lines.** H. HÖNL and F. LONDON (*Z. Physik*, 1925, **33**, 803—809).—Laws are obtained for the intensities of lines in band spectra with a zero branch, representing the more precise application of quantum theory to the formula deduced from the principle of correspondence. E. B. L.

**Excitation of the Band Spectrum of Helium.** T. R. MERTON and J. G. PILLEY (*Proc. Roy. Soc.*, 1925, **A**, **109**, 267—272).—The conditions are discussed for the excitation of the band spectrum of helium, now generally ascribed to the helium molecule. Experiments are described which show that it is possible to produce marked intensity changes within this spectrum by altering the type of discharge. More especially, conditions have been found under which a green band (between 5387 and 5277 Å.), normally so weak that it has not previously been described, becomes a conspicuous feature of the spectrum. Excitation of high-pressure helium by a continuous discharge or by continuous high-frequency oscillations results almost exclusively in the appearance of the line spectrum of helium. Discontinuous discharges produce also the band spectrum. In explanation of the present, and of former, observations, it is suggested that the energy required to excite the band spectrum must be greater than that required for the arc spectrum. With continuous, or low-frequency, discharges, the exciting electrons in the positive column do not acquire sufficient velocity to produce the bands. They can only do so with discontinuous high-frequency discharges, when the resistance of the gas in the positive column will rise to high values in the intervals between discharges. The green band mentioned above can apparently be excited by slower electrons than the rest of the bands. The use of a hydrogen discharge tube in place of a very small spark-gap is described. S. B.

**Band Spectra Associated with Carbon.** R. C. JOHNSON (*Nature*, 1925, **116**, 539—540).—The conditions associated with the appearance of the Swan bands lead to the tentative suggestion that they are due to a CH or (CH)<sub>2</sub> molecule, whilst the triplet system is due to a molecule of greater hydrogen content, possibly CH<sub>4</sub>. The CH band, at 4315 Å., and associated heads can be completely isolated from all other carbon spectra under suitable conditions. The author believes that the Ångström bands, the third positive bands, and possibly Cameron's new band spectrum arise from a neutral CO molecule, whilst Fowler's high-pressure bands probably arise from a more complex molecule. A. A. E.

**Measurements of the Rotation Spectrum of Hydrogen Chloride in the Long-wave Ultra-red.** M. CZERNY (*Z. Physik*, 1925, **34**, 227—244).—The absorption spectrum has been measured in the region 42 to 100  $\mu$ , and seven absorption maxima have been found with a constant difference of about 20/cm. The position of the bands can only be explained on the band theory by using half integral instead of integral quantum numbers. The comparison of this simple rotation spectrum with the rotation-oscillation spectrum in the shorter wave ultra-red shows good agreement. The isolation

of the radiation required was obtained by means of concave mirrors, a wire grating (used by Rubens), a celluloid film covered with lampblack, and a quartz lens. The radiation was received on an exceedingly sensitive micro-radiometer. E. B. L.

**Vibration of the Carbonate Ion.** S. CHAPMAN and A. E. LUDLAM (*Phil. Mag.*, 1925, [vi], 50, 822—824).—An attempt is made to modify Kornfeld's theory of the infra-red frequencies of vibration of the carbonate ion (this vol., ii, 12) in order to obtain a better agreement with observation. No modification, however, which neglects to take account of the ions surrounding the carbonate ion appears likely to remove the difficulty. A. B. M.

**Infra-red Absorption Spectra.** L. MÁRTON (*Z. physikal. Chem.*, 1925, 117, 97—128).—A method of measuring infra-red absorption spectra is described. Measurements of the absorption in a range extending from the visible to 4 or 5  $\mu$  were carried out with the following substances: hexane, cyclohexane and homologues, benzene and homologues, aliphatic aldehydes and ketones, chloroform, carbonyl chloride, and thiocarbonyl chloride. The closing of a ring shifts the bands towards the infra-red, and also increases intensities. Homologues differ chiefly in the intensities of the bands, the positions of which remain nearly the same, but some divergence of the principal bands occurs on passing from lower to higher homologues. Unsaturation results in a shift towards the violet. The theory of band spectra is considered mathematically, and a formula for calculating wave-lengths is derived which gives results agreeing well with the observed data.

L. F. G.

**Flame Spectra and Chemical Reaction.** (Miss) C. E. BLUKER (*Trans. Faraday Soc.*, October 1925, advance proof).—Previous measurements of the relative intensities of several members of the first and second subordinate series in the flame spectra of rubidium and caesium (*Z. Physik*, 1924, 27, 195) showed no such variation of relative intensity with temperature as should be expected on the basis of temperature radiation. Extension of the measurements to sodium and potassium flame spectra gave analogous results. It is suggested that, although the variation of relative intensity in the principal series of flame spectra may be explained on the temperature radiation basis, in the case of the subordinate series the effects are produced by the oxidation of the alkali metal atoms. A. E. M.

**Spectroscopic Determination of the Electron Affinity of the Halogens.** E. VON ANGERER and A. MÜLLER (*Physikal. Z.*, 1925, 26, 643).—The absorption spectra of the ionised vapour of potassium fluoride, sodium and caesium chlorides, potassium and caesium bromides, and potassium iodide have been examined at two different temperatures, 1050° and 2200°, and the electron affinity of the halogens has been calculated from the long-wave limit, which is the same at each temperature. The values obtained

for the above salts in cal./mol. are 94.0, 86.6, 89.6, 79.1, 81.3, and 71.3, respectively.

M. S. B.

**Duration of Fluorescence of Mercury Vapour.** R. N. GHOSH (*Physical Rev.*, 1925, [ii], **26**, 376—379).—Saha and Sur's explanation (A., 1924, ii, 803) of the after-glow of nitrogen is extended to the case of the fluorescence of mercury vapour. The fluorescing molecules are diatomic, and are given off by the liquid when the temperature is either rising or constant. Activation of each molecule occurs by absorption of energy corresponding with 6.7 volts.

A. A. E.

**Polarised Fluorescence in Solutions of Dyes.** F. WEIGERT and G. KÄPPLER (*Z. Physik*, 1925, **33**, 801—802).—It is suggested that in the experiments of Lewschin and Vavilov (see this vol., ii, 629, 739) the light was not sufficiently intense to show the increase in polarisation with increasing concentration.

E. B. L.

**Permanent Modifications in Fluorescent Liquids.** (MLLE.) M. ASTERBLUM (*Bull. Inter. Acad. Polonoise*, 1924, **A**, 7—8, 297—318).—Exposure of glycerol solutions of fluorescein to ultra-violet light results in a change in the colour of the fluorescence from green to blue. The intensity of fluorescence diminishes and after prolonged exposure the solution no longer gives out light. The solution does not recover its initial properties on long keeping. Indication of the formation of modifications on illumination is afforded by the appearance of a new band between 4900 and 4470 Å. in the fluorescence spectrum and the diminution in intensity of the band at 5500 Å. characteristic of normal fluorescence. On prolonging the action of the exciting light the new band in turn disappears. The absorption spectrum of the modified solutions shows a decreased absorption in the region 4900 Å. and an increased absorption in the region below 4600 Å. Purely chemical processes, *e.g.*, oxidation by the air, action of alkaline impurities, etc., may bring about similar changes. The maximum wave-length of the light capable of producing this modified fluorescence is about 2540 Å. Glycerol solutions of methylene-violet, corallin, crocein, æsculin, erythrosin, eosin, and rhodamine lose their fluorescent properties on exposure to the action of ultra-violet light. The rate at which these modifications are formed depends on the concentration, in general the rate being greater the more dilute the solution. Solutions of erythrosin, eosin, and rhodamine in benzyl alcohol are much more sensitive to the action of light than are the corresponding glycerol solutions.

J. S. C.

**Chemiluminescence.** H. KAUTSKY (*Trans. Faraday Soc.*, October, 1925, advance proof).—The adsorption compounds of rhodamine and rhodaminesulphonate with colourless oxidation products of siloxen are strongly coloured and fluorescent. Addition of potassium permanganate solution to the adsorption compounds promotes a strong chemiluminescence which is not exhibited when the adsorbent alone is oxidised in the same manner. The fluores-

cence and chemiluminescence spectra of the adsorption compounds are identical. The intensity of the chemiluminescence decreases with decreasing temperature, whilst that of the fluorescence increases in the normal manner. It is concluded that the energy of oxidation of the adsorbent is transmitted to the dyes, since they are adsorbed in the planes of the adsorbent and are thus in the direct neighbourhood of places of reaction. The results offer justification of the view that whereas in chemiluminescence the energy of a chemical reaction causes the radiation, in fluorescence it is the adsorbed light which has the same effect, and that therefore it should be possible to force a fluorescent substance to give chemiluminescence by using suitable reactions to activate its molecules.

A. E. M.

**Scintillations in Zinc Sulphide.** J. STALONY-DĄBROVSKI (*Rocz. Chem.*, 1925, **5**, 193—214).—The luminescence produced by thorium in thin layers of zinc sulphide is investigated. It is found that each scintillation, on examination through a lens magnifying up to 40 times, consists of a small bright spot of light surrounded by a diffuse aureole, the shape of which depends on the location of the thorium atom in the layer, and the diameter of which varies from 0.1 to 0.3 mm. The duration of the scintillations is determined in three ways, the first method being that of Wood (A., 1905, ii, 664), depending on the measurement of the length of the arcs of light appearing on the screen during its rapid rotation. In this way, the duration of the scintillations is shown to be of the order of  $1/200$  sec. and not, as Wood found,  $1/20000$  sec., the greater part of the arc being invisible at the high speeds of revolution used by him. In the second method, the number,  $N$ , of scintillations appearing per minute on a fixed screen of 1 sq. mm. surface is determined. Before this screen is placed a revolving opaque glass disc, possessing a window in the form of an arc of angle  $\alpha$ , and the number of scintillations per minute,  $N_{\alpha\beta}$ , is again counted, being less than  $N$  but greater than  $N\alpha/2\pi$ , the number which would appear if the scintillations were of infinitely short duration. The duration of the scintillations,  $t$ , is given by the formula  $t = (N_{\alpha\beta} - N\alpha/2\pi)/Nn$ , where  $n$  is the number of revolutions per second of the disc. The minimal values of  $t$  found were  $1/29$  sec. The third method is more convenient than the preceding ones, and gives more accurate results. A streak of radioactive matter is disposed radially on a glass disc, and is covered on the other side by a large sector of black paper. This disc is placed before a screen of zinc sulphide, of area 0.5 sq. cm., and revolved, the speed being reduced until the sparks cease to be visible, when  $t = \beta/2\pi n$ , where  $\beta$  is the angle between the streak of radioactive matter and the edge of the sector. In this way,  $t$  was found to be  $1/6$  sec., results of the same order being obtained using various samples of zinc sulphide. A disc phosphoroscope is also described, in which half the revolving disc is within a box containing the source of illumination, the other half showing bands of phosphorescence strikingly similar to those obtained using thorium as the excitant, i.e., a bright band



followed by a larger diffuse region ; this suggests that the mechanism of luminescence is the same in both cases. R. T.

### Electrification by Friction between Solids and Gases.

E. PERUCCA (*Z. Physik*, 1925, **34**, 120—130).—A stream of mercury vapour at a pressure less than  $10^{-5}$  mm. was directed against a plate of iron, which was raised to a negative potential of about 500 volts. When platinum was used in place of iron the potential only reached about 300 volts and the platinum became covered with mercury. When the collector was nickel-plated, there was no electrification. E. B. L.

### Mechanism of Breakdown of Damp Liquid Insulators.

A. GYEMANT (*Z. Physik*, 1925, **33**, 789—800).—The moisture is supposed to exist as an emulsion and the spherical particles to be elongated under the electrical stress. When they form a continuous chain, the insulation breaks down. A formula is obtained relating voltage and water content and verified experimentally for damp transformer oil. E. B. L.

### Spectrochemistry of Thiochromans, $\Delta^3$ -Thiochromens, and Thiochromanones.

F. KROLLPFEIFFER (*Ber.*, 1925, **58**, [B], 1677—1680; cf. Krollpfeiffer, this vol., i, 1305).—The following data, *inter alia*, are recorded : thiochroman,  $d_4^{173}$  1.1267,  $n_{He}^{173}$  1.61600; 6-methylthiochroman,  $d_4^{154}$  1.0907,  $n_{He}^{154}$  1.60227; 6 : 8-dimethylthiochroman,  $d_4^{151}$  1.0801,  $n_{He}^{158}$  1.59667; 4-methyl- $\Delta^3$ -thiochromen,  $d_4^{146}$  1.1310,  $n_{He}^{146}$  1.63315; 4 : 6-dimethyl- $\Delta^3$ -thiochromen,  $d_4^{129}$  1.1032,  $n_{He}^{129}$  1.62082; 6-methyl-4-ethyl- $\Delta^3$ -thiochromen,  $d_4^{156}$  1.0893,  $n_{He}^{156}$  1.61014; 4-phenyl-6-methyl- $\Delta^3$ -thiochromen,  $d_4^{997}$  1.0941,  $n_{He}^{997}$  1.62734; 4 : 6 : 8-trimethyl- $\Delta^3$ -thiochromen,  $d_4^{188}$  1.0829,  $n_{He}^{188}$  1.60637; thiochromanone,  $d_4^{137}$  1.2487,  $n_{He}^{137}$  1.64313; chromanone,  $d_4^{998}$  1.1291,  $n_{He}^{998}$  1.54598; 6-methylthiochromanone,  $d_4^{995}$  1.1376,  $n_{He}^{995}$  1.59171; 6 : 8-dimethylthiochromanone,  $d_4^{100}$  1.1204,  $n_{He}^{100}$  1.58634; tetrahydrobenzothiochromanone,  $d_4^{1005}$  1.1536,  $n_{He}^{1005}$  1.60589; 5 : 6-benzothiochromanone,  $d_4^{989}$  1.2162,  $n_{He}^{989}$  1.68556. H. W.

### Determination of the Principal Refractive Indices of Doubly Refracting Substances by Means of Federov's Plate.

C. PERRIER (*Atti R. Accad. Lincei*, 1925, [vi], 2, 22—29).—An outline is given of the theory of a method for measuring the principal refractive indices of both uniaxial and biaxial doubly refracting crystals. T. H. P.

### Rotatory Dispersion of Derivatives of Tartaric Acid. II.

**Acetyl Derivatives.** P. C. AUSTIN and J. R. PARK (*J. Chem. Soc.*, 1925, **127**, 1926—1934; cf. Austin and Carpenter, A., 1924, i, 1164).—In solution in dry acetone or ethyl acetate, diacetyl-tartaric anhydride does not exhibit mutarotation, but is dextro-rotatory showing "simple" dispersion. In the presence of water, the solution slowly becomes laevorotatory owing to hydrolysis of the anhydride ring, and the formation of diacetyltartaric acid, which may be isolated from the solution. The final readings depend on

the amount of water, owing either to association with water molecules or to ionisation of the acid. Diacetyltartaric acid has been obtained with  $1\frac{1}{2}$  mols. of benzene of crystallisation; the benzene is readily lost on heating, leaving the anhydrous acid (m. p.  $118^\circ$ ), of which the solution in acetone is strongly laevorotatory with "simple" rotatory dispersion, the anomalous dispersion of tartaric acid being eliminated by acetylation of the hydroxyl groups. Although both acid and anhydride show simple dispersion, the solution during the mutarotation shows anomalous dispersion owing to the difference between the dispersion constants of the final and end products in agreement with the theory of Arndtsen (*Ann. Chim. Phys.*, 1858, **54**, 421). W. H.-R.

**Optical and Magnetic Rotation Dispersion, Dispersion, Density, and Absorption Spectra of Chemically Homologous Compounds.** A. KRETHLOW (*Z. wiss. Phot.*, 1925, **23**, 233—282).—The law of Verdet, that the specific magnetic rotation of a dissolved substance should be independent of the concentration, was found not to hold for camphor in benzene solution, nor for 3-methylamyl bornylenecarboxylate; the magnetic rotation increases with decreasing concentration. Wiedemann's law, that the magnetic rotation is proportional to the natural rotation, was tested for five derivatives of methylenecamphor, and for the bornylenecarboxyl esters of 3-methylpentinol, 3-methylpentenol, and 3-methylpentanol. The law was found not to hold for any of these eight substances; with decreasing wave-length, the natural rotation increases more rapidly than the magnetic. The optical constants of the compounds were studied for a series of different wave-lengths. The simple Drude equation was investigated for the eight compounds. The value of  $\lambda_0$  was not constant, but showed a marked progression which was the same in each homologous series, but was different for different series. The characteristic frequencies calculated from the dispersion were found not to coincide with those of the rotation. Hagenbach's law, that in homologous series the rotation dispersion curves,  $f(\lambda)$ , of the individual homologues only differ from one another by a constant  $c$ , holds very well for the two series investigated. The Hagenbach constant provides a satisfactory means of testing whether substances belong to homologous series or not. Ordinary dispersion behaves in this respect differently from natural rotation. Although with dispersion a constant is obtained, it cannot be used for ascertaining homologous series. The theories of Lorentz and Livens and of Oseen do not agree with experimental facts. The Cotton phenomenon, that with yellow-coloured substances anomalous rotation in the visible region can be caused by an absorption band in the ultra-violet, agrees with the results of investigation of twenty-four compounds. No regularity in the absorption spectra of compounds of homologous series was observed in six series investigated. W. C.

**Theory of Rotatory Polarisation.** R. DE MALLEMANN (*Ann. Physique*, 1925, [x], **4**, 456—458; cf. this vol., ii, 840).—Theoretical.

Mistakes in earlier papers are pointed out and corrected. The rotatory power is independent of the choice of axes used to describe the symmetry of the molecule, but in anisotropic liquids or gases a structural rotatory power exists which is absent in ordinary liquids or gases.

W. H.-R.

**Diffusion of Light by Active and Inactive Molecules.** R. DE MALLEMANN (*Compt. rend.*, 1925, **181**, 371—374).—Theoretical. Optical activity is treated from the point of view of the Tyndall effect, which, except for the rotation of the plane of polarisation, is the same for optically active as for inactive substances. Simple equations are deduced for the diffusion of light through inactive substances, which are extended to optically active substances. Criticism is made of an observation by Gans (*Z. Physik*, 1923, **17**, 372).

F. G. S.

**Diffusion of Light by Methane and its Gaseous Homologues.** J. CABANNES and J. GAUZIT (*J. Phys. Radium*, 1925, [vi], **6**, 182—198).—The light diffused by saturated paraffin hydrocarbons in the gaseous state is not completely polarised. The factor of depolarisation, which for methane (illuminated by sunlight) is 0.015, varies but little as the series is ascended up to *n*-hexane. It is concluded that this depolarisation is due to the carbon atom not possessing exactly the symmetry of the regular tetrahedron. The intensity of the light diffused transversely by ethane, propane, and butane is in accordance with the values predicted by Rayleigh's formula when this is corrected for the anisotropy of the molecules. The experimental value for methane exceeds the theoretical value by nearly 10%.

E. E. W.

**Molecular Scattering of Light in Liquids.** K. S. KRISHNAN (*Phil. Mag.*, 1925, [vi], **50**, 697—715).—The intensity and imperfection of polarisation of the light scattered transversely by 65 different liquids has been measured. The liquids in glass bulbs were illuminated by a horizontal beam of sunlight. The bulbs were blackened except for suitable small windows and were immersed in a small rectangular tank of distilled water, which was also blackened, leaving similar openings. The scattered light was compared in intensity with that scattered by a block of Jena glass, using an Abney rotating-sector photometer. The Jena glass block was used as a secondary standard, being finally compared with a freshly prepared bulb of ethyl ether. The imperfection of polarisation of the scattered light was measured by Cornu's method. Some of the liquids are feebly fluorescent, as is shown by variations in the results when coloured filters were used in the incident beam and in the scattered beam. The relation between depolarisation and chemical constitution is briefly discussed. Comparison of the intensity of scattered light with that calculated from the Einstein-Smoluchowski formula, with a correction factor for imperfect polarisation, shows a satisfactory agreement except for liquids of high refractive index.

A. B. M.

**Measurement of the Coefficients of the Absorption of Light by Fluorescent Substances.** S. PIENKOVSKI and A. JABLONSKI (*J. Phys. Radium*, 1925, [vi], 6, 177—181).—The fall of intensity of the fluorescence formed by a beam of parallel monochromatic rays passing through the liquid is measured photographically. From this the coefficient of absorption of light can be calculated. The method is applicable both to visible and to ultra-violet light if it is monochromatic. Results obtained for fluorescein were found to be in good agreement with those obtained by other methods.

E. E. W.

**Valency Theories and the Magnetic Properties of Complex Salts.** L. A. WELO and A. BAUDISCH (*Nature*, 1925, 116, 606—607).—An application of theories of electron-sharing (cf. Sidgwick, T., 1923, 123, 725) to salts which have been studied magnetically. In certain diamagnetic salts, iron and cobalt attain the configuration of the diamagnetic element krypton; in certain salts of ruthenium and rhodium, the metallic atom attains the configuration of xenon, whilst in their diamagnetic salts, iridium and quadrivalent platinum attain the configuration of radon. The nearly diamagnetic substances potassium permanganate and potassium dichromate yield the configuration of argon if each oxygen atom removes 2 electrons and each potassium atom receives 1 electron. A different treatment is accorded in the case of salts giving magneton numbers which are not zero, the existence of stable configurations other than those of the rare gases being assumed. Chromium, nickel, and copper are examined from this point of view. A. A. E.

**Repulsive Action of Mutually Equal and Mutually Differing Groups in Saturated Organic Compounds.** J. BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, 28, 371—385).—A large number of measurements of the increase in conductivity of boric acid caused by the addition of various polyhydroxy compounds and hydroxy-acids (due to the formation of double compounds when the hydroxyl groups are situated close together) are adduced as evidence of the repulsive action of various groups in organic compounds, and supported by measurements of the heats of combustion and dissociation constants of the corresponding acetone compounds. In pentacyclic compounds where such repulsive action is inoperative owing to the ring structure, only *cis*-diols cause an increase in conductivity as in *cis*-cyclopentane-1:2-diol, mannitan, and the tartrimides, the action being independent of the nature of the remainder of the ring. In the  $\alpha$ -glycols the mutual repulsion of the hydroxyl groups forces them closer together as their number increases, this being evidenced by the increasing effect on the conductivity of boric acid on passing from ethylene glycol (most unfavourable position) to glycerol, erythritol, mannitol, dulcitol, and sorbitol, whilst in mannitan the position of the two hydroxyl groups on the same side of the five-membered ring has a larger effect than the six hydroxyl groups in mannitol. This mutual repulsion causes polyhydroxy compounds (e.g., sugars) to assume configurations very different from the conventional space

formulae, as is evidenced by the fact that mannitol combines easily with 3 mols. of acetone, the hydroxyl groups in the middle of the chain being favourably placed. Evidence for the mutual repulsion of hydroxyl groups is found in the fact that ethyl and benzylamine mesotartrates only yield *cis*-ethyl- or benzyl-tartrimide when heated below 115°, whilst at 165° the *trans* form is produced. The corresponding *cis*-methyltartrimide cannot be obtained, since at the necessary temperature (140—145°), the *trans* form is exclusively produced. Heats of combustion (the figures given being new determinations) for fumaric and maleic acids, mesaconic and citraconic acids, *d*- and *i*-ethyltartrimide (671.1 and 672.7, respectively), *d*- and *i*-benzyltartrimide (1237.8 and 1240.7, respectively), *cis*- and *trans*-hydrindene-1 : 2-diols (1098.5 and 1096.7, respectively), and *cis*- and *trans*-1 : 2 : 3 : 4-tetrahydronaphthalene-1 : 2-diols (1251.0 and 1249.4 cal./mol. at constant pressure, respectively) show that the *cis* form has always the larger value, indicating the lesser stability of this form. The repulsion of two methyl groups is indicated by the higher heat of combustion of *i*- (*cis*) *s*-dimethylsuccinic anhydride (681.0) than of the *trans* form (679.2 cal./mol.). In the tartaric acids and their esters, the repulsion of the carboxyl and carbethoxy groups causes the hydroxyl groups to approach more closely together in the active and racemic forms than in the *meso* form, as is evidenced by the greater increase produced in the conductivity of boric acid in the former cases. The mutual repulsion of phenyl groups is demonstrated by the greater dissociation constant for the acetone compound of racemic hydrobenzoin ( $K_{25}=8.55$ ) than for the *meso* form ( $K_{25}=0.44$ ), in agreement with the boric acid conductivity measurements and by the easy transition of *isostilbine* (*cis*) into the *trans* form. The ready transformation of *allo*- into ordinary cinnamic acids and the heats of combustion of a large number of substituted cinnamic and coumaric acids are cited as evidence of the mutual repulsion of the phenyl and carboxyl groups. The action of dilute acids on the oxide of 1-phenylcyclohexane-1 : 2-diol yields primarily the *trans* form of the diol, but this immediately reverts to the *cis* form, in opposition to steric effects, due to the repulsion of the phenyl and the 2-hydroxyl group, a result confirmed by the greater heat of combustion of the *trans* (8136 cal./mol.) than of the *cis* form (8132 cal./mol.). Boric acid conductivity measurements on the tartramides show that the carbamide group and the hydroxyl group repel each other with greater force than they do like groups. Thus the mean positions of molecules are greatly dependent on all the groups present and on their interaction one with another; rotatory power cannot be a simple function of the groups present, and the principle of optical superposition cannot be strictly valid (cf. Patterson and Patterson, A., 1915, ii, 78).

J. W. B.

**Spectrochemistry in the Ultra-red. IX. Origin of the Absorption Bands Incorrectly Attributed to the Groups  $-\text{CH}_3$  and  $-\text{CH}_2-$ .** G. B. BONINO (*Gazzetta*, 1925, 55, 576—582).—It has been shown (Bonino, A., 1923, ii, 711; this vol., ii,

838) that (a) even compounds not containing carbon exhibit an absorption band at  $3.4 \mu$ , (b) in its variation from compound to compound, the maximum absorption coefficient of this band quantitatively follows the variation in the number of hydrogen atoms and is independent of the number of carbon atoms present. On the basis of the Julius hypothesis, that the absorption band in question is due to the oscillation of the  $-\text{CH}_3$  or  $-\text{CH}_2-$  groups about the positions of equilibrium to which they are constrained by the valency-bonds which connect them to the rest of the molecule, although the effect of the small difference in the masses of  $-\text{CH}_3$  and  $-\text{CH}_2-$  on the position of the absorption maximum would be inappreciable, the value of  $K$  in the formula,  $\nu = (K/m)^{1/2}/2\pi$  (Kratzer, A., 1921, ii, 142) would be twice as great for  $-\text{CH}_2-$  as for  $-\text{CH}_3$ . Again, if the hydrogen atoms of ethane are substituted by halogen atoms, the above formula shows that  $\lambda_{\text{max}}$  ( $\lambda$  at the absorption maximum) would increase with the number of substituted halogen atoms; but experiment shows that all such halogen derivatives have  $\lambda_{\text{max}}$   $3.4 \mu$  (approx.). If the Julius hypothesis is accepted, it must be assumed that the valency-attraction between the carbons in pentachloroethane is seven times that between the carbons in ethane, a conclusion contrary to all known facts. The hypothesis also fails when confronted by the facts that completely halogenated compounds give no band at  $3.4 \mu$  and that the position of the corresponding band for the compound  $\text{CX}_3\cdot\text{CX}_3$  is the same as that of the corresponding band for the compounds  $\text{CX}_3\cdot\text{CX}_2$ . It therefore appears that the absorption band at  $3.4 \mu$  in the spectra of compounds containing hydrogen linked to carbon is due to the vibration of hydrogen atoms about the positions of equilibrium to which their valency bonds constrain them (cf. Ellis, A., 1924, ii, 218, 219).  
W. E. E.

**X-Ray Methods of Supplementing and Correcting Crystallographic Data.** K. YARDLEY (*Phil. Mag.*, 1925, [vi], 50, 864—878).—The limitations of the usual goniometric and X-ray methods of determining the dimensions and symmetry of the unit cell of a crystal are discussed, and it is shown how one method may supplement the other. X-Ray measurements are recorded of potassium hydrogen chloromaleate, ammonium chlorofumarate, and ammonium hydrogen fumarate, and are used to correct existing crystallographic data.  
A. B. M.

**Reflection of X-Rays by Alkali Halide Crystals.** (MISS) A. H. ARMSTRONG, W. DUANE, and R. J. HAVIGHURST (*Proc. Nat. Acad. Sci.*, 1925, 11, 218—221).—It is shown that crystals of caesium iodide and of potassium iodide are wont to exhibit abnormal peaks in their X-ray spectra, and that these peaks are probably due to rays reflected by small displaced crystals in the main mass.  
R. W. L.

**Reflection of X-Rays in Potassium Bromide Crystals.** H. KULENKAMPEFF (*Physikal. Z.*, 1925, 26, 657—658).—Early experiments by Duane and his colleagues seemed to show that

alkali halide crystals reflect the lines of the  $K$ -series of the halogen atoms. This has not been confirmed by later work. The author has examined, both by the revolving crystal method and by the Seemann method, potassium bromide crystals which, on account of their small size, were not likely to contain structural irregularities, and has found no selective reflection of noticeable intensity indicated on a photographic plate.

M. S. B.

**Compton Effect with Hard X-Rays.** D. L. WEBSTER and P. A. ROSS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 224—226).—A short preliminary note indicating the scope of the research and citing the evidence obtained with rays scattered by glass and by graphite which is in good quantitative agreement with the predictions of Compton's theory.

R. W. L.

**Wave-lengths of Scattered X-Rays.** S. K. ALLISON and W. DUANE (*Physical Rev.*, 1925, [ii], **26**, 300—309).—The scattering of molybdenum  $K\alpha$  rays by aluminium and lithium has been examined, and isolated experiments have been performed using beryllium, carbon, sodium, sodium chloride, magnesium, and sulphur as scatterers. The shift of the maximum intensity of the modified band is in agreement with Compton's quantum theory of scattering. For lithium, the width of the modified band is greater than that permitted by Compton's equation. Experiments in which tungsten primary rays were employed were less trustworthy, but the radiation was shifted as expected. Ross' observation, that the relative intensity of the shifted peak is greater for a given element than in the scattering of molybdenum rays, was confirmed.

A. A. E.

**Directed Quanta of Scattered X-Rays.** A. H. COMPTON and A. W. SIMON (*Physical Rev.*, 1925, [ii], **26**, 289—299).—As a result of measurements of the direction of X-ray scattering on stereoscopic cloud expansion photographs, it is held proved that a large proportion of the scattered X-rays proceed in directed quanta of radiant energy. The conclusion supports the view that energy and momentum are conserved during the interaction between radiation and individual electrons, but appears irreconcilable with the view of the statistical production of recoil and photoelectrons proposed by Bohr, Kramers, and Slater.

A. A. E.

**Non-existence of the Clark-Duane Secondary Spectra from Faultless Crystals.** A. P. WEBER (*Z. Physik*, 1925, **33**, 767—776).—Photographs were taken of X-rays reflected from faultless crystals of potassium bromide, rubidium alum, and copper sulphate, using the Seemann knife-edge method; the intensities of the lines were measured by means of a Moll photometer. No secondary lines appeared.

E. B. L.

**Asymmetric Emission of Electrons Produced by X-Rays.** II. W. SEITZ (*Physikal. Z.*, 1925, **26**, 610—615; cf. this vol., ii, 168).—Previous work has been extended to determine whether the asymmetrical emission of electrons from a metal film placed in

a beam of X-rays is confined to electrons from the outer levels, or extends to those from the X-ray levels. With a copper film asymmetrical emission of electrons from the *K*- and *L*-levels occurs, the asymmetry being the greater in the case of the *L*-electrons. The asymmetry of emission is less with silver than with copper. With lead the asymmetry is slight, although the ratio of the electron-emission from the surface from which the X-rays emerge to that from the incident surface increases in the region of high electron velocities.

F. G. T.

### **X-Ray Investigation of Black ("Metallic") Phosphorus.**

G. LINCK and H. JUNG (*Z. anorg. Chem.*, 1925, **147**, 288—292).—The density of "metallic" phosphorus is  $d_4^{20}$  2.699. The X-ray diagram yields the lattice constants  $a=5.96$  Å.,  $\alpha=60.47^\circ$ , corresponding with eight atoms per unit rhombohedral cell. The  $\Delta$ -parameter is approximately 0.17.

A. G.

**Crystal Structure of Manganese.** A. WESTGREN and G. PHRAGMÉN (*Z. Physik*, 1925, **33**, 777—788).—X-Ray photograms show that  $\alpha$ -manganese which is stable at the ordinary temperature is cubical; at higher temperatures, it changes into a  $\beta$ -form, likewise cubical but slightly denser. Electrolytic manganese is tetragonal, but has the same density as  $\alpha$ . Carbon dissolves in manganese in the same way as in iron, not by replacing atoms of the metal, but by lying between them.

E. B. L.

**Structure of Aragonite.** S. I. TOMKEIEFF (*Min. Mag.*, 1925, **20**, 408—434).—Based on the X-ray measurements of W. L. Bragg (*A.*, 1924, ii, 109), a new structure (leptonic) model is proposed for aragonite, although this does not explain the intensities of the X-ray spectra. The new model, which belongs to the space-group  $C_{2h}^1$ , explains the ready transformation of aragonite into calcite and also the shapes of the etch-figures developed by the action of acid on the different crystal-faces.

L. J. S.

**"Somatoid" Forms.** V. KOHLSCHÜTTER and C. EGG (*Helv. Chim. Acta*, 1925, **8**, 457—469).—The occurrence is discussed of minute particles of definite shape and structure which are deposited from mixed solutions and do not consist of a pure crystalline form. These "somatoid" forms depend for their characteristic shapes on the presence of impurities which influence crystal habit, twinning, and rate of crystallisation, and are regarded as definite physico-chemical units of individual character. The phenomenon is discussed with reference to the deposition of calcium carbonate from solutions of the hydrogen carbonate in a current of air and in presence of a variety of added impurities such as salts of the alkali metals, magnesium, strontium, and the heavy metals, and colloidal substances such as dyes. The first influence of the salts is to retard crystallisation and to favour the less stable forms—the faces of higher indices, the less stable crystal system, and finally a hydrated calcium carbonate. The dyes cause first a modification of crystal habit and then the deposition of definite shapes characteristic of the individual dye used, these effects being attributed to interference



with crystallisation by adsorption on to the surface of the growing crystal. The "somatoid" forms are also obtained in the presence of cobalt and nickel salts which yield colloids in solution, and the particles may be either modified crystal growths or complex aggregates consisting partly of colloidal material and not essentially crystalline in origin. The influences which contribute to their formation, such as lattice forces, retardation of diffusion by colloidal material, and the forces in the surface layer, are discussed in detail.

G. M. B.

**Alterations of the Habit and of the Modification of Calcium Carbonate by Substances in Solution.** V. KOHLSCHÜTTER and C. EGG (*Helv. Chim. Acta*, 1925, 8, 470—490; cf. preceding abstract).—Calcium carbonate is deposited from a calcium hydrogen carbonate solution below 30° in the form of primary calcite rhombohedra, but above 30° aragonite is obtained. With increasing concentrations of other salts present, such as sodium or potassium chloride, negative rhombohedra are deposited which are more and more acute, crystallisation being slower and the number of crystals fewer. Still higher concentrations of various salts cause the hydrate  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  to separate. The surface forces and energy relations involved in the production of these different crystals are discussed in detail.

G. M. B.

**Crystalline Structure of Perowskite.** G. R. LEVI and G. NATTA (*Atti R. Accad. Lincei*, 1925, [vi], 2, 39—46).—X-Ray examination by the Debye-Scherrer method indicates for perowskite a face-centred cubic lattice. In the conditions employed, however, this method gives less exact data than the optical and other physical data employed in determining the true symmetry of crystals. Laue's method confirms the view that the structure of perowskite is virtually that of a face-centred cube, the elementary cell having the side 7.68 Å. and containing 8 mols. of  $\text{CaTiO}_3$ . The crystallographic and optical results indicate that the pseudo-cube of perowskite is composed of the two rhombic forms (001) and (110), and of the Laue diagrams corresponding with the three pairs of faces of the pseudo-cube two are similar and the third is different. The fact that the symmetry of the photograms is apparently of higher order than that of rhombic crystals is possibly the result of superposition of differently oriented lamellæ.

T. H. P.

**Structure of Kaolin. Theory of the Structure of Silicates.** M. DOMINIKIEWICZ (*Rocz. Chem.*, 1925, 5, 252—290).—The space configuration of quartz is, on the basis of its crystal form, of its property of rotating the plane of polarised light, and of the tendency of oxy-silicon compounds, e.g., silicoformaldehyde, to form rings containing six silicon atoms, assumed to consist of spirally disposed rings each containing alternately six silicon and six oxygen atoms. On this assumption, the structural formulæ of various silicic acid derivatives are deduced. The difference between ortho- and meta-silicates depends only on different quantitative relationships between the metal and silicic acid, with the probability that

for salts of bivalent metals two silicic acid nuclei are joined by the metal. For the aluminosilicates only this type of formula can be considered, and the structure of semi-hydrated kaolin,  $H_{24}Al_{24}Si_{24}O_{96}$ , containing four silicic acid nuclei joined by  $-O\cdot Al\cdot O-$  groups is given. From this follows directly, by hydration, the structure of kaolin. This hydration is an ionic reaction, taking place at the eight  $-Si\cdot O\cdot Al-$  groups of the two inner saturated rings, and at the four free  $:Si:O$  groups in the two outer unsaturated rings. At these eight inner hydration points various other addition processes may occur, giving rise to other minerals connected genetically with kaolin, such as margarite, prismatine, nephelite, etc. R. T.

**Crystallographic Investigation of Diopside from Saulera (Val d'Ala).** M. LUCIANO (*Mem. Accad. Lincei*, 1924, [v], 14, 886—898).—Measurements of crystals of diopside from Saulera give:  $a : b : c = 1.0931 : 1 : 0.5892$ ,  $\beta = 105^\circ 47.5'$ ,  $d\ 3.289$ . Contrary to Strüver's statement, these crystals differ distinctly from those of Testa Ciarva. T. H. P.

**Crystal Structure of Silver Phosphate and Silver Arsenate.** R. W. G. WYCKOFF (*Amer. J. Sci.*, 1925, [v], 10, 107—118).—Crystals of silver phosphate and arsenate have been studied by the Laue and the powder methods of *X*-ray analysis. Two molecules are contained in the unit cube. The atomic arrangement is a new one, and the corresponding space-group is probably  $T_c-4$ . The position of the oxygen atoms could not be established in either crystal. The length of the edge of the unit cube is 6.00 Å. for silver phosphate and 6.12 Å. for the arsenate. S. B.

**Crystal Structures of the Sulphides of Mercury.** H. E. BUCKLEY and W. S. VERNON (*Min. Mag.*, 1925, 20, 382—392).—*X*-Ray examination of precipitated black mercuric sulphide (corresponding with metacinnabarite) shows the structure to be of the zinc-blende type with the edge of the unit cell  $a = 5.854$  Å. Cinnabar examined by the powder method gives spacings corresponding with a hexagonal space-lattice ( $D_3^4$ ) with three molecules per unit cell of dimensions  $a = 4.160$ ,  $c = 9.540$  Å. The mercury atoms are arranged on a simple rhombohedral lattice, whilst the sulphur atoms form spirals (of radius 0.87 Å.) running parallel to the vertical axis, corresponding with the optical activity of cinnabar. L. J. S.

**Crystallographic Data for Some Organic Compounds.** G. GREENWOOD (*Min. Mag.*, 1925, 20, 393—405).—Details are given for the following menthyl and glyoxaline derivatives: menthyl bromomethylenephénylhydrazonocarboxylate, menthyl bromomethylene-*p*-tolylhydrazonocarboxylate, 4 : 5-dibromo-1-methylglyoxaline hydrochloride (monoclinic), glyoxaline-4(5)-sulphonic acid (tetragonal), 2-methylglyoxaline-4(5)-sulphonic acid (monoclinic), 4(5)-bromoglyoxaline-5(4)-sulphonic acid (monoclinic), 4(5)-bromo-2-methylglyoxaline-5(4)-sulphonic acid (orthorhombic), 5-bromo-1-methylglyoxaline-4-sulphonic acid (monoclinic), and also for triphenylphosphine oxide, *p*-tolueneazobenzylformaldehyde oxime (this vol., i, 1193), a fission product of lupulon, and

5-carboline. The range in symmetry of the glyoxaline compounds is noted.

L. J. S.

**Significance of the Magnetism of the Rare Earths.** F. HUND (*Z. Physik*, 1925, **33**, 855—859).—From a consideration of the distribution of the electrons the magneton numbers are calculated for the elements with atomic numbers 54 to 68, and are in good agreement with the numbers calculated from experiments on the magnetic properties of the elements.

E. B. L.

**Magnetic Researches. XXVII. Magnetic Properties of some Paramagnetic Chlorides at Low Temperatures.** H. R. WOLTJER (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 536—543).—The dependence of the magnetic susceptibilities of anhydrous chromium, cobalt, and nickel chlorides on field strength and temperature has been studied, the magnetisation being determined from the attraction exerted on a small quantity of the substance in a non-homogeneous magnetic field. Down to the temperature of liquid nitrogen, the susceptibility is independent of field strength, but at the temperature of liquid hydrogen the susceptibility of chromium chloride decreases, whilst that of cobalt and nickel chlorides increases with the field. For a given field strength, the susceptibility of chromium chloride increases with falling temperature and of cobalt chloride decreases slightly; that of nickel chloride is independent of temperature except for weak fields, where it decreases slightly. Down to 64° Abs. all obey Weiss' law,  $\chi(T-\theta)=C$ , where  $\chi$  is the susceptibility,  $T$  the absolute temperature,  $C$  a constant, and  $\theta$  has the values 32.5°, 20°, and 67° for the chlorides of chromium, cobalt, and nickel, respectively.

M. S. B.

**Further Experiments with Liquid Helium. Magnetic Researches. XXVIII. Magnetisation of Anhydrous Chromium, Cobalt, and Nickel Chlorides at Very Low Temperatures.** H. R. WOLTJER and H. K. ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 544—549; cf. preceding abstract).—The magnetisation curves of the three chlorides have been determined at the temperatures of liquid hydrogen and liquid helium, i.e., below the Curie temperature. None of the chlorides shows hysteresis or residual magnetism. Chromium chloride is ferromagnetic to this extent, that its susceptibility decreases with increasing field strength. The magnetisation curves for nickel and cobalt chlorides are at first convex to the axis of magnetic field, becoming linear for higher fields. At very low temperatures the connexion between magnetisation and field strength for all the chlorides appears to be independent of temperature.

M. S. B.

**Orientations of Crystals in Electrodeposited Metals.** R. M. BOZORTH (*Physical Rev.*, 1925, [ii], **26**, 390—400).—When examined by the Debye-Scherrer X-ray method, electrodeposited films of copper, zinc, and cadmium are found to have the crystals oriented at random, whilst those of iron, nickel, and cobalt have special orientations. In the case of iron, the (111) planes tend to

lie parallel to the surface, as do also the (100) or (211) planes of nickel. Cobalt is less markedly, and silver only slightly, oriented. The production of orientation is ascribed to the tension present in the foils, presumably due to hydrogen being deposited with the metal; the metallic atoms take up positions farther apart than normally, but as successive layers are added, the hydrogen diffuses from the innermost layers, leaving the metal in a state of stress.

A. A. E.

**Very Thin, Transparent Metal Films.** C. MÜLLER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1925, 464—470).—Extremely thin films of nickel, gold, platinum, silver, and iron have been obtained by a modification of the method of electro-deposition on a thicker base, followed by the solution of the latter. The exact details of the process are not given, but it is stated that the metal film is coated with a thin protective layer which is very soluble, so that in the freeing of the film from its support it is exposed to the solvent only in the last stages of the process. Greater homogeneity of the film is thus obtained. Films of gold and nickel of  $0.01\ \mu$  thickness, and of the other metals of  $0.04\ \mu$  thickness, were obtained. The strength and elasticity of the nickel films are considerable; a  $0.04\ \mu$  foil, 6 cm. in diameter, has an elasticity of 1 mm., and a thicker foil,  $0.25\ \mu$  in thickness, supported by a gauze, withstood the pressure of a 25 cm. mercury column. The thickness of the heavier foils was estimated from their weight and bulk density, and that of the thinner foils by the amount of current used in their deposition compared with that required for thicker foils of equal area. The thickness of the thinner foils corresponded with a layer of 30 atoms only. The transparency of the films was high, permitting the photographing through them of a finely ruled scale. Those of gold showed a maximum transparency near  $5500\ \text{\AA}$ . In reflected light, gold films of  $0.04\ \mu$  thickness appeared golden-yellow, those of  $0.02\ \mu$  a deep rose. The surface of the thinnest films, under high magnification, appeared glassy and structureless, and their polarising effect was negligible. When heated in an oxidising atmosphere, a nickel foil,  $0.03$ — $0.04\ \mu$  thick, increases greatly in transparency. The reconversion of this film to its original condition by heating in hydrogen shows this to be due to oxidation, and not to loss of nickel. The current-carrying capacity of the films, owing to their large radiating surfaces, is high. A nickel foil,  $0.04\ \mu$  thick, will carry 0.3 amp. per cm. width without oxidising. Applications of these foils, based on their elasticity and conductivity, are suggested.

F. G. T.

**Plasticity of Single Crystals.** W. P. DAVEY (*J. Physical Chem.*, 1925, 29, 1211—1214).—A consideration of the positions of the planes of maximum atomic density (cf. A., 1923, ii, 768) indicates that plastic, ductile, and malleable metals have face-centred cubic structures, whilst relatively non-plastic metals have body-centred cubic structures. Iron is fairly plastic, but has the latter structure. Crystals of simple cubic structure have practically no plasticity. Single metal crystals which are ductile in the cold along certain

axes have a "hexagonal close-packed" structure; primary slip occurs in the (001) planes when the axial ratio exceeds 1.735 (e.g., zinc), and in the (100) planes when it is less than this number. A single zinc crystal stretched beyond its elastic limit exhibits "block-slip" along the (100) planes to a much greater extent than along the (001) planes, in agreement with the above theory. S. K. T.

**Heat of Formation of Lead Carbonate.** A. L. MARSHALL and B. BRUŽS (*J. Physical Chem.*, 1925, **29**, 1184—1186).—The heats of the reactions (1)  $\text{PbO} + \text{CO}_2 = \text{PbCO}_3$  and (2)  $\text{PbO} + \text{PbCO}_3 = \text{PbO} \cdot \text{PbCO}_3$  have been determined. The method used consisted in dissolving lead oxide, lead carbonate (as cerussite), and  $\text{PbO} \cdot \text{PbCO}_3$  in dilute nitric acid, using a calorimeter similar to that described by U. Fischer (*Z. anorg. Chem.*, 1912, **78**, 57). From the heats of solution thus measured, the heats of reaction have been calculated. The values of  $\Delta H$  given for (1) and (2) are  $-21,100$  and  $-340$  cal., respectively. The values of  $\Delta H$  calculated by the authors from the data given by Thomsen ("Thermochemische Untersuchungen," III, 333, 442) and by Berthelot ("Thermochemie," II, 345) for the reaction  $\text{PbO} + \text{CO}_2 = \text{PbCO}_3$  are  $-22,200$  cal. and  $-19,400$  cal., respectively, the new value  $-21,100$  cal. being approximately their mean. L. S. T.

**Method of Determining Molecular Weight.** G. RASTELLI (*Gazzetta*, 1925, **55**, 552—554; cf. Barger, T., 1904, **85**, 286; Rast, A., 1921, ii, 623).—Two solutions, one of a standard substance and the other of an unknown, of equal concentration, each contained in a calibrated glass tube of 2 mm. uniform internal diameter, ending in a bulb, are allowed to evaporate into a bulb containing an absorbent medium. After some hours, the amounts,  $a$  (from the solution of the standard) and  $b$ , of the solvent, which have left the two solutions, are read from the respective changes in the lengths of the columns of solution. Then  $M_2 = M_1 b/a$ , where  $M_1$  and  $M_2$  are the known and the unknown molecular weights, respectively. The method affords moderately accurate results. W. E. E.

**Cryoscopic Measurements with Benzene.** E. R. JONES and C. R. BURY (*J. Chem. Soc.*, 1925, **127**, 1947—1951; cf. Brown and Bury, this vol., ii, 32).—The use of benzene for cryoscopic measurements has been studied, using dry benzene in the presence of phosphoric oxide or alumina, and moist benzene in the presence of the salt hydrate pair  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , and also saturated with water. In calculating the molecular weights, little error is introduced by neglecting the water content of the benzene, provided that it is kept constant during the experiments. Azobenzene, triphenylmethane, picric acid, and trinitrotoluene show no definite evidence of solvation when dissolved in benzene, although they crystallise with 1 mol. of benzene of crystallisation. W. H.-R.

**Resistance of Platinum Films in Presence of Hydrogen.** A. W. GAUGER (*J. Amer. Chem. Soc.*, 1925, **47**, 2323—2325).—The electrical resistance of thin platinum films deposited on glass by thermal evaporation of the metal in a vacuum decreases with time,

the temperature coefficient of resistance being the reverse of that for the bulk metal. In two experiments out of three, the presence of hydrogen increased the resistance of the film. The deposition of the films is slow in starting at the ordinary temperature, but is rapid when once started; at liquid air temperatures, the deposition is rapid, but at high temperatures no film will form. The results, which were not reproducible at will, indicate that such films consist of numerous small aggregates of metal. S. K. T.

**Optical Constants of Magnesium and Zinc Crystals.** M. E. GRABER (*Physical Rev.*, 1925, [ii], 26, 380—389).—By means of the crystelliptometer (polarimetric method) the optical constants of magnesium and zinc have been measured between 4160 and 6500 Å., and 4550 and 6500 Å., respectively, values of the refractive index, index of absorption, and reflecting power for the horizontal and vertical positions of the crystal being tabulated. A. A. E.

**Characteristics of Tungsten and the Candle Power of a Black Body.** C. ZWIKKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, 28, 499—502).—Measurements have been made between 1200° and 3400° Abs. of the following properties of tungsten: spectral emissivity and brightness temperature (both for  $\lambda=0.665$ ), colour temperature, electrical resistance, total radiation, brightness, thermionic emission, rate of vaporisation, thermal conductivity, and (for the range 1800—2400° Abs.) of the Thomson effect. The electron emission is given by  $i=60 \cdot 2T^2 e^{-b/T}$  amp./cm.<sup>2</sup>, where  $b=52230$ . The rate of evaporation was determined from the decrease in diameter of a glowing tungsten filament maintained at a constant temperature, and is expressed by the formula

$$\log m = 11.92 - 4.84 \times 10^4/T - 0.368 \log T - 0.00016T.$$

The colour temperature of tungsten at a temperature  $T$  is defined as the temperature of a black body giving the same energy distribution in the visible spectrum as the tungsten. The ratio of the candle power  $B_1$  of the black body at  $T_c$  to the candle power  $B_2$  of tungsten at  $S$  is given by  $B_1/B_2 = e^{(C/2 \cdot 3\lambda)(1/S - 1/T_c)}$ , where  $T_c$  and  $S$  are the colour and brightness temperatures, respectively, and  $C$  is a constant. Measurements of the candle power of a black body, in conjunction with determinations of the brightness of a tungsten filament, give 0.00146 watt per international candle as the lowest value of the mechanical equivalent of light. F. G. T.

**Specific Heat of the Hydrogen Molecule.** A. PREDVODITELEV (*Z. Physik*, 1925, 34, 178—183).—A formula is obtained by considering the hydrogen molecule as a rotating dipole, without introducing quantum theory, and is in satisfactory agreement with experiment, particularly for low temperatures. A relationship is deduced between the energy of rotation and the b. p. E. B. L.

**Ratio of Specific Heats of Hydrogen.** J. R. PARTINGTON and A. B. HOWE (*Proc. Roy. Soc.*, 1925, A, 109, 286—291).—The ratio of the specific heats of hydrogen has been redetermined, and is

given as  $1.4113 \pm 0.0002$ . The previous determinations of the specific heats of hydrogen are discussed. S. B.

**Heat Capacity of Solid Aliphatic Crystals.** E. O. SALANT (*Proc. Nat. Acad. Sci.*, 1925, **11**, 227—231).—On the basis of the assumptions inherent in the Debye and Einstein functions of a linear oscillator, and in the Lindemann m. p. formula, the author proceeds to develop an expression for the atomic heat for a compound  $C_xH_yO_zN_w$  by a modification of the formal expression of the Neumann-Regnault-Kopp law. Values obtained in this way compare well with the known data and are given for formic acid, oxalic acid, methyl, ethyl, and *n*-butyl alcohols, glycerol, dextrose, acetone, and carbamide. R. W. L.

**Residual Affinity and Co-ordination. XXIV. Heats of Chelation of Dithiolated Metallic Halides.** G. T. MORGAN, S. R. CARTER, and W. F. HARRISON (*J. Chem. Soc.*, 1925, **127**, 1917—1925).—*Dimethyldithioethylene zinc chloride*,  $C_4H_{10}S_2 \cdot ZnCl_2$ , m. p.  $131^\circ$ , is prepared by passing chlorine into a suspension of zinc dust in ether, followed by addition of the disulphide to the filtered solution. It is unstable in the presence of moisture. *Dimethyldithioethylene zinc iodide*, m. p.  $169^\circ$ , is similarly prepared, using iodine in place of chlorine. *Dimethyldithioethylene cadmium chloride* and *bromide* are prepared by the action of the disulphide on dry alcoholic solutions of the halide; neither melts below  $285^\circ$ . *Dimethyldithioethylene cuprous iodide* is prepared by saturating an aqueous solution of copper sulphate with sulphur dioxide, and then adding the organic sulphide and potassium iodide. It is unchanged by cold water and has m. p.  $156^\circ$  (decomp.). The heats of reaction of dimethyldithioethylene with metallic halides are determined as follows: cupric chloride 14.85 cal., cuprous iodide 5.88 cal., zinc chloride, bromide, and iodide, 13.21, 15.35, 14.23 cal., respectively; cadmium chloride, bromide, and iodide, 12.16, 11.27, 9.96 cal., respectively; mercuric chloride, bromide, and iodide, 13.23, 11.33, and 4.83 cal., respectively; stannic chloride, bromide, and iodide, 28.06, 19.40, and 16.58 cal.; 12.0 cal. for the combination of 3 mols. of dimethyldithioethylene with 2 mols. of bismuth iodide to form the scarlet complex  $3SMe \cdot C_2H_4 \cdot SMe, 2BiI_3$ . W. H.-R.

**Heats of Formation of Quinonechloroimines and Quinonedichlorodi-imines.** (MLLE.) S. BLASZKOVSKA (*Bull. Inter. Acad. Polonaise*, 1924, **A**, 9—10, 409—428).—In an extension of previous work by Swientoslawski (A., 1909, ii, 862) the thermal values of the processes whereby the hydrochlorides of aromatic diamines and aminophenols react in aqueous solution with chlorine water or bleaching powder to precipitate quinonechloroimines have been evaluated. The following results have been obtained:—benzidine:

$C_{12}H_8(NH_2)_2 \cdot 2HCl + 3Cl_2 = C_{12}H_8N_2Cl_2 + 6HCl + 58.40 \text{ Cal.}$ ,  
 $C_{12}H_8(NH_2)_2 \cdot 2HCl + 3/2Ca(OCl)_2 = C_{12}H_8N_2Cl_2 + 3/2CaCl_2 + 3H_2O + 80.21 \text{ Cal.}$ ; dianisidine:  $C_{12}H_6(OMe)_2(NH_2)_2 \cdot 2HCl + 3/2Ca(OCl)_2 = C_{12}H_6(OMe)_2N_2Cl_2 + 3/2CaCl_2 + 3H_2O + 89.72 \text{ Cal.}$ ; *p*-aminophenol:  $OH \cdot C_6H_4 \cdot NH_2 \cdot HCl + 2Cl_2 = O \cdot C_6H_4 \cdot NCl + 4HCl + 39.92 \text{ Cal.}$ ;  
*p*-amino-*p*'-hydroxydiphenyl:  $OH \cdot C_{12}H_8 \cdot NH_2 \cdot HCl + 2Cl_2 =$

$\text{O}:\text{C}_{12}\text{H}_8:\text{NCl} + 4\text{HCl} + 30.99 \text{ Cal.}$  The formation of small quantities of decomposition products renders the thermal data obtained for picramic acid untrustworthy. It is not possible to determine the heats of formation of the corresponding bromine derivatives, the main reaction being always accompanied by a bromination of the nucleus.

From the present data and those of Swientoslawski (*loc. cit.*) on *p*-phenylene- and *p*-naphthylene-diamines a mean value of 21.92 Cal. is obtained for the difference between the heats of reaction using bleaching powder and chlorine water. Replacement of the benzene nucleus by diphenyl causes a mean decrease of 9.47 Cal. in the heat of reaction. Comparison of the thermal data for benzidine and dianisidine shows that the introduction of electropositive methoxy groups into the nucleus results in an increased thermal effect. 3 : 3'-*Dimethoxydiphenoquinone-4 : 4'-dichlorodi-imine* is formed as a reddish-brown, amorphous, unstable precipitate on treating solutions of dianisidine dihydrochloride with bleaching-powder solution. 4 : 6-*Dinitro-o-benzoquinone-2-chloroimine* is formed as a yellow precipitate on treating a solution of picramic acid in presence of hydrochloric acid with chlorine water in the cold. The substance, which has not yet been obtained pure, is very soluble in acetone, acetic acid, and alcohol.

J. S. C.

**Elasticity Modulus, Temperature, and M. P.** W. WIDDER (*Physikal. Z.*, 1925, 26, 618—622).—Examination of data for numerous metals shows that the elasticity modulus is a linear function of the temperature,  $E_t = E_0[1 - \epsilon_0(t - t_0)]$ . If it be assumed that the elastic modulus vanishes at the m. p., the temperature coefficient of the modulus at  $t_0$  is given by  $\epsilon_0 = 1/(t_m - t_0)$ , where  $t_m$  is the m. p. It is also shown that, for many metals, the ratio of the temperature coefficient of the elasticity modulus to the coefficient of linear expansion at the same temperature is approximately constant. The value of this constant is about 60. The divergences from this approximate relation are most marked with lead, cadmium, tin, manganese, and antimony.

F. G. T.

**Halides of the Fourth Group as Homopolar Compounds on the Basis of an Additive Relationship in M. P.** A. HANTZSCH and H. CARLSOHN (*Ber.*, 1925, 58, [B], 1741—1746; cf. Hantzsch, this vol., ii, 359; Paneth and Rabinovitsch, this vol., ii, 760).—The m. p. of the halides of the fourth group can be calculated from the m. p. of the *n*-valent element (M) and that of the halogen (X) according to the following empirical formula: m. p. of halide = (m. p. of  $\text{M} + n \times \text{m. p. of X}) / (n + 1)$ . It appears therefore that the atoms can be little changed by the union to form molecules; this hypothesis directly contradicts the deformation theory of Fajans and Joos (*A.*, 1924, ii, 750). The applicability of the rule to the halides of titanium, germanium, and silicon cannot be directly shown, since these elements are associated in the "free" state as indicated by their high m. p. Since, however, the m. p. of the chlorides, bromides, and iodides of silicon, titanium, germanium, and tin lie approximately on a straight line when the m. p. of the



halides of one of these elements as abscissæ are plotted against the m. p. of the halides of another of the elements just named as ordinates, the m. p. of the halides may be regarded as normal and, by application of the rule, the m. p. of "unassociated" titanium, germanium, or tin may be calculated. The possibility of "chemical association" of the halides is regarded as excluded if the relationship,  $\text{Abs. m. p.}/\text{Abs. b. p.} = 0.62$ , is fulfilled. H. W.

**Rare-gas Nature of Pseudo- and Non-electrolytes as Basis for the Calculation of their M. P. and B. P.** H. CARLSOHN (*Ber.*, 1925, 58, [B], 1747—1752; cf. Paneth and Rabinovitsch, this vol., ii, 760).—If association is taken into account, it is shown that the m. p. and b. p. of pseudo- and non-electrolytes are exactly directly proportional to the m. p. and b. p. of the rare gases corresponding with them. The halides of the elements of the fourth group, the hydrides of the metalloids, and organic halides are non-electrolytes constituted similarly to the rare gases. Association is little or non-evident in the solid inorganic compounds or molten organic derivatives. H. W.

**Thermochemical Researches on Diazo Compounds.** W. SWIENTOSLAWSKI (*Rocz. Chem.*, 1925, 5, 214—231).—The methods employed by the author (cf. A., 1920, i, 336) for the thermochemical investigation of diazo compounds are described and illustrated by the cases of aniline and *p*-bromoaniline. From these, and from previously published results (*loc. cit.*), the following conclusions are reached. Substitution in the benzene ring of electronegative groups has not a constant effect on the heats of various reactions of substituted anilines. Thus, where  $q_{am}$ ,  $q_{dz}$ ,  $q_n$ , and  $q_{is}$  are respectively the heats of formation of amine hydrochloride, of diazonium chloride, and of *n*- and *iso*-diazohydrate sodium salts,  $i_n$  and  $i_{is}$  the heats of isomerisation of the diazonium into the *n*- and *iso*-diazohydrate forms, and *A* and *B* the heats of diazotisation of amine and of coupling of *n*-diazohydrate with solid  $\beta$ -naphthol, the effect of electronegative substituents is to diminish  $q_{am}$ ,  $q_{dz}$ , and *A*, and to enhance  $q_{is}$ ,  $q_n$ , and *B*, whilst  $i_n$  and  $i_{is}$  remain unchanged. These differences may be considerable,  $q_{am}$  varying from 7.60 to 1.81 cal., *A* from 19.97 to 12.47 cal.,  $q_n$  from 3.77 to 5.65 cal., and  $q_{is}$  from 8.80 to 11.00 cal. *B* increases inversely with *A*, so that  $A + B + i_n = 50$  cal. is constant, and independent of substitution, the derivatives of *o*- and *p*-aminobenzoic and of sulphanilic acids deviating, however, from this rule. The mean values of  $i_n$  and  $i_{is}$  are +0.5 and -2.3 cal., and in all cases  $q_n < q_{is}$ , the difference being from 5 to 6 cal. Contrary to Hantzsch's statement,  $i_{is} - i_n$  gives a negative mean value of about 3 cal., although in the case of the isomerisation of salts heat is evolved, since  $q_n < q_{is}$ , so that  $(q_{is} + i_{is}) - (q_n + i_n) = +3$  cal., the salt of *p*-sulphodiazobenzene being, however, an exception to this rule. R. T.

**Thermochemical Researches on the Diazo Derivatives of Aminophenols.** W. SWIENTOSLAWSKI and (MLLE.) Z. BŁASZKOWSKA (*Rocz. Chem.*, 1925, 5, 233—251; cf. preceding abstract).—Certain reactions of picramic acid and of *p*-amino-*p'*-hydroxydi-

phenyl are examined thermochemically. The heats of formation of the hydrochlorides are, respectively, 0.746 and 6.0 cal., of formation of sodium salts 10.20 and 6.41 cal., of diazotisation 25.56 and 19.91 cal. The product of diazotisation of picramic acid is a quinonediazide which yields with sodium hydroxide a normal diazohydrate salt, 9.34 cal. being evolved. The heat of coupling of the quinonediazide with  $\beta$ -naphthol is about 41 cal. In the case of the aminohydroxydiphenyl, the heat of formation of the sodium salt of the diazohydrate is 24.13 cal., and of coupling with  $\beta$ -naphthol about 27 cal. Picramic acid exhibits greater divergences from the properties of other amines than the aminohydroxydiphenyl.

R. T.

**Density and Atomic Weight of Helium.** E. P. BAXTER and H. W. STARKWEATHER (*Proc. Nat. Acad. Sci.*, 1925, **11**, 231—234).—The technique developed by the authors for determining the density of oxygen has been applied to measure the density of helium. The average value for the density of helium is given as 0.17845 at 0° and 760 mm. at sea level lat. 45°.

R. W. L.

**Vapour Pressure. I. Nitroanilines.** J. F. T. BERLINER and O. E. MAY (*J. Amer. Chem. Soc.*, 1925, **47**, 2350—2356).—The vapour pressures of the isomeric nitroanilines have been determined by Nelson and Senseman's method (A., 1922, i, 245) using a U-tube levelling type of isotenoscope. All three isomerides decompose to some extent before their b. p. at atmospheric pressure are reached, *p*-nitroaniline decomposing completely, whilst the *o*-compound is only slightly decomposed. Below the decomposition temperatures, the observed vapour pressures agree closely with those calculated from the latent-heat equation. Determinations of the vaporisation entropies at a concentration of 0.00507*M* per litre of vapour indicate that the molten nitroanilines are not normal liquids.

R. B.

**Hypothesis of Molecular Association.** Y. ROCARD (*J. Phys. Radium*, 1925, [vi], **6**, 199—201).—Duclaux (*ibid.*, 1924, [vi], **5**, 331) maintains that the equation of state can be deduced equally well by substituting the idea of molecular association for van der Waals' conception of internal pressure, but it is now shown that this association theory leads to the expression  $\eta = \alpha \sqrt{T} (1 - 0.31be^{CT/T}/V)$  for the viscosity of a gas, and that this is not in agreement with the result of experiment. On the other hand, postulation of the existence of cohesive forces leads to an expression for the variation of the viscosity of a gas with temperature and pressure which is in excellent agreement with the facts (A., 1924, ii, 653).

E. E. W.

**Statistical Basis of Volmer's Equation of State for Adsorbed Substances, and the Concentration Formula.** S. C. KAR (*Physikal. Z.*, 1925, **26**, 615—618).—Theoretical. By a quantised statistical treatment based on the assumption that adsorbed molecules behave as a surface film, an equation of state of the same form as Volmer's equation (cf. this vol., ii, 539) is obtained. The treatment leads to a concentration formula different from Volmer's, but

identical with Langmuir's (A., 1918, ii, 430), and to an interpretation of the constant in that formula.

F. G. T.

**Cause of Surface Tension.** E. H. KENNARD (*Nature*, 1925, **116**, 463—464).

[Cause of Surface Tension.] N. K. ADAM (*Nature*, 1925, **116**, 464—465).

**Surface Tension Crystal v. Saturated Solution. The Concentration Cell: Finely Divided Salt | Supersaturated Solution | Saturated Solution | Large Crystals.** L. SOEP (*Phil. Mag.*, 1925, [vi], **50**, 675—680).—Equations are deduced relating the surface tension between a crystal surface and the corresponding saturated solution with the *E.M.F.* of the above cell, and further relating these quantities with the molecular heat of solution.

A. B. M.

**Scattering of Light by Liquid Boundaries, and its Relation to Surface Tension.** III. C. V. RAMAN and L. A. RAMDAS (*Proc. Roy. Soc.*, 1925, **A**, **109**, 272—279).—The surface-scattering of light by water and twenty-eight other liquids have been compared. It is found, in general, that the intensity of the surface opalescence increases when the surface tension is diminished or the refractive index increased. The effect of greasing the surface of the water has also been studied. With amounts of oleic acid just sufficient to stop camphor movements, the surface opalescence is approximately doubled. With excess of oleic acid over this quantity, the increase in brightness is far greater—perhaps a thousandfold. The surface is, however, no longer continuous, but contains microglobules of oil. These phenomena are correlated with recent work on surface films.

Experiments with liquid carbon dioxide show that the opalescence increases rapidly near the critical temperature, as would be expected. The scattering phenomena at the interface between carbon disulphide and methyl alcohol near the critical solution temperature are similar.

S. B.

**Behaviour of Crystals and Lenses of Fats on Surface of Water. I. Mechanism and Rate of Spreading.** A. CARY and E. K. RIDEAL (*Proc. Roy. Soc.*, 1925, **A**, **109**, 301—317).—An experimental study has been made of the "surface spreading" on water and dilute acid solutions of long-chain organic compounds terminating in a polar group, including acids, phenols, nitriles, etc. It has been found that unimolecular films spread from crystals as well as from liquid lenses, a definite equilibrium surface tension characteristic of each material being finally established. The rate of attainment of equilibrium is very much slower for the films formed by crystals than that for liquid films, and this observation has been utilised in examining the mechanism of the spreading. Equilibrium for the liquid films is reached too rapidly for dynamical experiments. A crystal of myristic acid, or other solid, was placed in contact with the surface, and the change in the surface tension

produced was measured by the ring method. It was found that the spreading could be separated into two stages, one during which the surface is covered with a unimolecular film under zero compression, the surface tension remaining constant meanwhile, and a stage during which packing of this expanded film occurs until equilibrium between surface solution and recondensation is attained. During this stage, the surface tension is altered, the changes obeying a unimolecular equation. The results indicate that for long-chain substances there is a limit at the ordinary temperature to the expansibility of a film, and that the molecules are unable to separate completely on the surface.

Experiments have also been conducted on the rate of spreading of the films from liquids on a free water surface. The rate is found to depend on the size of the liquid drop, but invariably a comparatively rapid extension for the first few cm. is succeeded by a slower but constant rate of spreading. The mean life of a molecule on the surface of a crystal in contact with water is calculated to be of the order of  $10^{-7}$  sec.

S. B.

**Behaviour of Crystals and Lenses of Fats on Surface of Water. II. Effect of Temperature on the Equilibrium Pressure.** A. CARY and E. K. RIDEAL (*Proc. Roy. Soc.*, 1925, **A**, 109, 318—330).—The surface tension of *N*/100-hydrochloric acid has been measured when the surface is saturated with a film in equilibrium with organic compounds in bulk over a temperature range including the m. p. of the compounds. The results and conclusions are as follows. When working with highly insoluble solid compounds, there is a definite temperature below which no effect on the surface tension could be observed with the most prolonged contact between crystal and surface. Between this temperature and the m. p. the surface tension falls linearly with rise of temperature. At the m. p., there is a sudden change in the slope of the surface tension-temperature curve, but the changes are still linear. With certain compounds (*e.g.*, stearic acid and octadecyl acetate), the surface tension above the m. p. of the bulk material increases rapidly with rise of temperature over a definite range, but above this range the decrease is resumed. Other compounds do not exhibit this double break, the surface tension decreasing steadily above the m. p. These phenomena are explained on the hypothesis, put forward by other workers on other grounds, that all films can exist in two states of aggregation—"condensed" and "expanded." The passage from a partly condensed to an expanded film is considered to take place at a definite temperature. If this temperature is below the m. p., then the surface tension-temperature curve will only show one break, at the m. p. If the transition temperature is above the m. p., the curve will have two breaks, one at the m. p., and the other at this transition temperature of the film. The phenomena are discussed from the point of view of the phase rule, the film being treated as a separate phase. By an application of the Clapeyron equation, the results of the experiments enable the latent heat of fusion of the compounds to be calculated.

S. B.

**Behaviour of Crystals and Lenses of Fats on Surface of Water. III. Effect of Polar Group on Equilibrium Pressure.**

A. CARY and E. K. RIDEAL (*Proc. Roy. Soc.*, 1925, A, **109**, 331—338).—The measurements described in the preceding abstract have been extended to include long-chain compounds with more complex polar heads. The results suggest that the slope of the surface tension-temperature curve up to the m. p. is determined by the hydrocarbon chain, whilst the slope between the m. p. and the film "transition" temperature is dependent on the polar group. Similar measurements have been made on mixtures of two compounds. With mixtures of octa- and hexa-decyl acetates, it was found that the relative proportions of the two compounds did not influence the results. Up to the m. p., the effect on the surface tension is the same as that of the component capable of producing the greater effect when present alone. Above the m. p., complex but interesting phenomena are observed. The influence of impurities is also described.

S. B.

**Measurement of Viscosity.** J. DUCLAUX and J. ERRERA (*J. Phys. Radium*, 1925, [vi], **6**, 202—204).—In order to avoid the errors introduced by the usual method of employing capillary viscosimeters for measuring the viscosity of liquids of low viscosity, an apparatus is devised which replaces the capillary by a cylinder of porous pot. It is shown experimentally that the rate of flow is proportional to the pressure, and that the results obtained by this method for ethyl ether, acetone, and other liquids of low viscosity are more accurate than those obtained with capillaries of 0.41 mm. and 0.26 mm. diameters.

E. E. W.

**Determination of the Coefficient of Viscosity of Water.**

P. LEROUX (*Ann. Physique*, 1925, [x], **4**, 163—248).—The absolute viscosity of water has been measured at different temperatures by the rotating cylinder method, the water being contained between two concentric cylinders, of which the outer was rotated at known velocity and the resulting twisting moment on the inner cylinder measured. The following values are given for the absolute value of  $\eta$ : 0.01704 at 1.5°, 0.01648 at 2.5°, 0.01551 at 4.1°, 0.01419 at 7.5°, 0.01276 at 10.9°, 0.01175 at 14°, 0.01121 at 16°, 0.01069 at 18°, 0.01018 at 20°, 0.00949 at 23.2°, 0.00883 at 26.4°, 0.008198 at 30°, 0.007500 at 34.3°, 0.006554 at 41.6°, and 0.006220 at 44.5°. No irregularity exists in the neighbourhood of 4°, and the values of  $\eta$  are independent of the speed of rotation of the outer cylinder, showing that water has no rigidity. The different methods of determining viscosity are critically discussed, and the elaborate precautions used in the present work are described.

W. H.-R.

**Relation between Viscosities of Liquids and their Molecular Weights.** D. B. MACLEOD (*Trans. Faraday Soc.*, 1925, **21**, 151—159).—See this vol., ii, 498.

**Physical Properties of Water.** D. B. MACLEOD. (*Trans. Faraday Soc.*, 1925, **21**, 145—150).—See this vol., ii, 498.

**Equal Viscosities.** W. HERZ (*Z. anorg. Chem.*, 1925, **147**, 293—294).—It is shown for about forty organic liquids that the ratio of the temperature at which the viscosity has the value 0.0040 C.G.S. unit, to the critical temperature, is approximately constant. The recorded ratios vary from 0.515 to 0.692 and the critical temperatures from 214° to 397°. A. G.

**Viscosities of Liquids at their B. P.** D. B. MACLEOD (*Trans. Faraday Soc.*, 1925, **21**, 160—167).—An attempt has been made to determine to what extent the b. p. of liquids may be regarded as corresponding temperatures. On the basis of previous determinations (this vol., ii, 492), the association factors of a number of liquids have been calculated and show a fairly close agreement with those given by Ramsay and Shields. Taking pentane as standard (b. p.=0.6578  $T_c$ ), the viscosities of other liquids have been compared (1) at the same reduced temperature, and (2) at the b. p. both with and without reduction of the free space to the same value as that given by pentane, viz., 0.1690. It has thus been shown that the viscosity at the b. p. bears no relation to the molecular weight. These quantities are, however, found to be proportional when the comparison is made under conditions of equal free space. It follows that the condition of equal free space corresponds very closely with that given by equality of reduced temperature on the basis of van der Waals' equation. M. S. B.

**Diffusion of Iodine in Pure and Mixed Solvents.** J. GRÖH and I. KELP (*Z. anorg. Chem.*, 1925, **147**, 321—330; cf. this vol., ii, 28).—The diffusion coefficient of iodine has been measured in benzene, chloroform, and carbon disulphide, in which the solutions are violet, and in ethyl alcohol and ether, in which the solutions are brown, owing, it is believed, to solvation. The coefficients in the first group of solvents are nearly equal after correction for the viscosities of the solutions. In ether, the coefficient is smaller, as was to be expected; in alcohol, it is greater, indicating that hitherto unsuspected factors are involved. The addition to carbon disulphide or chloroform of sufficient alcohol or ether (2 mols. per litre) to produce brown iodine solutions diminishes the diffusion coefficient. A. G.

**Densities and Compressibilities of Organic Liquids and Solutions: Polymerisation of Water.** T. W. RICHARDS and H. M. CHADWELL (*J. Amer. Chem. Soc.*, 1925, **47**, 2283—2302).—The densities of aqueous solutions of ethyl alcohol, urethane, ethyl ether, and methyl acetate, and of solutions of urethane in water, alcohol, ethyl ether, and benzene have been measured at 20°. The compressibilities of some of these solutions and solvents were also determined. The contractions observed in the formation of these solutions (excepting the first) are approximately proportional to the compressibilities of the solutes in the liquid state. Since urethane and water have comparable compressibilities, the large decrease in volume which occurs when urethane dissolves in water is attributed to depolymerisation of some of the water molecules. Equi-molar quantities of different substances have the same

depolarising effect. At 20° water appears to contain about 28% of "polyhydrol" (cf. Sutherland, A., 1906, ii, 603). In aqueous alcohol solutions, the alcohol polymerides, which are probably less bulky than those of water, appear to dissociate. S. K. T.

**Vapour Pressure of Organic Solutions and Application of Dühring's Rule to Calculation of Equilibrium Diagrams.**

E. H. LESLIE and A. R. CARR (*Ind. Eng. Chem.*, 1925, **17**, 810—817).—Dühring's rule agrees with experimental data satisfactorily enough for technical application. This has been proved by Baker and Waite (*Chem. Met. Eng.*, 1921, **25**, 1137) for aqueous solutions of salts. The vapour pressures of *n*-hexane, *n*-heptane, and *n*-octane, and of binary mixtures of these three substances, have now been determined in an apparatus similar to that used by Baker and Waite (*loc. cit.*) between 92.3 and 760 mm. It is found that the rule holds good for these binary mixtures of organic liquids. It is evident that by applying the rule the complete vapour pressure curve for any liquid can be plotted from two observations only. This facilitates technical investigations. Various applications are discussed.

W. A. S.

**Vapour Pressures of Hydrogen Chloride above Aqueous Solutions.**

I. S. MITSUKURI, T. ROKKAKU, and T. WATASE (*Sci. Rep. Tôhoku*, 1925, **14**, 251—258).—The partial pressure of hydrogen chloride in equilibrium with dilute hydrochloric acid solutions has been determined by passing air through a series of three saturators in a thermostat for several days and condensing the water vapour and hydrogen chloride in a bulb surrounded by ice. The conductivity of the condensate was measured and from these data the partial pressure of the gas over the original solution was calculated. The values obtained are much lower than those calculated from the vapour pressures of concentrated solutions of hydrochloric acid or from the *E.M.F.* of the cell  $H_2|HCl|AgCl|Ag$ , whereas Dunn and Rideal's values (A., 1924, ii, 306) were much higher. The authors reject the results of Dunn and Rideal on the ground that the method used involves a violent surface distillation, and they consider that the published data for concentrated hydrochloric acid solutions are also too high.

A. R. P.

**Equilibrium in the Liquid System Iron-Copper-Manganese with Varying Small Proportions of Carbon.**

F. OSTERMANN (*Z. Metallk.*, 1925, **17**, 278—282).—Pure copper and iron are miscible in all proportions in the liquid state, but in the presence of small quantities of carbon there is a more or less extensive range in which the metals are immiscible. On the addition of manganese, which alloys with both copper and iron in all proportions and has a great affinity for carbon, this range of immiscibility disappears. [Cf. B., 1925, 852.]

A. R. P.

**Law of Depression of Freezing Points in Metallic Alloys.**

K. HONDA and T. ISHIGAKI (*Sci. Rep. Tôhoku*, 1925, **14**, 219—233).—Measurements of the depression of the f. p. of many metals on the addition of a small amount of a second metal indicate that dilute

solutions obey the law of van 't Hoff whether a solid solution is formed or not. The atomic depression of the solvent is independent of the solute. [Cf. *B.*, 1925, 884.] A. R. P.

**Properties and Structure of Some Alloys of Aluminium and Chromium.** F. T. SISCO and M. R. WHITMORE (*Ind. Eng. Chem.*, 1925, **17**, 956—958).—Aluminium may be readily alloyed with chromium (up to 5%); photomicrographs of the alloys show scattered crystals of great hardness which probably have the composition  $\text{AlCr}_3$ . [Cf. *B.*, 1925, 852.] C. I.

**Mechanical Properties and Structure of Some Alloys with a Restricted Range of Mixed Crystals. Silver-rich Binary Solid Solutions containing Magnesium, Aluminium, Tin, Zinc, Cadmium, and Manganese.** F. SAEFTEL and G. SACHS (*Z. Metallk.*, 1925, **17**, 155—161, 258—264, 294—298).—Pure silver which has been hardened by cold work begins to soften at  $100^\circ$  and is completely soft at  $600^\circ$ , having a hardness of 25 and a tensile strength of 12.8 kg. per sq. mm. and giving an elongation of 48% before breaking. By adding magnesium, aluminium, tin, zinc, cadmium, or manganese in such quantities that the whole is retained in solid solution, the hardness and ductility increase, the tensile strength remains nearly constant, whilst the malleability decreases considerably, the reduction being nearly proportional to the amount of the second element added. The limiting amounts of zinc and aluminium retained in solid solution at the ordinary temperature are 20.4% and 5.7%, respectively, and the mixed crystal range in the silver-rich magnesium-silver alloys extends uninterruptedly to the compound  $\text{MgAg}$ . [Cf. *B.*, 1925, 853.] A. R. P.

**Hardness of Ternary Alloys of Lead, Bismuth, and Cadmium.** C. DI CAPUA (*Gazzetta*, 1925, **55**, 582—594).—A detailed study of the hardness-composition curves corresponding with certain sections of the f. p. diagram of this system shows that the ternary eutectic mixture possesses a minimum hardness, whereas the binary eutectic mixtures of the constituents (A., 1924, ii, 268, 553) are always characterised by a maximum hardness. This result is also met with in the ternary systems bismuth-tin-cadmium (where the minimum in question disappears on reheating) and lead-tin-bismuth (see following abstract). W. E. E.

**Hardness of Ternary Alloys of Lead, Bismuth, and Tin.** C. DI CAPUA (*Gazzetta*, 1925, **55**, 594—604).—Alloys of lead, bismuth, and tin or cadmium (cf. preceding abstract) show anomalies in the hardness-composition diagrams in that the binary eutectic mixtures show maxima, whilst the ternary eutectics show minima. These anomalies are eliminated by reheating. The reheating, moreover, increases the concentrations of the saturated solid solutions of lead and bismuth in tin. W. E. E.

**Expansion of Glasses. Boric Anhydride.** M. SAMSOEN (*Compt. rend.*, 1925, **181**, 354—356).—The linear coefficient of thermal expansion of boric oxide, determined by dilatometric



methods, is about  $15 \times 10^{-6}$  up to  $240^\circ$ , but then rapidly increases, again becoming constant at about  $200 \times 10^{-6}$ , between  $250^\circ$  and  $334^\circ$ . An approximate determination gave an average value of  $200 \times 10^{-6}$  over the region  $1100\text{--}250^\circ$ . [Cf. *B.*, 1925, 849.] A. COUSEN.

**Partition of Silver between Lead and Zinc.** W. A. NAISH (*Trans. Faraday Soc.*, 1925, 21, 102—113).—See this vol., ii, 506.

**Solubility of Slightly Soluble Chlorides in Concentrated Chloride Solutions.** J. KENDALL and C. H. SLOAN (*J. Amer. Chem. Soc.*, 1925, 47, 2306—2317).—The solubility of silver chloride in concentrated aqueous solutions of sodium, lithium, and magnesium chlorides, and of lead chloride in solutions of the chlorides of hydrogen, bivalent mercury, alkali, and alkaline-earth metals has been determined at  $25^\circ$ . In both series, the electrode potential varies in accordance with the rule previously given (cf. A., 1922, ii, 34), irrespective of the formation of double salts. New compounds of the type  $X, PbCl_2$  were isolated, where  $X = \frac{1}{2}LiCl, \frac{1}{2}NaCl, KCl, SrCl_2, BaCl_2, HgCl_2, CaCl_2$ , and  $MgCl_2$ , the last two compounds containing  $6H_2O$ . S. K. T.

**Solubility Relations of Isomeric Organic Compounds.**

**III. Mutual Solubility of the Three Dinitrobenzenes.** D. H. ANDREWS (*J. Physical Chem.*, 1925, 29, 1041—1047).—The mutual solubilities of the dinitrobenzenes, as indicated by f. p. observations, are recorded, and the results compared with those derived from calorimetric data. These solutions deviate but little, if at all, from the ideal, and this is taken to imply that the crystals of each isomeride which separate from ternary mixtures are pure, and that the mixing of the liquids is not attended by an appreciable change in volume or heat content. (For the method of experiment and the interpretation of the time—temperature curves, see this vol., ii, 852).

The solubilities of the three isomerides in different solvents have been interpolated from the observations of various workers and are given for reference. These also deviate but little from the ideal curve, which can therefore be used as a criterion of accuracy for such determinations.

The preparation of *p*-dinitrobenzene by diazotising *p*-nitroaniline in nitric acid solution and subsequent treatment with sodium nitrite and copper sulphate is outlined. L. S. T.

**Solubility Relations of Isomeric Organic Compounds.**

**IV. Mutual Solubility of *o*-, *m*-, and *p*-Nitroanilines and of *o*-, *m*-, and *p*-Chloronitrobenzenes.** G. T. KOHMAN (*J. Physical Chem.*, 1925, 29, 1048—1056; cf. preceding abstract).—The mutual solubilities of the three nitroanilines and of the three chloronitrobenzenes are recorded. As with the previous systems, the isomerides form solutions which are practically ideal, although calorimetric data for the chloronitrobenzenes are not available. It is probable that many such ternary systems will be found to be ideal, the solubility diagram affording the basis for a method of analysis.

The behaviour, on melting, of *o*-nitroaniline and of *m*-chloro-

nitrobenzene in binary mixture indicates the existence of an unstable form. A new method for the preparation of *m*-chloronitrobenzene from *m*-nitroaniline by diazotising in hydrochloric acid solution and subsequent treatment with cuprous chloride, giving 80–90% yield, is also described. L. S. T.

**Solubility Relations in Isomeric Organic Compounds. V. Construction of the Ideal Ternary Solubility Diagram, and its Use in Analysis.** G. T. KOHMAN and D. H. ANDREWS (*J. Physical Chem.*, 1925, **29**, 1317–1324).—A discussion of the construction and interpretation of solubility diagrams for ternary systems in which ideal or nearly ideal solutions (*e.g.*, those consisting of *o*-, *m*-, and *p*-isomerides) are formed. The use of these diagrams in the analysis of such mixtures is described. S. K. T.

**Formation of Metallic Deposits by Molecular Radiation.** I. ESTERMANN (*Z. Elektrochem.*, 1925, **31**, 441–447).—When a narrow stream of vapour from a heated metal impinges on a cold surface in a high vacuum, condensation takes place only below a critical temperature (*e.g.*,  $-50^{\circ}$  to  $-110^{\circ}$  for cadmium on glass) which varies with the density of the stream and the material of the surface. From the critical temperatures, the dimensions of the apparatus, and the temperature of the hot metal, the adsorption pressure of the condensed metal may be calculated. This quantity is of the order of  $10^{10}$  times the vapour pressure of the metal at the same temperature. The heats of adsorption may further be calculated; they are approximately 3500 cal./mol. for cadmium on glass, 3000 cal./mol. for cadmium on copper, 500 cal./mol. for cadmium on silver, and 2500 cal./mol. for mercury on silver. These values are from one-fifth to one-seventh of the heats of vaporisation. Since the work required to separate one atom from another is about one-fifth to one-seventh that required to detach an atom from a crystal surface, it would appear that the condensation nucleus consists of a simple pair of atoms. W. A. C.

**Adsorption of Gases by Graphitic Carbon.** H. H. LOWRY and S. O. MORGAN (*J. Physical Chem.*, 1925, **29**, 1105–1115).—The charcoals used in previous work on adsorption have proved to be hydrocarbons (Lowry, A., 1924, ii, 393); pure carbon, as graphite, is now shown capable of an adsorptive capacity equal to one-third or one-fourth that of the best adsorptive charcoals. Graphites of varying degrees of fineness were prepared by the oxidation of Ceylon graphite, previously treated to reduce the ash content, and exploding the resulting "graphitic acid" to produce "pyrographitic acid" or graphite in a fine state of division (see Burns and Hulett, *J. Amer. Chem. Soc.*, 1923, **45**, 572). Three samples of graphites of different adsorptive capacities were thus obtained. Experiments on pressed and unpressed samples of adsorbent showed no difference in adsorptive capacity.

Data for the three samples are given for (1) carbon dioxide at  $0^{\circ}$ ,  $35^{\circ}$ ,  $56.7^{\circ}$ ,  $80.4^{\circ}$ , and  $100^{\circ}$ ; (2) nitrogen at  $0^{\circ}$ ,  $56.7^{\circ}$ , and  $100^{\circ}$ , and (3) hydrogen at  $-191^{\circ}$ , and at pressures up to 1 atm. Graphite from

“graphitic acid” which was least oxidised ( $C:O=3.98:1$ ) adsorbed the least gas, and that from “graphitic acid” most completely oxidised ( $C:O=3.12:1$ ), the most. There is, however, no simple relation between the amount of gas adsorbed and the degree of oxidation. Support is given to the conclusion previously advanced (Lowry, *loc. cit.*) that large adsorptive powers are due to (1) large ratios of surface to mass and (2) unsaturation of the forces holding the atoms together in the solid.

Details of a method for measuring adsorption, eliminating the use of stop-cocks, are given. L. S. T.

#### Adsorption Capacities of Different Charcoal Powders.

F. KÖNIG (*Pharm. Zentr.*, 1925, **66**, 645—648).—The adsorption capacity of various medicinal charcoals for mercuric chloride has been measured, and found to bear no simple relation to the adsorption capacity for methylene-blue, although those samples which adsorb the former most readily are found to adsorb the latter strongly. These adsorption methods, combined with determinations of moisture, ash, soluble matter, and cyanogen compounds, are recommended for the examination of medicinal preparations. S. I. L.

#### Protein Films on Collodion Membranes.

D. I. НИТЧОК (*J. Gen. Physiol.*, 1925, **8**, 61—74).—The amount of protein (gelatin or egg-albumin) absorbed from an aqueous solution by a disc of collodion varies with the concentration of the protein. The results agree approximately with the hyperbolic formula proposed by Langmuir (cf. A., 1918, ii, 430) for the adsorption of a gas on a plane surface. If the  $p_H$  is varied, the absorption of protein is maximal at the isoelectric point; the absorption also varies when different quantities of inorganic salts are present, the variation being parallel to the changes in fluidity of the protein solution. The greater the permeability of the membrane to water, the larger is the amount of protein absorbed. Membranes which have absorbed protein become less permeable. Calculation of the capillary surface of the collodion from its permeability leads to the conclusion that the protein is adsorbed on the surface of the membrane. W. O. K.

#### Surface Concentration of Sodium Oleate and of Colloidal Sulphur.

J. M. JOHLIN (*J. Physical Chem.*, 1925, **29**, 1129—1139; this vol., ii, 388, 857).—The surface tension of 0.0001% to 1% sodium oleate solutions has been measured at 25° by the capillary rise method, and the change of surface tension with time studied. For the stronger solutions, this change is rapid, and may be represented by an equation of the form  $\sigma = a/t^n$ . It is considered probable that this change of surface tension with time occurs only with colloidal solutions in which the solute is in a highly dispersed state similar to that in true solutions. When alkali is added in increasing amounts to the 0.1% solution, the change in  $\sigma$  with time fluctuates in a periodic manner. Addition of sodium hydroxide diminishes the tendency towards the formation of stable foams.

Preliminary experiments with colloidal sulphur solutions show that, under certain conditions,  $\sigma$  changes with time according to the same equation. L. S. T.

**Structure of True Solutions and the Nature of the Changes Occurring Therein.** P. P. VON WEIMARN (*Kolloid-Z.*, 1925, **37**, 230—234).—The colour changes exhibited by solutions of the oleates of cobalt, nickel, chromium, iron, copper, and manganese in aromatic hydrocarbons on warming are similar to those shown by aqueous solutions of the chlorides and other salts of these metals. Hydrate and ionic theories are inapplicable to the hydrocarbon solutions, and the author, with many references to previous work, outlines his own theories of the colour changes and the nature of true solutions in general. The colour changes are attributed to alterations in the intensity factor of the volume energy of the molecules.  
N. H. H.

**Distribution of Particles in Colloidal Suspensions.** W. W. BARKAS (*Trans. Faraday Soc.*, 1925, **21**, 66—80).—See this vol., ii, 289.

**Law of Distribution of Particles in Colloidal Suspensions. Specific Volume of a Gamboge Suspension.** J. R. H. COUTTS (*Trans. Faraday Soc.*, 1925, **21**, 63—65).—See this vol., ii, 290.

**Colloid Systems in Nitrobenzene.** F. S. BROWN and C. R. BURY (*J. Physical Chem.*, 1925, **29**, 1312—1316).—Colloidal solutions of dehydrating agents (phosphorus pentoxide, calcium chloride, silica, alumina, zinc chloride) in nitrobenzene are formed in the presence of compounds containing hydroxyl groups (*e.g.*, alcohols, organic acids) on vigorous stirring. The hydroxy compound is adsorbed by the dehydrating agent, which is peptised and passes into solution. Traces of moisture cause rapid coagulation. Sufficiently concentrated solutions of phosphorus pentoxide and calcium chloride set to gels on keeping.  
S. K. T.

**Albumin Solutions.** I. M. KOLTHOFF (*Chem. Weekblad*, 1925, **22**, 489—494).—The albumins are distinct chemical individuals, since when they are obtained from the same source in the same way, they always give the same amino-acids in the same proportions. Their amphoteric properties arise from the presence of free amino and carboxyl groups, and not from the group  $-\text{CO}\cdot\text{NH}-$ , since diketopiperazine is entirely neutral, whilst other simple substances containing the group are not amphoteric. Adsorption is probably a purely chemical phenomenon, and although the law of mass action does not hold in its simplest form for the adsorption of acids or alkalis by proteins, yet since these substances must be polybasic and polyacidic, and the values of the coefficients of activity of multivalent ions are unknown, the law may well be found to hold and simple chemical action cannot be ruled out. Since the dissociation constants of the various acidic and basic groups in an albumin molecule probably differ but little, the ions may be regarded as spread over the whole surface of the molecule, forming with added hydrogen or hydroxyl ions a double surface layer, a knowledge of the forces within which is necessary to the understanding of the relations between electrolytes and albumins.  
S. I. L.

**Albumin Solutions.** H. R. KRUYT (*Chem. Weekblad*, 1925, 22, 473—475).—The author considers that the solutions are true colloidal systems. S. I. L.

**Solubility of Casein in Hydrochloric Acid.** K. LINDERSTRØM-LANG and S. KODAMA (*Compt. rend. Trav. Lab. Carlsberg*, 1925, 16, [i], 1—47).—When casein is shaken for 3 days with dilute hydrochloric acid the system does not reach equilibrium. Reproducible but arbitrary solubility values are obtained by dissolving casein in a solution of sodium hydroxide and adding a known quantity of hydrochloric acid, when the casein is liberated at the isoelectric point and then partly redissolves in the excess of acid. The equilibrium may be similarly approached from the acid side, and measurements of the solubility of casein at 18° in the resulting solutions of hydrochloric acid and sodium chloride have been made. The solubility increases with the activity of the hydrogen ions and with decreasing concentration of the chlorine ions, but the results are variable. With a given total quantity of hydrochloric acid, the solubility of casein diminishes with the amount of solid phase present, owing to adsorption of acid, but with a given concentration of hydrochloric acid in solution, the solubility of casein increases with the amount of the solid phase, indicating that solid casein is a mixture of different substances. By fractionation two portions of casein with slightly different solubility were obtained. W. H.-R.

**Is Casein a Homogeneous Substance ?** K. LINDERSTRØM-LANG (*Compt. rend. Trav. Lab. Carlsberg*, 1925, 16, [i], 48—62; cf. preceding abstract).—Pure casein was prepared from milk without exposure to hydrogen-ion concentrations greater than  $p_H$  4 or less than 7. Partial fractionation was effected by precipitating an acid solution with a base or *vice versa*. The various fractions all gave the casein reaction with rennin in a solution containing calcium salts, but showed distinct differences in the colloidal nature of the precipitate. The ratio of phosphorus to nitrogen varied between 0.0542 and 0.0194. The solubility of casein in mixtures of phosphoric acid and sodium phosphate is not independent of the quantity of solid phase, showing that casein liberated at the isoelectric point is not a single compound of phosphoric acid and protein, but a mixture of several substances. The results of Linderstrøm-Lang and Kodama (preceding abstract) with hydrochloric acid are confirmed with purer material. W. H.-R.

**Physical Properties of Serum on Addition of "Water-binding" Substances.** R. FÜRTH and R. PECHHOLD (*Kolloid-Z.*, 1925, 37, 193—199).—The effect of the addition of small quantities of methyl or isopropyl alcohol or acetone on the physical properties of bovine serum is analogous to that produced by the addition of ethyl alcohol (cf. A., 1924, ii, 313). The viscosity shows a minimum with 0.6—1.2% of added substance, the conductivity a maximum with 0.4—0.89%, and characteristic turning points are exhibited by the refractive index with 1.2% of methyl alcohol, 5% of isopropyl alcohol, and 2.4% of acetone. The results are explained on the

basis of Debye's dipole theory. Dilution of the serum with small quantities of water produces characteristic alterations in the above phenomena; in particular, the viscosity minimum is destroyed. This is held to explain the discrepancy between the authors' observations and those of Hayashi (this vol., ii, 663). N. H. H.

**Physical Chemistry of Colouring Matters. I. Measurement of the Electric Charge of Solutions of Colouring Matters.** R. FÜRTH (*Kolloid-Z.*, 1925, **37**, 200—204).—A method is described for determining the sign of the electrical charge on particles of colouring matter. The method is especially applicable to the study of the staining of animal tissues. The disadvantages inherent to the cataphoretic method are avoided. Two electrodes composed of "half-conducting" material are connected to a source of direct current at 200—600 volts and dip in a solution of the dye. The arrangement permits only a very small current to pass through the solution, but produces a high fall of potential at the liquid/electrode boundaries. The particles cling to the electrode having the sign opposite to their own. N. H. H.

**Titania Jellies.** S. KLOSKY and C. MARZANO (*J. Physical Chem.*, 1925, **29**, 1125—1128).—The production of titanium dioxide jellies from sodium titanate is described. The best results were obtained with a solution of the composition  $\text{HCl} \cdot \text{TiO}_2 \cdot x\text{H}_2\text{O}$  on addition of potassium, sodium, and ammonium carbonates as coagulating agents. Potassium carbonate gave the clearest jellies. Ferric oxide-titanium dioxide jellies were also obtained. L. S. T.

**Optical Activity of Gelatin Systems.** E. O. KRAEMER and J. R. FANSELOW (*J. Physical Chem.*, 1925, **29**, 1169—1177).—An extension of the work of Smith (A., 1919, i, 179), studying the optical activity of gelatin systems for  $p_H$  2.30 to 12.31 between 10° and 50°. Gelatin, with an ash content of less than 0.05%, was used and rotations were measured for  $\lambda=5461 \text{ \AA}$ . The Tyndall effect also was measured at 23°.

Above 27.5°, the  $p_H$ -specific rotation curve shows a minimum at  $p_H$  4.9, and another, less pronounced, at  $p_H$  7 to 9. The apparent temperature coefficient and the change in rotation with  $p_H$  for  $p_H$  3—11 (cf. Smith, *loc. cit.*) are both small. Below 27°, the curve changes in character, the minimum at  $p_H$  4.9 becoming a pronounced maximum; the other minimum at  $p_H$  7 to 9 also becomes a maximum, less pronounced, as before. That this change is quite distinct between 25° and 27.5° is shown by plotting specific rotation against temperature for a constant  $p_H$  value. The light-scattering capacities of these gelatin solutions show a pronounced maximum in the heterogeneity of the system at  $p_H$  4.7 (approx.). The Tyndall effect and optical activity are roughly parallel at  $p_H$  values less than 5, but show little resemblance at higher values.

A qualitative parallelism is shown between gel-forming tendency and the increase in optical activity at low temperatures.

The authors conclude that (i) there is insufficient evidence for supposing that gelatin contains two related molecular species (cf.

Smith, *loc. cit.*; Lloyd, A., 1920, i, 452; Wilson and Kern, A., 1923, i, 68); (ii) gelatin systems display in many ways the characteristics of disperse systems which include the properties to which the Donnan theory of membrane equilibrium may be successfully applied; (iii) in view of (i), the so-called "mutarotation" of gelatin is an indication of colloidal changes in a system tending to gel formation. Influences which inhibit gel formation likewise prevent mutarotation. The term is thus a misnomer when applied to gelatin. The optical activity of gelatin gels shows that these are optically more or less homogeneous, *i.e.*, the structure is very fine-grained, in spite of the pronounced light-scattering capacity. L. S. T.

**Elasticity of Gelatin Jellies and its Bearing on their Physical Structure and Chemical Equilibria.** H. J. POOLE (*Trans. Faraday Soc.*, 1925, **21**, 114—142).—See this vol., ii, 519.

**Plasticity in Relation to Gelatin.** S. E. SHEPPARD (*J. Physical Chem.*, 1925, **29**, 1224—1232).—The temperature at which plasticity appears in 1% to 8% gelatin solutions depends on the concentration and the method of preparation. The growth of elastic resistance with time is most marked for the more concentrated solutions. In the region between the m. p. and setting-point curves plasticity is well developed. S. K. T.

**Plasticity and Structure in Gelatin Systems.** R. H. BOGUE (*J. Physical Chem.*, 1925, **29**, 1233—1238).—The change from the plastic solid to the viscous liquid state in gelatin systems is gradual and continuous; the exact value of the transition point, which depends on the concentration, is governed by the sensitiveness of the instruments used. It is not a "critical equilibrium temperature," but a point on a continuous curve. The interpretation of these facts on the basis of the fibrillar structure theory for gelatin sols is discussed. S. K. T.

**Plasticity in Relation to Cellulose and Cellulose Derivatives.** S. E. SHEPPARD and E. K. CARVER (*J. Physical Chem.*, 1925, **29**, 1244—1263).—The plastic properties of cellulose nitrate and acetate films and sols are recorded, and a modified Bingham plastometer is described. Cellulose plastics resemble the metals in elastic properties, although the ultimate particles are more like those of rubber than those of the metals. Unless X-rays reveal a crystalline structure, the fibrillar structure theory is to be preferred for these sols, the fibrils being chains of molecules held together by residual valencies. On this view, Mardles' "metastable phase" (cf. A., 1923, i, 443) might consist of a brush-like structure of broken filaments. S. K. T.

**Plasticity as applied to Viscose and Artificial Silk.** C. S. VENABLE (*J. Physical Chem.*, 1925, **29**, 1239—1243).—Curves are given illustrating the effect of humidity on the plasticity of viscose silk. Viscose solutions (7% to 9%) behave almost like true solutions; their viscosities diminish with increasing temperature and pass through a minimum on ageing. [Cf. B., 1925, 912.] S. K. T.

**Limited Significance of Hydrogen-ion Concentration as a Factor in Determining the Condition of Lyophilic Sols.** H. R. KRUYT and H. C. TENDELOO (*J. Physical Chem.*, 1925, **29**, 1303—1311).—The electrolyte concentration of the medium determines the electrical condition of the colloid particles in gelatin solutions. The action of electrolytes on lyophilic colloids does not differ essentially from that on lyophobic colloids. The isoelectric point may be reached at various hydrogen-ion concentrations by adding a quantity of electrolyte just sufficient to produce discharge. The viscosity of positively charged gelatin is diminished by the addition of uni-univalent neutral salts, the diminution depending on the valency of the anions. Bi- and ter-valent cations increase the positive charge on the gelatin particles and this is accompanied by an increase in the viscosity. Emulsoid sols are to be regarded as hydrated suspensoids, the electric charge, which is one of the factors of stability, being influenced by electrolytes in all colloidal solutions in essentially the same manner. S. K. T.

**Action of Electrolytes on Colloidal Nitroalizarin.** S. LIEPATOV (*Kolloid-Z.*, 1925, **37**, 224—230).—With the object of throwing light on the constitution of alizarin lakes, the adsorption of various electrolytes by nitroalizarin and by its monosodium salt has been measured. In the coagulation of nitroalizarin sols by solutions of barium, calcium, cupric, aluminium, and ferric chlorides, of the sulphate and acetate of copper, and of other salts not designated, it is found that the degree of adsorption is influenced by the anion, *e.g.*, with the copper salts the more readily hydrolysable acetate is adsorbed more than the sulphate. The coagulates (lakes) vary in composition according to the concentration of salt in the solution. The principal rôle in the formation of the lakes is played by the cations. The anion is not adsorbed, and only affects the process in so far as the specific properties of the electrolyte depend on it. With free nitroalizarin, the salts of strong inorganic acids and the acids themselves, *e.g.*, barium and cupric chlorides, and hydrochloric acid, are not adsorbed at all, whereas cupric acetate is strongly adsorbed, giving lakes of variable composition. From a consideration of the properties of this and similar lakes and the effect on them of change of temperature and mineral acids, the author concludes that they are formed by a distribution of the base, cupric hydroxide, etc. between the two acids nitroalizarin and acetic acid. In the case of monosodium nitroalizarin, experiments with barium and cupric acetates show that a chemical compound of constant composition is formed, 2 mols. of the nitroalizarin reacting with 1 mol. of the acetate with the elimination of sodium acetate. These compounds have the same colours as the corresponding lakes of variable composition described above, and the latter are therefore regarded as the result of unsaturated chemical combination.

N. H. H.

**Action of Proteins on Gold Sols.** W. REINDERS (*Chem. Weekblad*, 1925, **22**, 481—484).—The variations in the protective effect of proteins in solutions of different degrees of acidity and



alkalinity have been followed by measurements of the gold numbers and the migration velocities for different values of  $p_H$  and different concentrations of protein. The results are in accordance with the known amphoteric character of the proteins. S. I. L.

**Separation Methods by Means of Specific Adsorption.**

A. FODOR and A. ROSENBERG (*Kolloid-Z.*, 1925, **37**, 234—236).—The disadvantages inherent to the usual biochemical methods of separating mixtures of albumin, peptone, carbohydrates, organic acids, etc., may be avoided by the use of a specific adsorption process which consists of first treating the mixture in fairly strong acid solution with talcum powder which removes organic acids, adsorbing the albumin from the filtrate, after diminishing its acid concentration, by means of kaolin, and finally removing starch from the kaolin filtrate by moist ferric hydroxide. Experiments are described which illustrate the efficacy of the process and demonstrate the influence of the constitution of oxalic, malonic, succinic, lactic, malic, glyceric, tartaric, citric, and pyruvic acids on the readiness with which they are adsorbed by talcum powder and by kaolin. N. H. H.

**Velocity of Coagulation of Antimony Trisulphide.**

K. JABŁCZYŃSKI and A. PRZEŹDRIECKA-JĘDRZEJEWSKA (*Rocz. Chem.*, 1925, **5**, 173—177; cf. this vol., ii, 203).—The velocity of coagulation on the addition of potassium chloride of colloidal antimony trisulphide is shown to agree with the equation  $\log \tan \alpha - \log \tan \alpha_0 = kt$ , where  $\alpha$  and  $\alpha_0$  are the initial and the final angles of rotation of polarised light over a period of time  $t$ , and  $k$  is the coefficient of coagulation. This equation was previously shown to hold for colloidal arsenic trisulphide (*loc. cit.*). During the first 24 hrs.  $k$  changes very slightly, but later it increases, probably as a result of the loss of hydrogen sulphide, which has a stabilising influence on the colloid;  $k$  remains constant after blowing hydrogen through the hydrosol until free hydrogen sulphide can no longer be observed, its value, however, being nearly quadrupled. R. T.

**Velocity of Coagulation of Mixed Colloids.**

K. JABŁCZYŃSKI and H. LORENTZ-ZIENKOVSKA (*Rocz. Chem.*, 1925, **5**, 178—181; cf. preceding abstract).—The velocity of coagulation of mixtures of colloidal arsenic and antimony sulphides follows the same law as for each colloid separately (cf. preceding abstract). The same result is obtained when the colloidal sulphides are prepared separately and then mixed, as when the colloids are produced together from a mixed solution. R. T.

**Electrical Dispersion of Liquids.**

V. COFMAN (*J. Physical Chem.*, 1925, **29**, 1289—1302).—Experiments are described in which the nature of current conduction across the boundary between aqueous potassium tri-iodide solution and nitrobenzene is investigated. Other solutes and liquids were also used. A critical *E.M.F.* must be attained before any current crosses. Ions, electrons, and larger complexes of ions and solvent are involved in the process. The phenomena at the electrodes depend on the *P.D.* applied;

dispersion occurs, generally in the solvent in which the substance produced by the current is insoluble, or only slightly soluble.

S. K. T.

**Rhythmic Reactions showing U-shaped Bands.** G. V. STUCKERT (*Kolloid-Z.*, 1925, **37**, 238—239).—The "corrosive" action of certain substances when placed on gelatin gels contained in test-tubes has been studied. Three effects were observed: (i) reversible or irreversible solvation of the gel; (ii) penetration of the gel by the substance, with the formation of different types of fissure; (iii) rhythmic reactions. With sodium aminoacetate and sodium tungstate the effects (i) and (iii) were obtained. The middle of the gel became solvated from top to bottom, and at the bounding surface between the sol so formed and the gel, horizontal bands, lower in the middle than at the sides (and thus like a wide U), made their appearance.

N. H. H.

**Simple Method for Preparing Ultra-filters.** E. MÜLLER (*Kolloid-Z.*, 1925, **37**, 237—238).—An apparatus, fully figured in the original, is described, with which the uniform impregnation of ultra-filters with gelatin or collodion may be effected. The disadvantages of Bechhold's method (*Z. physikal. Chem.*, 1907, **60**, 257) are avoided.

N. H. H.

**Equation of State and its Relation to the Laws of Thermodynamics.** N. J. KOLTSCHIN (*Z. anorg. Chem.*, 1925, **147**, 312—320).—In Lorenz's ("Festschrift z. Jahrhundertfeier d. Physikalischen Vereins," Frankfurt a.M., 1924) deduction of gas laws from the first two laws of thermodynamics and the conditions  $(\delta U/\delta v)_T=0$  and  $(\delta U/\delta p)_T=0$  there is the inherent assumption that  $F(p,v,T)=0$ . It is now shown that from the more general equations  $(p,v,T)dp + (p,v,T)dv + (p,v,T)dT=0$  and  $(\delta U/\delta v)_{T,p}=0$ ,  $(\delta U/\delta v)_{T,p}=0$  generalised forms of the equations of Clapeyron and Thomson may be derived. In order to deduce the equation of state it is necessary to add the condition  $(\delta S/\delta p)_{v,T}=0$  or  $S=S(v,T)$ . The conditions  $U=U(T)$  and  $S=S(p,T)$  are not sufficient. This is due to the particular form of the work equation  $dR=Ap \cdot dv$ , but a general form  $dR=f_1 dp + f_2 dv + f_3 dT$ , together with the conditions  $U=U(T)$  and  $S=S(v,T)$ , may be sufficient to deduce a differential form of the equation of state.

A. G.

**Theory of Interionic Attraction in Strong Electrolytes.** S. R. PIKE and G. NONHEBEL (*Phil. Mag.*, 1925, [vi], **50**, 723—728).—The theories of Milner (*ibid.*, 1912, [vi], **23**, 351; A., 1913, ii, 481) and of Debye and Hückel (A., 1923, ii, 459, 724) are compared in the light of recent experimental results, and it is shown that at present the evidence is insufficient to decide between them.

A. B. M.

**Activity Coefficients and Transport Numbers of Solutions of Hydrogen Chloride in Methyl Alcohol.** G. NONHEBEL and H. HARTLEY (*Phil. Mag.*, 1925, [vi], **50**, 729—749; cf. preceding abstract).—Activity coefficients and transport numbers for hydrogen

chloride in methyl alcohol solution have been determined from measurements of the *E.M.F.* of the cells  $H_2|HCl \text{ in } MeOH|AgCl:Ag$ , and  $Ag:AgCl|HCl(C_1)|HCl(C_2)|AgCl:Ag$ . The *E.M.F.* of the former cell has been measured at 25° for concentrations from 0.0004955 (*E.M.F.*=0.3861 volt) to 0.5574 mol. HCl per 1000 g. solvent (*E.M.F.*=0.0844 volt). The transport number of the hydrogen ion for dilute solutions at 25° is  $0.735 \pm 0.005$ . The results are discussed in conjunction with recent measurements of the activity coefficients of hydrogen chloride in aqueous and ethyl alcohol solutions. The observed values agree better with those calculated from Milner's theory than with those given by Debye's equation. The relation between the activity coefficients of hydrogen chloride in different solvents and the partial pressure of the vapour over the solutions is pointed out.

A. B. M.

**Dissociation Constant of Methyl Alcohol.** N. BJERRUM, A. UNMACK, and L. ZECHMEISTER (*Kong. Danske Vidensk. Meddel.*, 1925, 5, No. 11, 1—34; from *Chem. Zentr.*, 1925, i, 2680).—The dissociation constant of methyl alcohol at 18° is  $10^{-17.01}$ , calculated from the *P.D.* between hydrogen electrodes in methyl-alcoholic hydrochloric acid and in sodium methoxide, respectively, connected by methyl-alcoholic sodium chloride solution. The dissociation constant of methyl alcohol was also obtained from the degree of alcoholysis of ammonium acetate by measuring the increase in conductivity resulting from the addition of acetic acid and methyl alcohol, respectively. For the dissociation constant of ammonia and acetic acid, it was found that  $-\log K_{NH_3}=5.92$  and  $-\log K_{CH_3 \cdot COOH}=9.65-1.77\sqrt[3]{C}$  at 18°.

G. W. R.

**Ionic Equilibria across Semi-permeable Membranes.** N. KAMEYAMA (*Phil. Mag.*, 1925, [vi], 50, 849—864).—The results of Donnan and Allmand (T., 1914, 105, 1941) on the distribution of potassium chloride between two aqueous solutions separated by a copper ferrocyanide membrane, one of the solutions containing also potassium ferrocyanide, are discussed from the point of view of activity coefficients and the "ionic strength principle" of G. N. Lewis. The results are in agreement with this principle, except when the potassium chloride concentration is small compared with that of the ferrocyanide. A repetition of the experimental work, however, over this range with improved methods of analysis and technique renders it probable that the deviations mentioned are due to experimental error.

A. B. M.

**Equilibria in Systems in which Phases are Separated by a Semi-permeable Membrane. VIII.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, 28, 396—402).—The equations governing membrane diffusion and osmotic equilibria previously deduced for a theoretical membrane (cf. this. vol., ii, 538) are shown to be valid for a real membrane if the mass of the latter is small compared with that of the ternary systems involved; they also hold if one of the separate systems consists of substances

of constant composition between which a phase reaction occurs when water is added or removed. J. W. B.

**Equilibria in Systems in which Phases are Separated by a Semi-permeable Membrane. IX.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 489—498; cf. this vol., ii, 538, 869, and preceding abstract).—Theoretical. The membrane phase rule is applied to osmotic equilibria in which two ternary systems are separated by a semi-permeable membrane. Cases are considered in which both systems contain, respectively, one and two components in common. F. G. T.

**Equilibria in Systems in which Phases are Separated by a Semi-permeable Membrane. X.** F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 564—572; cf. preceding abstracts).—Osmotic equilibria in a group of systems, separated from one another by semi-permeable membranes through which water only can diffuse, are discussed, and also the osmotic action, under different conditions, of the double membrane formed when two systems, previously in osmotic contact through a semi-permeable membrane, are separated by two membranes between which a phase is interposed. M. S. B.

**Dissociation Pressures of Hydrated Double Selenates.** J. FERGUSON (*J. Chem. Soc.*, 1925, **127**, 2096—2100; cf. Caven and Ferguson, A., 1924, ii, 553).—Equilibrium pressures for systems of the type  $M''SeO_4 \cdot M'_2SeO_4 \cdot 6H_2O \rightleftharpoons M''SeO_4 \cdot M'_2SeO_4 \cdot 2H_2O + 4H_2O$  have been measured, and the stabilities of the hexahydrated double selenates compared by reference to the temperatures at which the dissociation pressures reach 50 mm. of mercury. If the salts are regarded as having the structure  $M'_2[M''(SeO_4)_2]$ , the stability increases with decreasing molecular volume of the anion, and with increasing atomic or molecular volume of the cation, but exceptions are noted, especially in the case of caesium. This rule is the reverse of that found for the stability of metallic ammines. The salts investigated contained ammonium, potassium, rubidium, or caesium and copper, cobalt, zinc, nickel, cadmium, and manganese. Nickel ammonium chromate was also examined. W. H.-R.

**Equilibrium in the Systems : Zinc Chloride-Pyridine : and Cadmium Chloride-Pyridine.** R. B. MASON and J. H. MATHEWS (*J. Physical Chem.*, 1925, **29**, 1178—1183).—Measurements of the solubility of zinc chloride in pyridine show that only one compound, viz.,  $ZnCl_2 \cdot 2C_5H_5N$ , is formed. The curve representing the solubility of cadmium chloride in pyridine shows a break at 9°. From 0° to 9° the solubility increases rapidly, whilst from 9° to 100° there is a gradual decrease. At the ordinary temperature, the solid phase is  $CdCl_2 \cdot 2C_5H_5N$ , whilst below 9° the stable compound is  $CdCl_2 \cdot 6C_5H_5N$ . The new compound forms large, clear, transparent crystals, which at the ordinary temperature crumble to a fine powder. An analogous compound,  $CdBr_2 \cdot 6C_5H_5N$ , has been described by Varet (A., 1891, 732). L. S. T.

**Condensed Ternary System Phenol-Water-Salicylic Acid.** C. R. BAILEY (*J. Chem. Soc.*, 1925, **127**, 1951—1965).—The system phenol-water has been examined, the critical saturation temperature being taken as the temperature of sudden thickening; the results in general agree with those of Timmermans (A., 1907, ii, 229). In the system salicylic acid-water, the eutectic ice-salicylic acid is determined as  $-0.07^{\circ}$  and 0.103% salicylic acid. The m. p. of salicylic acid is  $160.4^{\circ}$ . The values obtained agree with those of Walker and Wood (T., 1898, **73**, 620) up to  $30^{\circ}$ , but are slightly and uniformly larger at higher temperatures. In the system phenol-salicylic acid, a simple eutectic is formed at  $38.16^{\circ}$  and 5% salicylic acid; the f. p. data agree with the presence of single molecules of the acid. The ternary system has also been examined, using synthetic and analytical methods. No liquids exist below  $-1.3^{\circ}$ , the ternary eutectic composition being 6.5% phenol, 0.2% salicylic acid, and 93.3% water. Salicylic acid is much more soluble in mixtures of water and phenol than in either alone, but the results are very complex. W. H.-R.

**Reversible System  $\text{PbI}_2 + \text{ZnSO}_4 \rightleftharpoons \text{PbSO}_4 + \text{ZnI}_2$ .** C. G. STOFFELLA (*Boll. Chim. farm.*, 1925, **64**, 481—488).—No conversion at  $15^{\circ}$ , and only partial conversion at  $100^{\circ}$ , of zinc sulphate, in saturated solution, into zinc iodide occurs on the addition of an equimolecular amount, or more, of lead iodide. Complete conversion at  $15^{\circ}$  is attained only in extremely dilute solutions of zinc sulphate by the addition of an equimolecular amount of lead iodide. The yield of zinc iodide is best from a 1% solution of zinc sulphate at  $100^{\circ}$ . This behaviour is in accord with the solubility products of the components of the reaction, the ratio  $S_{\text{PbI}_2} : S_{\text{ZnSO}_4} : S_{\text{PbSO}_4} : S_{\text{ZnI}_2}$ , being 1 : 220 at  $15^{\circ}$  and 2 : 1 at  $100^{\circ}$ . F. G. T.

**Precipitation Laws.** P. P. VON WEIMARN (*Chem. Reviews*, 1925, **2**, 217—242).

**Heats of Oxidation of Carbon Monoxide and of Hydrogen by Manganese Dioxide at  $0^{\circ}$ .** J. C. W. FRAZER and C. E. GREIDER (*J. Physical Chem.*, 1925, **29**, 1099—1104).—A continuation of the work of Whitesell and Frazer (A., 1924, ii, 114). The heat changes accompanying the adsorption and oxidation of carbon monoxide by active manganese dioxide have now been measured. A large amount of heat is liberated during the admission of the carbon monoxide to the catalyst, indicating almost immediate oxidation. Equilibrium was not attained after several hours, however, owing to slow diffusion of the gases concerned: under modified conditions, thermal equilibrium was established in approximately 30 mins. It is assumed that (1) for every mol. of carbon dioxide removed, a corresponding amount of the dioxide is reduced to the oxide  $\text{Mn}_3\text{O}_4$ , and (2) all the carbon monoxide entering is oxidised. A deficiency in the amount of carbon dioxide desorbed suggests that a portion of the manganese dioxide is reduced to the monoxide, which then forms the carbonate, the catalyst showing a change from black to orange. The heats attending these reactions were evaluated

from the heat of formation, the heat of adsorption of carbon dioxide being taken equal to the measured heat of desorption. The heat data are (1)  $\text{MnO}_2 \rightarrow \text{MnO} (+\text{O})$ ,  $-7.0$  cal., (2)  $1.5\text{MnO}_2 \rightarrow 0.5\text{Mn}_3\text{O}_4 (+\text{O})$ ,  $-23.2$  cal., (3)  $\text{MnO} + \text{CO}_2 \rightarrow \text{MnCO}_3$ ,  $5.5$  cal., and (4)  $\text{CO} (+\text{O}) \rightarrow \text{CO}_2$ ,  $79.7$  cal. Further results indicate that when the catalyst has been reduced with pure carbon monoxide, it is re-oxidised with difficulty. Heat treatment over-night in air at  $150$ – $160^\circ$  does not restore the original activity; oxygen is more efficient in this respect. When hydrogen replaces carbon monoxide, a slow but continuous fall in pressure is observed, but the oxidation of the hydrogen is too slow for the heat of reaction to be determined. L. S. T.

**Aqueous Solutions of Sodium Silicates. I. Preparation and Electrical Conductivity.** R. W. HARMAN (*J. Physical Chem.*, 1925, **29**, 1155–1168).—An investigation of the system  $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$  at  $25^\circ$ . The system has been studied from the point of view of (1) conductivity, (2) transport numbers, (3) hydrolysis, (4) sodium-ion activity, (5) silicate ion, (6) lowering of vapour pressure and of f. p., and (7) heterogeneous equilibria.

Sodium metasilicate enneahydrate,  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , prepared according to Vesterberg's method (A., 1913, ii, 406), was used as the starting point and crystals of m. p.  $47^\circ$  (Vesterberg  $48^\circ$ ; Erdenberger  $47^\circ$ ) were obtained. Solutions having other values for the  $\text{Na}_2\text{O}:\text{SiO}_2$  ratio were prepared by electrolytic removal of the alkali (cf. Kröger, A., 1922, ii, 212). Solutions prepared in different ways gave identical results for the conductivity and other properties. Values of  $\Lambda$  at  $25^\circ$  are given for the ratios 2 : 1, 1 : 1, 1 : 1.5, 1 : 2, 1 : 3, and 1 : 4 at concentrations  $2N_w$  to  $0.005N_w$  ( $N_w$  = weight normality with regard to sodium content). The 2 : 1 and 1 : 1 solutions are excellent conductors, whilst 1 : 2, 1 : 3, and 1 : 4 are fair conductors in dilute solution, but abnormally poor in concentrated solutions (approx.  $1-2N_w$ ). The values for 1 : 1 agree with those of Kohlrausch (A., 1894, ii, 133; 1893, ii, 166). The high conductivity of  $\text{Na}_2\text{SiO}_3$  is attributed to the presence of hydroxyl ions formed by hydrolysis, but quantitative conclusions could not be reached. The low conductivity in concentrated solutions of 2 : 1, 1 : 1, and 1 : 1.5 is due to a decrease in hydrolytic dissociation. Hydrolysis is not sufficient, however, to account for some of the values obtained and calculations have therefore been made of the mobility of the silicate ion. Values for  $\Lambda_\infty$  have been assigned by extrapolation from the conductivity-log of concentration curve, and by Noyes' method (*Carnegie Inst. Pub.*, 1908, 63). The final values of  $\Lambda_\infty$  for ratios 1 : 1, 1 : 1.5, 1 : 2, 1 : 3, and 1 : 4 are 160, 121, 95, 91, and 88, respectively. The mobility of the silicate ion is calculated to be 60, 35, 43, and 41 for the ratios 1 : 1, 1 : 2, 1 : 3, and 1 : 4. Values of  $\Lambda_\infty$  derived from the curves and from the mobility data show good agreement.

It appears that the salts  $\text{Na}_2\text{O}, 2\text{SiO}_2$  and  $\text{Na}_2\text{O}, \text{SiO}_2$  exist in solution and that other ratios correspond with mixtures of these salts with sodium hydroxide and "hydrated" silica.

L. S. T.

**Conductivity of Solutions of Aluminium Chloride in Carbonyl Chloride at 25°, 0°, and -45°.** A. F. O. GERMANN (*J. Physical Chem.*, 1925, **29**, 1148—1154).—When a current is passed through a solution of aluminium chloride in liquid carbonyl chloride, the solvent is decomposed with the formation of carbon monoxide and chlorine (*Science*, 1924, **60**, 434). The conductivity of these solutions has been examined at 25°, 0°, and -45° in a specially constructed cell. The conductivity curve resembles those which have been previously obtained for solutions in weakly ionising solvents. The variation of the temperature coefficient is also similar to that observed by Franklin (A., 1911, ii, 1052) for solutions of potassium bromide and iodide in liquid sulphur dioxide, and the interpretation suggested by Franklin is accepted by the author.

L. S. T.

**Potential Difference between 0.1N and 3.5N Calomel Electrodes.** J. K. GJALDBÆK (*Kong. Danske Vidensk. Meddel.*, 1924, **5**, [9], 1—17; from *Chem. Zentr.*, 1925, i, 2679).—The potential of a 3.5N-calomel electrode measured against a standard electrode varied from 0.31 to -0.06 millivolt, according to the method of preparation. The values after 5½ months varied from 0.45 to 0.03 millivolt. For the 0.1N-electrodes the potential varied between 83.5 and 83.0 millivolts. The temperature coefficient of the 3.5N-electrode is 0.45 millivolt, and of the 0.1N-electrode 0.77 millivolt per degree. The mean value of the potential between 0.1N- and 3.5N-calomel electrodes is found to be 83.13 millivolts.

G. W. R.

**Decrease in Electromotive Force of Unsaturated Weston Cells.** W. C. VOSBURGH (*J. Opt. Soc. Amer.*, 1925, **11**, 59—61).—A slow decrease in the *E.M.F.* of an unsaturated Weston cell is to be expected on account of the diffusion of mercurous ion and its reaction with the cadmium of the amalgam electrode giving cadmium ion and mercury. The resulting increase in the concentration of cadmium sulphate in the electrolyte must cause a decrease in the *E.M.F.* Actually, the *E.M.F.* of a number of unsaturated cells were found to decrease at the average rate of 0.03—0.04 millivolt (0.003—0.004%) in a year.

S. B.

**Potentials of Copper and Zinc in Cyanide Solutions.** W. M. WALKER, J. H. SORRELS, and J. M. BRECKENRIDGE (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 113—124).—The potential of copper in cyanide solutions shows somewhat unsteady values for some hours, but gradually becomes more electropositive owing to atmospheric oxidation. The most electropositive potentials found were -0.7526 volt in 0.5N-sodium cyanide and -0.0765 volt in the same solution containing 0.125N-copper cyanide; -0.8598 volt and -0.1123 volt in the corresponding potassium cyanide solutions. Zinc tends to become more electronegative. In 0.5N-sodium cyanide it shows -0.9156 volt, in presence of 0.175N-zinc cyanide -0.8731 volt. The change of potential takes place more slowly when the electrolyte is covered with paraffin oil, more rapidly when oxygen is blown

over it. The rate of corrosion of the electrodes shows similar variations.

W. A. C.

**Reduction Potential of Dicyanoquinhydrone.** E. K. RIDEAL (*Trans. Faraday Soc.*, 1925, **21**, 143—144).—See this vol., ii, 546.

**Overvoltage and Surface Forces at the Lead Cathode.** S. GLASSTONE (*Trans. Faraday Soc.*, 1925, **21**, 36—41).—See this vol., ii, 301.

**Electrochemical Actinometers.** G. ATHANASIU (*Ann. Physique*, 1925, [x], **4**, 318—424).—The *E.M.F.* of the cells examined are not attributable to a photo-electric effect, but are due to three factors, (1) polarisation, (2) absorption of heat, and (3) chemical changes at the surface of the electrode-producing films, which may be comparatively inactive, as with zinc electrodes in zinc sulphate, or strongly actino-sensitive, as with copper in copper sulphate; in this case an *E.M.F.* of the order of 40 millivolts was obtained, the illuminated electrode being negative relative to the electrode in the dark. Greater effects can be obtained by coating metallic electrodes with films of suitable salts. Actinometers with electrodes of mercury covered with a film of mercurous halide or sulphide have been examined in monochromatic light of different wave-lengths, sulphuric acid being the electrolyte. The sensitivity is defined as the ratio of the *E.M.F.* produced to the intensity of the incident radiation. With films of mercurous halides, the illuminated electrode is positive, and the maximum sensitivity moves towards longer wave-lengths as the atomic weight of the halogen increases; the chloride and bromide are sensitive only to ultra-violet radiation, and photographic plates with this property have been prepared. With mercurous sulphide, the illuminated electrode is negative and shows a maximum sensitivity at about  $\lambda=4046 \text{ \AA}$ . The electrical conductivity of mercurous halides is increased by illumination, whilst the bromide and chloride give an orange fluorescence under the influence of ultra-violet light. Actinometers with oxidised copper electrodes in solutions of sodium or potassium chloride or sodium bromide show a marked maximum sensitivity at about  $\lambda=4046 \text{ \AA}$ , the illuminated electrode being positive. With silver electrodes coated with silver iodide, maximum sensitivity is shown at  $\lambda=4245 \text{ \AA}$ , with potassium chloride as electrolyte. If the chemical reaction involved is the decomposition of the halides, the critical wave-lengths and heats of reaction are in good agreement with the radiation theory of Lewis and Perrin. The electrical conductivities of all actino-active substances are affected by light, both effects being due to the displacement of the outer electrons, but the phenomena are distinct from the ordinary photo-electric effect.

W. H.-R.

**Electrolysis of Nitrobenzene with the Mercury-dropping Cathode. I. Reduction Potential of Nitrobenzene. II. Influence of Cathode Potential on Adsorption of Nitrobenzene.** M. SHIKATA (*Trans. Faraday Soc.*, 1925, **21**, 42—52, 53—62).—See this vol., ii, 304.



**Polarisation of Metals used as Electrodes.** M. DRESBACH and H. R. HOSMER (*Amer. J. Physiol.*, 1924, **68**, 122—123).—From observations of the changes produced in the plate-filament circuit of a three-electrode tube by altering the voltage in the grid-filament circuit, polarisation values in ascending order have been obtained for amalgamated zinc-zinc sulphate; silver-silver chloride; lead; zinc; tin; uncoated silver. A. A. E.

**Electrolytic Corrosion of Ferrous Metals.** W. M. THORNTON and J. A. HARLE (*Trans. Faraday Soc.*, 1925, **21**, 23—35).—See this vol., ii, 303.

**Effect of Superposed Alternating Current on Anodic Solution of Gold in Hydrochloric Acid.** A. J. ALLMAND and V. S. PURI (*Trans. Faraday Soc.*, 1925, **21**, 10—16).—See this vol., ii, 302.

**Electrochemical Corrosion Tests on Iron and Steel.** H. BEENY (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 135—149).—The polished test-piece serves as anode in a 0.2% sodium chloride solution contained in a rotating gilded vessel used as the cathode. The effective surface of the cathode is made forty times as large as that of the anode, so that cathodic polarisation is minimised. Experiments show that the amount of iron going into solution as  $\text{Fe}^{++}$  agrees with the quantity of electricity generated, and it is inferred that the corrosion is entirely electrochemical. W. A. C.

**Disintegration of Carbon Anodes in Nitric Acid.** H. J. M. CREIGHTON and W. H. OGDEN (*Trans. Amer. Electrochem. Soc.*, 1925, **48**, 161—165).—In the explosive disintegration of carbon anodes, a gas is evolved which consists mainly of air. The fragments are sometimes covered with minute yellow crystals. It is suggested that the disintegration is caused by formation and decomposition of graphitic acid. W. A. C.

**Physico-chemical Study of Some Organic Syntheses.** C. MATIGNON (*Bull. Soc. chim.*, 1925, [iv], **37**, 825—836).—The possibility of certain reactions taking place is investigated theoretically by a consideration of the equilibrium constant, the heat of reaction, and the formula  $\log K = -Q/4.57T + 3.50 \log T + C$ . The syntheses of methyl and ethyl alcohols, formaldehyde, acetone, acetic and propionic acids from carbon monoxide and hydrogen are dealt with; also syntheses involving ethylene (butane, hexane, acetone, and propyl alcohol); and syntheses of nitrogen compounds. L. L. B.

**Fundamental Factors in Corrosion.** G. M. ENOS (*Ind. Eng. Chem.*, 1925, **17**, 793—797).—The rate of corrosion of various steels in the atmosphere and in distilled water was determined, the former rate averaging about ten times the latter. No definite effect of varying carbon content in the steel could be traced. Chromium-vanadium steel and nickel-silicon steel showed lower rate losses. With increase in temperature, the increase in corrosion is a function of the temperature difference above that of the ordinary for a given

steel, the slope of the curve being similar whether the corroding agent was water, dilute sulphuric acid, or ferric sulphate solution. With increase in time, the rate of corrosion suffered an initial drop and then showed a linear increase. Ultra-violet light somewhat increases the rates of corrosion. [Cf. *B.*, 1925, 765.] C. I.

**Influence of Metallic Elements on the Corrosion of Iron and Steel.** Y. UTIDA and M. SAITÔ (*Sci. Rep. Tôhoku*, 1925, **14**, 295—312).—Addition of chromium to iron gives an alloy that is very resistant to 10% nitric acid solutions, but is readily attacked by dilute hydrochloric acid. Nickel in iron also retards its dissolution in cold 10% nitric acid, but not to the same extent as an equal amount of chromium. Nickel steels, on the other hand, are markedly resistant to 10% hydrochloric acid, and their resistance is increased by the addition of chromium. Copper and manganese first reduce the rate of attack of 10% nitric acid on iron, but with more than 1% of these elements the resistance of the metal to this acid is much reduced. Tungsten and copper increase the resistance of iron to sulphuric and hydrochloric acids. The rate of corrosion of nickel-chromium steel in cold 10% hydrochloric acid decreases with a rise in the carbon content from 0.1% to 0.7%. [Cf. *B.*, 1925, 884.] A. R. P.

**Solution of Zinc in Hydrochloric Acid at High Pressures.** W. IPATIEV and W. VERCHOVSKI (*Bull. Acad. Sci. St. Pétersbourg*, 1918, [6], 1—10; from *Chem. Zentr.*, 1925, i, 2525).—The pressure developed by the reaction of zinc with hydrochloric acid in glass test-tubes placed in a closed cavity over machine oil reaches a maximum of 1125 atm. This limiting value is not conditioned by the reverse reaction, but is related to the solubility of hydrogen in the oil, the contraction of the hydrochloric acid on saturation with zinc chloride, and the compressibility of the air present in the closed cavity. The limiting value is reached when some zinc still remains undissolved in the hydrochloric acid. When copper tubes are used instead of glass test-tubes, complete solution of the zinc occurs. G. W. R.

**Catalytic Decomposition of Acetoacetic Acid by Strong Acids and Bases.** H. VON EULER and A. OLANDER (*Z. anorg. Chem.*, 1925, **147**, 295—311).—Measurements have been made of the velocity of decomposition of the sodium derivative of ethyl acetoacetate in solutions of  $p_H$  11—15.1. In the less alkaline solutions, the reaction  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}=\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3+\text{CO}_2$  takes place exclusively, and the velocity constant is  $3.0\text{--}3.4\times 10^{-5}$  between  $p_H$  11.1 and 13.2. With increasing alkalinity, the velocity of this reaction diminishes rapidly and is zero at  $p_H$  14.2. The only reaction then taking place is  $\text{CH}_3\cdot\text{C}(\text{ONa})\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}+\text{H}_2\text{O}=2\text{CH}_3\cdot\text{CO}_2\text{Na}$ , and the velocity constant of this increases rapidly with increasing alkalinity from zero at  $p_H$  13.2 to  $1.3\times 10^{-3}$  at  $p_H$  15.1 (12.9 *N*-sodium hydroxide). The second acid dissociation constant of acetoacetic acid is  $10^{-13}$ . A. G.

**Acid Catalysis in Lactone Formation.** H. S. TAYLOR and H. W. CLOSE (*J. Physical Chem.*, 1925, **29**, 1085—1098).—An examination of Henry's results (A., 1892, 1303) indicates that the proportionality between the reaction velocity and the hydrogen-ion concentration is not exact, but that, as the concentration of the catalysing acid is increased, the reaction velocity increases faster than the hydrogen-ion concentration. The reaction has now been studied by varying the nature and concentration of catalysing acid and of the neutral salt, the temperature, and the solvent.

$\gamma$ -Hydroxyvaleric acid, prepared only as required, from its lactone, was the acid used, and the reaction velocity was measured in the usual way, after addition of the catalyst, with barium hydroxide as the titrating agent. The reaction was studied in presence and absence of salts over a temperature range 0—35°. In the experiments with different solvents, *o*-hydroxymethylbenzoic acid replaced  $\gamma$ -hydroxyvaleric acid, since the former is easily obtainable in the crystalline state and is stable when kept dry, and was converted into its lactone as in the previous case. The marked effect of moisture on the reaction velocity indicated that water plays an important rôle, and hence the velocity of lactone formation from this acid was also studied in ether-water mixtures with hydrogen chloride as catalyst. The reaction velocity is very much greater in wet ethereal solutions containing hydrogen chloride than in aqueous solutions of the same acid strength.

The results are in good agreement with those previously obtained (A., 1917, ii, 253), and confirm the similarity there found between acid catalysis in lactone formation and in ester hydrolysis, so far as deviations from proportionality to hydrogen concentration and the influence of neutral salts are concerned. Good agreement likewise exists with the data of Garrett and Lewis (A., 1923, ii, 476), although, unlike these authors, the use of the formula for opposed reactions,  $K_2 = (1/t) \log [a/(a-1.075x)]$ , has now been found necessary to eliminate a slight drift in the unimolecular constant.

The results indicate that the velocity is not dependent on the acid concentration, the undissociated acid molecule concentration, or the hydrogen-ion concentration as determined by conductance methods. A proportionality between reaction velocity and the thermodynamic activity of the hydrogen ions is suggested instead.

L. S. T.

**Catalysis of Oxido-reductions by Blood Pigments.** W. LIPSCHITZ (*Z. physiol. Chem.*, 1925, **146**, 1—43).—Hydroxylamine is rapidly decomposed by blood pigments with the formation of ammonia, nitrogen, nitrite, and nitrate, the pigment being transformed into methæmoglobin. Fresh frog's muscle, blood charcoal, bile pigments, chlorophyll, hæmin, and serum cannot effect this change. Hydroxylamine (1 mol.) and oxyhæmoglobin ( $\frac{1}{2}$  mol.) yield approximately ammonia (4/12 mol.), nitrogen (5/12 mol.), nitrite and nitrate (3/12 mol.). Hydroxylamine (1 mol.) and reduced hæmoglobin ( $\frac{1}{2}$  mol.) yield ammonia (6/12 mol.), nitrogen (4/12 mol.), nitrite and nitrate (1/12 mol.). About 1/12 of the hydroxyl-

amine-nitrogen is lost, but small amounts of nitrous oxide are detected. With carbon monoxide-hæmoglobin (1 mol.) the yield of ammonia falls to 4/12 mol. Nitric oxide-hæmoglobin and -methæmoglobin also act in this way. More than 24 mols. of hydroxylamine are decomposed by 1 mol. of pigment, but the rate of the reaction gradually decreases, probably on account of decreased adsorption of hydroxylamine by the hæmoglobin. Irradiation of hæmoglobin or precipitation by alcohol or colloidal ferric hydroxide does not influence its catalytic activity, but if the globin molecule be removed by heating, ammonia formation decreases to 10% or less.

P. W. C.

**Catalytic Action. X. Comparative Study of the Catalytic Activity of Reduced Copper, Reduced Nickel, and Thoria. I.**

S. KOMATSU and B. MASUMOTO (*Mem. Coll. Sci. Kyōtō*, 1925, [4], 9, 15—21).—A comparison of the products obtained when cyclohexanol is heated in presence of reduced copper, reduced nickel, and thoria, respectively, at 200° and at 300°, shows that reduced nickel acts principally as an oxidation catalyst, causing the formation of cyclohexanone and phenol, whereas thoria has a dehydrating effect, giving yields of dicyclohexyl ether, benzene, and tetrahydrobenzene. Reduced copper lies between the two in the nature of its activity and is the least affected by the change of temperature. With thoria at 300°, some dodecahydrotriphenylene is formed from cyclohexanol.

B. W. A.

**Promoter Action of Thoria on Nickel Catalysts.**

W. W. RUSSELL and H. S. TAYLOR (*J. Physical Chem.*, 1925, 29, 1325—1341).—The promoter action of thoria on nickel catalysts in the reaction  $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$  was studied. The results indicate that promoter action in supported catalysts cannot be explained by surface extension or by change in the relative concentrations of the adsorbed reactants. The former explanation partly suffices in the case of unsupported catalysts. The following theory of promoter action is advanced. The unsaturated metal atoms assumed to be responsible for catalytic activity are present in pure nickel in a higher concentration the lower the temperature of reduction. These atoms coalesce as the temperature rises, but the presence of thoria in supported nickel catalysts prevents sintering (coalescence) and, by the creation of thoria-nickel interfaces, increases the concentration of these atoms. The same may also occur in unsupported nickel, but on the other hand the surface may increase because of the promoter acting as a support, or because the ratio in which the reacting substances are adsorbed is favourably altered. [Cf. *B.*, 1925, 903.]

S. K. T.

**Catalytically Active and Inactive Forms of Ferric Oxide.**

L. A. WELO and O. BAUDISCH (*J. Biol. Chem.*, 1925, 65, 215—227).—The catalytic activity of different samples of magnetite varies with the mode of preparation, those made by precipitation of a mixture of ferrous and ferric sulphate being much more active than those made by precipitation of ferrous sulphate and subsequent

partial oxidation. The activity of active magnetite is not destroyed by oxidation, but both activity and magnetic properties are lost on heating at 550°. Comparison of the water absorption and X-ray diffraction spectra of active and inactive oxides indicates that the crystals of the former are smaller than those of the latter. It is thought that both magnetic properties and catalytic activity are related to the spatial arrangement of the atoms within the molecule.

C. R. H.

#### **Catalytic Action of Colloidal Metals of the Platinum Group.**

**XVII. Colloidal Cobalt.** C. PAAL and H. BOETERS (*Ber.*, 1925, 58, [B], 1542—1546; cf. A., 1914, ii, 642; 1915, ii, 171).—Colloidal solutions of cobalt are prepared by the action of hydrogen in the presence of palladium on sols or gels of cobaltic hydroxide (cf. this vol., ii, 1090). Reduction occurs slowly but completely, even with preparations rich in cobalt, although in the latter case the production of the sol is accompanied by that of an irreversible cobalt gel. In the solid form, the preparations of colloidal cobalt and sodium protalbate or lysalbate oxidise slowly when exposed to air, but otherwise remain colloiddally soluble for long periods; preparations of colloidal cobalt with free protalbic or lysalbic acid are considerably more stable. Attempts to obtain cobalt sols by the reduction of colloidal cobaltic hydroxide by hydrazine or formaldehyde in the presence of palladium sol were unsuccessful. Colloidal cobalt could not be obtained by the reduction of colloidal cobaltic hydroxide with hydrogen at 200—210°.

H. W.

**Physical State of Catalysts.** R. C. SMITH (*J. Physical Chem.*, 1925, 29, 1116—1118).—The catalytic activities of platinum, gold, and palladium have been studied in relation to the crystalline or amorphous state of the surface. Direct observations were made of the time taken for oxygen to be evolved from solutions of hydrogen peroxide, varying in strength from 0.2 to 10 volumes, placed on a plate of the metal. Polished platinum was found to decompose hydrogen peroxide (cf. Spring, A., 1896, ii, 92), but washing the metal surface with alcohol and water, or the presence of a film of grease, inhibited the decomposition. The change in the state of surface from amorphous to crystalline was also accompanied by a decrease in catalytic activity. The loss of activity pointed out by Thomas (A., 1923, ii, 64) in the case of nickel prepared at 650°, and by Vavon (A., 1914, ii, 189) in the case of platinum-black, is attributed to the formation of crystals in the finely-divided metal.

L. S. T.

#### **Thin Films of Platinum and Nickel and Catalytic Activity.**

A. W. GAUGER (*J. Amer. Chem. Soc.*, 1925, 47, 2278—2282).—The reaction  $C_2H_4 + H_2 = C_2H_6$ , both in the presence and absence of water vapour and of oxygen, is not catalysed by thin films of platinum or nickel deposited on glass wool. It is concluded that the influence of surface in catalysis is overestimated. It is probable that catalysts have electrons on other energy levels than is the case with the bulk metal, whereas the molecules in films probably have

the same electronic configuration as the latter. The active surface of a catalyst would consist, therefore, of molecules having electrons in the outer energy levels. This theory is developed briefly.

S. K. T.

**Electrolysis in Liquid Sulphur Dioxide.** H. P. CADY and R. TAFT (*J. Physical Chem.*, 1925, 29, 1075—1084).—The solubilities of various substances in liquid sulphur dioxide have been examined qualitatively and also the electrolysis of certain solutions in this solvent. Amongst other substances, potassium iodate, bromate, and chlorate, and silver nitrate, are appreciably soluble; sodium thiosulphate and cyanide and potassium dichromate very slightly soluble; and potassium perchlorate and permanganate, boric acid, and sodium insoluble in this solvent. A specially-constructed cell was used in the electrolysis experiments and precautions were taken to prevent the introduction of traces of moisture which probably account for the anomalous results previously obtained. The production of a deposit at the cathode causes reduction of the current, which is never large, to a very small value. No great advantage was found in the use of silver or copper cathodes as recommended by Bagster and Steele (A., 1913, ii, 15). In none of the electrolyses attempted (potassium iodate, iodide, ferriocyanide, etc.) were cathodic reduction products of the electrolyte obtained. Generally, the products possessed similar qualitative properties and are considered to be produced by the discharge of the ions of the solvent. The cathodic deposit, characteristic of so many of the solutions, gave reactions which indicated the presence of a sulphite, thiosulphate, and probably one or more salts of the thionic acids. Contrary to Bagster and Steel (*loc. cit.*), but in agreement with Centnerszwer and Drucker (A., 1923, ii, 370), no free sulphur was contained in these deposits. Anodic products are similar to those produced in the electrolysis of the substances in aqueous solution. A difficult feature encountered in this work was that retention of the solvent frequently led to misleading analytical results. The influence of current density on electrolytic oxidation and reduction is discussed and an explanation advanced.

L. S. T.

**Oxidation and Reduction.** H. P. CADY and R. TAFT (*J. Physical Chem.*, 1925, 29, 1057—1074).—In order to examine the truth of the conception that oxygen and hydrogen are respectively actually formed in oxidation and reduction reactions, electrolytic reduction was attempted in a system containing no hydrogen, and oxidation in one containing no oxygen. Ammonia was adopted as a suitable medium for oxidations, and phosphorus oxychloride,  $\text{POCl}_3$ , for reductions. Liquid sulphur dioxide proved unsatisfactory owing to the complex character of the cathodic processes involved (cf. preceding abstract).

Qualitative results for a number of inorganic substances are given. Nearly all solutions of these substances in this solvent are coloured. Phosphorus oxychloride is readily hydrolysed; it could be freed from the traces of hydrogen chloride formed by distillation over metallic potassium provided that certain precautions are taken to

prevent explosion. In the electrolysis of solutions of potassium iodate and of ferric chloride in phosphorus oxychloride, products were obtained which showed that reduction can take place in the absence of hydrogen. With liquid ammonia as solvent, the work was confined to solutions of thallous iodide, cuprous iodide, hydrazobenzene, and methyl- and ethyl-amine hydrochlorides, and it is concluded that oxidation in the absence of oxygen is established. A table of collected physical constants of liquid ammonia and phosphorus oxychloride is given.

L. S. T.

**Dissociation Theory and Photochemical Thresholds.** E. J. BOWEN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—The theory that absorption of a light quantum causes dissociation into free atoms or radicals has been fairly fruitful, especially in reactions to which a "chain" mechanism has been ascribed. It is not yet certain whether dissociation, if it occurs, is a unimolecular process or whether collisions of activated and unactivated molecules are necessary. There is no strong evidence for the existence of a connexion between heats of linking and activation energies corresponding with absorption spectra, as the one represents merely the difference between the energies of the lowest electron orbits in the free atoms and in the molecule, whilst the other is concerned only with the molecule. Clearer conceptions depend on a more complete knowledge of the physical meaning of absorption spectra. In general, heats of linking are less than the energies of the lower limits of absorption, and are therefore (except in the halogens) much less than the activation energies. There is little to justify a connexion between the so-called photochemical threshold and either the heat of linking or the lower limit of absorption. The conception of photochemical threshold has at present little value because there is no method of measuring it. Apparently the only work which throws light on the question of the minimum energy required to make a molecule active is in the rate of bimolecular thermal gas reactions (T., 1918, **113**, 471; 1924, **125**, 1841). In each case, the heats of activation are considerably less than the electronic activations obtained from absorption spectra, and appear to be unconnected with the heats of linking. It is difficult at present to form any clear picture of what constitutes an active molecule.

R. A. M.

**Relation between Quantum Sensitivity and Intensity of Radiation.** C. WINTHER (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—In photochemical reactions the quantum sensitivity decreases with increase of absorbed energy. The importance of measuring this variation experimentally in future photochemical work is emphasised.

A. B. M.

**Einstein's "Photochemical Equivalent Law."** A. J. ALLMAND (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—Einstein's deduction of the photochemical equivalent law is critically examined and the conditions of its validity are discussed. The available experimental work, and in particular that of Warburg, is summarised. In considering the application of the law a clear distinction must be

made between the primary and the complete reaction. The law seldom holds when applied to the complete reaction, as is shown by an examination of a variety of photochemical changes. A more complete examination of Einstein's deduction shows that the applicability of the law even to the primary reaction may fail under certain conditions, which are briefly discussed. A. B. M.

**Einstein's Law of Photochemical Equivalence.** N. R. DHAR and B. K. MUKERJI (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—The failure of Einstein's law of photochemical equivalence to be applicable in the majority of cases is discussed. The law is more applicable to endothermic than to exothermic reactions. The abnormally large yield obtained in the photochemical combination of hydrogen and chlorine is explained as due to electron emission during the interaction of activated chlorine molecules with hydrogen to form hydrogen chloride. The electrons thus emitted activate other chlorine molecules. A. B. M.

**Confirmation of Einstein's Law of the Photochemical Equivalent in a Very Simple Photochemical Reaction.** F. WEIGERT and L. BRODMANN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—The photochemical transformation of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid in acetone solution has been studied quantitatively. A reaction of this type, where the change takes place in the same molecule, is particularly suitable for testing the validity of the Einstein law. The source of light was a mercury arc, and the strong spectral groups at 436, 405, and 366  $\mu$ , respectively, were used. The concentration of the *o*-nitrosobenzoic acid produced was determined by conductivity measurements. The energy measurements were carried out by a surface bolometer of Lummer and Kurlbaum, and the proportion of the radiation absorbed by the *o*-nitrobenzaldehyde was calculated from Hyman's figures for the extinction coefficient. The efficiency ratio in all three spectral regions was found to be 0.5 within the limits of experimental error, thus proving the Einstein law for this reaction. Based on this value for the efficiency ratio, a suggestion is made as to the mechanism of the reaction. It appears probable that the orientation of the molecules with regard to the direction of vibration of the incident light is of significance. A. B. M.

**Mechanism of Photochemical Reactions.** M. BODENSTEIN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—A critical résumé attempting to clarify the general position. Einstein's law of equivalence in its simple form is practically never verified, for in almost all cases the original product is unstable and further transformations occur. Although the law is valid for the initial process, the molecule may communicate its increased energy by increasing thermal motion, by fluorescence, or by effecting a chemical reaction. If the period between two collisions is about  $10^{-8}$  sec. the fluorescence is extinguished; this fact agrees with other estimates of the life of an activated molecule. The existing data mainly apply to conditions



with short intervals between collisions, in which circumstances the competition is between chemical reaction and the communication of energy to other molecules. The mechanisms are best studied through the medium of chemical kinetics. The author discusses primary reactions in which the departure from the Einstein law is not of a high order and considers in detail the various mechanisms postulated to explain how two molecules of hydrogen iodide by absorption of one quantum result in the formation of hydrogen and iodine. He then treats the sensitisation of ozone decomposition by chlorine and the decomposition of ozone in the presence of inert gases. He concludes that the simple equivalence law is inadequate for a complete explanation of the phenomena observed even in such relatively simple systems. A critical discussion of secondary processes and "chain" reactions follows in which the syntheses of hydrogen chloride and hydrogen iodide are taken as examples.

R. A. M.

**Radiation Theory of Chemical Reaction.** J. RICE (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—The simple Lewis-Perrin radiation theory leads in the case of unimolecular reactions to a rate of activation about  $10^{-6}$  that determined experimentally. The simple collision theory of activation has to meet equally serious difficulties in the unimolecular reaction. The more general radiation theory postulates that the energy absorbed extends over a broad band and is not confined to the quasi-monochromatic beam (A., 1920, ii, 100; this vol., ii, 799). This postulate is a frank assumption (as the arguments hitherto advanced appear to be unsound), and it should be discussed on its merits and justified. The author analyses the assumptions involved in the revived theory and attempts to ascertain the conditions under which the generalised radiation theory may be valid. No serious numerical discrepancy as regards intensity of absorption is likely to be removed merely by quantising a classical expression unless an additional hypothesis is advanced. The simple collision theory cannot yield a unimolecular reaction (cf. Thomson, A., 1924, ii, 222), and can only account for a sufficiently rapid supply of active molecules by a hypothesis of rapid return of activation energy to the as yet unactivated mass. The G. N. Lewis-Smith (this vol., ii, 799) tubular "quant" mechanism also implies very rapid regeneration of "quants." It also involves that radiation of all frequencies above a threshold must be effective in activating. The "quant" mechanism is at variance with dispersion and interference phenomena, whilst recent work by the Copenhagen school has resulted in a correlation of the wave theory and the stationary atom theory by means of statistical conservation and the correspondence principle. Hence the author employs the latter to investigate the conditions under which the radiation theory may hold. He concludes (a) that absorption must go on uninterruptedly for a relatively long period, *i.e.*, the stationary state must persist for  $10^{-7}$  sec., (b) that the theory requires a gas like nitrogen pentoxide to possess intense reflecting power. Condition (a) is not normally fulfilled, but it may be the criterion for a

unimolecular reaction. Intense reflection may explain why light of the suitable wave-length does not seem to hasten the reactions.

R. A. M.

**Influence of Radiation on Chemical Reactions.** L. S. ORNSTEIN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—Lewis (A., 1920, ii, 100) has directed attention to the difficulty of finding the temperature coefficient of a unimolecular reaction from the radiation theory. The rate of reaction as derived from Planck resonators as well as from light quanta is too small to be observed. Franck considers that in the photochemical process excited molecules are formed by light, collisions transform the energy absorbed by the quantum absorption into chemical energy, and in the second stage newly-formed molecules lose their energy by way of quantum emission. The author shows mathematically that if Franck's view be accepted, Lewis' difficulty disappears provided the considerations are restricted to the direct chemical action of light.

R. A. M.

**Elementary Processes of Photochemical Reactions.** J. FRANCK (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—The elementary photochemical process consists usually in the excitation of a molecule. Stern and Volmer (A., 1920, ii, 461) showed that the primary reaction is not the first elementary process, which is instanced rather by the excitation of the molecule, e.g.,  $I_2 + h\nu = I_2^*$ . The conversion of excitation into chemical energy occurs only by collisions of the excited molecules with other molecules during the period of excitation. Molecules which are bound together by van der Waals forces can be separated into atoms by an adiabatic process. Illumination can cause either a dissociation into normal and excited atoms or else the formation of an excited molecule, in a single photochemical elementary process. Mecke's results (*Ann. Physik*, 1924, **71**, 104) on the band spectrum of iodine provide strong support for the views set forth.

R. A. M.

**Formation and Decomposition of Molecules.** M. POLANYI and E. WIGNER (*Z. Physik*, 1925, **33**, 429—434).—According to Born and Franck, molecules cannot be formed by simple association, nor can the reverse process take place, because the probability of the relative energy of the colliding atoms possessing the appropriate quantum of energy is vanishing small. On the assumption that the energy levels have a finite width, the authors show that the probability of the formation or dissociation of molecules, although small, is not infinitely so.

E. B. L.

**Activation of Hydrogen by Excited Mercury Atoms.** A. C. G. MITCHELL (*Proc. Nat. Acad. Sci.*, 1925, **11**, 458—463).—The work of Dickinson (A., 1924, ii, 841) on the reaction between hydrogen and oxygen in presence of excited mercury vapour has been extended and the influence of argon on the rate of reaction investigated. If the concentration of oxygen be kept constant, the rate of reaction increases with the pressure of hydrogen until a saturation value is reached. On addition of small quantities

of oxygen, the pressure of hydrogen being constant, the rate of reaction reaches a maximum at 0.01 mm. of oxygen and then falls to a lower limiting value. When the pressures of hydrogen and oxygen are maintained at a constant value and the pressure of argon is varied the rate of reaction falls with increasing argon concentration, addition of relatively large quantities completely stopping the reaction.

J. S. C.

**Reactions of Hydrogen Activated by Excited Mercury Atoms.** H. S. TAYLOR and A. L. MARSHALL (*J. Physical Chem.*, 1925, 29, 1140—1147).—Various gases react at the ordinary temperature with the hydrogen atoms produced by collisions of molecular hydrogen with mercury atoms excited by illumination with the resonance line (2536.7 Å.) of the mercury arc. This reactivity in the case of ethylene, carbon monoxide, and oxygen indicates that activation of hydrogen alone is a sufficient preliminary to catalytic reaction, activation of the compound reduced being unnecessary. The present work differs from that of previous investigators (Dickinson, A., 1924, ii, 841; Cario and Franck, A., 1922, ii, 809) in that the initial working pressures are much higher (average 0.5 atm.) and wider variations of conditions have been employed. The mercury arc system must be kept cold. Hydrogen and ethylene reacted smoothly according to the usual equation; with hydrogen and oxygen at an initial total pressure of 36 cm., the velocity of reaction was constant over the whole range of experiment. The reaction between hydrogen and carbon monoxide is complex, formaldehyde, solid polymerised products, and methane being produced. Formaldehyde is considered to be definitely the primary reaction product, and this thus represents a new synthesis at atmospheric pressure and temperature. Mixtures of hydrogen and carbon dioxide, and of nitrogen with excess of hydrogen showed no reaction under the conditions used. Hydrogen and nitrous oxide reacted more rapidly than did similar mixtures of hydrogen and oxygen. The velocities of reaction observed are about 100—40,000 times as great as in previous studies of this type, and it is suggested that the high yields may result from a chain mechanism of the kind obtaining in the photochemical combination of hydrogen and chlorine.

L. S. T.

**Photosensitisation and the Mechanism of Chemical Reactions.** H. S. TAYLOR (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—A *résumé* of earlier work on photosensitisation. and an account of a research carried out with Marshall (preceding abstract).

R. A. M.

**Some Conclusions from Recent Work on Photochemistry.** D. L. CHAPMAN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—Tramm (A., 1923, ii, 716) has shown that perfectly dry hydrogen and chlorine are unaffected by visible light. Electrolytically prepared gas cannot be dried sufficiently to ensure no reaction; probably enough oxygen is present to form a trace of water which on illumination initiates the chain of reactions. The author uses

as a working hypothesis the statement:— $\text{Cl}_2 + h\nu = \text{Cl}'_2$  (active);  
 $\text{Cl}'_2 + \text{H}_2\text{O} \rightleftharpoons \text{Cl} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix} < \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix}$ ;  $\text{Cl} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix} < \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} + \text{H}_2 = \text{H} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix} < \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} + \text{HCl}$ ;  
 $\text{H} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix} < \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} + \text{Cl}_2 \rightleftharpoons \text{Cl} \begin{smallmatrix} \text{O} \\ \text{H} \end{smallmatrix} < \begin{smallmatrix} \text{H} \\ \text{H} \end{smallmatrix} + \text{HCl}$ , etc. Without water, an active molecule of hydrogen chloride is assumed. Water is not essential under the influence of ultra-violet light. Chapman (T., 1923, **123**, 3079), in opposition to Baly and Barker (T., 1921, **119**, 653), finds that the rate of reaction is proportional to the intensity of the light. The reaction between iodine and potassium oxalate was found by Dhar (T., 1923, **123**, 1856) to be proportional to the intensity of the light, whilst Berthoud and Bellenot (A., 1924, ii, 327) found it proportional to the square root of the intensity. The latter view is confirmed (Walters, unpublished), with the addition that the mean life of an active molecule is  $>0.02$  sec. and may be as high as 1 sec. The implications of the verification are discussed.

R. A. M.

### Physical Antecedents of the Photo-activity of Chlorine.

W. TAYLOR (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—A theoretical examination of the optical properties of a medium containing activated molecules, and of the possibility of detecting their presence in photochemical reactions. Attempts to observe a change in the refractive index of chlorine when subjected to radiation containing the activating frequencies yielded negative results.

A. E. M.

**Photo-activation of Chlorine.** E. J. BOWEN (*Phil. Mag.*, 1925, [vi], **50**, 879—880).—An error in Taylor's deductions (this vol., ii, 811) is pointed out. No account was taken of the fact that the amount of light absorbed varies with the wave-length. When this is considered, the results lead to the conclusion that the Ribaud fine-structure bands are photo-active and that the rate of combination of hydrogen and chlorine is directly proportional to the number of light quanta absorbed. A similar error has been made by Coehn and Jung (this vol., ii, 142).

A. B. M.

**Mechanism of the Ozone-Chlorine Reaction.** A. J. ALLMAND (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—In the photochemical decomposition of ozone in the presence of chlorine it is suggested that the activated chlorine molecules produce activated oxygen molecules by collision, and that both are then effective in deoxygenation by collision with ozone molecules. Assuming that the life of an activated chlorine or oxygen molecule is long in comparison with the time taken to encounter an ozone molecule, it is shown that the reaction should be of zero order, as is observed experimentally.

A. B. M.

**Mechanism of Photochemical Reactions.** N. R. DHAR and B. K. MUKERJI (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—It is assumed that the first stage in a photochemical reaction consists of the activation of some at least of the molecules concerned. In the phenomenon of photo-sensitisation, e.g., by chlorine in the

decomposition of ozone, the molecules of the sensitiser are activated by the incident light and then pass on their energy to the reacting molecules. The mechanism of photo-inhibition is discussed. In certain cases, it appears to be related to the fluorescent nature of the inhibitor molecules, which transform the active short wavelengths of the incident light into less active light of longer wavelength. The temperature coefficients of photochemical reactions are considered, and it is shown that they may, and often do, possess values greater than unity.

A. B. M.

### **Photochemical and Thermal Decomposition of Ozone.**

R. O. GRIFFITH and A. McKEOWN (*Trans. Faraday Soc.*, Oct. 1925, advance proof; cf this vol., ii, 1076).—A comparison is made of the available results on the decomposition of ozone (1) by ultra-violet light, (2) by visible light, and (3) thermally, in the presence of oxygen only and with other diluent gases. The relative rates of decomposition in helium, nitrogen, and oxygen are given by the ratios 6.0 : 3.8 : 1 in ultra-violet light, and 5.3 : 4.4 : 1 in visible light. The helium : nitrogen ratio for thermal decomposition is 0.89 : 1, and the nitrogen : oxygen ratio is of about the same order as for photochemical decomposition. The catalytic effect of hydrogen is more difficult to measure, but appears to be much greater still. The temperature coefficient of the reaction increases with wave-length and is greatest in thermal decomposition. It is probable that the primary step in all cases is activation of the ozone molecule, but the subsequent course of the reaction may be different under different conditions. In the decomposition of ozone thermally or by visible light, the intermediate formation of atomic oxygen is improbable. Alternative mechanisms of the reaction are discussed.

A. B. M.

### **Rôle of Water in the Photosynthesis of Hydrogen Chloride.**

R. C. W. NORRISH (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—Coehn and Jung's results on the catalytic action of water on the photosynthesis of hydrogen chloride by visible radiation (this vol., ii, 142) cannot be accounted for by the theories of Coehn or Cathala (this vol., ii, 812). They are, however, in accord with the hypothesis that the effect is produced by a film of water on the surface of the vessel. It is assumed that the primary photochemical reaction,  $\text{Cl}_2 + h\nu = 2\text{Cl}$ , occurs at the surface and is proportional to the concentration of water existing there, and that the chain reactions extend into the gas phase and end again at the surface. The author's results on the induction period are explained on the same basis. A small quantity of ammonia can affect the reactivity of the surface, even after the removal of all gaseous ammonia. The velocity of the dark reaction between ethylene and chlorine is increased by 30% by so treating the surface of the vessel. It is suggested that other cases of catalysis by traces of water may be due to the formation of a surface film.

A. B. M.

### **Law of Photographic Blackening for Homogeneous X-Rays.**

W. BUSSE (*Z. Physik*, 1925, 34, 11—14).—The proportionality

between blackening and intensity is found to be linear. Variations from this law must be attributed to variation in development.

E. B. L.

**Formation of Polar Compounds by Photochemical Reactions.** W. A. NOYES (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—A discussion of the work of Moore and Noyes (A., 1924, ii, 748) on the reactions between oxygen and mercury, and nitrogen dioxide and mercury when the mercury was illuminated by wave-lengths both shorter and longer than the photo-electric threshold of mercury. It is considered probable that in such reactions leading to the formation of a highly polar compound the removal of electrons from the electropositive element by means of light may accelerate the reaction. The reaction  $4\text{Hg} + 2\text{NO}_2 = 4\text{HgO} + \text{N}_2$  is considered to take place through the scheme  $\text{Hg}(\text{liquid}) + \text{radiation} = \text{Hg}^+(\text{Hg liquid}) + \ominus$ ,  $\ominus + \text{NO}_2 = \text{NO}_2'$ , and  $\text{NO}_2' + \text{Hg} = \text{HgNO}_2 + \ominus$ , in which the electron is made available for more than one such cycle.

A. E. M.

**Reactions Produced by Sunlight in the Presence of Uranium Compounds.** J. ALOY and A. VALDIGUIÉ (*Bull. Soc. chim.*, 1925, [iv], 37, 1135—1140).—In neutral solution, uranium salts on exposure to sunlight in the presence of organic compounds for periods up to a few hours yield a violet precipitate of uranosouranic oxide,  $\text{U}_3\text{O}_8 \cdot 2\text{H}_2\text{O}$ , through partial reduction of the uranic salt. In acid solution, the reaction is indicated by the decolorisation of methylene-blue. The reaction is even more rapid on exposure in a vacuum. With saturated hydrocarbons, there is no reaction; with olefinic hydrocarbons, reaction takes place readily, amylene yielding amyl alcohol. Acetylenic hydrocarbons react even more readily, and in the case of acetylene the appearance of the violet compound is accompanied by the formation of aldehyde and formic acid. The reaction is sufficiently sensitive for the detection of double linkings. *cyclo*Hexane and the *cyclo*hexenes behave similarly, the former being unattacked, whilst the unsaturated compounds react readily. With benzene, no reaction occurs, but the introduction of side-chains facilitates reduction and reaction takes place with increasing readiness from toluene to xylenes and cymene. Benzoic acid is formed when only one side-chain is present. The introduction of electro-negative groups into the hydrocarbons favours reaction. Chloroform, bromoform, and iodoform react readily with formation of the hydrogen halide. With the alcohols, reaction takes place readily, yielding the corresponding aldehyde and acid, but the reaction proceeds less readily as the length of the carbon chain increases. Methyl alcohol reacts less readily than ethyl alcohol, but the slow reaction of the cyclic alcohols is probably due to their slight solubility. Reaction occurs with the aliphatic ethers, but not with phenolic ethers. With the aliphatic aldehydes, reaction proceeds more rapidly than with the corresponding alcohol, but with aromatic aldehydes the reaction is much slower. Ketones react very slowly, but fatty acids, with the exception of acetic acid, are readily decomposed and the decomposition is promoted by the

presence of hydroxyl or carbonyl groups in the molecule. Phenols do not undergo catalytic oxidation in this way; on the contrary, they prevent the catalysis in the presence of many acceptors of oxygen. Amines and amides do not react. R. B.

**Relation between Velocity of Photochemical Reactions and Dielectric Constant.** C. WINTHER (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—An examination of some results on the photochemical oxidation of iodoform and of the polymerisation of anthracene in several solvents shows that in general the reaction velocity decreases with increasing dielectric constant. A. B. M.

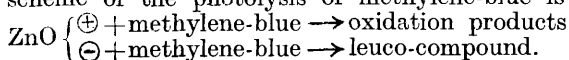
**Formation of Organic from Inorganic Substances under the Influence of Light.** O. BAUDISCH (*Chem.-Ztg.*, 1925, 49, 737).—In connexion with recent work of Baly and Heilbron, the author directs attention to his previous experiments on the formation of organic nitrogenous compounds (*e.g.*, formhydroxamic acid) by the action of ultra-violet light on mixtures of alkali nitrates and simple aldehydes or alcohols or on alkali nitrate solutions through which carbon dioxide is passed. Similar results have also been obtained by illuminating mixtures of formaldehyde and nitric oxide.

W. T. K. B.

**Activity of Various Radiations in Photosynthesis.** R. WURMSER (*Compt. rend.*, 1925, 181, 374—376).—The assimilation of carbon dioxide by marine algæ (*Ulva lactuca*) has been studied under slight illumination. The radiant energy absorbed was measured by the product of the intensity and the absorbing power of the chlorophyll, corrected for absorption due to its colourless constituents. The assimilation is evaluated as the chemical work in cal. involved in the reduction of the absorbed carbon dioxide to carbon. The efficiency, which is the ratio of assimilation to absorbed energy, is between 60 and 100 for red light (*cf. ibid.*, 1923, 177, 644). This result agrees with that of Warburg and Negelein (*A.*, 1923, ii, 718), but their conclusion that the efficiency is inversely proportional to the frequency is criticised. The ratio of the efficiency for radiation of wave-length 590—490  $\mu$  to that of wave-length 700—590  $\mu$  is 1.15. The greater efficiency of green light is connected with the fact that its frequency is such that  $2h\nu$  corresponds exactly with the energy required to reduce a molecule of carbon dioxide.

F. G. S.

**Photolysis of Methylene-blue, Sensitised by Zinc Oxide.** E. BAUR (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—Investigation of the photolysis of methylene-blue, sensitised by zinc oxide, offers corroboration of the idea that photolysis is molecular electrolysis (Baur, *A.*, 1918, ii, 284). The zinc oxide, in absorbing energy, is converted into a "phototrope" one-half of which oxidises a substance in its neighbourhood, whilst the other reduces it. The scheme of the photolysis of methylene-blue is considered thus:



A. E. M.

**Photochemical Sensitisation.** A. BERTHOUD (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—A discussion of various interpretations of the photochemical sensitising process. It is suggested that light may render a sensitiser chemically active and in consequence provoke a more or less complex chain of reactions at the end of which the sensitiser is regenerated (cf. preceding abstract). The hypothesis has been examined in connexion with the rate of addition of bromine to cinnamic acid and to stilbene, and is supported by the results.

A. E. M.

**Becquerel Effect on Copper Oxide Electrodes.** W. J. D. VAN DIJCK (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—For copper oxide electrodes in *N*-solutions of potassium nitrate, zinc nitrate, and sodium bromate subjected to wave-lengths between 5700 and 8600 Å. the Becquerel effect becomes zero at the same potential for all wave-lengths. It is concluded that the analogy with vacuum cells does not hold and that the effect does not consist in the neutralisation of positive ions in the liquid by the ejection of electrons from the electrode. Experiments with specially prepared electrodes show that cupric oxide and possibly cuprous oxide are light-sensitive. The Becquerel effect is then explained by the transport of oxygen resulting from the balance of the light reactions.  $2\text{CuO} \rightleftharpoons 2\text{Cu} + \text{O}_2$ ;  $2\text{Cu}_2\text{O} \rightleftharpoons 4\text{Cu} + \text{O}_2$  and  $4\text{CuO} \rightleftharpoons 2\text{Cu}_2\text{O} + \text{O}_2$ .

A. E. M.

**Absorption of Light by Solutions of Electrolytes.** H. VON HALBAN (*Trans. Faraday Soc.*, Oct. 1925, advance proof).—An examination of the validity of Beer's law. The molecular extinction coefficients of solutions of sodium nitrate, sodium picrate, and sodium dinitrophenoxide are constant only up to 0.5*N*-concentration, above which the variations are greater than the observational error. Addition of potassium, sodium, and calcium chlorides to potassium nitrate solutions has a powerful effect on the absorption of light by the nitrate ions. The influence of calcium chloride is greater than that of either the sodium or potassium salt. At 0.048*N*-concentration potassium and sodium nitrate show the same molecular extinction coefficient. The light absorption by a 0.048*N*-barium nitrate solution showed differences from that of the alkali nitrates in the same sense as those induced by adding calcium chloride to potassium nitrate solutions, and it is deduced that bivalent cations influence the light absorption of the univalent anion even in diluted solutions. Similar departures from Beer's law were found by adding various salts to solutions of sodium picrate and sodium dinitrophenoxide.

A. E. M.

**Action of Ammonia and of a Solution of Potassamide in Liquid Ammonia on certain Halides of Molybdenum and Tungsten.** F. W. BERGSTROM (*J. Amer. Chem. Soc.*, 1925, 47, 2317—2323).—Molybdenum and tungsten dibromides and tungsten dichloride yield slightly soluble ammonobasic halides on treatment with liquid ammonia. Molybdenum tribromide and pentachloride, and tungsten pentabromide and hexachloride dissolve in liquid



ammonia to give red solutions, the first named also giving a precipitate of ammonobasic bromides. Dilution of the solutions yields amorphous precipitates of indefinite composition. Molybdenum pentachloride absorbs 8 mols. of ammonia gas, giving a derivative of unknown composition. "Nitridation" takes place when an ammonia solution of molybdenum dibromide is kept for some days. *Potassium ammonomolybdate*,  $\text{Mo}(\text{NK})_2\text{NH}_2$ , is precipitated by adding excess of potassamide solution to molybdenum tribromide solution and keeping for some weeks. Free potassium is formed owing to reduction of the potassamide and "nitridation" of the molybdenum; hydrogen and nitrogen are simultaneously formed. The compound reacts vigorously with water and is soluble in dilute sulphuric acid; it loses  $0.5\text{NH}_3$  at  $120\text{--}130^\circ$  in a vacuum. The *sodium* salt is prepared using molybdenum pentachloride and sodamide. *Potassium ammonotungstite*,  $(?)\text{W}(\text{NK})_2\text{NH}_2$ , is precipitated as above, using tungsten pentabromide. It is pyrophoric, blackens in air, and reacts violently with water. If excess of halide is used in these precipitations, ammonobasic mixtures are obtained.

S. K. T.

#### Apparently Anomalous Protection against Oxidation.

S. E. SHEPPARD (*Nature*, 1925, **116**, 608—609).—When a strip of copper, brass, or bronze is dropped into a solution of potassium persulphate, it is blackened readily and completely, whereas if it is slowly lowered into the solution, blackening either does not take place or is merely a patchy tarnish. The oxide layer forms a soft, velvety pile which consolidates when rubbed to a smooth and semilustrous layer. The phenomenon is evidently associated only with the difference in the time of exposure of the metal to the air-solution interface, and normal blackening can be caused by mechanical or chemical protection of the metallic surface as it passes the interface, where molecular oxygen is accumulating as a result of reactions expressed by the equations: (i)  $\text{K}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O} = 2\text{KHSO}_4 + \text{O}$ ; (ii)  $\text{O} + \text{O} = \text{O}_2$ . In explanation of the oxygen interference, the formation of cuprous peroxide,  $\text{Cu}_2\text{O}_3$ , is postulated; alternatively, both cuprous and cupric peroxides may be formed, with subsequent mutual reduction.

A. A. E.

#### Is Orthoboric Acid, $\text{H}_3\text{BO}_3$ , Volatile in Steam? R.

ANSCHÜTZ and K. RIEPENKRÖGER (*Ber.*, 1925, **58**, [B], 1734—1735).—Orthoboric acid is volatile with steam only if the temperature is sufficiently high to cause dissociation into water and metaboric acid; the latter then volatilises and subsequently recombines with the condensed water to give orthoboric acid. If a solution of orthoboric acid in water is distilled under atmospheric pressure, the distillate does not contain orthoboric acid.

H. W.

#### Corrosion of certain Metals by Carbon Tetrachloride.

F. H. RHODES and J. T. CARTY (*Ind. Eng. Chem.*, 1925, **17**, 909—911).—Pure, dry carbon tetrachloride vapour reacts vigorously with aluminium yielding hexachloroethane,  $2\text{Al} + 6\text{CCl}_4 = 2\text{AlCl}_3 + 3\text{C}_2\text{Cl}_6$ . Other metals are only slightly corroded by prolonged

exposure to the dry liquid or its vapour, but in presence of water hydrogen chloride is formed by the interaction of the water with carbon tetrachloride (the metals acting as promoters) and corrosion proceeds accordingly. [Cf. *B.*, 1925, 852.] C. I.

**Preparation of "Phosgeno Salts."** A. F. O. GERMANN and C. R. TIMPANY (*J. Amer. Chem. Soc.*, 1925, **47**, 2275—2278).—An enclosed apparatus is described for the preparation of quantities of the pure metallic salts of the "phosgeno acid,"  $\text{COAl}_2\text{Cl}_8$ , which are soluble in volatile solvents. Reactions of the type  $\text{COAl}_2\text{Cl}_8 + \text{CaCl}_2 = \text{CaAl}_2\text{Cl}_8 + \text{COCl}_2$  are utilised. Vapour pressure measurements confirm the formula  $\text{CaAl}_2\text{Cl}_8 \cdot 2\text{COCl}_2$  for the calcium salt (cf. Germann and Gagos, A., 1924, ii, 861). A method of analysing these salts is also described. S. K. T.

**Combustion of Carbon.** III. H. F. SMITH (*Ind. Eng. Chem.*, 1925, **17**, 930—931; cf. this vol., ii, 888, 987).—Further experimental evidence is adduced to support the view that carbon monoxide is the initial product of the combustion of carbon at high temperatures. [Cf. *B.*, 1925, 835.] C. I.

**Phosphates of Zirconium and Hafnium.** G. VON HEVESY and K. KIMURA (*Z. angew. Chem.*, 1925, **38**, 774—776).—The pure phosphates, prepared by adding a solution of disodium hydrogen phosphate in 6*N*-hydrochloric acid to a solution of the oxychlorides in 6*N*-hydrochloric acid, were dried below 80°. Analytical results and general considerations point to the formula  $\text{MO}_2 \cdot \text{P}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$  ( $\text{M} = \text{Zr}$  or  $\text{Hf}$ ), but when heated at 700° they lose 2 mols. of water. Hafnium phosphate is less soluble than zirconium phosphate in hydrochloric acid, and the separation of the two should be carried out in concentrated acid. The solubility at 20° of hafnium phosphate is 0.00012 and 0.00009 mol. per litre of 10.21*N*- and 5.94*N*-hydrochloric acid, respectively, whilst of zirconium phosphate it is respectively 0.00023 and 0.00012 mol. per litre of 10.00*N*- and 6.01*N*-hydrochloric acid. Zirconium and hafnium may be separated as phosphates, but, even when working in strong acid solution, a large excess of phosphate should be used in the precipitation, which should also be carried out in the cold. W. T. K. B.

**Properties of Stannous Iodide.** P. FREUNDLER and (MLLE.) Y. LAURENT (*Bull. Soc. chim.*, 1925, [iv], **37**, 1133—1135).—Concentrated aqueous solutions of stannous chloride and sodium iodide deposit orange crystals of the monohydrate,  $\text{SnI}_2 \cdot \text{H}_2\text{O}$ , which on drying at 100° is converted into stannous oxide; the anhydrous iodide, obtained by spontaneous desiccation in the cold, or by warming a mixture of stannous chloride (1 mol.), sodium iodide (2 mols.), and hydrogen chloride (0.5 mol.), is stable at 100°. No double compound could be obtained in this case, but with potassium chloride in neutral solution the double compound,  $\text{SnI}_2 \cdot \text{KI} \cdot 3\text{H}_2\text{O}$ , described by Personne and Boullay, is obtained. The same compound is obtained in acid solution in the cold, but from warm solutions anhydrous stannous iodide is deposited, the temperature of transformation depending on the concentration of the potassium

iodide. In acid solution, the potassium double compound is readily oxidised, especially in sunlight, giving a dark brown solution which loses iodine on warming and probably contains a periodide. Under similar conditions, stannous iodide prepared from sodium iodide oxidises very slowly with separation of colloidal stannic acid. In view of these facts, the colloidal complex in *Laminaria flexicaulis* is now regarded as containing, at least temporarily, the complex iodine-rubidium-sodium (cf. this vol., ii, 22). The existence of rubidium iodide in association with protoplasm is further supported by the presence of rubidium and iodine in the equivalent proportions, by the absence of iodine and rubidium from the salts resulting from spontaneous desiccation, and by the similar behaviour of the compound obtained from *L. flexicaulis* and the rubidium-stannous iodide complex,  $2\text{SnI}_2 \cdot \text{RbI}$  (Auger and Karantassis, this vol., ii, 814), on exposure to sunlight. R. B.

**Lead Bromate and Diacetato-diplumbo-bromate.** E. GÜNZEL and E. MARCUS (*Z. angew. Chem.*, 1925, **38**, 929—930).—Lead bromate is quite insensitive to shock or friction. A hot solution of lead acetate and acetic acid, when treated with potassium bromate, gives no precipitate on cooling, but lead bromate crystallises out after cooling and seeding. A mixture left over-night without seeding yielded a solid which on drying exploded with fatal results; the solid was found to be a mixture of lead bromate and diacetato-diplumbo-bromate (cf. Weinland and Paul, A., 1924, ii, 45), the latter being a readily detonated substance. Preparation in presence of acetic acid is therefore dangerous. S. I. L.

**Doubly-refractive White Phosphorus.** D. VORLÄNDER, W. SELKE, and S. KREISS (*Ber.*, 1925, **58**, [B], 1802—1806).—Optically isotropic white phosphorus becomes converted into a doubly refractive variety (cf. Bridgman, A., 1914, ii, 647) when strongly cooled. The transition temperature of the two forms, determined from time-temperature curves and by observation with a specially-constructed polarisation microscope, is  $-68^\circ$  (Bridgman, *loc. cit.*, records  $-76.9^\circ$ ). The crystalline form of the doubly-refractive variety is indistinct, but appears to be either monoclinic or rhombic. Attempts to obtain well-defined crystals from carbon disulphide or other solvents at low temperatures showed that phosphorus remains permanently undercooled under these conditions and that production of the doubly-refractive variety does not occur (cf. Bridgman, *loc. cit.*). A corresponding, doubly-refractive form of arsenic could not be observed above  $-190^\circ$ . H. W.

**Effect of Sodium Chloride on Hydrogen-ion Concentration and Stability towards Alkali of Chromic Chlorides.** K. H. GUSTAVSON (*Ind. Eng. Chem.*, 1925, **17**, 945—952).—The addition of progressive amounts of sodium chloride to solutions of chromic chloride causes an initial increase in the value of  $p_{\text{H}}$ , followed by a later decrease with greater sodium chloride concentration. The latter effect is due to the increase in concentration of the chromium salt by hydration of the sodium chloride. The former change is

best marked in dilute solutions of lesser acidity. It is considered that it is due to changes in the composition of the internal sphere in the chrome complex, different modifications of the basic aquo-chromic chlorides existing analogous to the normal chlorides  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ ,  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2$ , and  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl}$ . Addition of sodium chloride will favour the formation of compounds with chlorine co-ordinatively attached, and the increase in chlorine ions is evidenced by decrease in the electric charges of the cation and by an increase in  $p_{\text{H}}$ . If sodium chloride is replaced by magnesium chloride, this effect is masked by the greater hydration tendency of the magnesium salt. The point at which precipitation occurs during addition of sodium hydroxide is not a function of  $p_{\text{H}}$ , but is proportional to the ratio of chlorine to chromium in the complex cation. C. I.

**Synthetic Potassium and Sodium Chromosilicates.** (MLLE.) H. KARFIOL (*Rocz. Chem.*, 1925, 5, 182—192).—Synthetic chromosilicates of sodium and potassium are prepared by the fusion of mixtures in various proportions of chromium sesquioxide, sodium, or potassium chloride and carbonate, and silica. The fused mass, after being heated for 10 hrs., is extracted with water. In the case of mixtures with potassium, the residue thus obtained had so low a potassium content that most of them appeared to be compounds of chromium sesquioxide and silica in various proportions, the potassium present being probably an impurity. The only product of this type which appeared definitely to be a chromosilicate had a composition corresponding with the formula  $\text{K}_2\text{Cr}_4\text{Si}_{13}\text{O}_{33}$ . The crystalline nature of these substances could not be determined, owing to the extremely small size of the particles. The sodium chromosilicates obtained are of very complicated composition, and seem to be additive compounds of sodium silicate and oxide to chromosilicates of the same type as the known series of aluminosilicates,  $\text{R}_3\text{Al}_2\text{Si}_n\text{O}_{2n+4}$ . All the sodium chromosilicates prepared are isomorphous, in spite of considerable differences in composition, the proportions of chromium sesquioxide to sodium metasilicate being as 1 : 2, 3, 4, 5, 6, 7, and 8. R. T.

**Decolorisation of Carbon Disulphide Solutions of Iodine by Red Phosphorus.** R. N. TRAXLER and F. E. E. GERMANN (*J. Physical Chem.*, 1925, 29, 1119—1124).—The work of Sestini (J., 1871, 24, 1005) on the action of moist red phosphorus on iodine in carbon disulphide has been repeated and verified. After decolorisation had occurred, the phosphorus was found to contain hydriodic and phosphorous acids, but no free iodine. The presence of these acids is ascribed to their insolubility in carbon disulphide, and not to adsorption. Decolorisation when dry phosphorus is added occurs only in dilute solution; more concentrated solutions give phosphorus tri-iodide. Dry red phosphorus and red phosphorus which had been heated for 2 hrs., when shaken with iodine in carbon disulphide, lost 18.5% of its original weight before losing its activity towards iodine. The reddish-brown solutions resulting from this addition yielded red crystals of phosphorus tri-iodide, m. p. 55°. The low

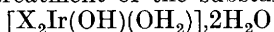
m. p. ( $55^{\circ}$  instead of  $61^{\circ}$ ) was probably due to the presence of the compound  $P_4S_3I_2$  (m. p.  $119.5^{\circ}$ ) derived from the sulphur in the carbon disulphide. The preparation of phosphorus tri-iodide using carbon disulphide freshly purified with mercury is recommended. L. S. T.

**Ferric Acid and Ferrates.** L. LOSANA (*Gazzetta*, 1925, 55, 468—497; cf. Baschieri, A., 1906, ii, 857; Frémy, *Compt. rend.*, 1841, 12, 23; Rossel, *J. Amer. Chem. Soc.*, 1895, 17, 760).—The authors have attempted to prepare the following ferrates: potassium, thallium, silver, mercurous, barium, strontium, calcium, mercuric, copper, lead, zinc, nickel, cobalt, manganese, magnesium, ferrous, aluminium, ferric, chromium, thorium. Potassium ferrate was prepared by oxidising with chlorine a suspension of ferric hydroxide in aqueous potassium hydroxide (Merz, *J. pr. Chem.*, 1867, 101, 269). Barium and calcium ferrates (Frémy, *loc. cit.*) and strontium and magnesium ferrates were obtained by double decomposition from the potassium salt; with three exceptions, the ferrates of the other metals were obtained by double decomposition of the nitrates, with an aqueous suspension of very finely divided barium ferrate. In the cases of the ferrates of silver, barium, strontium, calcium, copper, lead, zinc, nickel, and cobalt, the analysis was obtained and the thermal decomposition also studied. Those of iron (ferrous and ferric), aluminium, and thorium decompose on drying and only the combining ratios of their constituents were determined. Manganese, thallium, and bivalent mercury do not give definite compounds; magnesium ferrate was not obtained. Barium ferrate ( $+4H_2O$ ) and strontium ferrate ( $+2H_2O$ ) are stable over concentrated sulphuric acid in a vacuum, and controlled thermal decomposition shows that they can exist as anhydrides, but calcium ferrate ( $+2H_2O$ ) and copper ferrate ( $+H_2O$ ), which decompose in a vacuum over sulphuric acid, do not give anhydrides. The temperatures of decomposition of the ferrates studied are diverse. All lose oxygen continuously except barium ferrate, which possibly gives the intermediate compound,  $BaFeO_3$ . W. E. E.

**Co-ordination Chemistry. Chloroferrates of Substituted Ammonium Bases.** H. REMY and H. J. ROTHE (*Ber.*, 1925, 58, [B], 1565—1571).—According to the author's "law of homopolar combination" of atoms (A., 1921, ii, 501) compounds containing atoms with the co-ordination number 5 or 7 are to be expected among the chloro compounds of ferric iron if they are capable of existence. From analogy with osmium and ruthenium, the existence of the ions  $[FeX_4]'$ ,  $[FeX_5]''$ ,  $[FeX_6]'''$ , and  $[FeX_7]''''$  may be foreseen and stable compounds of the type  $M'_2[FeX_5]$  and  $M'_4[FeX_7]$  may be expected if the inherent instability of the corresponding complex ions is neutralised by combination with cations of suitable size and form. Such a series is found in the chloroferrates of substituted ammonium bases. The latter invariably also yield compounds,  $M'[FeX_4]$ , but their region of existence is nearly always smaller than that of the penta- and hepta-chloro

salts and their stability is generally less. Unfortunately, they are not sufficiently stable to permit measurements of molecular weight or conductivity. The following salts are described: *methylammonium tetrachloroferrate*,  $[\text{MeNH}_3][\text{FeCl}_4]$ , m. p. about  $211^\circ$ ; *methylammonium heptachlorohemiaquoferate*,  $[\text{MeNH}_3]_4[\text{FeCl}_7 + \text{H}_2\text{O}]$ , m. p.  $161^\circ$ ; *dimethylammonium tetrachloroferrate*, m. p. (indef.)  $97\text{--}104^\circ$ ; *dimethylammonium pentachloroferrate*,  $[\text{Me}_2\text{NH}_2]_2[\text{FeCl}_5]$ , m. p.  $98^\circ$ ; *dimethylammonium heptachloroferrate*, m. p. about  $48^\circ$ ; *trimethylammonium tetrachloroferrate*; *trimethylammonium pentachloroferrate*, m. p.  $143.5^\circ$ ; *tetramethylammonium tetrachloroferrate*, m. p. above  $308^\circ$ ; *ethylammonium tetrachloroferrate*, m. p. about  $85^\circ$ ; *ethylammonium heptachloroferrate*, m. p.  $117^\circ$ ; *propylammonium tetrachloroferrate*; *propylammonium heptachloroferrate*, m. p.  $118^\circ$  after softening at  $110^\circ$ ; *butylammonium tetrachloroferrate*, m. p.  $60.5^\circ$ .  
H. W.

**Iridium Halides.** F. KRAUSS and H. GERLACH (*Z. anorg. Chem.*, 1925, **147**, 265—287).—Attempts to prepare tetrahalides of iridium were unsuccessful. The formation of the trichloride from iridium and chlorine is accelerated by light and by the presence of carbon monoxide. Iridium tetrahydroxide readily reacts with chlorine when heated, yielding the trichloride, and with gaseous hydrogen chloride and bromide at the ordinary temperature, forming the substances  $[\text{X}_2\text{Ir}(\text{OH})(\text{OH}_2)]_2\cdot 2\text{H}_2\text{O}$ . When heated, these lose their water of crystallisation, and the resulting compounds  $[\text{X}_2\text{Ir}(\text{OH})(\text{OH}_2)]$  yield the acids  $[\text{X}_2\text{Ir}(\text{OH})_2]\text{H}$  when dissolved in water. By further treatment of the substances



with gaseous hydrogen chloride or bromide the compounds  $[\text{X}_3\text{IrOH}_2]$  are obtained. The compound  $[\text{Cl}_3\text{IrOH}_2]$  loses its water at  $310^\circ$ ; the bromine compound could not be dehydrated without decomposition, and when heated yielded the dibromide at  $440^\circ$  and the monobromide at  $485^\circ$ . The tribromide was prepared by heating the dibromide in a bomb tube with bromine. Iridium and iridium tetrahydroxide are not acted on by iodine, but hydrogen iodide readily reacts with the tetrahydroxide forming the substance  $[\text{I}_3\text{IrOH}_2]_2\cdot 2\text{H}_2\text{O}$ . When heated this loses water to form the compound  $[\text{I}_3\text{IrOH}_2]$ , which, when further heated, yields the monoiodide and probably the di-iodide. The acid  $[\text{I}_3\text{IrOH}]\text{H}$  is probably formed when the substance  $[\text{I}_3\text{IrOH}_2]_2\cdot 2\text{H}_2\text{O}$  is dissolved in water.

A. G.

**Preparation of Auric Chloride.** M. PETIT (*Bull. Soc. chim.*, 1925, [iv], **37**, 1141—1147).—The preparation of anhydrous auric chloride is best effected by the action of gaseous chlorine on gold leaf. In the apparatus described, the gold leaf is placed in a boat inside a tube (A) sealed on to a small flask. A current of chlorine at about 60—80 mm. in excess of atmospheric pressure is passed through the tube, leaving by a second tube, whilst a third tube at the bottom of the flask is connected with a test-tube in which the auric chloride is collected. The tube (A) and the adjacent side of

the flask are heated electrically, and at 245—250°, the optimal temperature, 0.15 g. of auric chloride is obtained per hr. (79% yield).  
R. B.

**Preparation of Beryllium.** A. STOCK, P. PRAETORIUS, and O. PRIESS (*Ber.*, 1925, **58**, [B], 1571—1580).—Technical beryllium oxide is purified from aluminium oxide by conversion into the basic acetate, which is dissolved in chloroform and finally distilled. Larger quantities of material are more conveniently obtained by slowly adding a solution of basic beryllium chloride to a solution of sodium carbonate through which a brisk current of carbon dioxide is passed; basic beryllium carbonate is thereby dissolved, whereas aluminium and iron hydroxides remain. Dissolved iron in the solution is removed by hydrogen sulphide. After addition of a quantity of hydrochloric acid sufficient to precipitate a fraction of the beryllium carbonate together with a little aluminium and iron which still remain, the bulk of the beryllium is precipitated as the basic carbonate, which is converted into the hydroxide. The fluorides,  $\text{NaBeF}_3$ ,  $\text{BaBeF}_4$ , and  $\text{BaBe}_2\text{F}_6$ , are prepared by dissolving the requisite amounts of beryllium oxide or hydroxide, sodium carbonate, and barium carbonate in hydrofluoric acid and ultimately heating the products before the blowpipe.

The electrolyte is contained in an Acheson graphite crucible, which serves as anode; it rests on asbestos inside a copper cylinder, the intervening space being filled with kryptol. The cathode is composed of an iron rod with internal water cooling. The crucible is filled initially with kryptol and electrically heated at 700—800°. The contents are removed and sodium beryllium fluoride is introduced, followed gradually by the fluoride,  $\text{BaBeF}_4$ . When the requisite temperature (1350°) is attained, the cathode is cleaned and reinserted and actual electrolysis begins, during which the fluoride  $\text{BaBe}_2\text{F}_6$  is added in small portions at frequent intervals. After 3 hrs., the process is interrupted and the beryllium is removed adhering to the cathode. A second and third run can be accomplished if the electrolyte is enriched by addition of the volatile sodium beryllium fluoride. The yield of beryllium is 45—51%, the current efficiency 75—80% in the first period, 60% in the second and third periods. Almost half of the fluorides is lost by volatilisation at the high temperature required for electrolysis. Beryllium is thus obtained in a compact, crystalline form,  $d^{18}$  1.842. It contains only traces of sodium or barium, its purity depending otherwise on that of the materials used. The iron content varies from 0% to 0.4%. The purity of the metal is most accurately determined by measurement of the hydrogen evolved when a known weight of it is dissolved in air-free, dilute hydrochloric acid. Traces of aluminium are determined by a modification of Atack's method (A., 1915, ii, 842), using sodium alizarinsulphonate. H. W.

**Colloidal Cobaltic Hydroxide.** C. PAAL and H. BOETERS (*Ber.*, 1925, **58**, [B], 1539—1541).—Colloidal solutions of cobaltous hydroxide are obtained by the alternate addition of small quantities of solutions of cobalt chloride and sodium hydroxide to solutions

of sodium protalbate or lysalbate, but the protective action of the latter substances is less marked than with nickel hydroxide, and turbidity ensues when more than 10% of cobalt is present. During dialysis, the cobaltous hydroxide is oxidised by the air to colloidal cobaltic hydroxide, which can be obtained in the solid, colloiddally soluble form by evaporation of the dialysed solution; stable preparations do not contain more than 10% of cobalt. If colloidal cobaltic hydroxide is directly prepared by the method described above, but in the presence of hydrogen peroxide, the stable, colloiddally soluble, solid form can be obtained with more than 20% of cobalt. H. W.

[Ultra-balance.] F. HOLTZ (*Ber.*, 1925, **58**, [B], 1924; cf. Holtz and Kuhlmann, this vol., ii, 319).—A reply to Kuhlmann (this vol., ii, 706). H. W.

**Elimination of Surface Devitrification on Laboratory Quartzware.** F. C. VILBRANDT (*Ind. Eng. Chem.*, 1925, **17**, 835—837).—The surface "devitrification" or frosting that gradually develops on fused silica laboratory vessels is frequently caused by the deposition of "slag" particles in the surface of the material. The phenomenon has been investigated by repeatedly evaporating water in fused silica dishes, by repeatedly incinerating wet filter-papers in crucibles, and by repeatedly quenching hot fused silica tube in water. In each case surface "devitrification" occurred. The deterioration was progressive; the ware gradually became brittle and eventually very fragile. The corroded surface layer is removed by hydrofluoric acid, and only by that acid. Vessels treated with hydrofluoric acid (by momentary immersion in the solution, which contains a little sulphuric acid) become clear and smooth again, and their life is prolonged. W. A. S.

**Calculations for and Calibration of the Haber-Löwe Gas Interferometer.** G. WERNER (*Z. angew. Chem.*, 1925, **38**, 905—911).—Equations are deduced for determining the percentage composition of gas mixtures, involving the scale reading of the interferometer, the refractive indices of the component gases, the absolute temperature, the pressure, and a constant for the instrument. Dry air, free from carbon dioxide, is used as standard, and any impure gas or mixture can be used for the same purpose after its relative refractive index (taking that of air as unity) has been determined. A single, short experiment enables the difference in refraction to be determined, by means of which the analysis of a gas mixture can be carried out independently of temperature and pressure. Mixtures of gases having widely different refractive indices can be analysed by using as standard a gas (*e.g.*, carbon dioxide) the refractive index of which lies between the two. W. T. K. B.

**Cryostat for Precision Measurements at Temperatures extending to  $-180^{\circ}$ .** J. E. WALTERS and A. G. LOOMIS (*J. Amer. Chem. Soc.*, 1925, **47**, 2302—2306).—A cryostat is described, based on that of Henning (*Z. Instrumentenkunde*, 1913, **33**, 33), which



maintains for 3 hrs. any required temperature between  $0^{\circ}$  and  $-180^{\circ}$  to within  $\pm 0.01^{\circ}$ . Aged liquid air is allowed to flow through a copper spiral immersed in petroleum or butane (for temperatures to  $-140^{\circ}$  and to  $-180^{\circ}$ , respectively) contained in a Dewar vessel, the rate of flow, controlled by a water head, being such that the bath tends to cool slowly. Change in the temperature of the bath is revealed by the gradual deflection of a galvanometer in the resistance thermometer circuit; the needle is constantly restored to zero by the momentary passage of a current through a resistance coil in the cryostat liquid. S. K. T.

**Porous Electrode for Oxidations or Reductions.** M. KNOBEL (*Ind. Eng. Chem.*, 1925, **17**, 826).—Knobel (A., 1923, ii, 608) and Schmid (A., 1924, ii, 324) have described a hydrogen electrode consisting of a platinised, but still porous, graphite tube. Similar electrodes can readily be prepared for use in electrolytic oxidation or reduction. The graphite tube (one end is closed) is electroplated with lead, copper, zinc, nickel, iron, or silver, a current of air being blown through the electrode in order to keep it porous. The metallic layer should be 1—2 mm. thick, because it does not adhere well to the graphite. [Cf. B., 1925, 855.] W. A. S.

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## Mineralogical Chemistry.

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**Rare Gases of Volcanic Exhalations.** A. PIUTTI and E. BOGGIO-LERA (*Mem. R. Accad. Lincei*, 1924, [v], **14**, 871—884).—In the various volcanic gases of different Italian localities examined, the ratio argon : nitrogen is constantly less than in the atmosphere, a value as low as 0.381 being obtained in one case. The ratio (helium+neon) : argon varies within wide limits, but, as with the gases of thermal springs, is always higher than with air. For the gases of any one volcanic region, the content of neon and helium increases as the temperature at which the gases issue falls. In no instance were more than traces of neon found. T. H. P.

**Albite and other Authigenic Minerals in Limestone from Bengal.** E. SPENCER (*Min. Mag.*, 1925, **20**, 365—381).—Small crystals of albite, together with crystals of quartz, mica, pyrite, rutile, and tourmaline, occur in certain zones in limestone beds near Raipura in Gangpur State. The albite crystals are twinned on the Roc Tourné type and are dark grey in colour due to carbonaceous inclusions. Analyses (I by K. B. SEN) show the mineral to be practically pure albite :

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	Ign.	Total.
I. ...	66.95	19.72	0.50	0.88	0.66	9.95	0.52	0.63	99.81
II. ...	67.10	19.95	0.55	0.70	0.50	10.30	0.60	0.85	100.55

A review, with bibliography, is given of the literature on the occurrences of small crystals of feldspars in limestones, and it is

concluded that the crystals have grown in place and are not the result of metamorphic processes.

L. J. S.

**Chlorophæite in Dolerites near Edinburgh.** R. CAMPBELL and J. W. LUNN (*Min. Mag.*, 1925, 20, 435—440).—Chlorophæite occurs as irregular patches in the dolerites (tholeiites) of Dalmahoy and Kaimes Hills near Edinburgh. On freshly-fractured surfaces it is bright olive-green with glassy lustre, but on exposure it soon changes, through dark-green, to black with pitchy lustre. This change in colour is not due to the action of light, but to oxidation. The material is mostly optically isotropic with  $n$  1.498; hardness 1.5,  $d$  1.81. Analysis by W. H. HERDSMAN gave :

SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.
32.95	0.62	5.40	12.37	9.18	0.33	4.75	3.05	1.68	0.36
H <sub>2</sub> O (at 105°).		H <sub>2</sub> O (+105°).		Total.					
23.90		5.20		99.79					

Several other occurrences of chlorophæite in Scotland are noted.

L. J. S.

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## Analytical Chemistry.

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**Use of the Quinhydrone Electrode for the Determination of  $p_H$  in Soils.** C. BRIOUX and J. PIEN.—(See i, 1227.)

**Standardisation of Solutions used in Iodometry. II.** S. POPOFF and J. L. WHITMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 2259—2275).—An electrometric study of the reaction between solutions of iodine in potassium iodide and of sodium thiosulphate shows that when the mixed liquids after titration are of large volume and the iodide concentration is therefore low (below 1%) a loss of iodine occurs. This loss is inappreciable when the iodide concentration is within 1% to 8% and the titration time, in the dilute solution, does not exceed 10 mins.; or when the 1% of iodide is replaced by its equivalent (0.06*N*) of hydrochloric acid, or by sulphuric acid up to 0.6*N*. Sunlight has no influence when the solutions contain up to 4% of iodide, although it vitiates the results when certain mineral acids are present. One % of iodide and 0.2*N*-acids may be used safely in diffused light. When the iodide concentration is less than 1% the order of mixing the solutions slightly influences the results. The conditions necessary for the accurate standardisation of thiosulphate solutions against iodine or potassium permanganate, dichromate, or bromate, are detailed. S. K. T.

**Diphenylamine Reaction [for Nitrates].** L. EKKERT (*Pharm. Zentr.*, 1925, **66**, 649—650).—The development of a coloration on addition of diphenylamine to a solution in sulphuric acid is not specific for nitric acid, but arises from the presence of many other oxidising agents. The colorations developed by the common oxidising agents when a solution in concentrated hydrochloric acid is treated with diphenylamine in glacial acetic acid, diluted, and

portions are shaken with chloroform and ether, are tabulated. Concentrated phosphoric acid gives even stronger colorations than sulphuric or hydrochloric acid.

S. I. L.

**Quantitative Kjeldahlisation of Nitrates with Phenol-sulphonic Acid and Potassium Sulphate.** B. M. MARGOSCHES and E. SCHEINOST [with V. WOYNAR] (*Ber.*, 1925, **58**, [B], 1850—1857).—Kjeldahlisation of sodium or potassium nitrate by sulphuric acid in the immediate presence of phenol and potassium sulphate gives low values for nitrogen. If, however, addition of potassium sulphate is delayed until the first main reaction is completed (about  $\frac{1}{2}$  hr. after commencement of the heating with a small luminous flame), accurate results are obtained. The success of the process appears to depend on the quantitative conversion of the nitrate into mononitrophenolsulphonic acids, since the corresponding polynitro compounds cannot be accurately kjeldahlised. The immediate addition of potassium sulphate disturbs the regular course of mononitration owing to the very considerable development of heat which it causes. Addition of compounds which are formed during the reaction (*e.g.*, potassium hydrogen sulphate) and do not evolve any considerable amount of heat when added to concentrated sulphuric acid is harmless even in the initial stages of the process.

H. W.

**Replacement of Monohydric by Dihydric Phenols in the Kjeldahlisation of Nitrates.** B. M. MARGOSCHES and E. SCHEINOST (*Ber.*, 1925, **58**, [B], 1857—1860; cf. preceding abstract).—Experiments with quinol, resorcinol, pyrocatechol, pyrogallol, phloroglucinol, and hydroxyquinol show that only resorcinol and phloroglucinol are suitable in place of phenol as fixing agents for nitrate nitrogen in the kjeldahlisation of nitrates in the absence of an accelerator. Complete kjeldahlisation of potassium nitrate can be effected in 4 hrs. in the presence of phloroglucinol and molybdic acid. Salicylic, *m*-hydroxybenzoic, and gallic acids are unsuitable.

H. W.

**Electrolytic Determination of Moderate Amounts of Arsenic.** J. MOIR and J. S. JAMIESON (*J. South African Chem. Inst.*, 1925, **8**, 16—18).—The apparatus is a modification of Thorpe's electrolytic apparatus with substitution of the generator cell by a narrow cylinder, and of the porous pot by an alundum crucible. A cadmium electrode is used (activated by reversal of the current and subsequent deposition of porous cadmium on restoring the normal direction) and platinum anode. The pressure of the anode liquid (1:5-sulphuric acid) prevents outward diffusion of the arsenical liquid. The cross tube is filled with lead acetate cotton wool, and the gas exit connected with silver nitrate tubes; the contents of these are titrated with dilute iodine solution after addition of a large excess of potassium iodide. [Cf. *B.*, Nov. 27th.]

D. G. H.

**Simple Apparatus for the Determination of Carbon Dioxide.** G. WITTIG (*Ber.*, 1925, **58**, [B], 1925).—An apparatus for the rapid,

accurate determination of carbon dioxide in carbonates is described and figured.  
H. W.

**Detection of Sodium as Oxalate.** L. W. WINKLER (*Pharm. Zentr.*, 1925, **66**, 669—670).—The conditions under which a precipitate is obtained on addition of a potassium oxalate solution to solutions containing various sodium salts are described. The test is best carried out in an alcohol-water solution containing 30% of alcohol by volume; a solution containing 2 mg. of sodium per c.c. gives an oxalate precipitate in 10 mins.  
S. I. L.

**Sodium Rhodizonate as a Reagent for Barium, Strontium, and Lead.** I. M. KOLTHOFF (*Pharm. Weekblad*, 1925, **62**, 1017—1020).—Solutions of sodium rhodizonate decompose on keeping in air. Fresh neutral solutions can be employed to detect lead, strontium, and barium in neutral solutions, but the utility of the reagent is limited. The sensitiveness to barium and strontium is much increased by addition of alcohol, 2 mg. of barium and 10 mg. of strontium per litre being detectable.  
S. I. L.

**Separation from Calcium of Magnesium, Iron, Aluminium, and Phosphoric Acid.** W. F. JAKÓB (*Rocz. Chem.*, 1925, **5**, 159—172; cf. this vol., ii, 69).—The addition of ammonium citrate to solutions containing calcium, in the presence of magnesium, trivalent metals, and phosphates, causes the calcium oxalate precipitated by the addition of ammonium oxalate to crystallise in octahedra of the approximate composition  $\text{CaC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$ . In this form, calcium oxalate does not tend to form solid solutions with magnesium oxalate, isomorphous with the monohydrate obtained in the absence of citric acid. Citric acid, further, owing to its tendency to the formation of complex ions, to a certain extent inhibits the precipitation of impurities such as iron, aluminium, phosphates, and magnesium. 200—300 C.c. of a faintly acid solution containing from 0.02 to 0.3 g. of calcium are treated with 20—25 c.c. of 10% ammonium citrate solution and warmed to 40—50°. A slight excess of 3% ammonium oxalate solution is then added, and the precipitate of  $\beta$ -hydrate collected, and boiled with dilute feebly acid citrate solution, thereby converting the precipitate into the stable monohydrate, and incidentally freeing it from impurities. The calcium is then determined as oxide.  
R. T.

**Detection of Minute Quantities of Material at Very Great Dilution.** F. L. HAHN (*Festschr. Physikal. Verein, Frankfurt a.M.*, 1924; from *Chem. Zentr.*, 1925, ii, 75).—Tincture of alkanet which contains hydroxyanthraquinones gives colour changes with many metals, including magnesium, which can be recognised by alterations in the absorption spectra. 1 : 2 : 5 : 8-Tetrahydroxyanthraquinone (quinalizarin) gives a bluish-violet solution in alkalis, which changes to a cornflower-blue in the presence of small quantities of magnesium and gives a blue precipitate with larger quantities. Ammonium salts mask or hinder the reaction. The test is sensitive to 1  $\mu\text{g.}/\text{c.c.}$  in the cold and 0.5  $\mu\text{g.}/\text{c.c.}$  when hot. The diphenylamine reaction for nitrates is not specific. A nitrate

is reduced to nitrite by lead salts and metallic lead and then detected by the diazo reaction. The reagents must be absolutely free from nitrate. The water is boiled with zinc dust and distilled. The lead and lead salt are obtained by strongly heating lead formate. A little of the solution to be tested is heated with some of the powder for 15—30 mins. at  $100^{\circ}$ , poured off from the lead, and treated with the diazo reagent (sulphanilic acid or  $\alpha$ -naphthylamine in acetic acid). Using 1—2 c.c. solution, 1 mg. of nitrate per litre gives a strong red and 0.1 mg. a distinct rose coloration. The diazo reagent is made more stable by using more than the usual amount of acetic acid and adding a suitable quantity of marble. If kept in a bottle filled with a stopcock tube, the quantity required may be obtained by the pressure of the carbon dioxide. A powder form of the reagent is obtained by mixing sulphanilic acid with acetnaphthylamide. This is boiled with acid or alkali just before using. The action of copper as an accelerator in the reaction between ferric salts and thiosulphate (resulting in ferrous salts and tetrathionate) can be used as a delicate qualitative and quantitative method for copper (cf. A., 1924, ii, 412). The disappearance of the ferric iron is followed by means of thiocyanate and the sensitiveness of the reaction raised to 0.03  $\mu$ g. in 25 c.c. A. C.

**Permanent Standards as a Possible Source of Error in Iron Determinations.** E. S. HOPKINS (*Ind. Eng. Chem.*, 1925, **17**, 832).—The determination of small amounts of iron in water by the procedure given in "Standard Methods of Water Analysis" (American Public Health Association) is liable to error for two reasons: (i) the cobalt chloride used in making up the standard solution may not be pure, and (ii) the Nessler tubes used may not be of an appropriate shape or capacity, the tints observed in different concentrations being differently related to one another in different sizes and shapes of tubes. The colour standards should be checked against actual iron solutions. W. A. S.

**Separation of Tantalum from Niobium, and Detection and Determination of Tantalum in Niobium Compounds.** A. R. POWELL and W. R. SCHOELLER (*Analyst*, 1925, **50**, 485—498).—Tantalum and niobium may be separated by a method depending on the differential hydrolytic dissociation between oxalotantalic and oxalonibic acids in the presence of tannin in slightly acid solution, and the method may be modified to allow of the detection and determination of small quantities of tantalum in niobium compounds. The two elements may be identified in admixture by the characteristic colours of the precipitates produced. [Cf. B., Dec. 11th.] D. G. H.

**Determination of Urobilin and Urobilinogen.** A. J. L. TERWEN.—(See i, 1351.)

**Determination of Uric Acid in Blood.** M. DELAVILLE and C. M. JONES.—(See i, 1344.)

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## General, Physical, and Inorganic Chemistry.

### Excitation of the Hydrogen Spectrum by Electron Impact.

P. M. S. BLACKETT and J. FRANCK (*Z. Physik*, 1925, **34**, 389—401).—The four possible modes of explaining the atomic spectra are: (1) The molecule is directly split up by the impact into a normal and an excited atom. (2) The molecule is excited by the impact and dissociated into a normal and an excited atom by collision while still in the excited state. (3) Normal free atoms produced by the discharge may be excited by the impact of an electron. (4) Atoms may also be excited by absorption of radiation, by collision with positive ions, and by successive collisions with electrons. The experiments show that electrons possessing sufficient kinetic energy can dissociate, in one elementary act, a normal hydrogen molecule into a normal atom and an excited atom. The broadening of the Balmer lines due to the Döppler effect is greater in this case than when free atoms are excited, owing to the great velocity with which the atoms separate in dissociation. A suggestion is made, with some reserve, that the impact of electrons may result in dissociation into two normal atoms, the excess energy being radiated as a continuous emission stretching from the far ultra-violet down to long wave-lengths.

E. B. L.

### Absorption of the Balmer Lines in Hydrogen. R. V.

JOLOWICZ (*Phil. Mag.*, 1925, [vi], **50**, 1089—1096).—Attempts have been made to observe absorption of the Balmer lines by hydrogen subjected to bombardment by electrons. Electrons from a glowing filament were accelerated by an electric field through a grid into a field-free space between the grid and a metal plate. A beam of light passed through the tube between grid and plate into a spectroscope, and was observed directly and also photographed. Experiments were carried out both with white light and with light from a hydrogen tube. Neutral glass wedges were used for the comparison of intensities (Nicholson and Merton, A., 1916, ii, 461). No trace of absorption was observed even with a specially designed apparatus in which a column of hydrogen 25 cm. long was subjected to electron bombardment. It is concluded either that the number of hydrogen atoms with electron moving in the second orbit is too small to produce absorption effects under the conditions of experiment, or that the ionisation is molecular, unaccompanied by dissociation.

A. B. M.

**Fine Structure of Hydrogen Lines.** G. HANSEN (*Physikal. Z.*, 1925, **26**, 678—680).—The structure of  $H_\alpha$  is the simplest case to which the relativistic fine structure can be applied. The author has used a long tube (cooled in the centre by liquid air) containing electrolytic hydrogen through which direct current is passed. The



measurements were made by a Lummer-Gehrcke plate and a registering photometer. For  $H_\alpha$ , in the short-wave group the records indicate a definitely unsymmetrical distribution of intensity among the components in the sense that the shorter wave is more intense. The effect is shown under widely diverging conditions. The value of  $\Delta\nu$  definitely increases for the lines  $\alpha \rightarrow \beta \rightarrow \gamma$ . The intensity ratio  $I_{\text{short-wave}}/I_{\text{long-wave}}$  of the doublet groups is dependent on pressure and current density, especially so in the case of  $H_\alpha$ ; e.g., at  $p=0.13$  and current density 0.039 the ratio is 1.05, whilst at  $p=0.015$  and current density 0.047 the ratio is 1.29. The separation  $\Delta\nu$  is 0.317/cm. The results are discussed theoretically.

R. A. M.

**Theory of the Fine Structure of H and He<sup>+</sup> Lines.** L. B. HAM (*Physical Rev.*, 1924, [ii], **23**, 107).—Application of Glitscher's method (*Ann. Physik*, 1917, [iv], **52**, 608) gave a value for the hydrogen doublet of the Balmer series twice that given by relativity. Similarly, results for the *L*-doublets of the X-ray spectra were incompatible with experimental values; Kunz's electromagnetic emission theory (*Physical Rev.*, 1914, [ii], **3**, 464) gives the same results as relativity. The mass variation of the electron in jumping from orbit to orbit is considered.

A. A. E.

**Recent Results in the Investigation of Fine Structure.** E. GEHRCKE (*Physikal. Z.*, 1925, **26**, 675—677; cf. A., 1921, ii, 565; 1922, ii, 3, 726; *Ann. Physik*, 1924, [iv], **74**, 575).—The fine structure of the Balmer lines of hydrogen shows that the relative intensity of the component lines can vary. This variability is greatest for  $H_\alpha$  and decreases with higher values for the series-term. In a tube 3 cm. wide at a pressure less than 0.1 mm.,  $H_\alpha$  is weaker than  $H_{\alpha_1}$ , whilst in a tube 1.5 mm. wide at a few mm. pressure  $H_\alpha$  is weaker than  $H_{\alpha_1}$ . By decreasing the pressure and somewhat narrowing the tube, the intensities of  $H_{\alpha_1}$  and  $H_\alpha$  can be made approximately equal. The relative intensity of the two components can therefore be altered at will without profoundly influencing line breadths in the entire system. The experimental separation of  $H_{\alpha_1}$  and  $H_\alpha$  is  $\Delta\lambda=0.128 \text{ \AA}$ . ( $\Delta\nu=0.296/\text{cm.}$ ).

An investigation of the fine structure of helium lines, especially the 4686 line, has been compared with Sommerfeld's theoretical classification. The three strongest components of the permitted lines show a separation in agreement with the theoretical predictions. The intensities of the other lines cannot, however, be reconciled with theory. Setting on one side the selection principle, the separation of the strongest lines leads to a lower value of  $\Delta\nu$ . Deviations of the same type from the requirements of theory have been observed by Bowen and Millikan for the doublet separation of Mg II, Al III, and S VI (this vol., ii, 252, 342). Therefore the lower value of  $\Delta\nu$  for helium is not without strong evidence. The experimental results are compared with earlier work by Paschen. The work is discussed with special reference to the 4686 line of helium, by Pachen, Joos, Sommerfeld, Smekal, and the author.

R. A. M.

**Spectrum of "Nebulium."** H. B. LEMON (*Physical Rev.*, 1924, [ii], 23, 766—767).—A study of 35 lines, of unknown origin, included in the spectra of the nebulae. A. A. E.

**New Combination Series in the Helium Spectrum.** J. S. FOSTER (*Physical Rev.*, 1924, [ii], 23, 293).—Direct measurements of wave-lengths of lines of the series  $1P-mP$ ,  $1P-mF$ ,  $1P-mG$ ,  $1P-mH$ , etc. for  $m=4$  to 6 differ in only one case by more than  $0.2 \text{ \AA}$ . from the calculated values. With higher fields, lines belonging to the series  $1S-mD$ ,  $1S-mF$ ,  $1S-mG$ , etc. have been recognised. A. A. E.

**Low-voltage Arc in Oxygen.** L. L. LOCKROW (*Physical Rev.*, 1924, [ii], 23, 553).—The critical potential for an ionisation process is 16.1 volts. The spectrum at 22 volts shows the negative bands, lines of the triplet system, and the one line  $4368 \text{ \AA}$ .,  $1S-3P$ , of the singlet system. A. A. E.

**Absorption in Excited Gases.** K. W. MEISSNER (*Physikal. Z.*, 1925, 26, 687—689).—In a mixture of neon and helium some strong lines suffer little or no absorption, whilst other equally intense lines are very strongly absorbed. For neon, lines requiring  $1s_3$  and  $1s_5$  terms are strongly absorbed and the  $1s_2$  and  $1s_4$  states are only weakly absorbed. The  $1s_3$  and  $1s_5$  states must therefore exhibit relatively long life-periods. The results are in good agreement with the term-scheme of neon. The work has been extended to argon. Similar differences in absorption are observed, but the series classification is as yet too defective to allow of rigorous conclusions. The work on neon has been extended in an ingenious manner, whereby the life-period of the  $S_5$  state has been calculated on the basis of the lines  $6402$ ,  $6143 \text{ \AA}$ ., and the value  $0.0038 \text{ sec}$ . obtained. The life-period of the  $S_3$  state is markedly shorter and more difficult to estimate. R. A. M.

**Red Neon Lines.** K. BURNS (*J. Opt. Soc. Amer.*, 1925, 11, 301—310).—The results from sixty-eight plates measured at the Allegheny Observatory indicated no appreciable change in the relative values of the mean wave-lengths of the red neon lines given by the Bureau of Standards. From their agreement amongst themselves and with the results of other observers, it is concluded that the Bureau of Standards values are sufficiently accurate to warrant the expressing of their means to  $0.0001$ . Under the observational conditions, the lines examined showed no complexities which interfered with the accuracy of measurement with orders of intensity up to 100,000. A. E. M.

**Distribution of Energy over the Lines of the Main Series of Neon in a Column Discharge.** H. B. DORGELO (*Physica*, 1925, 5, 90—100).—In a neon column (7 mm. pressure) with 350 volts and 50 milliamp., the energy is radiated practically entirely as  $2p-2s$  and  $2s-1s$  light. Values of the effective candle power are obtained by multiplication of the intensity of each line with the eye sensitivity factor for its wave-length. In the circumstances a

total 1.23 spheric candles per watt was calculated; direct measurement with a flicker photometer gave 1.66 spheric candles/watt. The average intensities of the multiplet components agreed with the intensity rules previously given; the energy distribution was, however, materially different from that in an excitation tube.

CHEMICAL ABSTRACTS.

**Spectrum of Singly Ionised Silicon.** M. SAHA (*Nature*, 1925, **116**, 644).—Certain lines, ascribed by Fowler to singly ionised silicon, but not included in his scheme of classification, can be arranged in a group of quadruplets. A. A. E.

**Chlorine Spectrum in the Extreme Ultra-violet.** J. J. HOPFIELD (*Physical Rev.*, 1924, [ii], **23**, 766).—Many new strong lines have been observed, as well as lines corresponding with those occurring in the vacuum spark spectrum. A new group of bands of aluminium chloride was observed at 2620 Å. A. A. E.

**Arc Spectrum of Titanium from 7496 to 2273 Å.** K. BEHNER (*Z. wiss. Phot.*, 1925, **23**, 325—341).—Using titanium sulphate in the arc between copper electrodes, about 1330 lines between wave-lengths 7496 and 2273 were measured. Wave-lengths are given to 0.001 Å., the maximum mean error being seldom more than 0.002 Å. Data of intensities of lines and of regular groups of multiplets are given. Nearly all the lines described by earlier workers were found, and in the ultra-violet a number of arc lines were measured which previously were considered to be spark lines. The new are compared with older measurements, with the view of reducing the Rowland values to the international system. From a comparison of Rowland's original values with his own, the author presents a new "error" curve, in which the correction curves of Kayser and Hartmann are also included for comparison. Marked deviations from both correction curves are found, although in some regions the agreement with either the Kayser or the Hartmann curve is good, so that for titanium neither can be considered the better. Individual lines show a marked deviation, and in general these are the lines for which Rowland found extreme values. Although a conversion from the Rowland to the international system is possible on the average, it is not so for individual lines. The author's results are compared with those of other workers, in particular with those of Crew (*Astrophys. J.*, 1924, **60**, 108—121). Crew's method of graphical interpolation for measuring his plates does not give the highest degree of accuracy. W. C.

**Vacuum Spark Spectrum of Zinc in the Region 2100—4000 Å.** R. A. SAWYER and E. J. MARTIN (*Physical Rev.*, 1924, [ii], **23**, 766).—In addition to 250 new lines, all the spark lines given by Exner and Haschek appeared, but of the arc spectrum only the subordinate triplets  $2p-3s$ ,  $2p-3d$ , and  $2p-4d$  appeared with considerable intensities. The new lines are grouped to some extent in the regions 2400—2700 Å. and 3500—4000 Å. A. A. E.

**Infra-red Line Spectrum of Zinc and Cadmium.** H. M. RANDALL and W. N. ST. PETER (*Physical Rev.*, 1924, [ii], **23**, 766).—The spectra of zinc and cadmium were examined in the region 1–5  $\mu$ . A. A. E.

**Change of Wave-lengths for certain Lines of Zinc, Cadmium, and Mercury in a Condensed Discharge.** M. FUKUDA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1925, **3**, 183–192).—When a condensed discharge was passed between metal poles in a fused silica Geissler tube, certain spectral lines were shifted. The shifts increased with the distance of a spark gap inserted in series with the discharge tube. Many spark lines appeared in the spectrum of the condensed discharge, increasing in number and intensity as the spark gap was widened. The appearance of these lines was accompanied by augmented displacements of some lines. The shifted lines generally belonged to the sharp series and the displacements were of the order of 1 Å. towards the red. Under comparable conditions for lines having the same notation, the magnitude of the shift was in the order: cadmium (highest), mercury, zinc. In most cases, the lines of the diffuse series were displaced towards the red, but a few, e.g., the yellow lines of mercury, were shifted in the reverse direction. It was concluded that the shift was due to the intermolecular electric field arising from close packing of ions and electrons in the capillary. R. A. M.

**Series Relations in the Spectra of Doubly Ionised Gallium and Indium.** J. A. CARROLL (*Physical Rev.*, 1924, [ii], **24**, 205).—The hot spark spectra of gallium, indium, thallium, and mercury have been examined from 500 Å. upwards. The principal pairs of the doublet systems of Ga III and In III are at 1495.2–1534.6 ( $\delta\nu=1720$ ) and 1625.3–1748.8 ( $\delta\nu=4350$ ), respectively, the outer electron being assigned a 4-quantum and a 5-quantum orbit. The line 1414.57 Å. is probably 1S–2P in Ga II. A. A. E.

**Structure of the  $K\alpha$  Lines of Molybdenum.** F. K. RICHTMYER and R. C. SPENCER (*Physical Rev.*, 1924, [ii], **23**, 550–551).—Energy-wave-length diagrams show that the line  $K\alpha_2$  is broader than  $K\alpha_1$ ; the width of the latter is probably not greater than 0.0003 Å. The distribution of energy over the focal spot is not uniform. A. A. E.

**Arc Spectrum Regularities for Ruthenium.** W. F. MEGGERS and O. LAPORTE (*Science*, 1925, **61**, 635–636).—The condensed spark under water shows 85 distinct absorption lines between 2255 and 4709 Å. The lowest term of ruthenium is 5-fold with the separations 392.2, 621.7, 900.9, 1190.8  $\text{cm}^{-1}$  and inner quantum numbers 0, 1, 2, 3, 4; it is regarded as a quintuplet  $D$ -term. The  $D$ -term combines with 46 or more higher levels, accounting for the majority of the strong lines in the ruthenium arc spectrum. In agreement with a general rule that the most sensitive lines of a spectrum always involve a quantum jump with  $\Delta K=1$ , the “raies ultimes,” 3436.74 and 3498.95 Å., occur also in a  $^5D$ – $^5F$  combination. A. A. E.

**Width of the  $K_{\alpha}$  Absorption Discontinuity in Silver.** F. K. RICHTMYER and R. C. SPENCER (*Physical Rev.*, 1924, [ii], **23**, 760—761).—An experimental verification of the conclusion that with a perfect crystal, a target of uniform energy distribution, and a slit system of angular width  $\alpha$ , then if the absorber has a perfectly sharp discontinuity showing no structure, (i) the width of the observed discontinuity should be  $\alpha$ , and (ii) the shape of the energy curve through the discontinuity should be made up of two parabolas.

A. A. E.

**Line Spectra of Tungsten and Nickel in the Afterglow of a Discharge through a Mixture of Nitrogen and Argon.** A. G. WORTHING and R. RUDY (*Physical Rev.*, 1924, [ii], **23**, 767).—With tungsten electrodes, two afterglows were obtained in a discharge through a mixture of argon (99.8%) and nitrogen (0.2%) at 300 mm.; the spectrum of the orange glow showed strongly the first and second groups of positive nitrogen bands, and that of the blue glow showed the tungsten lines superposed on a faint background consisting of a continuous spectrum and nitrogen bands. In the conditions favouring the latter, a dark deposit, probably tungsten nitride, is formed. With nickel electrodes, the blue glow gave place to a green one showing strong nickel lines. Glows obtained in pure nitrogen were much feebler. No argon lines were observed during the discharge or in the afterglow.

A. A. E.

**Excitation Function of the Mercury Spectrum.** J. A. ELDRIDGE (*Physical Rev.*, 1924, [ii], **23**, 294).—For low pressures and currents, ionisation plays an unimportant rôle in spectrum excitation. Lines which originate in electrons falling from an  $S$ ,  $D$ , or  $d_2$  orbit become stronger, and those from an  $s$ ,  $d_1$ , or  $d_3$  orbit weaker with increasing energy of the primary electrons.

A. A. E.

**Behaviour of Mercury Arc Lines after Removal of the Exciting Potential.** L. J. HAYNER (*Physical Rev.*, 1924, [ii], **23**, 294).—The line 2537 Å. was particularly strong in the after-spectrum, and exhibited also a second type of persistence between 40° and 200°. Its rate of decay appeared to determine the interval between the extinction of the arc lines and their reappearance. Principal series lines were not found in this after-spectrum. The extinction of the arc lines immediately after removal of the potential is probably due to absorption by excited atoms in the  $2p$  state (Kurth, *ibid.*, 1923, **22**, 202).

A. A. E.

**Excited Atoms in the Striated Glow Discharge in Mercury Vapour.** W. H. MCCURDY, L. A. TURNER, and K. T. COMPTON (*Physical Rev.*, 1924, [ii], **23**, 776).—It is suggested that ionisation in the striations is cumulative, depending on the existence of  $2p_{1,2,3}$  excited atoms; the action of slight impurities, only in presence of which striations are possible, is to reduce the concentration of these excited atoms and prevent their diffusion into the dark spaces. The metastable states  $2p_{1,2}$  are relatively most prominent; absorption involving inter-system transitions is less probable than that in one system.

A. A. E.

**Completion of the Series in the Arc Spectrum of Lead.** H. GIESELER and W. GROTRIAN (*Z. Physik*, 1925, **34**, 374—388).—The spectrum was excited by a stream of electrons from a glowing filament in a long silica tube containing lead and surrounded by an electric furnace. Many new lines were found and measured. Several new series were found, of which two are the diffuse and sharp series with a  $P_o$  term, and two others are described as combinations  $pf$  and yield a calculation of a Bergmann series.

E. B. L.

**X-Ray Absorption Coefficients in the Neighbourhood of  $K$ -Limits.** F. W. WARBURTON and F. K. RICHTMYER (*Physical Rev.*, 1924, [ii], **23**, 291—292).—Atomic absorption coefficients on both sides of the respective  $K$ -limits have been determined for molybdenum, silver, tin, tungsten, gold, and lead. Values of  $kN^4\lambda^3$  in  $\mu_a = kN^4\lambda^3 + \sigma_a$  are proportional to  $N^4/(N-b)^6$  when in the expression  $\sqrt{\mu} \propto (N-b)$ ,  $b=7$ ; the change in the values on passing the  $K$ -limit decreases as  $N$  becomes large. For elements of higher atomic number, a smaller proportion of the absorbed energy is radiated as  $K$  fluorescence radiation.

A. A. E.

**X-Ray Spectra from a Ruled Reflection Grating.** A. H. COMPTON and R. L. DOAN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 598—601).—Spectra of ordinary X-rays have been obtained by reflection at very small glancing angles from a grating of space  $2 \times 10^{-3}$  cm., ruled on speculum metal. Measurements made with this grating gave as the wave-length of the molybdenum  $K\alpha_1$  line  $0.707 \pm 0.003$ , which is in good agreement with the value  $0.7078 \pm 0.0002$  Å. obtained by crystal measurement. Measurement with a copper target gave wave-lengths of 1.4—1.5 Å. or values intermediate between the  $\alpha$  and  $\beta$  lines of copper.

A. E. M.

**Zeeman Effect on the Helium Bands.** W. E. CURTIS and W. JEVONS (*Nature*, 1925, **116**, 746—747).—The band near 4650 Å. has been studied, using magnetic fields up to 20,000 gauss; many other band lines also appear on the plates. The band lines exhibit no Zeeman effect of a "normal" order of magnitude, except in the case of the first member of each of the three branches, *i.e.*,  $Q(1)$ ,  $R'(1)$ , and  $P(2)$ , which are broadened, but not resolved into components. In  $Q(1)$  and  $P(2)$ , the component corresponding with vibrations parallel to the field is much broader than the "perpendicular" component, the reverse being the case for  $R'(1)$  and for series lines. The effect is greatest in  $Q(1)$ , of which the extreme width in a field of about 20,000 gauss corresponds with a separation of about 0.27 Å. The effect of the magnetic field on the molecule is largely determined by the state of rotation of the latter, being relatively small for the higher speeds of rotation.

A. A. E.

**Fine Structures of Spectrum Lines.** A. E. RUARK and R. L. CHENAULT (*Phil. Mag.*, 1925, [vi], **50**, 937—956).—The fine structure of spectral lines arising from complex levels, *i.e.*, levels with several components all characterised by the same total, azimuthal, and

inner quantum numbers, is discussed. An analysis is made of nearly all the available data on fine structures. It is shown that the fine structures examined cannot be due to isotopy. They are due probably to slight quantised variations in the configuration of loosely bound underlying electron shells. In the case of thallium, a fine quantum number  $f$  may be introduced, with a selection principle to govern its changes, but for other elements no selection principle has been discovered. Fine structures have proved to be an aid in classifying spectral lines.

A. B. M.

**Primed Terms in the Spectra of the Lighter Elements.** O. LAPORTE (*J. Washington Acad. Sci.*, 1925, **15**, 409—413).—A theoretical paper in which the work of Millikan and Bowen (this vol., ii, 916) is criticised. These authors consider that if the atom of aluminium is in its normal state, two of its electrons are in  $3s$ , one in  $3p$  orbits obtaining the  $2P'$  state when one electron is in  $3s$  and two are in  $3p$ . It is in contradiction with the alternation law to have several electrons in the same  $s$  or  $p$  orbit and moving in the same doublet-energy diagram. A new explanation is put forward in which the arc spectrum is built up from the spectrum of the ionised atom. Further considerations clarify the position with regard to the fact that  $pp'$  groups follow the irregular doublet law.

R. A. M.

**Summation Rules for the Intensities of Spectral Lines.** R. H. FOWLER (*Phil. Mag.*, 1925, [vi], **50**, 1079—1083).—A theoretical discussion of the summation rules of Ornstein, Burger, and Dorgelo for the intensities of the components of complex lines (A., 1924, ii, 282, 361, and 433). It is shown that if the intensities are reckoned in numbers of quanta per second, then the summation rules ought to be fulfilled to the degree of accuracy with which the Fourier coefficients of the original electronic system are left unaltered by the superposed perturbation which splits the radiation up into the associated group of lines.

A. B. M.

**Explanation of Complex Spectra. II.** F. HUND (*Z. Physik*, 1925, **34**, 296—308; cf. this vol., ii, 912).—The elements in the fourth and fifth groups of the periodic system are chiefly considered, and a scheme is developed indicating to which series limit the single terms of the multiplets correspond by transition to higher orbit numbers. The spectrum of neon is also discussed and the bearing of the Zeeman effect.

E. B. L.

**Minimum Velocity of Impact to Produce Secondary Electrons from Tungsten.** O. STUHLMAN, jun. (*Physical Rev.*, 1924, [ii], **23**, 296—297).—The minimum potential for tungsten is 3.72 volts.

A. A. E.

**Post-arc Conductivity and Metastable Helium.** C. ECKART (*Physical Rev.*, 1925, [ii], **26**, 454—464).—The abnormal conductivity observed by Kannenstine to persist for 0.007 sec. after the extinction of an arc in helium is not due to metastable excited helium atoms, but to positive ions and accompanying electrons. The only

evidence in favour of a very long life ( $10^{-2}$  to  $10^{-3}$  sec.) of metastable helium atoms is therefore inadmissible, although the metastable states in helium have a longer life than other excited states.

A. A. E.

**Mechanics of Electrons and Light Quanta.** K. SCHAPOSCHNIKOV and W. S. FEDOROV (*Z. Physik*, 1925, **34**, 402—405).—Theoretical.

E. B. L.

**Chemical Statics of Electronic Phenomena.** L. ROLLA and G. PICCARDI (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 173—177).—It follows from the principle of mobile equilibrium, since it has been shown that the potential of ionisation of elements is independent of temperature, that the logarithm of the electronic equilibrium constant, at constant temperatures, should be a linear function of the heat of ionisation. This latter, further, is proportional to the ionising potential. This linear relation is shown to hold for a number of elements for which the values of the ionising equilibrium constant and the ionisation potential were known. The slope of the line obtained by plotting  $\log K$  against the ionisation potential indicates that only those elements the ionising potentials of which are below 8 volts may be expected to show ionisation in a Bunsen flame. The above relationship is used to calculate the ionising potentials of barium, strontium, copper, and molybdenum from observations of their flame spectra. The calculated values are in accord with those determined by other methods.

F. G. T.

**Predicted Ionisation Potentials of Niton [Radon] and Hydrofluoric Acid.** G. GLOCKLER (*Phil. Mag.*, 1925, [vi], **50**, 997—1001).—By extrapolation of the ionisation potential—atomic number curve for the rare gases, the ionisation potential for radon is found to be 10 volts. From Eve's rule, that the product of ionisation potential and atomic radius is constant, and from the value for the atomic radius ( $2.80 \pm 0.25$  Å.) calculated from the diffusion coefficient in air, the ionisation potential is again calculated to be 10 volts. The ionisation potential of hydrogen fluoride, estimated by a method based on thermochemical considerations, is 15 volts. Both values differ from those obtained by Turner (A., 1924, ii, 797) on the basis of a linear relation between quantum defect and atomic number.

A. B. M.

**Structure of the Hydrogen Molecule Ion.** H. C. UREY (*Proc. Nat. Acad. Sci.*, 1925, **11**, 618—621).—When the condition of dynamic stability is ignored, the steady state of lowest energy of the ionised hydrogen molecule is that in which the electron vibrates in a straight line perpendicular to the line joining the nuclei at its mid point. The energy of this state has been calculated and a formula obtained by means of which values for the ionisation potential of the molecule and critical potentials of the hydrogen atom have been calculated. These are in agreement with the determinations of Olson and Glockler (A., 1923, ii, 455), whose results are explained. The heat of dissociation of the hydrogen molecule and its moment of inertia calculated from this model are



in agreement with the results of other investigators. It is predicted that there should be an ultra-violet spectrum of the ionised hydrogen molecule, free from that of the neutral molecule, in the region 850—714 Å.

A. E. M.

**Probability of Ionisation of Gas Molecules by Electron Impacts.** K. T. COMPTON and C. C. VAN VOORHIS (*Physical Rev.*, 1925, [ii], 26, 436—453).—Values as follows are tabulated for  $N$ , the number of ions per cm. path produced by an electron moving through a gas at 1 mm. pressure,  $V_a$ , the maximum accelerating potential, and  $P$ , the corresponding probability that a collision will result in ionisation of the hit molecule:—hydrogen, 3.55, 145, 0.29; helium, 1.65, 210, 0.209; neon, 3.2, 340, 0.254; argon, 10.33, 140, 0.466; nitrogen, 9.96, 175, 0.423; mercury, 19.44, 135, 0.239; hydrogen chloride, 17.3, 130, 0.558. The weak ionisation observed in nitrogen at 10 volts was possibly associated with the presence of active nitrogen.

A. A. E.

**Impact Ionisation by Low-speed Positive Ions.** M. A. TUVE (*Physical Rev.*, 1924, [ii], 23, 111).—Positive ions produced by electronic collision in mercury vapour were caused to collide with mercury atoms, and the electron current in the ionisation chamber was measured. The current was again measured when positive ions or  $\delta$ -rays were prevented from entering the chamber. The ratio of the difference to the total current was measured, giving definite upper limits of the amount of impact ionisation.

A. A. E.

**Spectroscopic Evidence of Impact Ionisation by Positive Ions in Mercury Vapour.** J. T. TATE (*Physical Rev.*, 1924, [ii], 23, 293—294).—When positive sodium ions are accelerated at more than 40 volts into an ionisation chamber containing mercury vapour, both sodium and mercury arc lines appear. The ionising potential was not necessarily critical for positive ions, but impact ionisation by positive ions is indicated. When positive mercury ions were accelerated into the chamber at above 70 volts, mercury arc lines appeared.

A. A. E.

**Impact Experiments in Compound Gases. Ammonia.** (MISS) A. T. WALDIE (*J. Franklin Inst.*, 1925, 200, 507—518).—Ammonia has been shown to possess a critical ionisation potential at about 11 volts. The result was obtained both with photo-electrons and with thermions. With photo-electrons, the results indicate that the dissociation through ultra-violet light is slow, and that of the dissociation products hydrogen is more or less effectively removed by the nickel which was used as the electron source. In the thermionic experiments, the critical points determined in the direct region of the filament were principally those of hydrogen, indicating that, in that region, the ammonia is almost completely dissociated. Only when arrangements were made so that the electron impacts occurred at some distance from the filament could the above value for the ionisation potential be obtained.

A. E. M.

**Theory of Electrodeless Discharge in Gases.** P. LASAREV (*Bull. Acad. Sci. St. Pétersbourg*, 1919, [6], 127—132; from *Chem. Zentr.*, 1925, ii, 519).—The author derives formulæ for the ionisation and fluorescence of gases in electrodeless discharge, on the assumption that the number of ionised atoms is proportional to the total number of atoms and the strength of the field, and that the formation of molecules from ions (molisation) is a unimolecular reaction. G. W. R.

**Mobility of Argon and Hydrogen Ions in Air.** H. A. ERIKSON (*Physical Rev.*, 1925, [ii], 26, 465—468).—Two positive ions and one negative ion were found in both cases, and in that of air. In the case of hydrogen, and probably also with argon, the initial positive ion becomes transformed into the second. Initial positive and negative ions of argon, air, and carbon dioxide, and the initial positive ion of hydrogen, have the same mobility in air at normal pressure; negative hydrogen ions possess an unexpectedly larger mobility. A. A. E.

**Photo-electric Action of Total Radiation of a Solid Body.** A. BECKER (*Ann. Physik*, 1925, [iv], 78, 83—111).—The photo-electric action of light from an incandescent tungsten ribbon on an aluminium plate was investigated. The number of electrons emitted is related to the absolute temperature of the source of radiation by the formula  $n = \text{const.} \times \theta^x e^{-c/\lambda_0 \theta}$ ;  $x$  is greater than 2, and probably between 3 and 4. The distribution of velocities in the photo-electrons is identical with that of electrons emitted by hot bodies. The most probable velocity of escape is proportional to the absolute temperature of the radiator and of the same order of magnitude as for thermionic emission. The optical properties of the metal (absorption) do not affect the distribution of velocities, and the absolute value of the velocities only slightly.

E. B. L.

**Magnetism and the Structure of Atoms and Molecules.** B. CABRERA (*J. Phys. Radium*, 1925, [vi], 6, 241—258).—It is possible on the basis of a formula due to Larmor to calculate the mean radius of the electronic orbits of an atom from its magnetic susceptibility. By adopting the Bohr scheme of stable atomic levels, true atomic radii can be calculated which apply even to the "surface" of the atom. The magnetic susceptibility and certain derived constants exhibit the Mendeléev periodicity exceedingly well. From the values of  $\chi_A$  (atomic susceptibility) found by Pascal (A., 1914, ii, 618, 764) and Hector (A., 1924, ii, 854) the following atomic radii have been calculated:  $r_A \times 10^8$ , helium 0.57, neon 0.54, argon 0.85, krypton 1.03, xenon 1.44; for ions of the argon type, the following values are deduced: phosphorus ( $P^{+++}$ ) 1.37, 1.11; sulphur ( $S^{++}$ ) 1.13, 1.01; chlorine ( $Cl^+$ ) 0.98, 0.92; argon 0.85; potassium ( $K^+$ ) 0.76, 0.80; calcium ( $Ca^{++}$ ) 0.69, 0.74. The results are in good agreement with those obtained by Fajans, Grimm, and Herzfeld by a different procedure (A., 1921, ii, 168, 174). The values for the atomic radii of the rare gases obtained

by Jeans on the basis of the kinetic theory are about twice those obtained by the author. The results of Bragg (A., 1920, ii, 537) are not in agreement. By employing Sommerfeld's model for the hydrogen molecule, the author deduces from  $\chi_4$  its moment of inertia and the value  $1.6 \times 10^{-40}$  is of the right order.

Dia- and para-magnetism are discussed in the light of modern atomic theory, and special consideration is given to Sommerfeld's interpretation of the Gerlach-Stern experiments. The author affirms that (a) The Bohr magneton is the natural unit of the magnetic moment of a free electronic orbit. (b) The Weiss magneton is the highest common factor of the magnetic moments of all electronic orbits and is therefore the unit applicable to cations and paramagnetic atoms. The two magnetons are probably related, the Bohr magneton being nearly five times the Weiss magneton. (c) Free atoms orient themselves under the action of an external field according to the principle of space-quantisation. Free orientation cannot occur in solutions or in solids. The data lead to the rejection of interpretations of the paramagnetism of cations based on the Bohr magneton and on the form of quantisation suggested by Pauli and Sommerfeld. The real existence of the Weiss magneton is confirmed. The orientation should be regarded as that of the magnetic axis rather than the atoms themselves. The real explanation is probably similar to that of Ehrenfest, which involves a reversal of the direction of movement of an electron in its orbit, and a distribution of the two movements governed by the Boltzmann probability law. This idea of reversal should be replaced by that of the constancy of the magnetic moment. The electronic orbits will then be distributed so that the resultant magnetic moment will always be a definite multiple of the Weiss magneton. To explain the effect of temperature on paramagnetism it is suggested that the orientation of the magnetic axis follows from the reorganisation of superficial electronic levels after collisions. R. A. M.

**Separation of Chlorine into Isotopes (Isotopic Elements) and the Whole Number Rule.** W. D. HARKINS (*Proc. Nat. Acad. Sci.*, 1925, **11**, 624—628).—Evidence in support of the whole number rule for the atomic weights of isotopes (Harkins and Wilson, A., 1915, ii, 543) has been obtained by the separation by diffusion of hydrogen chloride to give a lighter fraction in which the atomic weight of the chlorine was 35.4177, or 0.04 unit lighter than ordinary chlorine. The separation thus obtained amounts to 60% of that indicated by the theory. A. E. M.

**Isotopic Composition of the Element Chlorine: The Atomic Weight of Meteoric and Terrestrial Chlorine.** W. D. HARKINS and S. B. STONE (*Proc. Nat. Acad. Sci.*, 1925, **11**, 643—645).—Determinations of the atomic weight of chlorine obtained from a meteorite, and from rocks of non-marine origin such as wernerite, apatite, and sodalite, gave the same results as ordinary chlorine found on the earth. It is concluded that the chlorine from the three sources has the same isotopic composition. It is

suggested that this result in conjunction with that of Baxter for nickel indicates that elements had originally the same isotopic composition as they have at present, or that the composition has changed at the same rate in all localities. A. E. M.

**Isotopic Composition and Atomic Weight of Chlorine in Meteorites.** A. W. C. MENZIES (*Nature*, 1925, **116**, 643—644).—The atomic weight of chlorine from the "shale balls" associated with the Canyon Diablo, Arizona, meteorite, is identical with that of "ordinary" chlorine to within 1 part in 2000 parts, which is within the estimated experimental error. The extra-terrestrial nature of this chlorine and of that examined by Harkins and Stone (cf. preceding abstract) remains in doubt. A. A. E.

**Isotopes of Lead.** H. BRENNEN (*Ann. Chim.*, 1925, [x], **4**, 127—155).—A fuller account is given of earlier work (this vol., ii, 174) with a review of the literature. The author has repeated the work of Dillon, Clarke, and Hinchy (A., 1922, ii, 710) and of Atkinson (A., 1923, ii, 689) which claimed to make a partial separation of the isotopes of ordinary lead, and has found that with an experimental error of 0.01 in the determination of atomic weight these methods do not lead to any separation of isotopes. The values 206.19 and 206.14 have been obtained for the atomic weight of two samples of lead extracted from pitchblende from Belgian Congo. R. A. M.

**Radioactivity of Potassium, Rubidium, and other Elements.** W. D. HARKINS and W. G. GUY (*Proc. Nat. Acad. Sci.*, 1925, **11**, 628—630).—By balancing the natural leak of the ionisation chamber against that due to  $\beta$ - and  $\gamma$ -rays from uranium oxide, the absence of  $\beta$ -ray activity greater than  $3.3 \times 10^{-6}$  that of uranium was proved for the salts of fifteen elements and ten single elements. The measured activity of various potassium salts was found to be directly proportional to the amount of potassium present. The radiation from rubidium salts is not homogeneous. Rubidium is 1.39 times as radioactive as potassium, but the radiation from rubidium is ten to fifteen times less penetrating than that from potassium. The results indicate that the activities of rubidium and potassium salts cannot be traced to a common source such as the presence of radioactive impurities. The source of the radioactivity of potassium salts is discussed. A. E. M.

**Scattering of  $\alpha$ -Particles by Atomic Nuclei and the Law of Force.** (SIR) E. RUTHERFORD and J. CHADWICK (*Phil. Mag.*, 1925, [vi], **50**, 889—913).—The scattering of  $\alpha$ -particles by a number of elements has been observed. The angle of scattering was kept constant at  $135^\circ$ , and the velocity of the incident  $\alpha$ -particles was varied by the interposition of suitable mica screens. The number of particles scattered and the distribution of velocity in the scattered beam were observed. Within the accuracy of experiment, the results for gold, platinum, silver, and copper showed no deviation from the simple laws of scattering, which assume that the particles can be regarded as point charges and that the inverse

square law of force holds. The light elements, magnesium and aluminium, however, showed a marked departure from these laws. The scattering decreased as the energy of the incident  $\alpha$ -particles was diminished, falling to a minimum for particles of range about 5 cm. in air, increasing again, and approaching the theoretical value for particles of small range. The scattering by uranium was compared with that of gold, but showed no indication of a departure from the usual laws, although a fast  $\alpha$ -particle would be expected to penetrate deeply into the nuclear structure of the uranium atom. The scattering by gold, determined by Chadwick's method (A., 1921, ii, 7), over wide ranges of scattering angle and energy of incident  $\alpha$ -particles, was shown to be normal to within about 2%. The gold nucleus behaves as a point charge and the law of force is the inverse square for distances of approach between  $3.2 \times 10^{-12}$  and  $10^{-11}$  cm. The  $\alpha$ -particles scattered by aluminium are accompanied by protons liberated by disintegration of the aluminium nucleus. The evidence is at present insufficient to decide the fate of an  $\alpha$ -particle which succeeds in ejecting a proton from the nucleus. From experiments on the absorption of ejected protons, it is estimated that they acquire a minimum critical speed of about  $2.4 \times 10^9$  cm. per sec. in escaping from the nucleus. The scattering curves for aluminium and magnesium showed the same type of deviation from normal with a scattering angle of  $90^\circ$  as with one of  $135^\circ$ . Neither the assumption that the scattering may be governed by quantum conditions nor Bieler's assumption (*Proc. Roy. Soc.*, 1924, A, 105, 434) of an inverse fourth power law of attraction superimposed on the ordinary repulsion force appears adequate to account for the deviations observed. A tentative explanation of the experimental results is made, based on the assumption that the aluminium nucleus consists of a central charged core surrounded by a satellite distribution of positive and negative charges.

A. B. M.

**Penetrating Radiations Observed at Sea-level.** G. HOFFMANN (*Physikal. Z.*, 1925, 26, 669—672).—An apparatus has been devised employing very thick lead screens for registering the intensity of the penetrating radiations akin to  $\gamma$ -radiation. The results seem to prove that there is nothing mysterious about the penetrating character of these radiations at the sea-level and that the rays can be explained entirely as coming from known radioactive elements. A more detailed account is promised.

R. A. M.

**Measurements of Radioactivity.** C. MATIGNON and (MLLE.) G. MARCHAL (*Chim. et Ind.*, 1925, 14, 503—510).—An account of the methods used for the determination of radioactive material. The methods outlined depend on (1)  $\alpha$ -ray activity, (2) activity of radium emanation, and (3)  $\gamma$ -ray activity. The use of the gold-leaf electroscope, the chemical methods of opening up radioactive minerals, and the three types of apparatus used by Curie (*J. Physique*, 1912, [v], 2, 813) for  $\gamma$ -activity, are described and illustrated.

L. S. T.

**Half-value Period of Radium-E.** G. FOURNIER (*Compt. rend.*, 1925, 181, 502—504).—Bastings (this vol., ii, 9) found the period of

decay of radium-*E* to be 4.98 days instead of 4.85 days as found by Thaller (*Sitzungsber. Akad. Wiss. Wien*, 1912, **121**, 1611). Lead containing radium-*D* + *E* has been used. The separation of radium-*E* from this is described. The period of decay was measured by employing a piezo-electrometer, and for sources prepared in different ways the values 4.86, 4.86, and 4.84 days were obtained, confirming Thaller's value. R. A. M.

**Behaviour of Lead Containing Radium- $\Omega$  in the Formation of Formaldehyde by Thunberg's Method.** A. STOLFI (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 195—197).—By using lead carbonate, prepared from the radioactive mineral cotunnite, it has been found that the presence of radium- $\Omega$  is without influence on the preparation of formaldehyde by Thunberg's method (A., 1923, i, 1271). F. G. T.

**Photographic Action of H-Particles from Paraffin and Aluminium.** M. BLAU (*Z. Physik*, 1925, **34**, 285—295).—The impact of  $\alpha$ -particles on a paraffin film ejects hydrogen nuclei with high velocity. With polonium as the source of  $\alpha$ -particles of 4 cm. range, the H-particles produced an effect on a photographic plate similar to that of the  $\alpha$ -particles. When lamp-black was substituted for paraffin, little or no effect was obtained, which is to be expected, as there is no hydrogen present, and the disintegration of the carbon nucleus takes place to a very small extent only, if at all. With radium-*C* as source of  $\alpha$ -particles, the other radiations fogged the plates in spite of precautions taken to avoid this. E. B. L.

**Transmutation of Mercury to Gold.** H. NAGAOKA (*J. Phys. Radium*, 1925, [vi], **6**, 209—216; cf. this vol., ii, 835).—When a high-tension condensed discharge of 600,000 volts is passed between electrodes of mercury and tungsten wire, both of which are immersed in hydrocarbon oils, the very intense field causes artificial disintegration with production of a small quantity of gold. The mercury used was redistilled two or three times in a vacuum at temperatures below 200°, and control tests indicated the absence of gold from the product. After the discharge had been passed for several hours, the viscous black mass of carbon, oil, mercury, etc. was examined in various ways. Reliance was placed on the formation of ruby glass as a test for gold. Positive results were obtained. The gold appeared to be largely colloidal and adsorbed on the carbon. When the discharge is passed across drops of mercury falling between iron electrodes immersed in oil, both gold and a complex white metal (largely silver) are formed. The simultaneous production of gold and silver is significant because gold is usually found with silver rather than with mercury in terrestrial minerals. It is pointed out that if the isotopes of mercury are arranged in order of ascending mass number and 80 is subtracted from each number, the mass numbers of the isotopes of tin are found, so that the mercury nucleus may be regarded as compounded of krypton and tin nuclei. Krypton was not detected in the experiments. R. A. M.

**Structure of Cadmium.** H. COLLINS (*Chem. News*, 1925, **131**, 290—294).—Speculative; the structure of cadmium is deduced to be  $\text{Na}_2\text{Zn}$ .  
A. R. P.

**Force of Attraction and Repulsion in Atoms.** A. KORN (*Atti R. Accad. Sci. Torino*, 1925, **60**, 41—45).—A suggestion is made, based on the author's mechanical theory of gravitation, that, in addition to protons and electrons, atoms contain "gravitational" particles. These three constituents are of identical composition, and differ from one another only in dimensions and in their inherent type of vibration. To explain the stability of systems built up from these units, it is necessary to assume that the usual force laws of Newton and Coulomb become invalid for very small distances, and that a modified force law operates. This force is assumed to originate in the vibration of the particles in the atom. These vibrations are similar to, but different in magnitude from, those to which the author attributes the ordinary gravitational and electrical forces. The mutual reactions of these three types of unit are discussed, and the conditions are formulated for stability in a system composed of them. It is a corollary of these conditions that the size of the gravitational particles must be greater than that of either the electron or proton. Structures are suggested for the atoms up to chlorine.  
F. G. T.

**Estimation of Maximum Coefficients of Absorption.** R. C. TOLMAN (*Physical Rev.*, 1925, [ii], **26**, 431—432).—On the basis of the correspondence principle, Einstein's coefficient of absorption may be estimated from the equation  $B_{na} = 2\pi^3 e^2 Q^2 / 3h^2$ , where  $e$  is the charge and  $Q$  the amplitude of the virtual oscillator which corresponds with the transition by absorption from state  $S_n$  to state  $S_a$ . Values of  $(B_{na})_{\text{max}}$  are in agreement with those previously calculated.  
A. A. E.

**Whittaker's Atomic Model.** J. A. ELDRIDGE (*Proc. Roy. Soc. Edin.*, 1925, **45**, 245—248).—Whittaker has suggested an atomic model designed to absorb and emit radiation by quanta (A., 1922, ii, 632). It is pointed out that a mechanism involving the existence of unipolar magnets has been employed. The assistance of the ether must be invoked in order to retain conservation of momentum. The criticism is regarded by Whittaker (in a note) as due to the confusion of bar-magnets with the new concept of "magnetic current." The idea that momentum can be stored by the ether is regarded as proved. Allen (in a note) suggests that the criticism is only valid for a particular case and proposes a way out of the difficulty.  
R. A. M.

**Treatment of Radiation-pressure and Gas-pressure as due to Intermolecular Forces.** J. Q. STEWART (*Physical Rev.*, 1925, [ii], **26**, 491—494).—Calculation of the average repulsive force between two gas molecules associated respectively with the emission and absorption of radiation affords a justification of Eddington, in his theory of stellar constitution, regarding the total pressure as the sum of the gas- and radiation-pressures. The fiction ascribing gas-

pressure to the effect of statistical repulsive forces between the molecules is examined mathematically. A. A. E.

**Soft X-Ray Levels and the Bohr Scheme of Atomic Structure.** F. L. MOHLER (*Physical Rev.*, 1924, [ii], **23**, 765).—A survey of data on critical radiation potentials of solids and gases yields results consistent with the conclusions of Bohr and Coster regarding the probable course of soft X-ray levels on the Moseley diagram. A. A. E.

**Fulcher Lines in the Hydrogen Spectrum.** C. R. BURY (*Phil. Mag.*, 1925, [vi], **50**, 1139—1143).—It is suggested that the 10 triplets in the many-lined spectrum of hydrogen, which were arranged by Fulcher in two bands, are each the three brightest lines of ten different bands. These bands are arranged in two series and each band consists of two branches. A number of the lines in the spectrum have been classified on this basis. A. B. M.

**Measurement of Negative Oxygen Bands in the Visible Spectrum Region.** F. HOLLAND (*Z. wiss. Phot.*, 1925, **23**, 342—363).—Results of measurements of three groups of negative oxygen bands are given. For group I, from 6226 to 5807 Å., 403 lines are given; for group II, from 5644 to 5509, 274 lines; and for group III, from 5295 to 5196, 225 lines. Mean errors of measurements are given and discussed, together with the intensities and the wave-lengths in air and after reduction to vacuum. W. C.

**Relations between the Band Spectra of Zinc, Cadmium, and Mercury and their Atomic Spectra.** E. HULTHÉN (*Nature*, 1925, **116**, 642).—It is concluded that the metal atoms remain in their metastable  $2p_i$  states during the molisation act with the hydrogen atom, the other hydrogen atom carrying away the energy not to be quantised by the molecule. The electron transition is located in the metal atom, the hydrogen atom being optically inactive. A. A. E.

**Resonance Radiation from Cadmium Vapour.** A. D. POWER (*Physical Rev.*, 1924, [ii], **23**, 293).—If cadmium vapour in an evacuated silica tube is illuminated by a spark discharge, the wave-lengths 3262 Å. ( $1S-2p_2$ ) and 2289 Å. ( $1S-2P$ ) are radiated strongly by the freshly-formed vapour. The presence of thallium as an impurity was revealed in this radiation, but not by the spark. A. A. E.

**Terms of the Mercury Hydride Bands.** H. LUDLOV (*Z. Physik*, 1925, **34**, 485—495).—The terms of the mercury bands are represented by Kratzer's formula (*ibid.*, 1923, **13**, 82) and the structure of the mercury hydride molecule is discussed. The moment of inertia is not greatly affected by the orbit of the radiating electron, nor does this electron greatly influence the combination of the nuclei; it revolves about the mercury hydride ion at a relatively great distance. The spectrum is also produced by the passage of active hydrogen over mercury. In common with the hydrides of cadmium and zinc, the states of lower energy have the



greater moments of inertia; the nearer the radiating electron approaches the nuclei the feebler becomes their mutual attraction.

E. B. L.

**Structure and Distribution of Band Spectra.** H. DESLANDRES (*Compt. rend.*, 1925, **181**, 410—412; cf. this vol., ii, 930, 1023).—For the substances of simple composition hitherto examined the position of the principal absorption bands is given by sub-multiples of the universal constant,  $d_1$ , 1062.5, and is simply related to the number and size of the constituent atoms. For eleven spectra in the infra-red and twenty-nine in the visible and ultra-violet, the most intense band has a frequency which is a multiple of  $d_1$ . The same law applies to the strongest lines in the spectra of the atoms. It is suggested that 1062.5 is a fundamental frequency, related on the one hand to Planck's quantum of action and on the other to the unknown law for the mutual action of electric charges on atoms and molecules at very small distances apart.

E. B. L.

**Energy Levels in Band Spectra.** O. S. DUFFENDACK (*Astro-phys. J.*, 1925, **61**, 209—222).—A study of the relation between the radiating potentials of the molecule and its band spectrum. There are, in addition to a change in its translational motion, three ways in which a molecule may absorb energy (instead of only one, as for the atom) associated with changes in (a) the electronic configuration of the molecule, (b) the configuration of the nuclei of the constituent atoms, and (c) the rotational state of the molecule, the amount of energy gained or lost decreasing in that order. The rotational and vibrational spectra are in the infra-red, but spectra due to electronic shifts may be in the visible spectrum or the ultra-violet. The normal state of the molecule is that of the zero electronic and vibrational states, coupled with some rotational state  $m$ . The first band system should therefore consist of a single set of bands with frequencies related in a second Deslandres progression, but succeeding systems should consist of groups of bands. The extent of a band system is limited by the overlapping of energy levels, and by the stability and the ionisation of the molecule. The minimum radiating potential of a system is the potential of the zero vibrational level.

A. A. E.

**Use of Half-quantum Numbers in Interpretation of Hydrogen Chloride Absorption Bands.** W. F. COLBY (*Physical Rev.*, 1924, [ii], **23**, 295).—Assignment to the electronic momentum of a value  $\frac{1}{2}h/2\pi$  accounts for the missing centres of the well-known bands and for the lines of a new faint combination band observed for hydrogen chloride at 300°.

A. A. E.

**Effect of Pressure on the Infra-red Absorption of Hydrogen Chloride.** G. BECKER (*Z. Physik*, 1925, **34**, 255—272).—The observations were made on the rotation-oscillation band at  $3.4\mu$ , by comparing the effect of compression of the hydrogen chloride with the effect of addition of air, the product of length of column by density being kept constant. The increase in absorption is due to

broadening of the lines composing the band; the breadth does not depend solely on the number of molecular collisions. E. B. L.

**Emission and Absorption Bands of Carbon Dioxide in the Infra-red.** J. W. ELLIS (*Physical Rev.*, 1925, [ii], **26**, 469—474).—A new weak absorption band of carbon dioxide was observed, using a self-registering infra-red quartz prism spectrograph of an auto-collimation type, at  $2.02\mu$ , forming a linear, although not harmonic, frequency series with known bands at  $2.73\mu$  and  $4.25\mu$ ; it was identified with a band at  $1.99\mu$  in the Bunsen flame emission spectrum. The emission region at  $2.7\mu$  was resolved into equally intense components at  $2.58\mu$  and  $2.76\mu$ . The temperature of the Bunsen flame is computed to be about  $2000^\circ$  Abs. A. A. E.

**Vibration of the Carbonate Group.** P. A. TAYLOR (*Phil. Mag.*, 1925, [vi], **50**, 1158—1160; cf. Chapman and Ludlam, this vol., ii, 1025).—Kornfeld's treatment of the problem of the infra-red vibrations of the carbonate group in crystals is modified by the introduction of terms for the force between the oxygen atoms. The discrepancy between theory and observation is thereby made worse, emphasising the difficulty, pointed out by Chapman and Ludlam, of explaining the observed infra-red vibrations of the carbonate group by a simple theory. A. B. M.

**Optical Researches on Sulphurous Acid and its Alkali Salts, Especially Potassium and Ammonium Pyrosulphites.** R. DIETZEL and S. GALANOS (*Z. Elektrochem.*, 1925, **31**, 466—473).—The absorption spectra of aqueous solutions of sulphur dioxide show that these contain chiefly molecules of unchanged sulphur dioxide and of its hydrate, and only small amounts of sulphurous acid and its ions. Alcoholic solutions absorb much more strongly than aqueous solutions, from which it follows that a new substance, possibly an alcoholate with the formula  $O_2HS \cdot OC_2H_5$ , is formed. Aqueous alkali hydrogen sulphite solutions show similar results to sulphur dioxide solutions. Aqueous and alcoholic solutions of potassium and ammonium pyrosulphites show no spectrum characteristic of the ion  $S_2O_5^{--}$ . It is concluded that the equilibrium in these cases also is similar to that in aqueous sulphur dioxide solutions. On being exposed to light or warmed, solutions of hydrogen sulphites and pyrosulphites show after some time an alteration in the absorption, which is increased and displaced in the direction of longer wavelength. This effect is due to a photo-oxidation of the  $HSO_3^-$  ions which results in formation of the normal sulphate, sulphurous acid, and the hydrate of sulphur dioxide. Schafer's assumption of an isomerisation of the  $HSO_3^-$  ions to explain this phenomenon is unnecessary. N. H. H.

**Behaviour of Benzene in Aqueous Solutions. Ultra-violet Absorption as a Function of  $p_H$ .** F. VLÈS and (MLLE.) M. GEX (*Compt. rend.*, 1925, **181**, 506—509).—Benzene in the proportion of 0.5 c.c. per litre was added to various solutions of hydrochloric acid or sodium hydroxide. The resulting solutions were kept for different periods in completely filled closed flasks. On opening, the

absorption spectra were photographed, and the  $p_H$  values measured, as quickly as possible. The results are expressed by plotting  $\phi$  (ratio of absorptive powers at 260 and 254  $\mu$ ) against  $p_H$  values (cf. this vol., ii, 472). The curve exhibits well-defined maxima at  $p_H$  values 1.2, 5, 9.5, 13, which occur whether the solutions were examined 7 or 24 hrs. after preparation; in the latter case, however, the values of  $\phi$  are uniformly lower. The results are considered to prove that the benzene molecule is not inert towards hydrogen ions or towards electrolytic equilibria into which they enter.

R. A. M.

**Absorption Spectra of Some Ketones.** S. L. LANGEDIJK (*Rec. trav. chim.*, 1925, **44**, 931—934; cf. this vol., i, 408).—A reply to Plotnikov (this vol., ii, 837).

G. M. B.

**Hæmatoporphyrin.** R. FABRE (*Compt. rend.*, 1925, **181**, 623—625; cf. Dhêré, Schneider, and van der Bom, A., 1924, ii, 643).—The curve of spectral distribution of fluorescence of hæmatoporphyrin has a maximum at 6350 Å., is best defined at a dilution of 1 in 8000, is more characteristic than the absorption spectrum of hæmatoporphyrin, and disappears after 12 hrs.' irradiation by a mercury vapour lamp. The absorption curve loses its characteristics after irradiation for 8 hrs.

L. F. H.

**Fluorescence Radiation of Nitrogen.** O. OLDENBERG (*Proc. Nat. Acad. Sci.*, 1925, **11**, 595—597).—When a condensed spark occurs in nitrogen which is at a pressure of a few tenths of a mm. and special arrangements are made to prevent glow discharges, it is possible to observe the fluorescence radiation excited by the spark. The fluorescence spectrum is different from that of the spark and contains the bands: 3755, 3805, 3894, 3914, 3943, 3998, 4059, 4142, 4201, 4239, 4281, 4344, 4416, 4489, 4574, 4653, and 4709 Å. From the work of Wien (A., 1923, ii, 349), it is certain that the bands 4709, 4281, 4239, 3914, and probably some others, are due to the ionised nitrogen molecule, whilst the others originate in the neutral molecule. It is suggested from analogy with the alkaline earths that two-electron jumps occur within the molecule and that the absorption of a wave-length beyond the limit of a series would ionise the atoms and at the same time excite the ion.

A. E. M.

**New Experiments with Crookes' Tube.** A. DAUVILLIER (*Compt. rend.*, 1925, **181**, 601—603).—The hypothesis that the appearance of bubbles in the walls of Crookes' tubes after prolonged use is connected with the disappearance of gas from the tube has been shown to be erroneous by exposing pieces of glass cut from tubes which had shown this effect, to a homogeneous beam of cathode rays, under conditions in which negative luminescence and ionic discharge were absent. The green fluorescence of these test-pieces disappeared after  $\frac{1}{2}$  hr. exposure, and the glass became violet-brown in colour. Thin sections, showing no visible fluorescence, showed the same coloration, which was deep-seated and unaffected by aqua-regia. It disappeared easily on heating, without triboluminescence, but with the formation of bubbles. Fusion of the

coloured test-pieces by cathode ray bombardment gave the same result. It is suggested that the coloration is due to the liberation of atoms of alkali metals by the destruction of negative ions, the freed electrons passing to adjacent positive ions. The formation of gas bubbles is due to the decomposition of the glass by the alkali metal, and is independent of the absorption of gas, and of fluorescence. The disappearance of gas is attributed to polymerisation in the negative luminescence. The author's theory of the origin of the Crookes' dark space ("La Technique des Rayons-X," p. 14) is supported by the production of a positive stream in a secondary dark space in a tube containing neon.

F. G. T.

**Polarised Fluorescence of Dyes. VI.** W. L. LEVSHIN (*Z. Physik*, 1925, **34**, 330—336; cf. this vol., ii, 13, 629).—By comparing the polarised fluorescence from dyes in viscous solutions and in colloidal solutions, the conclusion is reached that the total polarisation in the latter is the sum of the polarisation in the single phases.

E. B. L.

**Luminous Efficiency of Chemi-luminescence Reactions.** E. Q. ADAMS (*Physical Rev.*, 1924, [ii], **23**, 771).—The ratio of light production to energy input in the case of phosphorus (nitrogen saturated with phosphorus vapour being brought into contact with air) is slightly above 1 lumen per kilowatt at either 25° or 40°.

A. A. E.

**Decay and Regeneration of Radio-luminescence.** C. H. VIOL, G. D. KAMMER, and A. L. MILLER (*Science*, 1925, **61**, 489).—The decrease in the glow of niton (radon) in glass tubes and in the luminescence of phosphorescent zinc sulphide is believed to be due to the masking of the radiation luminosity by the colour which the material acquires, due to the action of the radiation. When the colour is discharged by just sufficient heating the luminescence returns.

A. A. E.

**Oscillation Phenomena in Diffraction Spectra.** E. BUCHWALD (*Physikal. Z.*, 1925, **26**, 672—675).—The blue colour of the sky owes its existence to fluctuations in the density of the diffracting molecules of air. Opalescence has a similar cause. The continuous ground in X-ray diffraction images is affected by thermal motion of the crystal particles. The paper is theoretical and consists of an attempt to clarify the mathematics of the oscillation phenomena entering into those enumerated.

R. A. M.

**Effect of Light on the Thermal Conductivity of Selenium.** R. E. MARTIN (*Physical Rev.*, 1925, [ii], **26**, 475—485).—A selenium cell which was not sensitive electrically was also not sensitive thermally. The red end of the spectrum is more effective than the shorter wave-lengths. The results furnish additional evidence that thermal and electrical conductivities in metals largely depend on the same factors.

A. A. E.

**Method for Determining the Dielectric Constants of Electrolytes which Conduct Well.** H. HELLMANN and H. ZAHN (*Physikal. Z.*, 1925, **26**, 680—682).—The method, based on

high-frequency oscillations, leads to accurate values for small differences in the constant and has been tested by a determination of the influence of the addition of small volumes of acetone to solutions of sodium and potassium chlorides. R. A. M.

**Dielectric Constants of Ethane, Ethylene, Acetylene, and Butylene, and the Symmetry of Unsaturated Bonds.** C. P. SMITH and C. T. ZAHN (*J. Amer. Chem. Soc.*, 1925, 47, 2501—2506).—The method of Zahn (A., 1924, ii, 809) was employed and the values obtained are in accord with Debye's theory of dielectrics as applied to gases. The molecules of the gases studied have no electric moment except  $\alpha$ -butylene, which has a small moment. The electronic structure of an unsaturated linking is symmetrical, but with a stronger field of force around it than that around a saturated linking, so that if the unsaturated linking is unsymmetrically located in the molecule, the induced electronic shifts will give a moment to the molecule as a whole. W. T.

**Electric Moment of Gaseous Hydrogen Chloride and Hydrogen Bromide Molecules.** K. T. COMPTON and C. T. ZAHN (*Physical Rev.*, 1924, [ii], 23, 781—782).—Measurements were made of the dielectric constant of gaseous hydrogen chloride and hydrogen bromide throughout a temperature range of 400° beginning just above the liquefaction point. The data accurately obey Debye's equation based on the existence of fixed moments in the molecule. For hydrogen chloride the moment is  $1.03 \times 10^{-18}$  c.g.s.u., and for hydrogen bromide,  $0.7881 \times 10^{-18}$  c.g.s.u. A. A. E.

**Dielectric Fatigue in Rochelle Salt.** J. VALASEK (*Physical Rev.*, 1924, [ii], 23, 114).—Rochelle salt behaves as though it contained conducting elements insulated from one another. Anomalous effects have been observed only between  $-20^\circ$  and  $+25^\circ$ , the range in which the crystal is piezo-electrically active. There is a corresponding piezo-electric fatigue due to the same causes. A. A. E.

**Colour-vision Spectrometer.** W. PEDDIE (*Proc. Roy. Soc. Edin.*, 1925, 45, 302—307).—A new design is described for a spectrometer which can be employed both for the three-standard and the two-standard colour methods of determining colour sensation curves. R. A. M.

**Scattering of Light in Mixtures of Air and Carbon Dioxide.** D. BANERJI (*Physical Rev.*, 1925, [ii], 26, 495—499).—The intensity of the light scattered transversely by a mixture of the two gases varied linearly with the percentage of carbon dioxide. The ratio of the intensities of the components polarised horizontally and vertically varies in accordance with Raman's theory. A. A. E.

**Dispersion Constants and Critical Electron Velocities of Molecular Hydrogen.** H. SCHÜLER and K. L. WOLF (*Z. Physik*, 1925, 34, 343—346).—The experimental values for the index of refraction of hydrogen are represented by a dispersion formula containing two terms which are discussed in connexion with the critical velocities found for the impact of electrons on the hydrogen

molecule. It is suggested that these terms are the frequencies at the centres of gravity of two regions of continuous absorption, of which the long wave-length limits correspond with 13 and 16 volts, respectively.

E. B. L.

### Dispersion of Potassium Chloride and Sodium Chloride.

K. F. HERZFELD and K. L. WOLF (*Ann. Physik*, 1925, [iv], **78**, 35—56).—In these simplest heteropolar crystals, the metal will have lost an electron and the halogen will have gained one; both will then possess an outer electron shell containing eight electrons and will thus resemble the noble gases. Sodium chloride will give ions resembling neon and argon, but the sodium ion will hold its electrons more firmly than neon on account of its positive charge and the chlorine less firmly than argon because of its negative charge. From these considerations, dispersion formulæ are developed which consist of three members, one for the cation and two for the anion. The two positions taken for the absorption of the chlorine ion are the resonance line and the centre of gravity of the continuous absorption in the far ultra-violet, resulting from the complete loss of an electron. This requires, in addition to the work done against the electron affinity, the work done against the attraction exerted by the other points in the lattice. In this way, the desired wave-lengths can be calculated. Conversely, from the wave-lengths for the cation, the ionisation potentials of the potassium and sodium ions can be calculated.

E. B. L.

### Molecular Dissymmetry and Optical Activity. E. DARMOIS

(*J. Phys. Radium*, 1925, [vi], **6**, 232—240).—The inadequacy of Drude's electromagnetic theory has led to various new theories of rotatory power (A., 1918, ii, 283; *Ann. Physik*, 1915, [iv], **48**, 1—56; *Phil. Mag.*, 1920, [vi], **40**, 713). The theory of de Malleman (*Ann. Physique*, 1924, [x], **2**, 5—239) is discussed at some length. On this theory, optical anisotropy of liquids is due to elliptical vibrations resulting from the superposition of effects due to rotatory power and birefringence. The molecular rotatory power is a mean effect varying with changes in the orientation of the molecules. Evidence supporting this has been obtained by de Malleman for orientation in an electric field and by Longchambon for the rotatory power of active crystals. Gouy's relation  $\delta^2 = \phi + 4\omega^2$  ( $\phi$  the birefringence,  $\omega$  the rotatory polarisation) is found to hold when the birefringence is feeble. It is claimed for de Malleman's theory that it correlates birefringence, rotatory power, concentration, and temperature effects. The author considers that the purely physical theories cannot, however, explain the large variations of rotatory power with dilution and temperature changes. Physico-chemical mechanisms must be employed such as association of active molecules with each other (*e.g.*, tartaric acid) or with the solvent. In other cases, definite evidence of chemical reaction between the active substance and the solvent (*e.g.*, malic acid and molybdates) must enter into the mechanisms put forward. The author considers the Kerr and Cotton-Mouton effects. The relations between

chemical constitution and the existence of circular dichroism are also discussed.

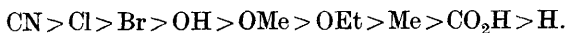
R. A. M.

**Rotation-Dispersion of Optically Active Compounds. Dimethoxysuccinates and Pyridine.** T. S. PATTERSON and J. D. FULTON (*J. Chem. Soc.*, 1925, **127**, 2435—2444).—With the object of determining whether the rotation values on both sides of a maximum or minimum in the temperature-rotation curve for an optically active substance and its derivatives fall on a single characteristic diagram, the temperature-rotation curves between 0° and 100°, for six different wave-lengths, have been examined for benzyl *d*-dimethoxysuccinate in the homogeneous state and in solution, as well as for *d*-dimethoxysuccinic acid and its methyl ester, and benzyl tartrate in solution. The dispersion ratios calculated from the rational zero give values approximating to that of ethyl tartrate (T., 1913, **103**, 145). As little variation of the temperature-rotation curve is shown, and no definite maximum or minimum, nicotine has also been examined. Rotations on either side of the zero of rotation have been obtained, but no suitable solvent could be found to bring the region of anomalous dispersion under observation. The dispersion ratios for nicotine, whether in the homogeneous condition, in an inert solvent, or as a salt, show good agreement.

M. S. B.

### Optical Activity and the Polarity of Substituent Groups.

**II. Menthyl Esters of Substituted Acetic Acids.** H. G. RULE and J. SMITH (*J. Chem. Soc.*, 1925, **127**, 2188—2194).—The rotatory powers of menthyl esters of the acids  $\text{CH}_2\text{X}\cdot\text{CO}_2\text{H}$ , where  $\text{X}=\text{CN}$ ,  $\text{CO}_2\text{H}$ ,  $\text{OH}$ ,  $\text{OMe}$ , and  $\text{OEt}$ , have been determined at temperatures between 20° and 95° and for light of four different wave-lengths. Where possible, the compounds have been examined in the homogeneous state. In all cases, the observed rotations may be expressed within the limits of experimental accuracy, by a Drude equation of one term. Temperature has little effect on the results. The values of  $\lambda_0^2$  vary between 0.0238 and 0.0316 for homogeneous esters. Observations made with menthyl cyanoacetate, glycollate, and hydrogen malonate in benzene and chloroform solution show that, in these cases also, dispersion is apparently simple in character. By comparison with molecular rotations for menthyl esters of other monosubstituted acetic acids, as determined by earlier investigations, the relative effect of substituents on optical activity appears to be as follows :



This corresponds very closely with the general polar effect of the groups as shown by their influence on molecular inductive capacity (Rule and Paterson, this vol., i, 29) and the dissociation constants of the acids (Betti, A., 1923, ii, 674). There is no indication of positive groups affecting the rotatory power in an opposite sense to negative groups as illustrated by the behaviour of the benzoates.

M. S. B.

**Varying Valency of Platinum with Respect to Mercaptanic Radicals. II.** (STR) P. C. RÂY and K. C. B. RAY (*J. Indian Chem. Soc.*, 1925, **2**, 178—190).—Further evidence is brought forward in support of the view that in compounds with certain mercaptanic radicals platinum behaves as a bi-, ter-, quinque-, sexa-, and octa-valent element, respectively (cf. Rây, T., 1923, **123**, 133). The determination of the mol. wt. of the compound  $\text{Et}_2\text{S}_2\text{PtCl}$  obtained by the interaction of ethyl disulphide and platinic chloride (Rây, *loc. cit.*) shows that the molecular formula is treble the empirical formula, the compound having a ring structure in which the platinum is ter- or quinque-valent. By the interaction of sodium dithioethylene glycol and platinic chloride in acetone, the compounds  $\text{C}_2\text{H}_4\langle\text{S}\rangle\text{Pt}\langle\text{S}\rangle\text{C}_2\text{H}_4$  and  $[(\text{C}_2\text{H}_4\text{S}_2)_2\text{:Pt}\cdot\text{S}\cdot\text{CH}_2\cdot]_2$ , in which the metal is respectively quadri- and quinque-valent, are obtained. By the interaction of ethyl sulphide and platinic chloride, the following products, in which platinum varies from ter- to octa-valent, have been isolated, those to which no reference is given being new compounds: (1)  $\text{Et}_2\text{SPTCl}$ , not melting below  $250^\circ$ , (2)  $(\text{Et}_2\text{S})_2\text{PtCl}_2$ , which has been isolated in six isomeric modifications, the products obtained depending on the temperature of the reaction and the active mass of the reactants,  $\alpha$ , golden-yellow needles, m. p.  $108^\circ$  (cf. Tschugaev and Malzschewsky, A., 1924, i, 934);  $\beta$ , white, m. p.  $108^\circ$ ;  $\gamma$ , greenish-yellow, m. p.  $110^\circ$  (cf. Tschugaev and Malzschewsky, *loc. cit.*);  $\delta$ , colourless, m. p.  $104^\circ$ ;  $\epsilon$ , m. p.  $96^\circ$ ; the sixth isomeride, m. p.  $77^\circ$ , was obtained by Rây (*loc. cit.*); (3)  $(\text{Et}_2\text{S})_2\text{PtCl}_3$ , orange-red, m. p.  $109^\circ$ , which is a molecular compound of (2) and (4) [cf. Tschugaev and Benevolenski, A., 1913, i, 1149; Loir, *Ann. Chim. Phys.*, 1853, **39**, 441, who, by crystallisation from boiling alcohol, evidently decomposed the compound into its two components and isolated (4) only]; (4)  $(\text{Et}_2\text{S})_2\text{PtCl}_4$ , yellow needles, m. p.  $198^\circ$  (cf. Rây, *loc. cit.*); (5)  $(\text{Et}_2\text{S})_2\text{PtCl}_5\cdot 2\text{H}_2\text{O}$ , orange needles, m. p.  $90^\circ$ . The constitution of these compounds on Werner's co-ordination theory is discussed. Crystallographic data for the compounds (2)  $\epsilon$  and (4) are given. J. W. B.

**Colour and Molecular Geometry. IV. Explanation of the Colours of Cyanine Dyes.** J. MOIR (*J. Chem. Soc.*, 1925, **127**, 2338—2343; cf. this vol., ii, 634).—The inactive portions of a dye molecule lying outside the two positive colour centres produce a "loading" effect on the colour, raising the position of the absorption bands by an amount varying between 0.5% and 10%. The colour bands of diquinolymethane may be deduced from those of dipyridylmethane by multiplying by the square of the colour factor 1.105, thus showing that the effect of "loading" with a portion of a benzene ring is the same as in the ordinary naphthol-phenol dicyclic family of dyes. There is only a minute difference between the colours of pseudoisocyanine and of activated di-2-quinolymethane, the methyl colour factor being apparently 1.005. The azocyanine family is abnormal in that the unmethylated member does not become activated with acid. Thus the effect of the methyl



groups is large, the factor being 1.06 instead of 1.005. All the cyanines have two bands close together, and the ratio of the absorption centre wave-lengths for the two bands of each substance is practically always 1.065. By a coincidence, the bands of the cyanines are calculated from those of the *isocyanines*, and the bands of the latter from those of the *pseudocyanines*, by multiplying by 1.065 also, the same factor holding good for the carbocyanine series. The bands of activated dipyridylmethane are explained on the author's spatial theory of colour.

M. S. B.

**Atoms and Isomorphism.** A. N. WINCHELL (*Science*, 1925, **61**, 553—557).—A discussion of isomorphism in relation to valency and atomic domain. Although substances which are chemically closely similar are often isomorphous, the miscibility of substances in crystals is determined by the relative sizes of the atoms, and not by their valency.

A. A. E.

**Law of Periodicity and the Theory of Cyclic Unsaturated Compounds.** P. PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1925, [ii], **111**, 23—35).—A survey of published data on the mutual influences of various portions of an organic molecule leads to the generalisation that the approximation and accumulation of one and the same substituent causes a diminution or even a reversal of the usual influence of the particular group on the character of the molecule. Examples are afforded by the unexpectedly low ionisation constant of trichloroacetic acid as compared with that of the monochloro derivative, where the strongly acidic influence of the substituting chlorine is depressed by its accumulation, and by the low basicity of hydrazobenzene as compared with benzidine, where the basic character of each nitrogen atom is depressed by its proximity to the other. A similar explanation applies to dibasic acids, diketones, and ketonic acids, containing the grouping  $-\text{CO} \cdot [\text{CH}_2]_n \cdot \text{CO}-$ , where instability increases with decreasing value of  $n$  down to  $n=1$ , whilst when the two carbonyl groups are adjacent the compounds are perfectly stable. This explanation removes the anomaly of the strong dissociation of the second carboxyl group of oxalic acid, which is contrary to Ostwald's rule that the dissociation of the second carboxyl group in dibasic acids is less the nearer the two carboxyl groups approach one another. Similar, quantitative data are quoted for the influence of  $-\text{Cl}$ ,  $-\text{CO}_2\text{H}$ ,  $-\text{OH}$ , and  $-\text{C}_6\text{H}_5$  groups in analogous series. Thus, whilst the dissociation constant of phenylacetic acid is 3 times that of acetic acid, that of benzoic acid is only 0.2 of that of formic acid, owing to the close proximity, in benzoic acid, of the phenyl group to the carboxyl group. Similar regularities are observed amongst diamines, of which hydrazine can be considered as an extreme case. The increase in acidity produced by the etherification of an  $\alpha$ -hydroxy group in carboxylic acids is explained analogously, and the explanation is extended to include the increase in acidity of boric acid in presence of glycerol, and the acidity relationships of polybasic mineral acids, where the anhydro-acid is stronger than the simple compound (cf. Hantzsch, A., 1923, ii, 475). The "accumulation influence" can be considered

similarly to explain the inactivity of conjugated unsaturated systems, and an analogy is drawn in this sense between the groupings  $-\text{C}:\text{C}:\text{C}:\text{C}-$  and  $-\text{C}:\text{CX}-$  ( $\text{X}=\text{halogen}$ ), both of which exhibit unexpected passivity. Analogy is drawn between the activity relationships of the series  $\text{CH}_2:\text{CH}:\text{CH}_2\text{X}$ ,  $\text{CH}_2:\text{CHX}$ ,  $\text{CH}_2:\text{CX}_2$ , in which the middle term represents the least reactive compound, and those observed by Vorländer (A., 1901, i, 444) amongst carboxylic acids, and this analogy is extended to the three unsaturated, conjugated ring systems in *cyclooctatetraene*, benzene, and *cyclobutadiene*, where increasing proximity of active groups (unsaturated linkings) first depresses the total activity and then, reversing the effect, enhances it. A form of periodicity is thus set up, and can be experimentally demonstrated by a study of reactivities in suitable series (cf. this vol., ii, 802), although in many cases it may be impossible to discover the full "wave" of the periodicity curve. Similar considerations can be applied to condensed and heterocyclic ring systems.

F. G. W.

**Born's Dipole Theory of Anisotropic Liquids.** G. SZIVESSY (*Z. Physik*, 1925, **34**, 474—484).—According to Born's theory, an anisotropic liquid should exhibit an electric charge at its boundary when its molecules are subjected to an external force which would cause them to be parallel to each other. This should be the case when a magnetic field is applied, but no such effect was observed, although one-millionth of the predicted effect could have been detected.

E. B. L.

**Magnetochemistry of Closed Chains.** P. PASCAL (*Compt. rend.*, 1925, **181**, 656—658; cf. this vol., ii, 371, 634).—The magnetic properties of three-, four-, and five-membered ring compounds were investigated. The diamagnetism decreases with progressive unsaturation. *cyclopentanes* behave magnetically, like the corresponding chain compounds; the same holds when one or two carbon atoms are substituted by nitrogen atoms, or when an unsaturated linking is introduced. The magnetic susceptibilities of the compounds investigated vary in proportion to the angular strains predicted from Baeyer's theory.

S. K. T.

**Structure and Molecular Dimensions of Non-metallic Hydrides.** H. G. GRIMM (*Z. Elektrochem.*, 1925, **31**, 474—480).—The principle is put forward that atoms preceding the inert gases in the periodic classification by one to four places alter their properties by taking up  $\alpha$  hydrogen atoms, where  $\alpha$  is one to four, in such a way that the resulting complexes behave as pseudo-atoms having similar properties to the atoms  $\alpha$  groups to the right of the original atoms. The work involved in the dissociation of oxygen and nitrogen is calculated from measurements of ionisation by collision, and from these figures the work of dissociation of non-polar molecules is determined. The true diameter of simple non-metallic hydrides is calculated. With the aid of these and other data, models of simple organic molecules are described which seek to elucidate their dimensions and physical properties.

N. H. H.

**Average Cross-sectional Areas of Molecules by Gaseous Diffusion Methods.** E. MACK, jun. (*J. Amer. Chem. Soc.*, 1925, **47**, 2468—2482).—A simple method for the determination of the diffusion coefficients of volatile substance is described, and the average cross-sectional areas of the molecules of iodine, benzene, naphthalene, anthracene, toluene, diphenyl, aniline, and benzidine are calculated by the equation of Stefan, Maxwell, and Jeans. The results obtained agree with those proposed by Bragg from X-ray analysis. They do not agree so well with values determined from Huggins' models. The carbon atoms in the chain of the *n*-octane molecule are probably arranged in a zigzag manner. The diffusion method confirms the conclusion, based on chemical evidence, that diphenyl and benzidine have a "collapsed" structure. W. T.

**Search for the Element 93. I. Examination of Crude Manganese Compounds and Isolation of Element of Atomic Number 75.** J. G. F. DRUCE (*Chem. News*, 1925, **131**, 273—277).—From theoretical considerations it seems possible that an element related to manganese, and of atomic number 93, may exist in quantity sufficient to make it readily accessible to chemical analysis. An investigation of the impurities in 100 g. of crude manganese sulphate has therefore been made. From the solution which could not be precipitated by hydrogen sulphide 75 mg. of a light brown oxide, soluble in acids but not in sodium hydroxide, has been obtained. Examination in an X-ray spectrograph indicated, in addition to well-known elements, the presence in appreciable quantity of an element with the characteristic radiations 1.43 Å. and 1.233 Å., corresponding with lines in the characteristic *L* radiation of the element rhenium (atomic number 75), recently discovered (cf. Noddack, Tacke, and Berg, this vol., ii, 939). No trace was found of any line corresponding with the characteristic radiations to be expected from an element 93. M. S. B.

**Eka-cæsium.** F. H. LORING and J. G. F. DRUCE (*Chem. News*, 1925, **131**, 289).—X-Ray examination of a specimen of crude rhenium oxide disclosed a faint line corresponding with the *L* $\alpha$  line of element 87 (eka-cæsium). A. R. P.

**Eka-cæsium and Eka-iodine.** F. H. LORING and J. G. F. DRUCE (*Chem. News*, 1925, **131**, 305).—A preparation of crude rhenium oxide from pyrolusite gave an X-ray spectrum containing lines of wave-length 1.040 and 0.895, corresponding with the *L* $\alpha$  lines of elements 85 (eka-cæsium) and 87 (eka-iodine), respectively. A. R. P.

**Allotropy of Manganese.** A. J. BRADLEY (*Phil. Mag.*, 1925, [vi], **50**, 1018—1030; cf. Westgren and Phragmén, this vol., ii, 1035).—A number of specimens of manganese have been examined by the method of the X-ray powder photograph. The varying types of photograph obtained have been shown to be due to the existence of three allotropic forms of the element. Two of these,  $\beta$  and  $\gamma$ , are present normally in commercial manganese. The  $\beta$ -form is stable in the range 150—850°, and the  $\gamma$ -form from

650° upwards. Within the region 650—850°, both forms are stable, and the element appears to show the phenomenon of isodynamic allotropy, an equilibrium mixture of the two allotropes corresponding with each temperature. The pure  $\gamma$ -form is easily obtained by raising the temperature above 850° in a vacuum, and suddenly quenching. It does not appear easy to obtain pure  $\beta$ -manganese by heat treatment alone, but it is formed from the  $\gamma$ -form by sublimation in a vacuum at 1105°. The third allotrope,  $\alpha$ , has only been obtained electrolytically. X-Ray measurements show that the  $\alpha$ -form can be regarded either as a face-centred tetragonal structure with axial ratio  $a:c=1:0.9445$ , or as a body-centred tetragonal structure with axial ratio 1.34:1. It is apparently stable only at low temperatures. On heat treatment,  $\alpha$ -manganese is converted into the  $\beta$ - and  $\gamma$ -forms, but the change does not appear to be reversible.

A. B. M.

**Amorphous Carbon and Graphite.** O. RUFF, G. SCHMIDT, and W. OLBRICH (*Z. anorg. Chem.*, 1925, **148**, 313—331).—The conclusion of Debye and Scherrer (A., 1917, ii, 437) and of Kohlschütter (A., 1919, ii, 151, 152) that amorphous carbon is merely a finely divided form of graphite is shown to be probably incorrect. Amorphous carbon is a true modification which at 1100° begins to pass into a "paracrystalline" form, the properties of which approach those of graphite. The numerous forms of amorphous carbon are to be attributed to the presence of varying proportions of graphite, amorphous carbon, and the "paracrystalline" form. Only true amorphous carbon can be activated, activation being associated with the property of adsorption from solution. The authors' conclusions are supported by examination of the röntgenograms of various carbons and of the röntgenograms, resistivity towards oxidising agents, and electrical conductivity of graphites prepared by heating lamp-black at 1600—2600°, either with or without catalysts (*e.g.*, metals). The conversion proceeds stepwise; the nature of the atmosphere in the furnace probably has some influence. The conditions governing the effect of the catalysts are also considered.

S. K. T.

**X-Ray Investigation of Palladium-Silver Alloys containing Hydrogen.** F. KRUGER and A. SACKLOVSKY (*Ann. Physik*, 1925, [iv], **78**, 72—82).—Hydrogen forms a solid solution in palladium up to a certain saturation accompanied by expansion of the lattice. Addition of silver also expands the lattice, and if this expansion has not reached the limit given by hydrogen alone in palladium, then the alloy will absorb hydrogen. With 70% of silver, this point has been reached and palladium with 70% of silver will not absorb hydrogen.

E. B. L.

**X-Ray Analysis of the Crystal Structure of Lead Dioxide.** A. FERRARI (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 186—191).—An examination, by the Debye method, indicates a tetragonal structure of the rutile type. The dimensions of the elementary cell, which contains the molecule  $\text{PbO}_2$ , are  $a=4.98$ ,  $c=3.40$  Å. The value,

$c/a=0.682$ , of the axial ratio differs slightly from that determined crystallographically. The density, calculated from the dimensions of the unit cell, is 9.42, and agrees excellently with that determined directly. In preparing lead dioxide by different methods, no evidence was obtained of the hexagonal modification reported by Geuther and Lüdecke.

F. G. T.

**X-Ray Examination of Maleic and Fumaric Acids.** K. YARDLEY (*J. Chem. Soc.*, 1925, **127**, 2207—2219).—Examination of monoclinic maleic acid crystals by the X-ray spectrometer shows that the unit cell contains four asymmetric molecules, so that the planosymmetry usually ascribed to maleic acid from chemical considerations has no existence in the crystalline state. The dimensions of the cell are  $a=7.49$ ,  $b=10.14$ , and  $c=7.12$  Å.,  $\beta=117^{\circ}7'$ . Perfect cleavage is obtained parallel to the (001) plane, and imperfect cleavage parallel to (010), and the crystals can be bent and twisted in certain directions without fracture. Twinning takes place with great facility, and almost invariably on the (100) plane. The crystals belong to the space group  $C_{2h}^5$  and a probable structure is suggested. The unit cell of fumaric acid is triclinic,  $a=7.56$ ,  $b=15.00$ , and  $c=6.20$  Å., whilst  $\alpha=90^{\circ}40'$ ,  $\beta=88^{\circ}30'$ , and  $\gamma=89^{\circ}48'$ . The cell appears to contain either six simple molecules, forming a single asymmetric unit if the crystals are pedial, or, if they are pinakoidal, the six molecules are arranged in two groups of three, each group being asymmetric in itself but centro-symmetric with respect to the other. The significance of this structure with reference to the physical properties of fumaric acid is discussed. Very complex twinning takes place. X-Ray examination of derivatives of maleic and fumaric acids does not indicate association in the solid state in any other case (cf. this vol., ii, 1033).

M. S. B.

**X-Ray Diffraction Measurements on the Pyroxenes.** R. W. G. WYCKOFF, H. E. MERWIN, and H. S. WASHINGTON (*Amer. J. Sci.*, 1925, [v], **10**, 383—397).—X-Ray diffraction photographs have been made of the different types of minerals (in powder form) usually classed as pyroxenes, thus dividing them into groups with related X-ray patterns, i.e., showing the same type of crystal structure, namely, diopside, enstatite, wollastonite, and rhodonite. The exceptions are clino-enstatite, babingtonite, spodumene, pyroxmangite, alamosite, and sobralite, each of which has a diffraction pattern unlike any other. In spite of varied composition, the spacings of diopside-like minerals, with the exception of jadeite, which is probably formed under conditions of very high pressure, show remarkable similarity. This indicates that (1) atoms of magnesium and ferrous iron have practically the same effective volumes in this structure, (2) the volume of manganese atoms is somewhat larger, and (3) that of calcium atoms is considerably larger. Measurements on the diopside group also indicate that there is no apparent connexion between the excess of aluminium and ferric oxides present and the sizes of the unit cells. Density calculations, combined with the X-ray spacing measurements, prove

that these oxides cannot be present in the molecules in addition to the diopside-like metasilicate molecule. It is not possible, however, to distinguish between the possibility of some kind of isomorphous replacement and the formation of intimate mechanical mixtures with the excess oxides in forms of similar density to that of the diopside-like constituents.

M. S. B.

**X-Ray Study of Cyanite and Andalusite.** J. T. NORTON (*J. Amer. Ceram. Soc.*, 1925, 8, 636—639).—Natural, raw cyanite and andalusite have different atomic structures, both the positions and the relative intensities of the lines in the diffraction patterns showing distinct variations. After having been heated to about 1450° and about 1600°, respectively, the two compounds exhibit the diffraction pattern of artificial sillimanite.

F. S.

**Differentiation between Mullite and Sillimanite by their X-Ray Diffraction Patterns.** L. NAVIAS and W. P. DAVEY (*J. Amer. Ceram. Soc.*, 1925, 8, 640—647).—X-Ray diffraction patterns were obtained for natural sillimanite, mullite (prepared by fusing alumina and silica), and calcined china clays and ball clays. The patterns of two substances were taken, one above the other, on the same film, the lower one in each case being that of mullite, so that direct comparison was possible. In the patterns for sillimanite and mullite, distinct differences in the positions of lines in the region of 2.12—1.70 Å. were apparent. The specimens were prepared by the powder method. Sillimanite and mullite showed entirely different characteristics when ground to give a maximum particle size of 0.06 mm.; the lines of the sillimanite pattern were smooth, whereas those of the mullite were scratchy in appearance, indicating that the mullite fragments had “packed” to form lumps. The negative results obtained by other investigators are accounted for by this packing tendency. Mullite ground to an average particle size of 0.002 mm. and annealed for 2 hrs. at 900—1000° gave lines as smooth as those of sillimanite. Re-examination of the diffraction patterns previously obtained for calcined china clays and ball clays confirmed the conclusion that the crystalline phase of fired clays is mullite. [Cf. *B.*, 1925, 546.]

F. S.

**Method of Following the Course of certain Chemical Reactions by Means of X-Rays. Oxidation of Unsaturated Fatty Acids.** J. J. TRILLAT (*Compt. rend.*, 1925, 181, 504—506).—Very small quantities of saturated fatty acids deposited on a plane piece of metal yield intense X-ray spectra by the rotating crystal method (this vol., ii, 752). The work has been extended by attacking lead with thin films of oleic, linoleic, and linolenic acids containing one, two, and three double linkings, respectively. The lead salts catalyse oxidation by air. In oleic acid, the first effect is shown by the appearance of an intense spectrum with a reticular distance of  $d=29.8$  Å. After a few hrs., a new spectrum  $d=37.5$  Å. appears, and after about 40 hrs. the preparation shows no spectrum. The first spectrum is attributed to lead oleate and the second to its oxidation product and the subsequent absence of structure to

non-oriented polymerides. For linoleic acid, the first spectrum  $d_1 = 37.1 \text{ \AA.}$  appears at once, followed after 2—3 hrs. by  $d_2 = 49.2 \text{ \AA.}$ , with subsequent disappearance of structure. Thus oxidation of both double linkings in the lead salt occurs simultaneously, since no intermediate stage is observed. Linolenic acid shows three stages,  $d_1 = 21.2$ ,  $d_2 = 28$ ,  $d_3 = 34.4 \text{ \AA.}$  (ill-defined) on the way to random distribution in the fully "dried" oil. The oxidation of this acid is very rapid and  $d_1$  is regarded as due to the first product. Thus in all three acids oxidation of a double linking is accompanied by a molecular lengthening of 6—7  $\text{\AA.}$  Unstable products are formed by the fixation of oxygen, and polymerisation follows. R. A. M.

**Reality of the Compton Effect.** J. A. BECKER, E. C. WATSON, W. R. SMYTHE, R. B. BRODE, and L. M. MOTT-SMITH (*Physical Rev.*, 1924, [ii], **23**, 763).—Unambiguous evidence is adduced in support of the reality of the Compton effect. A. A. E.

**Theory of Impulse-radiation and Compton's Scattered Radiation.** G. MIE (*Physikal. Z.*, 1925, **26**, 665—669; cf. this vol., ii, 844).—The inert period between energy-jumps postulated by the older quantum theory is replaced in the newer theory of Bohr, Kramers, and Slater by the time occupied in the actual radiation process, without any change in the atom itself occurring during the emission. The more recent treatment of the theory has been extremely fruitful in the direction of reconciling interference and polarisation with quantum mechanisms, but impulse-radiation and Compton's scattered radiation have so far not been explained by Bohr and his colleagues. The author advances a theory which is at variance with the newer quantum theory. Collision between an electron and a light quantum occupies a finite period of time, and the electron can either gain mechanical energy without radiating, or it can be excited, whereupon it may radiate energy. Similarly, absorption inside the atoms can occur in two ways resulting respectively in the Compton effect and the photo-effect. In opposition to Bohr, Kramers, and Slater, the radiation from a single excited electron must be strictly monochromatic. The views advanced by the author are discussed by Smekal, Sommerfeld, and Bothe.

R. A. M.

**Theory of the Number of  $\beta$ -Rays Associated with Scattered X-Rays.** G. E. M. JAUNCEY and O. K. DE FOE (*Physical Rev.*, 1925, [ii], **26**, 433—435).—By the application of a correction factor to the ratio  $\sigma/\tau$ , better agreement for long wave-lengths is obtained for the equality of this ratio with that of the number of recoil electron tracks to that of photo-electron tracks (cf. Compton and Simon, this vol., ii, 347). A. A. E.

**Wave-length of Molybdenum  $K\alpha$  Rays Scattered by Light Elements.** A. H. COMPTON and Y. H. WOO (*Physical Rev.*, 1924, [ii], **23**, 763).—Radiators of lithium, boron, graphite, and water were employed; the spectra observed in each case showed a faint line identical with the primary  $K\alpha$  line and a stronger line of wave-

length greater by  $0.039 \text{ \AA.}$ , in agreement with the quantum theory of scattering. The relative intensities of the modified and unmodified lines do not depend on whether the radiator is crystalline or amorphous. A. A. E.

**X-Ray Diffraction Effects from Solid Fatty Acids.** R. W. G. WYCKOFF, F. L. HUNT, and H. E. MERWIN (*Science*, 1925, **61**, 613—614).—Microscopical examination shows that films of palmitic acid, obtained by solidification from a single point outwards, exhibit large areas having a common optical orientation; X-ray examination shows the characteristic several orders of large spacing. Even more definite results were obtained with large plates from solution in acetone or 1-chloronaphthalene. Films obtained by solidification at many points yield lines typical of a powder photograph. Thus the acid appears to be truly crystalline, and not in a smectic or other sub-crystalline state. The symmetry of palmitic acid is either monoclinic or triclinic; the long carbon chains are inclined at an angle to the reflecting face, so that the increase in spacing with the number of carbon atoms is not a simple and direct measure of carbon-to-carbon distances. A. A. E.

**Relative Number of *K* and *L* Electrons Expelled by X-Rays.** F. K. RICHTMYER (*Physical Rev.*, 1924, [ii], **23**, 292).—With certain assumptions, the part of the ( $L+M$ ) absorption which is due to the *L* electrons only may be computed. The ratio of *K* to *L* absorption is then almost equal to that of the respective ionisation potentials, whence the ratio of the probabilities of ejection of *K* and *L* electrons is independent of the relative numbers of those electrons, and is inversely proportional to the ionisation potentials, a result at variance with Compton's theory of scattering. A. A. E.

**Crystal Structure and Chemical Constitution. I. Transformation Properties of Matter.** K. WEISSENBERG (*Z. Physik*, 1925, **34**, 406—419).—A theoretical discussion of the principles underlying the present conception of the properties of matter. Matter being regarded as a discontinuum in space and time, it is shown that physical as well as geometrical properties of matter may be finally referred to the invariance of the properties of an object under change of the system of co-ordinates by which it is described. W. A. C.

**Crystal Structure and Chemical Constitution. II. Structural Theory of Crystals.** K. WEISSENBERG (*Z. Physik*, 1925, **34**, 420—432).—A complete geometrical theory of crystal structure can only be based on the transformation properties of matter. The 230 space-groups of Schoenflies' system may thus be derived; but this system is conceived rather with a view to the practical investigation of crystals. A much larger number of different space-groups is possible. Exhaustive examination of crystal symmetry must lead to a definite number of space-groups of about 10,000. W. A. C.



**Crystal Structure and Chemical Constitution. III. Analysis of Crystal Structure.** K. WEISSENBERG (*Z. Physik*, 1925, **34**, 433—452).—Crystals are built up of “islands” consisting of a definitely grouped number of atoms such that the “island” repeats itself subject to the symmetry of the crystal. The simplest “island” has a finite number of atoms and a finite volume, but others are possible in which an infinite number of atoms forms a chain, a flat network, or a space-lattice. A second form of atomic grouping is called a “dynad,” the characteristic of which is that its constituents are held together by atomic forces, whereas the “island” is a purely geometrical grouping. All “dynads” are “islands,” but not *vice versa*. Both kinds of groups must be arranged, in a crystal, in one or other of the extended series of space-groups based on transformation properties. W. A. C.

**Crystal Structure of Some Simple Inorganic Substances (Condensed Gases, Sulphates, etc.).** H. MARK (*Z. Elektrochem.*, 1925, **31**, 523).—X-Ray examination of solid carbon dioxide and solid ammonia by the powder method indicates four molecules to the cell in both cases. Barium, strontium, and lead sulphates, potassium permanganate and perchlorate are found to crystallise in the space-group  $Q_h^{16}$ , anhydrous calcium sulphate in  $Q_h^{17}$ . The arrangement of the atoms is such that any metal atom is not surrounded by equidistant anion groups, but that one of the latter stands in an exceptional position towards the former. W. A. C.

**Crystal Structure of Copper-Manganese Alloys.** R. A. PATTERSON (*Physical Rev.*, 1924, [ii], **23**, 552).—In the formation of solid solutions by the addition of manganese (up to 30%) to copper, copper atoms in the face-centred cubic lattice are replaced by manganese atoms, with an increase in the side of the cube from 3.60 to 3.70 Å. Further addition of manganese causes the formation of a new lattice. The minimum m. p. at 30—35% Mn is in accord with Rosenhain's view that the straining of a lattice by the substitution of new atoms lowers the m. p. A. A. E.

**Crystal Structure of Potassium Dihydrogen Phosphate and its Isomorphs.** O. HASSEL (*Z. Elektrochem.*, 1925, **31**, 523—529).—Crystals of potassium and ammonium dihydrogen phosphates (tetragonal-scalenohedral) have been examined by the rotating-crystal method with X-rays. There are four molecules to the cell, with spacings for the potassium salt  $a=7.42$ ,  $c=6.97$  Å., for the ammonium salt  $a=7.48$ ,  $c=7.56$  Å. The halvings indicate a body-centred cell of the space-group  $D_{2d}^{12}$ . An arrangement of atoms in the cell is proposed, in which the free oxygen atoms are equivalent and grouped tetrahedrally about the phosphorus atom. From the identity of the  $a$ -spacings in the two salts, it follows that the potassium or ammonium points in the lattice lie in line with the phosphorus points along the  $c$ -axis. This result had been previously inferred by Groth from the goniometric data. W. A. C.

**Theories on the Constitution of Natural Silicates.** G. N. RIDLEY (*Chem. News*, 1925, **131**, 305—308).—A review of modern

theories of the constitution of natural silicates and aluminosilicates with especial reference to the hexite-pentite theory of W. and D. Asch. A. R. P.

**Structure of Quartz.** (SIR) W. H. BRAGG (*J. Soc. Glass. Tech.*, 1925, 9, 272—282).—It has already been shown that the quartz crystal consists of a set of similar and similarly placed spirals with three  $\text{SiO}_2$  molecules to each turn of the spiral, but four parameters still remained to be determined to fix completely the separate atoms. The solution now suggested is based on the change of  $\alpha$ - to  $\beta$ -quartz which occurs at  $575^\circ$ , for the former has a trigonal structure, the latter hexagonal. Proof of the difference is obtained by the study of crystal symmetry, from pyro- and piezo-electrical properties, from X-ray Laue photographs, and from elasticity determinations on crystal sections. The structure of  $\beta$ -quartz is more easily elucidated, since the four parameters then reduce to one, the silicon atom being fixed and the oxygen atoms lying on certain straight lines. Intensity measurements then serve to determine the position of the oxygen atoms. The most probable value so obtained gives a structure in which the silicon atom is at the centre of a regular tetrahedron, the corners of which are occupied by oxygen atoms. Evidence favours the assumption that the  $\alpha$ -form only differs from  $\beta$ -quartz in the relative positions of the atoms in the unit cell. This change, probably only involving a twist of individual units through  $8^\circ$ , would readily account for the various twinings of  $\alpha$ -quartz. A. COUSEN.

**Cristobalite.** L. LONGCHAMON (*Compt. rend.*, 1925, 181, 614—616).—It has been observed that in the crystallisation of tridymite from a solution in which cristobalite is dissolving, between  $870^\circ$  and  $1470^\circ$ , the crystals of tridymite form in oriented positions on the dissolving cristobalite crystals. The transformation appears to be gradual, the tridymite crystal having the same direction of extinction, and preserving the skeleton of the cristobalite. This arranging of the cristobalite molecules according to the tridymite lattice in a continuous manner exemplifies an indirect oriented polymorphism. The quasi-identity of the crystal lattices of cristobalite and tridymite is supported by the fact that the densities of these substances are almost identical near  $1000^\circ$ . In the crystallisation of quartz between  $870^\circ$  and  $1470^\circ$ , it has been found that, if the quartz is powdered and sieved so as to eliminate very fine powder, tridymite is obtained, but that from unsieved powdered quartz cristobalite is produced, owing to the supersaturation induced by the rapid solution of the impalpable dust. The statement of Weil (this vol., ii, 757) that the transformation of cristobalite in the neighbourhood of  $200^\circ$  occurs at a constant temperature for each crystal or part of a crystal is not confirmed. The transformation appears to be subject to fortuitous retardations dependent on the previous treatment of the crystal. F. G. T.

**Structure of Ultramarine.** M. DOMINIKIEWICZ (*Rocz. Chem.*, 1925, 5, 308—339; cf. this vol., ii, 1036).—The structural formulæ of various forms of ultramarine are derived from that of kaolin,

the sulphur being attached at the eight internal additive points of the molecule, namely, two points each on each side of the aluminosilicate radical. For ultramarines of low sulphur content, a variety of points of attachment is thus available, leading to the existence of numerous isomerides. In all ultramarines, the sulphur is bound to both aluminium and silicon atoms, the colour depending on the existence of polysulphide bindings,  $\cdot\text{Al}\cdot\text{S}\cdot\text{S}\cdot\text{Al}\cdot$ , together with sulphides of the type  $\cdot\text{Si}\cdot\text{O}\cdot\text{SNa}$ . In colourless ultramarines, the sulphur exists only as  $\cdot\text{Al}\cdot\text{SNa}$  and  $\cdot\text{Si}\cdot\text{O}\cdot\text{SNa}$ . The large inner aluminate radicals have no influence on the coloration of ultramarine, since ultramarines of the highest sulphur content can be divided, by elimination of these aluminate radicals, into two halves, each of which still fulfils all the necessary conditions for the possession of colour, and represents a variety of ultramarine of high silica content, called natrolite ultramarine. In the preparation of this, by fusing silica, kaolin, and sodium hydroxide, the kaolin molecule breaks down into two natrolite molecules, whilst the aluminate radical thus liberated combines with two silicic acid molecules to form a third molecule of natrolite. The colour of ultramarine is explicable by the same theory as for organic dyes, the aluminosilicate radicals playing the part of chromogens, the polysulphide bindings that of chromophores, and the sulphide groups that of auxochromes.

R. T.

#### Determination of Crystal-orientation in Conglomerates.

G. TAMMANN (*Z. anorg. Chem.*, 1925, **148**, 293—296).—Careful inspection of the geometry of the etched figures produced when metallic surfaces are treated with ammonium persulphate solution and determination of the relative numbers of certain well-defined types of structures furnish trustworthy information regarding the orientation.

J. S. C.

#### Isotropic Ions, Building of Molecules and the Crystal Lattice.

F. HUND (*Physikal. Z.*, 1925, **26**, 682—685).—The shape of a molecule and the type of lattice in which a substance crystallises follow in principle from the conception of isotropic ions, which considers three properties only, their charge  $Ze$ , the mutual attractions or repulsions given by  $b/r^m$ , and their polarisability by an electric field (Born and Heisenberg, *A.*, 1924, ii, 434), the strength of which is denoted by  $a$ .  $Z$ ,  $b$ ,  $n$ , and  $a$  define the properties of an isotropic ion. The conception is admittedly crude, but it serves to prove that a structure for ions cannot be deduced from the shapes of either molecules or crystals. It is not claimed that the reasoning is adequate for all molecular or crystalline forms; crystals made up of neutral atoms are specifically excluded.

R. A. M.

#### Change of State of Aggregation and Polymorphism. V.

K. SCHAUM [with W. NAUMANN, K. UNGER, and H. HOFFARTH] (*Z. anorg. Chem.*, 1925, **148**, 217—224).—Investigations on undercooled vapours, supercooled liquids, and supersaturated solutions support the authors' assumption of the existence of space-lattice fragments in "fresh" solutions and fused masses (*A.*, 1922, ii, 264).

J. S. C.

**Isomorphism of the Molybdates of the Rare Earths with those of Calcium, Strontium, Barium, and Lead.** F. ZAMBONINI and R. G. LEVI (*Atti R. Accad. Lincei*, 1925, [vi], 2, 149—152).—In pairs of isomorphous salts, in which the substituent atoms have the same valency, the difference of molecular volume of the compounds, expressed as a percentage of the smaller molecular volume, has values between 40 and 50. For isomorphous pairs in which the substituent atoms have different valencies, the corresponding figure is about 150. The latter, however, give normal values if the volumes of equivalent weights of the compounds, instead of molecular volumes, are used in the calculation. The rule has been shown to apply also to mixed crystals. Extended to crystal structure, the rule implies that the unit cells of isomorphous pairs and of mixed crystals contain equivalent volumes of the component. An X-ray investigation of the crystal structure of the molybdates of calcium, strontium, barium, lead, lanthanum, praseodymium, neodymium, samarium, and of tervalent cerium has been made to establish this rule. F. G. T.

**Isomorphism of Quadrivalent Uranium and Zirconium Compounds.** L. FERNANDES (*Atti R. Accad. Lincei*, 1925, [vi], 2, 182—186; cf. this vol., ii, 748).—The compounds  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  and  $\text{U}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$  are isomorphous, and form mixed crystals over the range 99.14—10.3%  $\text{Zr}(\text{SO}_4)_2$ . They are isomorphous also with the corresponding compounds of cerium and thorium. F. G. T.

**Magnetic Quality in Crystals.** J. FORREST (*Phil. Mag.*, 1925, [vi], 50, 1009—1018).—The theory of the magnetic quality of crystals has been developed from the point of view of the magnetic potential energy in a homogeneous assemblage of equal magnetic doublets, and has been experimentally tested for about twenty different crystalline substances. The results are here summarised, the full theoretical discussion and experimental details being published later. The longitudinal and transverse components of the intensity of magnetisation produced by an external field of varying orientation, in circular plates cut in chosen planes from selected crystals, were measured. By comparison with the theoretical variations of internal field appropriate to the various possible lattices, the lattice arrangement of the centres of the doublets, *i.e.*, the magnetic lattice, was determined. In many cases, the solution is unique, but in others more than one lattice gives the actual relative positions of maxima and minima. For magnetite, iron crystals, the cubic alums, calcite, and some others, there is agreement between the magnetic lattice and the atomic lattice found by X-ray analysis. In other cases, *e.g.*, iron pyrites, cobaltite, fluorspar, etc., these do not correspond, unless the magnetic maxima and minima are interchanged. For potassium sulphate and ammonium sulphate more than one magnetic lattice gives the correct relative intensities, but that corresponding with the X-ray lattice best explains the behaviour of the crystal in the field. Possible explanations are suggested for the interchange of positions

of maxima and minima occurring in some cases, and for a constant effect found in the parallel component in all cases and not accounted for by the theory. The results of a theoretical investigation of the stability of the types of magnetic lattice met with are briefly summarised.

A. B. M.

**Constitution of Magnetic Iron.** F. GROSS (*Bol. Assoc. Brasil. Pharm.*, 1924, 5, 216—223; from *Chem. Zentr.*, 1925, ii, 708).—Since ferroso-ferric oxide is the only magnetic oxide of iron, it is suggested that it contains the nucleus  $\begin{smallmatrix} \text{Fe} \\ | \\ \text{Fe} \end{smallmatrix} > \text{Fe}$ . Magnetic

properties are attributed to the presence in the molecule of atoms of differing valency, according to Ampère's cross-current theory of magnetism.

G. W. R.

**Recrystallisation Phenomena as Functions of the Crystal Growth after Hot Deformation.** H. HANEMANN (*Z. Metallk.*, 1925, 17, 316—319).—For copper and steel, the curves showing the relation between the grain size and degree of deformation and between the temperature at which recrystallisation takes place and the deformation are in each case hyperbolas. The parameter of the grain size hyperbola for steel is a linear function of the recrystallisation temperature, whilst the curve of this relation for copper is a segment of a circle. If  $r$  is the radius of this circle,  $v$  the degree of deformation,  $\phi^2$  the grain size, and  $t$  the temperature of recrystallisation, then  $2v\phi^2 = (b \pm \sqrt{r^2 - (t - c)^2})^2$  for copper and  $2v\phi^2 = a^2(t - t_R)^2$  for steel, where  $t_R$  is the minimum temperature at which recrystallisation takes place, and  $a$ ,  $b$ , and  $c$  are constants. For steel  $t_R$  is  $620^\circ$  and for copper  $235^\circ$ . [Cf. *B.*, 1925, 925.] A. R. P.

**Molecular Physics. I. Relationship between Elastic Limit and Atomic Concentration.** P. LASAREV (*Bull. Acad. Sci. St. Pétersbourg*, 1919, 13, 1005—1006; from *Chem. Zentr.*, 1925, ii, 514).—The elastic limit of a metal is proportional to  $N^{5/3}$ , where  $N$  is the number of atoms per c.c. This relationship holds approximately for silver, gold, platinum, palladium, and iron, but is inapplicable to lead and copper. It has a theoretical basis if it be assumed that intermolecular force is proportional to atomic concentration, and a certain power, the same for all metals, of intermolecular distance.

G. W. R.

**Changes in the Conductivity of Coloured Films on Bleaching.** N. SCHTSCHODRO (*Bull. Acad. Sci. St. Pétersbourg*, 1919, 13, 727—746; from *Chem. Zentr.*, 1925, ii, 521—522).—A platinum film deposited on a quartz plate was so treated as to leave two comb-shaped electrodes with teeth interlacing. A colouring matter was then fixed on the plate, by means of a collodion film. The colouring matters used were cyanine, pinaverdol, and pinachrome. A current was then passed between the electrodes and a condenser arranged in series, the potential of the condenser being measured by a quadrant electrometer. The rate of increase of potential of the condenser served as a measure of the conductivity of the film. Conductivity increased when the film was bleached

through being submitted to illumination. The effect ceased when bleaching was complete. Independently of the light effect the strength of current increased with the time on account (a) of polarisation, which gradually sinks to zero when the current is interrupted, (b) of irreversible changes produced in the film by the current. The light effect was independent of the potential used. The conductivity of the film increased with the duration of illumination according to a curve which was concave to the time axis. When the illumination was interrupted, the conductivity decreased according to a curve which is convex to the time axis. The increase in conductivity,  $L$ , under illumination could be represented by the equation  $L=L_0+a(1-e^{-bJ})$ , where  $L_0$  is the conductivity in darkness,  $J$  the intensity of illumination, and  $a$  and  $b$  are constants. The effect on conductivity was greatest for that wave-length which is most absorbed by the dye used. The increase in conductivity was almost directly proportional to the absorption of light energy. G. W. R.

**Plant for Liquefaction of Helium. Some Measurements made with the Aid of Liquid Helium.** W. MEISSNER (*Physikal. Z.*, 1925, **26**, 689—694).—The paper contains a description of the liquefying apparatus, a discussion of certain physical properties of helium, and measurements of supra-conductivity at the temperature of liquid helium. The fraction total helium/liquid helium is denoted by  $\varepsilon$ . The value of  $\varepsilon$  calculated from Nernst's equation is negative and from the law of corresponding states is 0.06; the observed value is 0.2. Hence helium shows a very strong deviation from the law due to quantisation of translational energy. The author has examined the conductivity of various metals in order at a later date to decide whether supra-conductivity is a property of all metals in the pure state at a sufficiently low temperature. If  $r=R_T/R_0$ , where  $R_T$  is the resistance at  $T^\circ$  and  $R_0$  that at  $0^\circ$ , for constantan wire  $r$  is 0.9569 at  $4.21^\circ$  Abs. and 0.9552 at  $2.62^\circ$  Abs.; for lead wire the value is already  $< 1 \times 10^{-8}$  at  $4.21^\circ$  Abs.; for tin wire it is  $7.89 \times 10^{-4}$  at  $4.20^\circ$  and  $< 2 \times 10^{-8}$  at  $3.61^\circ$  Abs. A long series of measurements has been made on gold. The highest conductivity obtained corresponded with a value of  $r=0.39 \times 10^{-3}$ . Gold wire was altered by heating for  $3\frac{1}{2}$  hrs. at  $350^\circ$ . The treated wire showed a resistance one-tenth as great at the temperature of liquid helium as the original wire. A series of single crystal wires was also examined, with the result that a polycrystalline wire after being subjected to heat treatment exhibited the same values of  $r$  as the single crystal wires. This means that gap-resistance in the treated wire cannot occur between the single crystals in the polycrystalline mass. R. A. M.

**Thermo-electric Power and the Hall Coefficient.** C. W. HEAPS (*Phil. Mag.*, 1925, [vi], **50**, 1001—1009).—The effect of a magnetic field on the thermo-electric power of bismuth, antimony, graphite, and carbon has been measured and compared with the Hall coefficient for the same substances. The specimen to be

investigated was soldered across two parallel brass tubes, and placed between the poles of an electromagnet. Steam was passed through one tube and cold water through the other. The thermo-electric power was measured for different values of the magnetic field. The Hall coefficients for the same specimens of bismuth and graphite had previously been determined (*Physical Rev.*, 1918, [ii], 12, 340). For the other substances, it was measured in the usual way by connecting the potentiometer to side arms on the specimen and sending a current through the latter, using the brass tubes as terminals. Theory requires a linear relation between  $E_H - E_0$ , the change in thermo-electric effect, and  $\log R_H$ , where  $R_H$  is the Hall coefficient. This relation is satisfied by the results for bismuth, and the slight deviation in the case of graphite can be attributed to experimental error. The change in thermo-electric power was different for transverse and longitudinal magnetic fields. The effects for antimony are very small, but the changes are in the right direction. For carbon no change in thermo-electric power was observed with the strongest field used, and  $R_H$  was constant within the limits of experimental error. The relation for ferromagnetic elements appears to be more complicated.

A. B. M.

**Thermo-electric Effect in Single Crystal Zinc Wires.** E. G. LINDER (*Physical Rev.*, 1925, [ii], 26, 486—490).—The ratio of thermo-*E.M.F.* to the temperature difference between the ends of the crystal is not linear, but increases more rapidly with the latter. For wires with the angle of orientation (between the vertical axis of the crystal and the axis of the wire)  $\theta = 14^\circ$  and  $\theta = 86.5^\circ$  the *E.M.F.* (directed at the hot junction from the latter to the former) with  $t = 250^\circ$  is  $6.50 \times 10^{-4}$  volt.

A. A. E.

**Thermal Conductivity and Thermo-electric Force of Single Metal Crystals.** P. W. BRIDGMAN (*Proc. Nat. Acad. Sci.*, 1925, 11, 608—612).—The thermal conductivity at the ordinary temperature and the thermo-*E.M.F.* over the range from the ordinary temperature to  $100^\circ$  have been measured as a function of the orientation for single crystal rods of bismuth, zinc, cadmium, and tin. Within wide limits of experimental error, the thermal conductivities of the four metals have rotational symmetry about the axis and also the electrical resistance is an inverse linear function of the thermal conductivity. These results are in agreement with the deductions of Voigt. The generalised Wiedemann-Franz law does not hold for all directions in the crystals. In the thermo-*E.M.F.* the Thomson effect is directly proportional to the resistance, whilst, except with cadmium, no such relationship exists for the Peltier effect. The Thomson effect shows rotational symmetry, whilst the Peltier effect does not. Considerations of the internal Peltier effect lead to the assumption that an electron functions as a dipole and that when moving in different directions in the non-isotropic force-field of a crystal it assumes different orientations.

A. E. M.

**Measurements on Small Tungsten Arcs.** W. DE GROOT (*Physica*, 1925, 5, 121—129).—Determination of the temperature (by radiation pyrometry) of the small spherical electrodes in a tungsten arc, combined with voltage and current measurement, permits verification of some theoretical considerations on the energy balance of the electrodes. The anode receives an amount of heat  $U_a \geq i\phi$ ; the cathode  $U_k \leq -i\phi + ne(V_i + fV)$ ; where  $i$  is the current,  $\phi$  Richardson's constant,  $n$  the number of positive ions reaching the cathode,  $V_i$  ionisation potential,  $f$  a factor varying from  $\frac{1}{2}$  to 1 and depending on the cathodic field concentration. Besides the obvious condition (if  $V < 2V_i$ ) that  $ne \leq \frac{1}{2}i$ , it can be expected that  $ne < (U_k + i\phi)/(V_i + \frac{1}{2}V)$ . In neon these relations were completely confirmed by the results; at low current values (high potential) the fraction mentioned approaches  $\frac{1}{2}i$ ; in argon and mercury the ion current is slightly higher. The arc voltage, which converges to  $V_i$  at high current values in neon and in argon, approaches 15.2 V in mercury, far above  $V_i$ . Thomson's condition for an arc: voluntary electron emission of cathode  $i - ne = i_R$ , the thermionic electron stream, is satisfactorily borne out for neon and mercury; for argon the values of  $i_R$  are a little too low.

CHEMICAL ABSTRACTS.

**Refractive Index of Air in the Visible Spectrum between 0° and 100°.** A. PÉRARD (*J. Phys. Radium*, 1925, [vi], 6, 217—227).—The index of refraction of air has been obtained by the observation of interference fringes in a vacuum and then in dry air free from carbon dioxide for five lines in the spectra of cadmium and mercury at temperatures varying between 0° and 100°. The refraction  $(N-1)$  is nearly proportional to the pressure at 600 and 760 mm. The variation of the refractive index with temperature is given by  $N_0 - 1/(1 + \alpha\theta) = N_\theta - 1$ , where  $N_0$  and  $N_\theta$  are the indices at 0° and  $\theta^\circ$ , respectively, and  $\alpha$  is a constant, which does not appear to depend on the wave-length. The average value for  $\alpha$  is  $0.003716 \pm 0.000007$ . The following are the most probable values:

$\lambda$ in $\mu$ .	0.4358	0.5461	0.5780	0.5086	0.6438
$(N_0 - 1) \cdot 10^6$	296.68	293.34	292.73	294.21	291.77

The following general formula is valid for pressures up to 1 atm., temperatures 0—100°, and wave-lengths in the visible  $(N-1) \cdot 10^6 = (288.02 + 1.478/\lambda^2 + 0.0316/\lambda^4)h(1 + \beta h)/760(1 + 760\beta) \cdot 1/(1 + 0.003716\theta)$ , where  $\lambda$  is the wave-length in  $\mu$ ,  $h$  is the pressure in mm. The value of  $\beta$  is small and may be neglected. A list of previous determinations and numerical results is given. R. A. M.

**Optical Properties of Ethylenic Isomerides.** J. ERRERA and V. HENRI (*Compt. rend.*, 1925, 181, 548—550; cf. A., 1913, ii, 815).—The ultra-violet absorptive power of *trans* isomerides is greater than that shown by the *cis* forms. Similarly the refraction for the sodium D-line is higher for the more strongly absorbing isomeride. The differences in extinction coefficient increase with decreasing wave-length. The data include molecular refractions



for *cis*- and *trans*-dichloroethylenes (20.25, 20.56), bromoethylethylenes (27.8, 27.9), bromomethylethylenes (27.8, 27.85), chloroiodoethylenes (28.6, 29.5), maleic and fumaric esters (42.23, 42.9), methyl citraconate and mesaconate (37.2, 38), *isocrotono*- and *crotono*-nitriles (20.5, 20.7), *isocrotonic*, m. p. 15.5°, and *crotonic*, m. p. 72°, acids (21.4, 22.85). The absorption spectra for the first four pairs of isomerides are recorded and generally the ratio  $e_{trans}/e_{cis}$  is 1.0—1.5. The work enables the solid crotonic acid and its corresponding nitrile to be classified as *trans* isomerides.

R. A. M.

**Metastability of Matter and Physical Constants.** E. COHEN (*Z. Elektrochem.*, 1925, **31**, 539).—Attention is directed to the desirability of taking possibilities of monotropic or enantiotropic diversity into account in laying down the physical constants of solids.

W. A. C.

**Specific Heat of an Elastic Gyroscopic Model of the Hydrogen Molecule.** J. H. VAN VLECK (*Physical Rev.*, 1924, [ii], **23**, 308).—Even when the vibrational degree of freedom is considered, the specific heats of the Born model and the author's non-gyroscopic model of the hydrogen molecule are almost identical if in each case the probability is taken proportional to the total angular momentum. The Born model is in agreement with specific heat observations up to 2000° Abs., provided the moment of inertia and vibrational frequency are  $1.98 \times 10^{-41}$  g.cm.<sup>2</sup> and  $1.46 \times 10^{-14}$  per sec., respectively.

A. A. E.

**Specific Heat of Liquids according to the Theory of Corresponding States.** E. FOA (*Atti R. Accad. Sci. Torino*, 1925, **60**, 160—166).—Theoretical. By combining thermodynamic relationships with the principle of corresponding states it is deduced that, at the same reduced temperature, the difference between the molar heat capacity,  $C_v$ , of a substance as a liquid and its molar heat capacity at constant pressure,  $C_p$ , when in the condition of a perfect gas, is the same for all substances which conform to the principle of corresponding states. This relationship has been tested for water, ammonia, carbon dioxide, and sulphur dioxide at a series of reduced temperatures between  $\theta=0.5$  and  $\theta=0.95$ , and is found to be approximately valid. The value of  $C_v - C_p$  rises from 9.7 at  $\theta=0.5$  to about 23.0 at  $\theta=0.95$ . For the reduced temperature  $\theta=0.6$ , the relation is satisfied by chloroform, ethyl ether, acetone, and benzene, the value of  $C_v - C_p$  averaging 11.9.

F. G. T.

**Theory of the Specific Heats of Electrolytes.** F. ZWICKY (*Physikal. Z.*, 1925, **26**, 664—665).—A solution of  $n$  mols. of a non-electrolyte such as sugar in  $n_0$  mols. of water (specific heat  $c_0$ ) shows a specific heat given by  $C=n_0c_0+nc$ , where  $c$  is the specific heat of 1 mol. of the non-electrolyte in the solid state. Thus  $C$  is always greater than  $n_0C_0$ , in contradistinction to the view that for electrolytes  $C$  is generally less than  $n_0c_0$ . The electric charges exert a two-fold influence. The electric work  $A_e$  given by  $e^2(D-1)/2aD$  ( $D$  is dielectric constant of water,  $a$  ionic radius) is

necessary to annul electric polarisation of water. The work  $A_x$ , equal to the negative work of compression, is required to counteract the pressure effect of the charges. The free energy  $f$  of 1 mol. of electrolyte solution will then be given by  $f=f_0-A_e-A_x$ , where  $f_0$  is the value for a non-electrolyte. The energy of the electrolyte solution is then  $U=f-T\delta f/\delta T$  and  $C_v=(\delta U/\delta T)_v$ . The smallness of the specific heat of an electrolytic solution is due much more to the  $A_x$  than to the  $A_e$  factor.

The foregoing may be tested by using the dipolar moment of water as an unknown constant, and the relation  $\delta C_p/\delta T=-T\delta^2 v/\delta T^2$  for calculating the specific heat of water at increased pressures from measurements of specific volume at high pressures. Good agreement with experiment is obtained; the data, however, are not given in this preliminary paper. The reasoning may be extended to other physical properties of electrolytes with the proviso that the Debye-Hückel theory must be introduced as occasion requires.

R. A. M.

**Errors Introduced in certain Thermochemical Data and the Correction Coefficients of these Data.** W. SWIENTOSLAWSKI (*J. Chim. physique*, 1925, **22**, 391—394).—Mainly introductory to following papers. The systematic errors which occur in determinations of heats of combustion are tabulated. The majority of previous investigations contain a systematic error arising from the acceptance of the specific heat of water given by Regnault (error +0.13%) and neglect of the correction of the thermometer to the hydrogen scale (0.30% error). The chief of other errors lies in the determination of the constant for the calorimetric bomb. Berthelot's method is discussed. The correction coefficient for given data is evaluated by comparing the heats of combustion,  $A_1, A_2$ , etc., of several substances as found with freshly determined values  $A_1', A_2'$ , etc. (benzoic acid, 6324 Cal. at 15° for 1 g. in air is taken as standard). The mean value of the ratios  $A_1':A_1, A_2':A_2$ , etc. is the correction coefficient to be applied.

L. S. T.

**Correction of the Thermochemical Data of P. Lemoult.** W. SWIENTOSLAWSKI and M. POPOV (*J. Chim. physique*, 1925, **22**, 395—398; cf. preceding abstract).—The correction coefficient for the data on heats of combustion by Lemoult has been evaluated from a redetermination of the figures for naphthalene, *p*-aminoazobenzene, and  $\beta$ -naphthylamine. The mean of three ratios gives  $0.99489 \pm 0.01\%$ . A table of uncorrected and corrected data for all substances investigated by Lemoult is given.

L. S. T.

**Correction of the Thermochemical Data of A. Valeur.** W. SWIENTOSLAWSKI and (MLLE.) H. STARCZEWSKA (*J. Chim. physique*, 1925, **22**, 399—401; cf. preceding abstracts).—The coefficient of correction for the data of Valeur (A., 1901, i, 154) evaluated from the redetermined values of the heats of combustion of benzoquinone,  $\beta$ -naphthol, and anthraquinone, is  $0.9974 \pm 0.01\%$ . Corrected and uncorrected values of all substances examined are again given.

L. S. T.

**Simple Method for the Indirect Determination of Molecular Heats of Vaporisation.** J. NARBUTT (*Z. Elektrochem.*, 1925, **31**, 511—512).—An apparatus for determining the molecular heat of vaporisation from the equation  $\lambda = RT^2/p \cdot dp/dT$  is described. A water manometer is recommended as being as accurate as a mercury instrument and more easily made. The error in the values obtained by this method is less than 0.2%.  
N. H. H.

**Latent Heat of Fusion of Camphor.** N. N. EFREMOV (*Bull. Acad. Sci. St. Pétersbourg*, 1919, **13**, 765—776; from *Chem. Zentr.*, 1925, ii, 524).—The latent heat of fusion of camphor calculated from the freezing-point depression with different compounds is 8.39 cal./g.  
G. W. R.

**Heat of Dissociation of Calcium Carbonate and the Entropy of Carbon Dioxide.** H. L. J. BÄCKSTRÖM (*J. Amer. Chem. Soc.*, 1925, **47**, 2443—2449).—The heat of dissociation of calcite at 25° has been obtained from the heat of solution of calcite in hydrochloric acid and the heat of solution of calcium oxide in the acid; the value obtained is  $42,600 \pm 200$  cal./mol. On the basis of this value a free energy equation for the reaction  $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$  has been derived, which represents the dissociation pressure measurements within limits of error. The entropy of carbon dioxide was found to be 50.85 units, which is in good agreement with values obtained from other sources.  
W. T.

**Thermochemical Researches on the Oximes. IV. Acetaldoxime.** (MLLE.) A. DORABIALSKA (*Rocz. Chem.*, 1925, **5**, 386—394; cf. A., 1922, ii, 548; 1924, i, 646).—The heats of neutralisation by sodium hydroxide of various preparations of acetaldoxime fall into two series, one varying about 4.6 cal., the other about 3.6 cal. It is hence deduced that ordinary preparations of acetaldoxime are mixtures of two unstable stereoisomerides of varying composition. The heat of transformation of the  $\alpha$ - into the  $\beta$ -isomeride is about -2 cal.  
R. T.

**White and Black Diamonds and their Relation to [other Forms of] Carbon.** W. A. ROTH and W. NAESER (*Z. Elektrochem.*, 1925, **31**, 461—466).—The heats of combustion of different forms of carbon have been measured, with the following results:  $\beta$ -graphite,  $7856 \pm 1$ ;  $\alpha$ -graphite,  $7832 \pm 1$ ; white diamond,  $7873 \pm 4$ ; black diamond (carbonado),  $7884 \pm 2$  cal./g. The results of Berthelot and Petit (*Ann. Chim. Phys.*, 1889, **18**, 80), which showed a lower heat of combustion (and therefore a greater stability) for white diamond at the ordinary temperature than for graphite, are thus refuted. Several different forms of natural and artificial graphite were measured. The  $\alpha$ -form is that stable at higher pressures. The high value for carbonado is explained by the assumption that it consists of normal crystals of white diamond permeated with amorphous carbon, the heat of combustion of which is about 8060. This is in general agreement with the X-ray work of Gerlach (A., 1924, ii, 753).  
N. H. H.

**Density and Temperature.** V. W. HERZ (*Z. Elektrochem.*, 1925, **31**, 512—514; cf. A., 1924, ii, 524).—From the consideration of a large number of substances cited, it is shown that the temperature, expressed as a fraction of the critical temperature (both in absolute units), at which the density in the liquid state bears any given relation to that of the saturated vapour, is very nearly the same for all substances. Other temperature-density relationships connected with the above are demonstrated. N. H. H.

**Density of Beryllium Halides.** C. MESSERKNECHT and W. BILTZ (*Z. anorg. Chem.*, 1925, **148**, 152—156).—The following data are recorded: beryllium chloride,  $d_4^{25}$  1.901; bromide,  $d_4^{25}$  3.465; iodide,  $d_4^{25}$  4.325. The density of the chloride is in agreement with the value obtained by Hönigschmid and Birckenbach (A., 1922, ii, 214). J. S. C.

**Additivity of Boiling Points.** J. J. VAN LAAR (*Physica*, 1925, **5**, 130—134).—Objection is raised to the use of  $\sqrt{a}$  values calculated from measurements of the b. p. (cf. van Arkel and de Boer, this vol., ii, 734, 758) instead of the critical point; the b. p. is not a "corresponding" temperature and may give untrustworthy  $\sqrt{a}$  values. The use of methane and carbon tetrachloride values happens to be rather unfortunate, since these substances show large discrepancies from the rules originally given.

CHEMICAL ABSTRACTS.

**Additive Properties of Boiling Points.** II. A. E. VAN ARKEL and J. H. DE BOER (*Physica*, 1925, **5**, 134—141; cf. this vol., ii, 734, 758, and preceding abstract).—For many organic halogen compounds, particularly methyl halides, it is a sufficient condition for the additivity of the b. p. that  $\sqrt{a_x/b_x}$  has the same value for every halogen; this leads to a b. p. formula  $T_s = K(\Sigma V - V_c)^2/\Sigma V = K_2(\Sigma \sqrt{a_x})^2/\Sigma V$  ( $V$  is the Kopp molecular volume). If this equation is applied to ethane compounds,  $K$  is found to have a lower value; this may be due to a mutual screening effect of the halogen atoms ( $X$ ), with a consequent decrease of  $\sqrt{a}$ . The authors express this effect in an empirical screening coefficient to be subtracted from  $\sqrt{a}$ . Values of the b. p. of the pure halogens and of iodine monochloride and monobromide calculated in this manner agree well with the facts.

CHEMICAL ABSTRACTS.

**Value of  $\sqrt{a}$  Calculated from the Vapour Tensions of Alkali Metals and Halides in Relation to the Additive Nature of this Quantity.** J. J. VAN LAAR (*Z. anorg. Chem.*, 1925, **148**, 235—255; cf. this vol., ii, 950).—From existing data, the vapour-pressure equations of the type,  $\log p = -A/T - B \log T + C$ , are derived for the alkali metals and halides, the value of  $B$  being practically zero in the case of the salts. From the values of  $A$ , the magnitude of the quantity  $a_0$  in the author's equation of state is calculable. The value of  $\sqrt{a_0}$  for the halides is approximately

the sum of the corresponding values for the metal and halogen concerned.

J. S. C.

**Vapour Pressure of Sodium.** W. H. RODEBUSH and T. DE VRIES (*J. Amer. Chem. Soc.*, 1925, **47**, 2488—2493).—The vapour pressure has been found from the weight of vapour passing through a small opening in a definite time at constant temperature, and has been determined over the range 181.8—597°. The following equation holds for the vapour pressure from 180° to the b. p.:  $\log p = -5922/T - 1.6184 \log T + 12.9605$ . The entropy of sodium vapour at 298° Abs. and 1 atm. is calculated to be  $35.7 \pm 0.5$  units.

W. T.

**Kinetic Theory of Vaporisation. II.** S. C. BRADFORD (*Phil. Mag.*, 1925, [vi], **50**, 1147—1158; cf. this vol., ii, 26).—The equilibrium between liquid and vapour is considered on the basis of the kinetic theory, and the following expression for the vapour pressure is deduced:  $p = 81.84 T \lambda e^{-9.656 S v A^{2/3} / T \delta' \lambda^2} / A \Phi$ , where  $\lambda$  is the ratio of the average velocity of the molecules in the liquid to that in the vapour,  $A$  is the factor giving the state of aggregation of the liquid,  $\Phi$  the co-volume of the liquid,  $S$  the surface tension,  $v$  the volume of a mole of the liquid, and  $\delta' \times 10^{-8}$  the nearest distance of approach of the centres of the molecules in the liquid;  $\lambda$  is calculated from data for a few almost unassociated liquids and shown to be a function of density and temperature only. The formula is applied to a number of liquids at different temperatures and gives good agreement between calculated and observed values.

A. B. M.

**Existence of Liquid Racemates.** F. D. AGUIRRECHE (*Anal. Fis. Quím.*, 1925, **23**, 409—418).—The existence of racemic compounds in the liquid state implies molecular association, and may therefore be best studied by means of those properties which are affected by association. The principal physical properties of ethyl *d*-tartrate and ethyl *r*-tartrate are compared. The viscosity of the latter is less than that of the former. The differences in density, refractive index, and surface tension are insignificant.

G. W. R.

**Theory of State of Matter. II. Internal Pressure, Co-volume, and Association.** F. SCHUSTER (*Ber.*, 1925, **58**, [B], 2183—2186; cf. this vol., ii, 951).—Expressions are deduced for the internal pressure and molecular co-volume of substances and the constants are calculated for an extended series of inorganic and organic compounds. The factor of association at the b. p. under normal pressure is calculated for many substances, the results being in agreement with the data obtained by other methods.

H. W.

**Determination of Surface Tension from Photographic Records of the Formation of Drops.** T. MOLODYI and F. PAVLOV (*Bull. Acad. Sci. St. Pétersbourg*, 1920, **13**, 241—258; from *Chem. Zentr.*, 1925, ii, 750).—The formation of drops of a liquid

in an atmosphere of its own vapour was followed kinematographically. From the records the critical value for the diameter of the "neck" of a forming drop at the point of destruction of equilibrium was obtained and the surface tension was calculated from Tate's formula  $\pi d\gamma = P$ , where  $d$  is the critical diameter,  $\gamma$  the surface tension, and  $P$  the weight of the drop. The following values were obtained: water at  $14.9^\circ$ ,  $7.24$ — $7.46$ ; at  $16.5^\circ$ ,  $7.29$ — $7.38$ ; aniline at  $16.1^\circ$ ,  $4.31$ — $4.42$ ; *m*-xylene at  $14.7^\circ$ ,  $2.76$ — $2.89$ ; benzene at  $14.7^\circ$ ,  $2.97$ — $3.05$ ; ethyl alcohol at  $15^\circ$ ,  $2.39$ — $2.47$ . G. W. R.

**Viscosity of Liquids under Pressure.** P. W. BRIDGMAN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 603—606).—The relative viscosities of forty-three liquids, including water, have been measured at  $30^\circ$  and  $75^\circ$  under pressures from atmospheric to 12,000 kg. per sq. cm. The values for water have been determined also at  $0^\circ$  and  $10.3^\circ$ . At low temperatures and pressures, the viscosity of water decreases with increasing pressure, passing through a pressure minimum, and then increases. With increasing temperature this minimum flattens and disappears finally at about  $25^\circ$ , above which temperature the viscosity increases continuously with increasing pressure. The viscosity of the other liquids increases uniformly with increasing pressure. The increase under a pressure of 12,000 kg. per sq. cm. varies from 10-fold for methyl alcohol to at least  $10^7$ -fold for eugenol. The temperature coefficient of viscosity increases with increasing pressure. The results are not in accord with the theories of Phillips (*ibid.*, 1921, **7**, 172) and Brillouin (*J. Phys. Radium*, 1922, [vi], **3**, 326, 362), and since the pressure effects are greatest with substances with more complicated molecules, it is suggested that there is an interlocking of these which the theories neglect.

A. E. M.

**Diffusion of Helium through Different Glasses.** C. C. VAN VOORHIS (*Physical Rev.*, 1924, [ii], **23**, 557).—Measurements were made between  $200^\circ$  and  $500^\circ$ . Increase of silica and boron trioxide increases the permeability; increase of basic oxides decreases the permeability, but oxides only slightly acidic or basic, *e.g.*, lead oxide and alumina, have scarcely any effect. A. A. E.

**General Theory of Solvent Systems.** A. F. O. GERMANN (*J. Amer. Chem. Soc.*, 1925, **47**, 2461—2468).—Based on a study of the analogy between reactions in water and in carbonyl chloride solutions, a general theory of acids, bases, and salts in their relation to a parent solvent has been outlined, and its application to sulphuryl chloride, selenium oxychloride, and thionyl chloride as solvents is discussed.

W. T.

**Vapour Pressures and Miscibilities of Binary Liquid Mixtures.** K. F. HERZFELD (*Z. Elektrochem.*, 1925, **31**, 536—539).—By a simplification of van der Waals' method of treating liquid mixtures, the following expression for the energy of a mixture is arrived at:  $U = -\lambda_A \cdot x - \lambda_B(1-x) + \lambda_{AB}x(1-x)$ , where  $\lambda_A$  and  $\lambda_B$  are the latent heats of the components and  $\lambda_{AB}x(1-x)$  is the heat

of mixing at the molecular concentration  $x$ . It would follow that the same heat is evolved when little of component  $A$  is dissolved in much of component  $B$  as *vice versa*. A formula for the ratio of partial pressures in the vapour phase is developed, according to which the vapour-pressure curve is convex or concave upwards, according as the heat of mixing is negative or positive. All pairs of liquids have an azeotropic mixture below the temperature given by  $T = \lambda/R \log_e p_A/p_B$ , where  $\lambda$  is the heat of mixing; the temperature range in which azeotropy can no longer exist may, however, be out of practical bounds. The upper critical temperature of miscibility may be expressed by the formula  $T_K = -\lambda(2R)$ , from which the molecular ratio of components should always be 1:1 at the critical point; this is approximately confirmed by the available data.

W. A. C.

**Selective Solvent Action. IV. Cryoscopy in Mixed Solvents.** R. WRIGHT (*J. Chem. Soc.*, 1925, **127**, 2234—2238; cf. T., 1922, **121**, 2252; 1923, **123**, 2493; A., 1924, ii, 838; 1898, ii, 17).—The addition to the mixed solvents nicotine-water, alcohol-benzene, acetone-benzene, and alcohol-ethylene dibromide of a substance soluble only in one constituent raises the freezing point of the other constituent. It appears that a semi-solute forms solvates with the constituent in which it is soluble, and thus raises the freezing point and vapour pressure of the one in which it is insoluble. When the added substance is also soluble to a slight extent in the second constituent, the freezing point of this constituent is first raised and then lowered as the concentration of the solute is increased. If the solute is completely miscible with each constituent of a 50% mixture, then the effect on the freezing point indicates which constituent has the greater attraction for it. Thus the lower members of the aliphatic alcohol series show a greater attraction for ethyl alcohol than for benzene, whereas the higher alcohols and aromatic compounds have a greater attraction for benzene.

A. G.

**Theory of [Solid] Solutions.** P. LASAREV (*Bull. Acad. Sci. St. Pétersbourg*, 1919, **13**, 207—214; from *Chem. Zentr.*, 1925, ii, 515).—The author calculates the force exerted on a molecule lying on the interface between two phases by the molecules of each phase. The force acting between any two molecules is an unknown but constant function of the distance between them, and consists of two terms, of which one is proportional to, and the other independent of, the dielectric constant of the medium. Since a solid substance attracts its superficial molecules with a force proportional to its atomic concentration, and as the latter is proportional to the hardness, the solubility must vary inversely with hardness.

G. W. R.

**Nature and Constitution of Glass.** W. E. S. TURNER (*J. Soc. Glass Tech.*, 1925, **9**, 147—166).—Investigation of the constitution of glass in the light of published physical and chemical data gives indeterminate results. Molecular association is suggested by surface-

tension determinations and by the analogy of certain properties with those of other liquids. On the other hand, relationships between percentage oxide composition, various physical properties, and chemical durability suggest a state of dissociation. Silica probably enters into loose combination with the silicates present and it may form a sponge or network soaked in silicates or their products of dissociation. [Cf. *B.*, 1925, 920.] A. COUSEN.

**Constitution of Glass.** F. ECKERT (*J. Soc. Glass Tech.*, 1925, 9, 267—272).—The constitution of the final product is dependent on the previous heat treatment of the glass, that is, on the initial state and on the time which the material has had to adjust itself to the temperature range, since the velocity of internal reactions (molecular interaction, dissociation, etc.) is a function of the temperature. Recent determinations of optical constants and density of glasses have indicated variations of properties determined by the past history of the glass. Similar changes are shown in the viscosity and in hardening phenomena observed with rapidly cooled glass. A. COUSEN.

**Constitution and Density of Glass.** A. Q. TOOL and E. E. HILL (*J. Soc. Glass Tech.*, 1925, 9, 185—207).—The hypothesis is advanced that when glass is cooled under proper conditions, certain practically reversible processes occur, involving some or all of the molecules and so preventing other possible processes often associated with cooling, such as segregation, crystallisation, etc. The character and rate of the processes are determined by the temperature of the glass, and when the latter is maintained at any given value the reactions proceed until equilibrium is attained. In proof of the theory, samples of flint and of pyrex glass when heated to various temperatures in the range 360—750° and maintained at these temperatures until equilibrium is attained, were found on cooling in air to have varying densities according to the temperature of treatment, although strain was absent in each case. Preliminary tests have shown that the change in the refractive index of the flint glass is approximately proportional to that of the density. [Cf. *B.*, 1925, 920.] A. COUSEN.

**Glasses as Supercooled Liquids.** G. TAMMANN (*J. Soc. Glass Tech.*, 1925, 9, 166—185).—Conditions governing the supercooling of liquids are (1) the number of crystallisation centres in unit volume, which, with easily fusible substances, generally reach a maximum at about 100° supercooling, and (2) the rate of crystallisation, which, when not exceeding 3—4 mm. per min., generally reaches a maximum at about 30° supercooling. The formation of crystal centres is subject to the laws of probability. Liquids are mobile for about 90° supercooling, then become viscous, and at 20° lower brittle and hard. At normal pressures glasses are unstable, but the growth of crystal centres is so slow as to be practically negligible. The temperature of maximum crystallisation centre formation is influenced little by impurities, but the actual number



of centres formed is greatly affected. Supercooling conditions for mixed salts and for glasses are considered. [Cf. *B.*, 1925, 920.]

A. COUSEN.

**Viscosity of Glass.** V. H. STOTT (*J. Soc. Glass Tech.*, 1925, 9, 207—225).—The log. viscosity-temperature curve of a soft laboratory glass gave a point of inflexion at about 500°. The heating curve indicated heat absorption beginning at 535°. Application of the Michelson load-displacement formula also indicated a state of discontinuity between 486° and 529°. All these phenomena are probably caused by the same change of constitution. The extended form of the Le Chatelier viscosity-temperature equation for glass, namely,  $\log . \log \eta/\eta_0 = Mt + P$ , is not capable of general application. [Cf. *B.*, 1925, 921.]

A. COUSEN.

**X-Ray Diffraction Measurements on Some Soda-Lime-Silica Glasses.** R. W. G. WYCKOFF and G. W. MOREY (*J. Soc. Glass Tech.*, 1925, 9, 256—257).—Glasses crystallising with greatest difficulty give broad X-ray powder bands; easily crystallisable glasses give lines when the glasses contain a considerable proportion of readily crystallisable components. [Cf. *B.*, 1925, 921.]

A. COUSEN.

**Cause of Inverse Segregation [in Alloys].** G. MASING (*Z. Metallk.*, 1925, 17, 251—257).—The conditions for the occurrence of inverse segregation in an alloy are that there must be a tendency for the primary crystals to grow in a dendritic form, a tendency for the formation of mixed crystals having zones of differing composition, and a considerable difference in the composition of the crystals first formed and the remaining liquid (cf. Bauer and Arndt, *ibid.*, 1921, 13, 497). Iokibe (*B.*, 1924, 297) has shown that inverse segregation occurs in zinc-copper alloys in which zinc predominates, and that such alloys expand on solidification. This work has been confirmed, and similar observations on certain copper-tin and aluminium-copper alloys show that expansion on solidification is the primary cause of inverse segregation, whilst a tendency to supercooling is a secondary cause. Simple contraction on cooling is shown mathematically to have no influence on inverse segregation. [Cf. *B.*, Dec. 24th.]

A. R. P.

**Chemical Resistance of Metals and Alloys, especially Those Containing Molybdenum.** W. GUERTLER and T. LIEPUS (*Z. Metallk.*, 1925, 17, 310—315).—The resistance of more than one hundred alloys containing two or more of the metals cobalt, nickel, iron, chromium, manganese, tungsten, molybdenum, copper, silicon, tin, and aluminium, against attack by acid, alkaline, and neutral salt solutions has been examined. Whilst a considerable number of the alloys, especially those containing nickel, cobalt, and molybdenum or iron, are very resistant to alkaline reagents, it is found that only certain alloys of the nickel, chromium, and cobalt or molybdenum series resist nitric acid. The most resistant alloys to hydrochloric acid consist of nickel with silicon and molybdenum,

nickel-cobalt-molybdenum, and cobalt-manganese-molybdenum. Nickel containing small amounts of molybdenum with or without aluminium and chromium is the only metal that is not corroded by mercuric chloride solutions. [Cf. *B.*, 1925, 925.] A. R. P.

### Solubilities of the Phosphates of Zirconium and Hafnium.

G. HEVESY and K. KIMURA (*J. Amer. Chem. Soc.*, 1925, **47**, 2540—2544).—The composition of zirconium and hafnium phosphate precipitated from 6*N*-hydrochloric acid corresponds with  $\text{MO}(\text{H}_2\text{PO}_4)_2$ . On ignition, the precipitates lose 2 mols. of water. The solubility of the zirconium phosphate in 6*N*-hydrochloric acid is 0.00012 and that of the hafnium phosphate 0.00009 mol. per litre. In 10*N*-hydrochloric acid the values are 0.00023 and 0.00012. The importance of the phosphate precipitation for the detection and determination of the two elements is discussed. W. T.

### Solubility of Ammonium Salts in Presence of Ammonia.

E. WEITZ (*Z. Elektrochem.*, 1925, **31**, 546—549).—Ammonium salts of monobasic acids are in general more soluble in ammonia than in water alone; those of polybasic acids are less soluble, and may be salted out of solution by passing in ammonia gas. The difference is attributed to the formation of soluble ammonia additive compounds by monobasic salts, but not by polybasic salts. Fluoride, iodate, periodate, and borate behave as if the acids were polybasic, probably owing to polymerisation. On the other hand, the persulphate and the dithionate show the same effect as monobasic salts, possibly because the substituted hydrogen atoms are on two distinct branches of the structural molecule. Ammonium isophthalate and benzene-*m*-disulphonate also stand out as exceptions, although their *o*- and *p*-isomerides follow the polybasic rule. W. A. C.

**Influence of Electrolytes on the Solubilities of Some Organic Acids.** N. A. YAJNIK, M. P. JAIN, and D. NATH (*J. Indian Chem. Soc.*, 1925, **2**, 115—128).—The influence of several electrolytes and of their respective anions and cations on the solubility of *o*-, *m*-, and *p*-nitrobenzoic, *p*-amino- and *p*-hydroxy-benzenesulphonic acids in water, at varying concentrations and temperatures, has been studied. The results obtained for the sulphates, nitrates, and chlorides of ammonium, sodium, potassium, calcium, strontium, and barium at 25°, 35°, and 45° in the case of the nitrobenzoic acids, and 20°, 30°, and 40° in the case of the sulphonic acids, are tabulated and discussed. With increase in the concentration of the electrolyte, the solubility of the *o*- and *p*-acids first increases, reaches a maximum (that of the *para* isomeride being greater than that of the *ortho*), and then decreases again, whilst in the case of the *m*-acids an initial rapid decrease in the solubility is followed by a more slow and regular decrease. With rise of temperature, the influence of the nitrates and chlorides of the alkali metals decreases, whilst that of the corresponding salts of the alkaline-earth metals increases. The influence of the cations increases in the order given above, whilst the influence of the anions

varies in the order  $\text{NO}_3' > \text{Cl}' > \text{SO}_4''$ . The nature of the acid also affects the results, the solubility of the stronger acids being influenced to a greater extent than that of the weaker, the nitro-acids more than the amino-acids, which in turn are more influenced than the hydroxy-acids.

J. W. B.

**Cause of Surface Tension.** E. H. KENNARD (*Nature*, 1925, **116**, 643).—Polemical.

A. A. E.

**Variation in the Surface Tension of Solutions as a Function of the Concentration.** J. SCHECHTMANN (*Bull. Acad. Sci. St. Pétersbourg*, 1919, **13**, 657—662; from *Chem. Zentr.*, 1925, ii, 530—531).—The surface tension of solutions of naphthalene in benzene, as determined by capillary rise is represented by  $\gamma = 28.65 + 1.1079c$  where  $\gamma$  is the surface tension at  $20^\circ$  and  $c$  the molar concentration. The temperature coefficient  $1/\gamma \cdot d\gamma/dt$  at  $20^\circ$  is 0.00453. Density and concentration are connected by the relation-ship  $d = 0.8787 + c/51.654$  at  $20^\circ$ .

G. W. R.

**Orientation of Molecules in the Surfaces of Liquids.** W. D. HARKINS (*2nd Colloid Symposium Monograph*, 1925, 141—173).—A consideration of the development of the concept of interfacial orientation, the wedge theory of emulsions, molecular orientation as exhibited by the relations between the energy of surface formation and that of vaporisation, energy of thermal emission, adsorption and distribution of substances between different phases, relations at surfaces and interfaces, and adsorption at interfaces.

CHEMICAL ABSTRACTS.

**Unimolecular Soap Films in Emulsions.** W. RIEMAN 3RD and P. A. VAN DER MEULEN (*J. Amer. Chem. Soc.*, 1925, **47**, 2507—2514).—Emulsions of the oil-in-water type, containing a solution of phenol in toluene as the internal phase and sodium oleate as the emulsifying agent, have been studied (cf. A., 1924, ii, 389). The average area of interface covered per mol. of soap depends primarily on the concentration of soap in the external phase of the dilute emulsion. Most of the phenol passes from the toluene to the water layer and may partly displace the soap in the interface. The results are in agreement with the hypothesis that the protective film is composed of a single layer of oriented molecules. With soap concentrations up to 0.01M, an average area of  $17 \text{ \AA}^2$  per soap mol. was found, and it is suggested that this may be the average cross-sectional area of the hydrocarbon chain of oleic acid. Soaps of stearic acid are not sufficiently soluble to give satisfactory emulsions.

W. T.

**Multimolecular and Unimolecular Films.** W. D. HARKINS and J. W. MORGAN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 637—643).—Measurements of the variations of compressibility with change in area have been made for a number of surface films on water and on aqueous salt solutions, principally calcium chloride. The results are discussed in connexion with the preceding work (A., 1923, ii,

127). In general, multimolecular films are much weaker than unimolecular ones. Mixtures of two substances, each of which gives a unimolecular film when alone, give rise to unimolecular films. When mixed films composed of two substances one of which is normally unimolecular and the other multimolecular are compressed, the substance giving the multimolecular film slides over the other, leaving a unimolecular film of the latter beneath it.

A. E. M.

**Adsorption Forces and their Electrical Nature. II. The Electrical Moment of the Adsorbed Molecule and the Surface Energy of the Adsorbent.** B. ILIN (*Phil. Mag.*, 1925, [vi], 50, 1144—1146; cf. A., 1924, ii, 663).—The electrical theory of adsorption leads to a relation between heat of adsorption and the electrical moment of the adsorbed molecules ( $\tau$ ), permitting calculation of the absolute value of the latter. This calculation is applied to Titov's results for the adsorption of gases by charcoal ( $\tau$  varies from  $4.1 \times 10^{-19}$  for hydrogen to  $20.5 \times 10^{-19}$  for ethylene), and Langmuir's results for mica ( $\tau$  varies from  $3.0 \times 10^{-19}$  for hydrogen to  $15.0 \times 10^{-19}$  for ethylene). These results are of the same order of magnitude as given by other methods. The data are shown to lead also to an approximate value of the surface energy of the solid adsorbent, giving for charcoal 1000 ergs/cm.<sup>2</sup>

A. B. M.

**Absorptive Power of Lipoid Mixtures.** A. SCHÄFER (*Biochem. Z.*, 1925, 159, 250—256).—The distribution of ferric thiocyanate between water and a second medium consisting of ether, benzene, oil, an ether-benzene mixture, or an ether-oil mixture indicates that the solvent power of the ether is diminished by the presence of either benzene or oil.

P. W. C.

**Adsorption of Iodine by Starch.** E. ANGELESCU and J. MIRCESCU (*Soc. Romana Stiinte, Bul. Chim.*, 1924, 27, 59—64).—The adsorption of iodine by starch is independent of the concentration of potassium iodide between 2% and 15%, the general adsorption equation holding good within these limits. The constants of the equation:  $C_{\text{starch}} = kC_I^p$  are  $p = 0.166$  and  $k = 0.27$ . The fact that a rise in the concentration of the iodide increases the solubility of iodine but does not increase the amount adsorbed by starch is evidence in favour of the formation of a definite starch-iodine compound.

A. R. P.

**Nature of Hydrolytic Adsorption with Reference to the Adsorption of Electrolytes and of Water. I. General and Theoretical Introduction.** J. N. MUKHERJEE (*J. Indian Chem. Soc.*, 1925, 2, 191—224).—A theoretical paper in which the author develops his view regarding the distribution of ions in the Helmholtz double layer (cf. A., 1922, ii, 689) to account for hydrolytic adsorption in systems where acids and alkalis are liberated by the interaction of solutions of salts having a neutral reaction and insoluble substances which give no acid or alkaline extract with

water. Four simple types of reactions, attributable to the preferential adsorption of one ion by the adsorbent, are discussed, and a brief summary of the experimental evidence (to be published in detail later) in support of each type is given. The four types are (1) interaction between a neutral electrolyte and adsorbed acids of which the anion is primarily adsorbed; (2) interaction between a neutral electrolyte and adsorbed alkali of which the cation is primarily adsorbed; (3) generation of acids or alkalis during the precipitation of barium sulphate from neutral salt solutions; (4) adsorption of water and its constituent ions in their relation to hydrolytic adsorption. It is shown that when well-washed barium sulphate and other precipitates are left in contact with potassium chloride solution, the liquid develops an acid reaction, the acidity depending on the conditions under which adsorption takes place. The acidity developed in contact with pure water is almost negligible. In the precipitation of barium sulphate, if the potassium sulphate is in excess, the medium becomes alkaline ( $p_H$  11), whilst with an excess of barium chloride it becomes acid ( $p_H$  5). Theoretically possible types of interaction between adsorbed water molecules, its constituent ions, and ions in solution, are illustrated by the primary adsorption of anions by hydrated silica, which shows, in contact with water, a marked negative charge which is decreased by the addition of acids and increased by alkalis. In reference to the dependence of adsorption on the degree of hydration of a substance, it is shown that whilst the primarily adsorbed layer is probably only one molecule thick, the adsorbed water molecules which hydrate the surface form a layer several molecules in depth.

J. W. B.

### Theory of Permeability of Membranes for Electrolytes.

L. MICHAELIS (*J. Gen. Physiol.*, 1925, 8, 33—59).—Experiments are described on the diffusion of electrolytes across membranes, such as apple skin, parchment-paper membrane, and dry collodion, including the measurement of the *E.M.F.* developed. The velocity of the anions is much reduced as compared with that of the cations, and in the case of membranes of collodion and apple skin there is practically complete impermeability to anions. The theory of the diffusion process is worked out in detail for the case where the velocities of the two ions across the membrane are different but finite, and also where the membrane is permeable to anion but impermeable to cation. The theoretical results are compared with those of experiment, and for univalent cations it is found that the order of the ionic mobilities through a collodion membrane is the same as in aqueous solution, but that the differences are very much increased. For example, the hydrogen ion has a mobility approximately 900 times that of lithium ion, whereas in aqueous solution it is only ten times as great. Further, it appears that the mobility of bivalent cations is very small and indefinite, whereas that of trivalent cations is of the same order as that of univalent cations. The mobility of anions, even of hydroxyl, appears to be exceedingly small, if not zero.

W. O. K.

**Electrical Properties and Ionic Permeability of Membranes.**

**III. Potential Differences at Parchment Membranes.** A. FUJITA (*Biochem. Z.*, 1925, **159**, 370—378).—If two solutions containing different concentrations of the same electrolyte are separated from each other by a parchment membrane, the potential difference is not the same as when the two solutions are directly in contact. The change is such as would be brought about if the mobility of the anions had been diminished to a larger extent than that of the cations. For the cations the effect diminishes in general with rise in valency, but is very small in the case of hydrogen ions. For the anions the effect increases with rise in valency. H. D. K.

**Cryoscopy of Solutions of Gases in Various Solvents.** F. GARELLI (*Atti R. Accad. Lincei*, 1925, [vi], **2**, 120—124).—Cryoscopic observations on solutions of gases have shown their tendency to enter the solid phase (Garelli and Falcicola, A., 1904, ii, 312). In the present work, the apparatus used is of the usual Beckmann type, but it is shut off from the atmosphere and provided with a side tube by which the gas-stream passes into the solvent. In benzene and dimethylaniline, acetylene dissolves in the form of simple molecules, the saturated solutions containing 0.744 g. and 0.737 g. per 100 g. of the respective solvents. The following solubilities, in grams of acetylene per 100 g. of solvent, are also obtained: in aniline, 0.800 g.; in *cyclohexane*, 0.3107 g.; in nitrobenzene, 0.5537 g. In most solvents, nitrogen, carbon monoxide, and helium first produce very slight elevations of m. p. On expelling these gases, however, this higher value of the m. p. generally persists and, on resaturation, the m. p. is often depressed. It is therefore thought that the elevation is due to the removal by the gas-stream of slight impurities of the solvent (cf. Falcicola, A., 1908, ii, 1015). In benzene, nitrogen ultimately gives a depression of  $0.005^\circ$  and nitric oxide one of  $0.04^\circ$ ; on the assumption of simple molecules of solute, the latter corresponds with a concentration of 0.235 g./100 g. of benzene. In bromoform, nitrogen and nitric oxide ultimately give depressions of  $0.005^\circ$  and  $0.025^\circ$ , respectively; nitrogen in nitrobenzene depresses the m. p. by  $0.005^\circ$  and nitric oxide gives a depression of  $0.135^\circ$ , whence the concentration is 0.058 g./100 g. In *cyclohexane* the depression caused by nitrogen is  $0.005^\circ$ , whilst nitric oxide gives  $0.225^\circ$ , the concentration thus being 0.337 g./100 g. In no case is it certain that helium produces a depression. The ultimate depression caused by carbon monoxide in benzene is  $0.03^\circ$ ; according to Just's absorption coefficient, the depression should be  $0.032^\circ$ . In nitrobenzene, the ultimate depression is  $0.025^\circ$ ; Just's value is  $0.022^\circ$ . Considering the high constant of bromoform, the depression of  $0.02^\circ$  in this solvent shows that carbon monoxide is practically insoluble. W. E. E.

**Hydration of Ions.** J. BABOROVSKY (*Chem. Listy*, 1925, **19**, 297—300).—Starting from the assumption that the hydrogen ion is attached to 1 mol. of water, the author deduces from the results of various investigators that the chlorine ion is combined with 6,

the sodium ion with 22—25, the potassium ion with 10, and the lithium ion with 35 mols. of water.

A. R. P.

**Uric Acid. III. Nature of the Hydrotropic Super-saturated Solution of Uric Acid.** R. STERN (*Biochem. Z.*, 1925, **159**, 192—198).—Hydrotropically dissolved uric acid (in presence of "atophan") causes a rise in the concentration of hydrogen ions, this acid being dissociated to about the same extent as when present in true solution. The hydrotropic effect is based on the formation of loosely combined, dissociating compounds between "atophane" and uric acid (cf. this vol., ii, 34, 196, 504).

P. W. C.

**Electrolytes in Solutions of Low Dielectric Constant.** P. GROSS and O. HALPERN (*Physikal. Z.*, 1925, **26**, 636—642).—From Debye and Hückel's mathematical development of the theory of inter-ionic forces in solution (A., 1923, ii, 459, 724; this vol., ii, 171), it can be shown that, for solutions of salts in liquids of low dielectric constant at low temperatures, the influence of the ions on osmotic effects may be not only small but even negative. The solute will thus appear to be associated, the apparent association increasing with the electrical conductivity. From a consideration of the thermodynamic equilibrium conditions, it is shown that the activity may increase with decreasing salt concentration, to a limit not of 1, but of  $\infty$ . This rapid change of activity with concentration should result in an increase of ionisation with increasing concentration giving anomalous concentration-conductivity curves which display maxima and minima. This phenomenon is comparable with the increase of ionisation of a weak electrolyte in aqueous solution by the addition of ions. If solvents with successively decreasing dielectric constants are considered, the concentration at which the minimum appears ought to become lower. All these deductions, which depend solely on the electrical effect postulated between the ions, are in qualitative agreement with experimental facts.

M. S. B.

**Colloidal Oxide of Manganese.** A. ANAGYROS (*Compt. rend.*, 1925, **181**, 419—421).—Potassium permanganate in the presence of sodium protalbinat was reduced by means of sodium arsenite at 65—70°, giving a brown, colloidal solution which could be kept for more than a month. The amount of chlorine liberated from hydrochloric acid corresponded with the formula  $Mn_2O_3$ , but this does not exclude the possibility of a mixture of other oxides. The colloidal solution rapidly liberates oxygen from hydrogen peroxide, acting more rapidly in alkaline than in neutral solution.

E. B. L.

**Colloidal Kaolin. I. Properties.** W. J. POPE and T. M. HAINES (*Lancet*, 1925, I, 1123—1124).—Kaolin which remained in aqueous suspension for a week was flocculated on the addition of 0.3% of hydrochloric acid or 1.3% of sodium chloride. It is a negative colloid and adsorbs iodine and basic dyes.

CHEMICAL ABSTRACTS.

**Colour of Colloidal Silver and Mercury.** R. FEICK (*Ann. Physik*, 1925, [iv], **77**, 573—596).—The author has recalculated the absorption curves for silver hydrosol according to the theory of Mie (cf. *Ann. Physik*, 1908, [iv], **25**, 377; Müller, *ibid.*, 1911, [iv], **35**, 500). He concludes that this theory in its simplest form is not in agreement with the experimental results (cf. Zsigmondy, A., 1906, ii, 679; Schaum and Lang, A., 1921, ii, 506; Schaum and Marx, A., 1922, ii, 696). However, so far as it concerns the diffuse radiation of the silver particles it is in agreement with experiment; the conclusion that the absorption colour should be complementary to the true colour of the particles is also satisfied in this case. The extension of Mie's theory proposed by Gans (A., 1912, ii, 508; 1920, ii, 256; *Ann. Physik*, 1925, [iv], **76**, 29) explains some of the difficulties met with in the application of the simple theory, although the complicated phenomena met with in the colours of the photohalides are still unexplained. In this connexion, Weigert has pointed out that the older Maxwell-Garnett theory has a certain range of validity (*Z. Physik*, 1921, **5**, 410). The radiation and absorption of colloidal mercury are calculated from the results of Meyer (*Ann. Physik*, 1910, [iv], **31**, 1017), in the same way as for colloidal silver. The results are in agreement with experiment so far as can be seen from the data available, which are, however, only qualitative. The spectrometric results and the determination of the dispersity of the sols is difficult owing to their instability, but this work is proceeding. The author discusses the reasons why complete concordance between the calculated and the experimental results should not be expected.

D. C. J.

**Chemical Properties of Colloidal Starch Derivatives.** SAMEC (*Compt. rend.*, 1925, **181**, 477—479; cf. A., 1921, ii, 707).—By heating to 120° and fractional electro-dialysis, electrolyte-free sols have been obtained from starch; these differ in the colour produced with iodine (red to blue), in mol. wt. (90,000—156,000), and in protective-colloid function. The colour produced with iodine appears to be independent of the presence of electrolytes, of the degree of dispersion, and of the protective-colloid properties.

L. F. H.

**Sols with Non-spherical Particles.** H. FREUNDLICH (*2nd Colloid Symposium Monograph*, 1925, 46—56).—Vanadium pentoxide sol shows the Majorana phenomenon (double refraction in a magnetic field) and streaks when stirred; this is due to "dityndallism," which is consequent on the elongated shape of the particles—probably rod-like crystals. Other similar phenomena are discussed.

CHEMICAL ABSTRACTS.

**Determination of the Distribution of Size of Particles in Emulsions.** A. J. STAMM (*2nd Colloid Symposium Monograph*, 1925, 70—79).—The principle of the method is similar to that of Wiegner (*Landw. Versuchs-Stat.*, 1918, **91**, 41) and of Ostwald and Hahn (A., 1922, ii, 205), but so modified and improved that emulsions with a rising dispersed phase may be studied, *e.g.*, benzene in



soap solutions. The distribution curves showing particle sizes were obtained from the experimentally determined accumulation curves by Svedberg's method, and duplicate determinations check fairly well. Changes in concentration alter the maximum but slightly. Potassium oleate tends to give emulsions with larger drops than potassium palmitate, in harmony with the wedge theory. Homogenisation increased dispersity with soaps, but broke emulsions with gelatin or fatty acids as stabilisers.

CHEMICAL ABSTRACTS.

**Oriented Wedge Theory of Emulsions.** W. D. HARKINS and N. BEEMAN (*Proc. Nat. Acad. Sci.*, 1925, **11**, 631—637).—A continuation of previous work by Harkins and others. The size distribution of oil particles in an emulsion is the same, within experimental error, whether sodium, potassium, or caesium soaps are used as emulsifying agents. When water-in-oil emulsions are produced by soaps of bi- or ter-valent metals, the distribution of the water particles is the same as that of the oil particles in the former cases. These results are not in agreement with the oriented wedge theory of Langmuir, for, according to this, the size of the particles should decrease with increasing size of the positive radical in the soap. If soaps are regarded as completely ionised there is little ground for supposing that the shape of the emulsifying molecules should affect the size of the particles produced.

A. E. M.

**General Principles of Ion Effects on Colloids.** L. MICHAELIS (*2nd Colloid Symposium Monograph*, 1924, 15 pp.).—The addition of ions to a sol may produce two effects: (a) electrostatic, due to its fixation by adsorption or combination, (b) hydrophilic or lyotropic, due to competition for water between micelles and dissolved ions. In the first case an electric double layer may be produced by (a) appositional adsorption, the ion most highly adsorbed determining the particle charge, (b) dissociation tendency in colloidal particles, and (c) orientation of polar water molecules at indifferent surfaces. Acidoids, *e.g.*, silicic acid, nucleic acid, resin acids, are insoluble, but tend to dissolve, and in the absence of easily adsorbable ions form a layer of hydrogen ions which may have diffusivity, but need not be unimolecular; they tend to emit hydrogen ions and become negative. Gelatin, casein, etc. may be termed ampholytoids; cellulose, collodion, agar, gas bubbles, etc. form double layers without active participation of the colloidal phase. It is tentatively supposed that hydroxyl ions have a greater capillary activity than hydrogen ions, so that any aqueous interface will be charged negatively against the mass of water, unless forces come into play which disturb the distribution spontaneously aimed at. Orientation of water molecules at the interface might account for the charge. Although flocculation by electrolytes usually involves adsorption, hydrochloric acid coagulates mastic sol by suppressing its tendency to emit hydrogen ions; in most other cases "exchange adsorption" occurs. The hydrogen ion is exceptional in its power of reducing swelling, *e.g.*, of agar, its effect exceeding that of tervalent ions.

CHEMICAL ABSTRACTS.

**Coagulation of a Colloidal Solution by Hydrogen Ions.**

A. B. WEIR (*J. Chem. Soc.*, 1925, **127**, 2245—2248).—Prussian-blue sols were precipitated by sulphuric, hydrochloric, citric, and acetic acids, and the  $p_H$  of the supernatant liquid was determined by means of a hydrogen electrode when precipitation was just complete. The values for the first three acids were nearly equal (1.80—1.91), but for acetic acid the  $p_H$  was higher (2.27). In the absence of the colloid the same concentrations of acid have slightly lower  $p_H$  values, indicating adsorption by the colloid. A more dilute Prussian-blue sol, prepared by grinding with water without the addition of acid, was precipitated by oxalic acid at  $p_H$  0.8—0.9, compared with 2.6 for hydrochloric acid. A. G.

**Precipitation of Colloidal Gold by Proteins.**

H. A. KREBS (*Biochem. Z.*, 1925, **159**, 311—324).—Colloidal gold may be precipitated either as a result of mutual precipitation of the two oppositely charged colloids or by the formation of a protein-gold complex as a result of adsorption of the gold by the protein. For the first type of precipitation, the acidity of the medium must be greater than that of the isoelectric point of the protein. Precipitation occurs only when the quantities of protein are small (0.002 mg. per 10 c.c. of gold solution), is mostly irreversible, and is indicated in all cases by colour changes of the gold and the formation of a small amount of blue precipitate. For the second type, the formation of the protein-gold complex takes place with any concentration of protein, is completely reversible on the addition of acid or alkali (so long as the  $p_H$  is outside the isoelectric zone), and is indicated by the appearance of cloudiness followed by precipitation of coarse, red particles. It is often possible to obtain both types simultaneously. The work is extended to a consideration of the effect of colloidal protein on colloidal solutions of gum mastic. P. W. C.

**Influence of Some Stable Colloids on the Flocculation of Sols and Suspensions.**

A. BOUTARIC and (Mlle.) G. PERREAU (*Compt. rend.*, 1925, **181**, 511—513).—The action of varying amounts of gum arabic, gelatin, albumin, casein, and dextrin on negatively charged suspensions has been examined. In most cases addition of small amounts of the colloid renders sols more sensitive to the action of electrolytes. With larger quantities the increase in sensitivity falls gradually to zero and still larger quantities cause the appearance of a more or less definite protective action. Very large additions of colloid, however, cause flocculation of the sols even in the absence of electrolytes (cf. this vol., ii, 526). R. A. M.

**Protective Action of Soaps and Further Evidence in Favour of the Chemical Theory of Adsorption. III.**

S. S. BHATNAGAR, M. PRASAD, and D. C. BAHL (*J. Indian. Chem. Soc.*, 1925, **2**, 11—22; cf. this vol., ii, 293).—The protective action of soap on sols of arsenic, antimony, and cadmium sulphides has been examined for various concentrations of soap, the drop pipette method (cf. Donnan, A., 1900, ii, 201) being employed. The surface tension of soap solutions decreases with increasing concentration of the soap, but in the

case of the sulphide sols the colloidal particles produce no change in the surface tension of the dispersion medium. When the soap solution and the sol are mixed, the concentration of the soap as indicated by the drop number is greatly reduced, affording evidence of the adsorption of the soap molecules by the particles of the sulphide sols. Similar results were obtained with various solid absorbents. The ratio of the amount of soap adsorbed to the quantity of solid employed decreases as the concentration of the soap solution is decreased. The adsorbed soap, although shown by chemical tests to be present in the washed coagula after the colloidal solutions had been coagulated by a 0.1*N*-solution of barium chloride, loses its property of dissolving in, and lowering the surface tension of water, since the drop numbers for the aqueous extracts of the coagula are the same as for pure water. Experiments on the adsorption of dyes by fine precipitates gave similar results, the adsorbed dye losing its capacity to dissolve in water. These facts support the chemical theory of adsorption. J. W. B.

**Hydrophilic Effect of Ions on Agar and Protoplasmic Components.** D. T. MACDOUGAL and B. L. CLARKE (*Science*, 1925, **62**, 136—137).—Sodium, potassium, calcium, and magnesium chlorides, at 0.001—0.0001*M*, cause excessive hydration of sections of agar; the effects of the cations are distinctive, and differences are shown by the nitrate and sulphate ions. Excessive swelling was observed with 0.0001*N*-hydrochloric acid, in solutions containing weak hydroxides, glycine, histidine, phenylalanine, asparagine, or alanine over the range  $p_H$  4.2—11. A. A. E.

**Kino-ultramicroscope.** E. O. KRAEMER (*2nd Colloid Symposium Monograph*, 1925, 57—69).—Various colloid phenomena were studied with the kino-ultramicroscope. With gelatin the viscosity appears to increase gradually, although in the later stages the motion appears to be localised more than would correspond with a simple viscosity effect; with magnesium arsenate and dibenzoyl-cystine gel formation occurs comparatively suddenly following an induction period which probably corresponds with an initial state of supersaturation followed by condensation. In the last-named case, moving fibres were observed. Gelatin gel shows local preferential melting. An alkaline solution of bismuth tartrate is reduced by light, and a Carey Lea silver solution is coagulated by light. In the initial stages, the aggregation of particles seems to be spontaneously reversible, so that the union between particles in agglomerates must be loose and flexible. CHEMICAL ABSTRACTS.

**Polar Emulsifying Agents.** H. N. HOLMES and H. A. WILLIAMS (*2nd Colloid Symposium Monograph*, 1925, 135—137).—In a clean bottle, 2 c.c. of methyl alcohol give an emulsion stable for at least a week with 10 c.c. of water and 10 c.c. of benzene, the methyl group being apparently oriented towards the benzene, and the hydroxyl group towards the water. Good results were also obtained with stearic, palmitic, oleic, linoleic, and linolenic acids, sodium  $\beta$ -naphthylaminesulphonate, benzonitrile, or rancid fats as

emulsifying agent, slight effects with phenol, butyl alcohol, resorcinol, sulphonic acids, or neutral fats, and negative results with higher alcohols, glycol, glycerol, sugars, naphthols, benzyl alcohol, ketones, nitro and amino compounds. Oleic acid lowers the surface tension benzene/water, but not benzene/air, and should accumulate as a film at the interface. Molecular association does not seem to be a factor. There is a great difference in the emulsifying powers of the soaps and the lower alcohols; certain substances in true solution form distinct emulsions.

CHEMICAL ABSTRACTS.

**Plasticity in Colloid Control.** E. C. BINGHAM (*2nd Colloid Symposium Monograph*, 1925, 106—113).—The formula  $V = \mu(F - f)r$ , where  $\mu$  is the mobility, *i.e.*, the reciprocal of the consistency,  $F$  the shearing stress, and  $r$  the distance between the shearing planes, is probably applicable over a wide range of shearing stresses. In suspensions the flow is a linear function of the shearing stress, and is independent of the dimensions of the instrument; for emulsoids this is not the case. The distinction is ascribed to two causes providing the internal friction: diffusional viscosity, resulting from inter-diffusion of molecules having different amounts of transitional energy, and collisional viscosity caused by actual spatial interference as the layers are sheared over each other. In suspensions a third cause is the rotation of the particles in the shearing process. In many cases *m. p.* is without scientific value.

CHEMICAL ABSTRACTS.

**Mobility of the Particles in Gold Hydrosols.** P. A. THIESSEN and J. HEUMANN (*Z. anorg. Chem.*, 1925, **148**, 382—390).—The mobility of the particles in gold hydrosols is about  $3 \times 10^{-4}$  cm./sec. under a potential gradient of 1 volt/cm., and is independent of their size and of the method of preparation of the sols. Prolonged dialysis and protective colloids (*e.g.*, gum arabic) are also without influence. Addition of sodium carbonate raises the mobility, probably because of the adsorption of hydroxyl ions; addition of electrolytes such as barium and strontium chlorides diminishes the mobility, coagulation setting in before the particles are completely discharged.

S. K. T.

**Influence of Neutral Salts on the Combination of Gelatin with Acids.** J. CSAFÓ (*Biochem. Z.*, 1925, **159**, 53—57).—The capacity of gelatin to combine with sulphuric, nitric, and hydrochloric acids is increased by  $K^+$ ,  $Na^+$ ,  $Ba^{++}$ ,  $Ca^{++}$ , in ascending order, and by  $Cl^-$ ,  $NO_3^-$ ,  $I^-$ , but is diminished by  $SO_4^{--}$ . The amount of acid absorbed in 0.02—0.03*N*-sulphuric acid is less than in the same concentration of hydrochloric acid.

E. C. S.

**Effect of Temperature on the Hygroscopicity of Hydrogels of Aluminium Oxide, Ferric Oxide, and Silica.** B. AARNIO (*Geol. Kommiss. Finland Geotekn. Meddel.*, 1920, No. 25, 1—12; from *Chem. Zentr.*, 1925, ii, 525).—Hydrated ferric oxide precipitated by ammonium hydroxide contains, after drying at 100°, 10% of water and has a hygroscopic coefficient of 34%. At 200°, the corresponding values are 1.5% and 42%; at 300°, 1% and 29.6%;

at 700°, it becomes anhydrous and completely loses its hygroscopicity. The hygroscopic coefficient of hydrated aluminium oxide is 24% at 100°, 45% at 400°, 44% at 800°, 17% at 1000°, and 0.53% at 1200°. At the last temperature, the water content is 0.2%. The hygroscopic coefficient of hydrated silica is 41% at 100°, 56% at 200°, 45% at 400°, 50% at 500°, 0.62% at 1000°, and 0.5% at 1100°.

G. W. R.

**Electrodialysis of Agar. Preparation of the Free Agar Acid.** W. F. HOFFMAN and R. A. GORTNER (*J. Biol. Chem.*, 1925, **65**, 371—379).—Electrodialysis of a suspension of agar for 18 hrs. resulted in almost complete removal from the latter of calcium, but there was no change in the sulphur or silicon. The resulting agar acid, in approximately 0.78% solution, had  $p_H$  2.475 and was about 56% ionised. All the sulphur is in the form of sulphuric acid, and the formula is therefore probably  $R \cdot O \cdot SO_2 \cdot OH$ , where R is a polysaccharide residue. Titration data and the percentage of alkaloid in the alkaloid compounds of the acid indicate that the mol. wt. of the latter is about 3000. Neutralisation of sols of the acid with inorganic or organic bases gives rise to rigid gels.

C. R. H.

**Mechanism of the Liesegang Phenomenon.** A. STEPOUE (*Bul. Soc. Romana Stiinte*, 1924, **27**, 51—58).—The mechanism of the formation of Liesegang rings in extremely thin gelatin layers containing potassium chromate on the addition of a drop of silver nitrate solution is discussed. Under the microscope, these rings are seen to consist of several bands separated by a very narrow band of clear gel and each ring is separated from the next by a wider band of clear gel. The origin of these phenomena is ascribed to three causes, viz., a diminution of the viscosity of the gel caused by a slight increase in temperature due to the heat of reaction, the diffusion of the water added with the silver nitrate, and the greater velocity of diffusion of the silver ion compared with the chromate ion. These factors contribute towards periodic denudation of the solution in chromate ions so that the silver chromate is deposited in rings surrounding the drop of silver nitrate solution. This explanation is in accord with the fact that the central bands of each ring are denser than the outside bands.

A. R. P.

**Electro-ultrafiltration.** H. BECHHOLD (*Z. Elektrochem.*, 1925, **31**, 496—497).—An apparatus for the accelerated removal of crystalloids from colloidal solutions is described, which involves a combination of ultrafiltration and electro-dialysis. A comparison between the results obtained by its use and those obtained by other methods is distinctly favourable to the former.

N. H. H.

**Equilibrium of Carbon Dioxide with Carbon Monoxide and Oxygen in the Corona Discharge.** G. L. WENDT and M. FARNSWORTH (*J. Amer. Chem. Soc.*, 1925, **47**, 2494—2500).—Carbon dioxide or a mixture of carbon monoxide and oxygen under the influence of the corona discharge reaches an equilibrium corresponding with the decomposition of 28.54% of the carbon dioxide;

thermodynamically this would correspond with a temperature of 2600°, whereas the temperature in the corona was not more than about 35°. W. T.

**Dissociation Constants of Organic Complexes.** H. LEY and R. GRAU [and, in part, W. EMMERICH] (*Ber.*, 1925, **58**, [B], 1765—1775; cf. Ley and Pfeiffer, A., 1921, i, 335).—The dissociation constants of additive compounds of amines with trinitrobenzene have been determined from measurements of the solubility of the latter in solutions of the amine in chloroform at 17.5°. The additive compounds of dimethylaniline and dimethyl-*p*-toluidine with trinitrobenzene are very extensively dissociated, so that the intense colour of the solutions is remarkable. Dimethyl-*o*-toluidine depresses the solubility of trinitrobenzene in chloroform; in this case, the solubility effect which reduces the concentration of the nitro derivative in the saturated solution and the complex formation effect (which is only very slight) are superposed. A similar solubility effect is observed with the dimethylxylydines in which at least one methyl group is contiguous to the dimethylamino group. The dissociation constants of the compounds of trinitrobenzene with dimethylaniline and dimethyl-*o*-toluidine have also been determined photometrically, the results being in fair agreement with those given by the previous method, but the procedure is not completely satisfactory for compounds which are so considerably dissociated. Determinations of the dissociation constants are also obtained from the apparent mol. wts. of the additive compounds in boiling chloroform. The results agree in order of magnitude with those of the photometric method, but are somewhat smaller than those of the solubility method. H. W.

**Heterogeneous Equilibria between Tungsten and Oxygen, and Tungsten and Water Vapour at High Temperatures.** H. ALTERTHUM and F. KOREF (*Z. Elektrochem.*, 1925, **31**, 508—511).—The calculations of Wöhler (A., 1917, ii, 455; 1921, ii, 633; 1923, ii, 471) for the equilibria between tungsten and oxygen and between tungsten and water vapour do not take into account the vaporisation of the oxides of tungsten at high temperatures. The heats of vaporisation of the oxides have been calculated from the modified Trouton's law. The disappearance of the oxide film from the tungsten filament in a lamp, and the appearance of the Tyndall effect in the gas space are used to estimate the b. p. The equilibrium constants are calculated from the heats of vaporisation by the Nernst heat theorem. They show that with rise of temperature the action of oxygen on tungsten decreases, whilst that of water vapour increases greatly. N. H. H.

**Magnetic Transformation Points in the System Ferric Oxide-Magnesia.** H. FORESTIER and G. CHAUDRON (*Compt. rend.*, 1925, **181**, 509—511; cf. this vol., ii, 534).—The variation with temperature of the magnetic transformation point (t. p.) of mixtures of ferric oxide and magnesia has been studied by the direct method of Curie and by a differential dilatometric method.

When the proportion of ferric oxide is between 2% and 50%, the t. p. remains constant at 310°, and the compound  $\text{Fe}_2\text{O}_3 \cdot \text{MgO}$  exists in the free state. Between 50% and 56% of ferric oxide the t. p. rises to 400° and a solid solution of the double compound in ferric oxide is formed. Between 56% and 100% of ferric oxide the t. p. of pure ferric oxide at 675° is always observed. Magnesium ferrite is stable below its m. p. (1700°). Magnetic ferrites of nickel, calcium, and cadmium have been prepared by the general method of adding sodium hydroxide to a mixture of chlorides and strongly heating the precipitate. Nickel ferrite shows a magnetic t. p. at 590° and is stable at high temperatures. Cadmium and calcium ferrites lose their magnetic properties irreversibly when heated at 400° and 700°, respectively.

R. A. M.

**Chemical Equilibrium between Lead Sulphide and its Roasting Products.** III. R. SCHENCK (*Z. anorg. Chem.*, 1925, **148**, 351–368; cf. this vol., ii, 419).—The nine possible bivariant equilibria with lead sulphide in the gaseous phase are considered and the conditions necessary for the formation of various products are outlined. Some of the diagrams previously given are modified. [Cf. *B.*, Dec. 24th.]

S. K. T.

**Equilibria in Fused Salts (Reactions between Alloys of Alkali and Alkaline-earth Metals and their Chlorides).** K. JELLINEK (*Z. Elektrochem.*, 1925, **31**, 542–545).—When fused chlorides are electrolysed with cathodes of molten lead, tin, antimony, and bismuth or carbon anodes, equilibria are attained between the salt and the cathodic alloy of its base. A number of binary mixtures of chlorides have been thus examined. When alkalis alone or alkaline earths alone are concerned, quotients such as  $(\text{Ba})(\text{CaCl}_2)/(\text{Ca})(\text{BaCl}_2)$  are found constant. With mixed alkalis and alkaline earths, however, the equilibrium constant takes the form  $(\text{Na}_2)(\text{BaCl}_2)/(\text{Ba})(\text{Na}_2\text{Cl}_2)$ . Hence molten alkali metals and alkali chlorides appear to be associated to double molecules.

W. A. C.

**Camphor and Nitrophenols.** N. N. EFREMOV (*Bull. Acad. Sci. St. Pétersbourg*, 1919, **13**, 255–286; from *Chem. Zentr.*, 1925, ii, 523–524).—The author presents the following data for the eutectic points of camphor with certain compounds, the molecular percentage in the eutectic mixture of the compound mentioned being given in each case. With *o*-nitrophenol, 11.8° and 45.5%,  $z=8$ ; with *m*-nitrophenol, 16° and 41.5%; with nitrophenol, –2° and about 36%; with 2:4-dinitrophenol, 69.3° and 30.7%,  $z=6.5$ ; with picric acid, 66.4° and 30.5%,  $z=3.8$ ; with 2-nitroresorcinol (m. p. 84.8°), 4.63° and 39.3%,  $z=\text{about } 11.0$ ; with 2:4-dinitroresorcinol (m. p. 142.3°), 47.2° and 29%,  $z=16$ ; with nitroquinol, 26.4° and 33.2%; with 3-nitropyrocatechol (m. p. 83.8°), 25.8° and 38%. In no case was there any indication of the formation of a compound. Photomicrographs are given for some of the systems.

G. W. R.

**Binary System consisting of *o*-Cresol and *p*-Cresol.** A. E. HILL and I. MOSBACHER (*J. Amer. Chem. Soc.*, 1925, **47**, 2544—2545).—Evidence has been obtained of the formation of a 1:1 compound with a congruent m. p. of 7·8° existing between the limits of 37% and 59% of *o*-cresol. The eutectics of the compound with *o*-cresol and *p*-cresol, respectively, are at 0° and 1·57°.

W. T.

**Ternary System Sodium Metasilicate–Calcium Metasilicate–Silica.** G. W. MOREY and N. L. BOWEN (*J. Soc. Glass Tech.*, 1925, **9**, 226—262).—The system  $\text{Na}_2\text{SiO}_3$ – $\text{CaSiO}_3$ – $\text{SiO}_2$  has been studied by heating the glasses at definite temperatures until in equilibrium and then quenching. From the results the ternary diagram and the binary diagrams  $\text{Na}_2\text{SiO}_3$ – $\text{SiO}_2$ ,  $\text{Na}_2\text{SiO}_3$ – $\text{CaSiO}_3$ , and  $\text{Na}_2\text{Si}_2\text{O}_5$ – $\text{Na}_2\text{O}$ ,  $2\text{CaO}$ ,  $3\text{SiO}_2$  were constructed. In addition to the known compounds  $\text{Na}_2\text{SiO}_3$ ,  $\text{Na}_2\text{Si}_2\text{O}_5$ ,  $\text{CaSiO}_3$ , and  $\text{SiO}_2$ , three new substances were obtained, namely, (1)  $2\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $3\text{SiO}_2$ , giving isometric pyritohedral crystals, refractive index ( $n$ )=1·571, which decompose at 1141° to (2)  $\text{Na}_2\text{O}$ ,  $2\text{CaO}$ ,  $3\text{SiO}_2$ ; this forms crystals of indeterminate symmetry, showing twinning, with  $n_\gamma$ =1·599,  $n_\alpha$ =1·596, (3)  $\text{Na}_2\text{O}$ ,  $3\text{CaO}$ ,  $6\text{SiO}_2$ , orthorhombic crystals with  $n_\gamma$ =1·579,  $n_\alpha$ =1·564,  $2V$  about 75°. Many mixtures within the region solidify at the ternary eutectic  $\text{CaO}$  5·2%,  $\text{SiO}_2$  73·5%, and at a temperature of 725°. Outside the above region, the compounds  $\text{Na}_4\text{SiO}_4$  and  $\text{Na}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{SiO}_2$  have been prepared. Comparison of the results with published surface tension and viscosity data affords no evidence of correlation between the equilibrium relations and these properties. [Cf. *B.*, 1925, 921.]

A. COUSEN.

**Dehydrogenation of Methyl Alcohol and Formaldehyde with Copper as Catalyst. Conditions of Equilibrium in the System  $\text{CH}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$ .** J. C. GHOSH and J. N. CHAKRAVARTY (*J. Indian Chem. Soc.*, 1925, **2**, 142—149; cf. Ghosh and Mali, this vol., i, 116).—The equilibrium attained in the dehydrogenation of methyl alcohol in the presence of a copper catalyst between temperatures ranging from 155° to 350° has been studied by a static method similar to that employed by Rideal (*A.*, 1921, i, 389). It is found that the yield of formaldehyde and its decomposition into carbon monoxide and hydrogen depend more on the nature of the catalyst than on the rate of flow. The observed equilibrium constants for the reaction  $\text{CH}_3\cdot\text{OH} \rightleftharpoons \text{CH}_2\text{O} + \text{H}_2$  are not in agreement with the theoretical values, but for the reaction  $\text{CH}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$  the experimental data are satisfactorily represented by the equation  $\log_{10} K_p = -11800/4\cdot571T + 1\cdot75 \log_{10} T - 0\cdot001T + 0\cdot3$ . The most probable value for the chemical constant of carbon monoxide is 2·7.

J. W. B.

**Phase Rule and its Application to Problems of Luminescence and Ionisation of Gases.** M. SAHA (*J. Indian Chem. Soc.*, 1925, **2**, 49—60).—A theoretical paper in which the thermal ionisation of the elements is considered from the thermodynamic point of view. The ionisation of calcium in a closed vessel and in an



atmosphere containing an excess of electrons, as represented by  $\text{Ca} \rightleftharpoons \text{Ca}^+ + e$ ,  $\text{Ca}^+ \rightleftharpoons \text{Ca}^{++} + e$ , is discussed. Reference is made to the range within which certain metastable states may occur.

J. W. B.

### Thermodynamic Properties of Calcite and Aragonite.

H. L. J. BÄCKSTRÖM (*J. Amer. Chem. Soc.*, 1925, **47**, 2432—2442).—The heats of solution of calcite and aragonite in *N*-hydrochloric acid and in the same acid saturated with carbon dioxide have been determined. These data give the heat of transformation of aragonite into calcite at 298° Abs. as  $30 \pm 20$  cal./mol.; this corresponds with a change of  $0.74 \pm 0.2$  entropy unit per mol. The third law of thermodynamics gives 22.3 and 19.9 for the entropies of calcite and aragonite under standard conditions, respectively, the difference being 2.4. This value is probably inaccurate because of an error in the specific heat curve for calcite at low temperatures, which is not in agreement with the Debye equation. The difference of entropy derived from solubility measurements is 2.9 units, but reasons are given for not accepting this value. The calibration of thermocouples for use in calorimetric work is discussed.

W. T.

**Higher Oxides of Silver. II.  $\text{Ag}_2\text{O}_2$ .** F. JIRSA (*Chem. Listy*, 1925, **19**, 300—306).—The active oxygen content of silver dioxide may be accurately determined by means of the reaction  $\text{Ag}_2\text{O}_2 + \text{N}_2\text{H}_4 = 2\text{Ag} + 2\text{H}_2\text{O} + \text{N}_2$ . The heat of formation of silver perchlorate, calculated from the heats of reaction of silver perchlorate in aqueous solution with hydrochloric, hydrobromic, and hydriodic acids, is (Ag, Cl, 40 aq.) = 12,622 cal. From the heats of reaction of silver monoxide and dioxide with perchloric acid the heat of formation of the dioxide is  $2\text{Ag}_2\text{O}_2 = 2\text{Ag}_2\text{O} + \text{O}_2 + 2000$  cal. This value agrees with that calculated from the heats of reaction of silver oxides with nitric acid and with hydrazine. The heat of formation of the dioxide from its elements is  $-5440$  cal., and its dissociation pressure at 25° is  $1.37 \times 10^3$  derived from the Nernst equation. The dioxide yields a continuous series of solid solutions with the monoxide formed by its decomposition, and its dissociation ceases in the presence of water as soon as the liquid is saturated with silver hydroxide.

A. R. P.

### Decomposition of Metallic Sulphates by Heat. (MLLE.) G.

MARCHAL (*J. Chim. phys.*, 1925, **22**, 412—431).—Reactions of the types (i)  $\text{RSO}_4 \rightleftharpoons \text{RO} + \text{SO}_3$ , (ii)  $3\text{MnSO}_4 \rightleftharpoons \text{Mn}_3\text{O}_4 + 2\text{SO}_3 + \text{SO}_2$ , and (iii)  $2\text{Ag}_2\text{SO}_4 \rightleftharpoons 2\text{Ag}_2\text{O} + 2\text{SO}_3 + \text{O}_2$ , followed by  $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$ , have been studied with reference to the conditions under which the systems become univariant. Using the equation of Bodenstein and Pohl (cf. A., 1905, ii, 581) to find  $K_c$ , expressions are derived in each case for calculating the partial pressures of the sulphur trioxide, dioxide, and oxygen from the measured total pressure. The sulphates were heated in a platinum-wire-wound furnace in a vacuum and the equilibrium pressures measured. Results are quoted for the sulphates of silver, manganese, nickel, cobalt, cadmium, beryllium, and magnesium at temperatures around

1000°, showing that conditions for a univariant equilibrium are obtained.

L. S. T.

**Apparent Molecular Heat and Viscosity of Solutions of Naphthalene in Organic Solvents.** N. DE KOLOSOSOVSKY (*Bull. Soc. Chim. Belg.*, 1925, **34**, 221—231).—The method suggested for the derivation of the apparent molecular heat of dissolved substances (cf. this vol., ii, 879) has been applied to the determination of the apparent molecular heat of naphthalene in benzene, toluene, chloroform, and carbon tetrachloride solutions. Using the author's formula, the values obtained for various solvents from the data of Forch (A., 1903, ii, 632) all approximate closely to 44 cal., whence it follows that the work necessary to overcome the viscosity is equal in all solvents. Since the value calculated for the real molecular heat is 39 cal., this work is equivalent to 5 cal. Measurements of the viscosity of the pure solvents and of the naphthalene solutions give for the work necessary to overcome the viscosity of the solutions per degree rise in temperature a mean value of 3 cal. (the extreme values being 0 and 6), in good agreement with that derived above.

J. W. B.

**Conductivity of Uni-univalent Salts in Methyl Alcohol.** J. E. FRAZER and H. B. HARTLEY (*Proc. Roy. Soc.*, 1925, **A**, **109**, 351—368).—The electrical conductivity between  $N/10,000$  and  $N/500$  of fifteen uni-univalent salts in methyl alcohol has been measured. Kohlrausch's law of the independent mobility of ions has been found applicable. The empirical relation of Kohlrausch  $\Lambda_0 - \Lambda_c = k\sqrt{c}$  ( $\Lambda_0$  and  $\Lambda_c$  are the equivalent conductivities at infinite dilution and at concentration  $c$ ) also holds. In these respects, the results are in agreement with Debye's theory of conductivity, but some difficulties arise. If  $\Lambda_c$  is plotted against  $\sqrt{c}$ , the slope of the straight-line graph obtained varies for different salts of which the ions have approximately the same mobilities. This is not anticipated by the theory.

S. B.

**Calculation of the Equivalent Conductivity of Strong Electrolytes at Infinite Dilution. I. Aqueous Solutions.** A. FERGUSON and I. VOGEL (*Phil. Mag.*, 1925, [vi], **50**, 971—985).—As a preliminary to a discussion of Storch's dilution formula (A., 1896, ii, 288), the values of  $\Lambda_0$ , the equivalent conductivity at zero concentration, have been recalculated for a series of thirty-seven electrolytes. For this purpose, the equation  $\Lambda = \Lambda_0 - BC^n$  has been used. A simple and direct method of determining the most probable values of the constants  $\Lambda_0$ ,  $B$ , and  $n$ , from the experimental data, is described. For all the electrolytes considered, the available data are shown to lead to consistent values of  $\Lambda_0$  over ranges of concentration  $C$  from  $10^{-4}$  to  $10^{-2}$  g.-equiv./litre. A further test of consistency by applying Kohlrausch's law of the independent migration of the ions gives better agreement using the present values than using Kohlrausch's own values for  $\Lambda_0$ . Certain regularities are observed in the variation of  $B$  and  $n$  for elements belonging to the same group of the periodic table.

A. B. M.

**Measurement of Single-phase Boundary Potentials.** E. BAUR (*Z. Elektrochem.*, 1925, **31**, 514—517).—Cells of the type calomel electrode|KCl (1) in water|KCl (2) in amyl alcohol|CaCl<sub>2</sub> (3) in amyl alcohol|CaCl<sub>2</sub> (4) in water|calomel electrode have been measured. The potential between (1) and (2) may be neglected, whilst that between (2) and (3) may be eliminated by a bridge of 0.1*N*-hydrochloric acid in amyl alcohol. The *E.M.F.* measured is thus due to the phase boundary potential between (3) and (4).

N. H. H.

**Potential of Fluorine from Measurements of the Decomposition Voltages of Fused Fluorides.** B. NEUMANN and H. RICHTER (*Z. Elektrochem.*, 1925, **31**, 481—488).—From measurements of the decomposition voltages of the fused fluorides of potassium, sodium, lithium, calcium, strontium, barium, magnesium, and beryllium, the value  $1.923 \pm 0.01$  volt at 18° has been obtained for the potential of fluorine. This has been used to obtain a new value for the potential of aluminium by measuring the decomposition voltage of aluminium fluoride. The result, 0.829 volt at 18°, when combined with those given by other methods furnishes the mean value  $0.844 \pm 0.015$  volt. The potential difference between hydrogen and fluorine has also been obtained directly from the decomposition voltage of fused acid potassium fluoride, the result being 1.928 volts at 18°. The heats of formation of the fluorides investigated have been calculated from the above measurements and show in many cases good agreement with calorimetric determinations.

N. H. H.

**Saturated Standard Cells with Small Temperature Coefficients.** W. C. VOSBURGH (*J. Amer. Chem. Soc.*, 1925, **47**, 2531—2539).—By substituting for the cadmium amalgam electrode of the normal Weston cell a cadmium-tin amalgam electrode the *E.M.F.* is increased to 1.01901 volts at 25° and the temperature coefficient is reduced to about two-fifths that of the normal Weston cell. The new cell was found to be as nearly constant over short periods of time as the Weston cell. The replacement of tin by lead is not satisfactory, the temperature coefficient being increased, whilst the presence of lead increases the tendency of cadmium to react with the hydrogen ion of the electrolyte. For the cadmium-lead amalgam the *E.M.F.* is 1.01918 volts at 25°. When a cadmium-bismuth amalgam is substituted for the cadmium amalgam the *E.M.F.* is 1.01976 volts at 25° with a positive temperature coefficient equal to the negative temperature coefficient of the cadmium-tin amalgam electrode. The presence of copper does not appreciably alter the *E.M.F.* or the temperature coefficient of the Weston cell.

W. T.

**Oxidation-Reduction. VIII. Methylene-blue.** W. M. CLARK, B. COHEN, and H. D. GIBBS (*U.S. Pub. Health Repts.*, 1925, **40**, 1131—1201; cf. this vol., i, 25).—Methylene-white solutions are sensitive to light; the rate of oxidation by air varies as the fifth root of the hydroxyl-ion concentration. Buffer solutions

containing citrates are described, and oxidation-reduction potentials are measured at different  $p_H$  values. Methylene-blue is a very strong base, whilst Lauth's violet has a basic dissociation constant of  $1.9 \times 10^{-3}$ . The basic dissociation constants of the two amino groups are: for methylene-white,  $K_1 = 1.4 \times 10^{-8}$ ;  $K_2 = 6.3 \times 10^{-10}$ ; for leuco-Lauth's-violet,  $K_1 = 3.8 \times 10^{-9}$ ;  $K_2 = 4.5 \times 10^{-10}$ . The characteristic potentials at  $p_H 0$  are 0.532 volt for methylene-blue and 0.563 volt for Lauth's violet. The corresponding free energies of hydrogenation are calculated and an equation is given for its dependence on  $p_H$ .  
CHEMICAL ABSTRACTS.

**Streams of Gas Bubbles Directed by Electrolysis.** A. COEHN (*Z. Elektrochem.*, 1925, **31**, 552—554).—When a very small platinum point electrode in the tip of a finely-drawn-out glass tube is made the anode in 0.005*N*-sulphuric acid at a high *P.D.* of approximately 300 volts, the disengaged bubbles are found to rush backwards over the electrode. The same occurs under similar conditions at the anode in 0.005*N*-potassium hydroxide solution. The explanation is offered that in the very steep potential gradient a high velocity is imparted to the ions, which then carry a stream of liquid and of gas bubbles with them.  
W. A. C.

**Passivity of Nickel.** F. EISENKOLB (*Z. Elektrochem.*, 1925, **31**, 503—507).—The potential at which nickel changes from the active to the passive state is about the same (in most cases 0.3—0.4 volt, referred to the normal hydrogen electrode) with the oxy-acids, sulphuric, nitric, perchloric, phosphoric, acetic, oxalic, citric, and tartaric, and with hydrofluosilicic acid, and is little affected by the acid concentration. With hydrochloric, hydrobromic, and hydriodic acids, much higher values are given, which vary with dilution, whilst in the most dilute solutions (0.01*N* and beyond with hydrochloric acid) the passivity ceases. With hydrofluoric acid the potential shows a maximum (1.38 volts) with a 0.1*N*-solution. The addition of potassium sulphate to sulphuric acid lowers the potential given in the latter alone, whilst addition of hydrochloric acid has the opposite effect. Mixtures of hydrochloric acid and potassium chloride give higher potentials than the former alone. In 0.1*N*-sulphuric acid rotation of the electrodes is without effect, but in hydrochloric acid the potential is increased with increasing speed of rotation and finally the passivity disappears. The theory that there is a difference in the valency of the active and passive states of a metal passing into solution is found to be without support in the case of iron and nickel.  
N. H. H.

**Electrolytic Oxidation of Double Cyanides of Quadri-valent Molybdenum.** O. COLLEBERG and B. ANDERSEN (*Z. Elektrochem.*, 1925, **31**, 558—565).—In connexion with the preparation of double cyanides of quinquevalent molybdenum, it is found that the electrolytic oxidation of tetrapotassium molybdenum octacyanide (0.06 mol./litre) proceeds smoothly and completely at platinum anodes in 0.2*N*-sulphuric acid solution, preferably at a temperature of 45° and a current density of 0.0056

amp./dm.<sup>2</sup> In alkaline solutions, the oxidation can only be carried to the extent of 72%. Neutral solutions are unsatisfactory, since complex decompositions set in.

W. A. C.

**Electrolytic Reduction of Tungstic Acid in Presence of Oxalic Acid.** O. COLLENBERG and K. WILSON (*Z. Elektrochem.*, 1925, **31**, 555—558).—Electrolysis of solutions containing 11.2 g. of potassium tungstate and 16 g. of oxalic acid in 100 c.c. at a current density of 0.01—0.03 amp./dm.<sup>2</sup> and a temperature of not less than 70° with lead or tin cathodes leads to a complete reduction of tungsten to the quinquevalent stage and no further. The method is well adapted to the preparation of quinquevalent tungsten compounds.

W. A. C.

**Electrodeposition of Silver-Cadmium Alloys.** A. H. W. ATEN and M. F. VAN PUTTEN (*Rec. trav. chim.*, 1925, **44**, 861—865).—Electrolysis of a solution containing potassium cyanide, potassium silver cyanide, and potassium cadmium cyanide with current densities up to 0.8 amp./dm.<sup>2</sup> gives a deposit of silver containing not more than 2% of cadmium. With a current density of 1.2 amp./dm.<sup>2</sup> and an atomic ratio of 2 : 1 of cadmium to silver in solution there is obtained a yellow deposit containing 25% of cadmium. The variation with composition of the *E.M.F.* between cadmium-silver alloys and solutions containing the above-mentioned salts in various proportions, has been determined and an expression deduced for the potential difference between silver and cadmium metals in contact with them.

G. M. B.

**Electrochemical Reduction of Solid Electrodes.** K. FISCHBECK (*Z. anorg. Chem.*, 1925, **148**, 97—129).—A coulometer is described capable of reading to 10<sup>-3</sup> coulomb, the volume of hydrogen evolved by the electrolysis of dilute sulphuric acid being measured in a capillary tube. From electrodes of platinum, mercury, and lead, theoretical volumes of hydrogen were obtained, but when a platinum cathode was covered with a reducible powder, the evolution of hydrogen was reduced by an amount which was a measure of the efficiency of the reduction process. With stannic oxide, copper pyrites, and galena, the efficiency diminished with increasing current density; with copper sulphide and copper oxide no hydrogen was evolved; in the latter case a difficultly reducible electrolyte, *e.g.*, potassium nitrate, could also be reduced. The current was varied from 0.003 to 0.05 amp. with a circular electrode of 1.5 cm. diameter. The reduction was also studied of solid electrodes of stibnite, iron pyrites, copper pyrites, galena, and cassiterite, crystals of each mineral being so mounted that one face only was exposed to the electrolyte. The following relation holds:  $I_r = A \log (1 + B \cdot I)$ , where  $I$  is the total current,  $I_r$  that used in reduction, and  $A$  and  $B$  are constants. In a third series of experiments, silver electrodes covered with a layer of an insoluble silver salt were reduced. Above a certain minimum value, the *E.M.F.*-current relation is linear, and the initial portion of the curve may be continued backwards by reversing the direction of

the current. The break corresponds with a change from metallic to electrolytic conduction by the salt layer, and occurs, not at zero current, but at a cathodic polarisation of the order of 0.01 volt.

A. G.

**Some Electrode Phenomena in Electrolysis.** J. A. CROWTHER and R. J. STEPHENSON (*Phil. Mag.*, 1925, [vi], 50, 1066—1079; cf. *ibid.*, 50, 86).—The phenomena occurring when an increasing potential difference is applied to an electrolytic cell, one of the electrodes of which is of comparatively small area, have been further investigated. The small electrode consisted of a platinum disc or wire of about 0.5 cm.<sup>2</sup> area. Evidence is adduced to show that a contact or transfer resistance exists between the electrolyte and electrode. This resistance is inversely proportional to the external pressure on the cell. From this it is inferred that the transfer resistance is attributable to a thin gas film. When the current density exceeds a certain critical value, the resistance at the electrode is very largely increased. For solutions of sulphuric acid of varying concentration the critical voltage increases and the critical current diminishes with increasing specific resistance. The critical current diminishes with diminishing external pressure. The extra resistance of the cell when in the highly resistant state is confined to a layer which does not extend more than 0.02 mm. from the electrode. The suggestion is made that it is due to the liquid being thrown into the spheroidal state by the heat generated in the transfer resistance owing to the passage of the current through it.

A. B. M.

**Application of Quanta in the Theory of Chemical Reactivity.** S. C. ROY (*Z. Physik*, 1925, 34, 499—509).—In spite of the severe criticism to which the radiation theory of chemical reactivity has been subjected, its value remains great in the absence of any other valid hypothesis. The velocity of the change  $AB \rightarrow A+B$  is determined by the number of collisions of  $AB$  with light quanta, and the reverse process by the number of collisions between  $A$  and  $B$ . From considerations of the effective diameter of quanta and atoms an expression is obtained for the velocity constants of the two reactions and is extended to include molecules previously activated. Ionisation of a gas is regarded as the simplest type of chemical change; thermal ionisation of gases and thermionic emission of hot bodies are treated as special cases of heat reactions.

E. B. L.

**Critical Increment of Chemical Reactions.** W. E. GARNER (*Phil. Mag.*, 1925, [vi], 50, 1031—1033).—Polemical, in reply to Hinshelwood (this vol., ii, 874).

A. B. M.

**Energy Distribution Law Appropriate to the Theory of Chemical Reaction Velocity.** C. N. HINSHELWOOD and C. W. THORNTON (*Phil. Mag.*, 1925, [vi], 50, 1135—1139).—The fraction of the total number of molecules possessing the necessary energy of activation to react is usually written  $e^{-E/RT}$ , where  $E$  is the critical energy. This is not rigidly true for all forms of energy, and the possibility of determining which form of molecular energy

is responsible for activation, or of distinguishing between cases in which one or other form of energy preponderates, is discussed. An examination of the data for three bimolecular reactions (cf. A., 1924, ii, 749) from this point of view, however, shows that the variations which would be observed fall within the experimental error.

A. B. M.

**Thermal Decomposition of Ozone.** R. O. GRIFFITH and A. McKEOWN (*J. Chem. Soc.*, 1925, 127, 2086—2096).—The thermal decomposition of ozone in glass tubes at 100° follows approximately a bimolecular course although the velocity coefficients increase slightly with time. For ozonised oxygen mixtures, at pressures between 300 mm. and 1000 mm., the bimolecular coefficient  $k$  (expressed in the units litres/moles-minutes) is given by the expression  $k=11,500/(300+P)$ , where  $P$  is the gas pressure in millimetres of mercury. The velocity of decomposition is accelerated by the addition of argon, nitrogen, carbon dioxide, and helium, the "catalytic" efficiency being in the order given. The magnitude of the velocity coefficient varies from tube to tube and is retarded slightly by coating the walls with sulphuric acid. The reaction is therefore regarded as partly homogeneous and partly heterogeneous. A mechanism is suggested explaining the retardation of the reaction by added oxygen and its acceleration by inert gases.

E. E. W.

**Keeping Properties of Standard Sodium Thiosulphate Solution.** E. COLLARD, jun. (*Ann. Chim. analyt.*, 1925, [ii], 7, 291—292).—A 0.1N-solution of sodium thiosulphate remained practically unchanged in strength (24.76 as against 24.80 g. per litre) after 3½ yrs.

D. G. H.

**Keeping Properties of Tincture of Iodine.** E. COLLARD, jun. (*Ann. Chim. analyt.*, 1925, [ii], 7, 292—293).—Tincture of iodine keeps well, and a sample stored in an ordinary ground glass-stoppered flask for 3 yrs. only showed a very slight loss of alcohol and a formation of hydriodic acid less than that allowed in the French Codex. [Cf. B., 1925, 989.]

D. G. H.

**Periodic Crystallisation of Pure Substances.** E. S. HEDGES and J. E. MYERS (*J. Chem. Soc.*, 1925, 127, 2432—2434).—The periodic crystallisation of thin films of solutions of chrome alum and of barium nitrate has been observed on a microscope slide. With chrome alum, crystallisation proceeds at first at a fairly rapid rate with the formation of a large number of small particles, and then at a slower rate with the formation of a smaller number of larger particles, the two speeds thereafter alternating; the bands thus consist of alternate zones of small and large spherulites. Periodicity is only observed when the metastable, spherulitic form appears, and it seems probable that periodic phenomena are a general characteristic of such metastable systems. When benzoic acid is crystallised from a mixture of equal volumes of sulphuric acid and ethyl alcohol, rings about 1 cm. apart can be obtained.

These consist of layers of closely-packed crystals separated by spaces containing mostly solution with sufficient crystals to give rigidity to the whole. A. G.

**Temper-colours of Iron-Carbon Alloys and of the Mixed Crystals Fe-Ni, Fe-V, Fe-Al.** G. TAMMANN and G. SIEBEL (*Z. anorg. Chem.*, 1925, **148**, 297—312).—The rates of change with time of the temper-colours of primary cementite, pearlite, pearlitic cementite, and troostite, in their relation to temperature, and of nickel-, vanadium-, and aluminium-iron alloys in their relation to temperature and composition have been investigated. On plotting the thickness of the equivalent air films ( $\mu$ ) against the logarithm of the time, the resulting isotherms are in general linear or consist of two intersecting lines, indicating the validity of the equation  $t = a \cdot e^{by} - a$ , where  $t$  represents time,  $y$  the thickness of the film of oxide,  $a$  a constant, and  $b$  a coefficient (Schwächungskoeffizient), correcting for the decreased availability of oxygen;  $b$  decreases with increasing temperature according to the equation  $\log b_T = \log b_{T_0} - c(T - T_0) \log e$ ,  $c$  being a constant. The behaviour of nickel alloys is complicated. The discontinuous nature of the alteration in the  $b$  values and in the thickness of the temper-film with increasing nickel content is, however, to be explained when the changes in the nature of the alloys consequent on the passage of the iron into  $\alpha$ - and  $\gamma$ - and the nickel into  $\alpha$ - and  $\beta$ -modifications are considered. The discontinuity in the case of vanadium alloys is likewise connected with the  $\alpha \rightarrow \gamma$  change of iron. Addition of aluminium results in a markedly reduced rate of oxidation.

J. S. C.

**Mechanism of Reduction. IV.** H. J. PRINS (*Rec. trav. chim.*, 1925, **44**, 876—888; cf. A., 1923, ii, 839).—A study of the action of nitrobenzene in acetic acid solution on lead gives results closely resembling those obtained with zinc, and the same formula is applicable to both. Up to a critical concentration of nitrobenzene the velocity of solution is directly proportional to the concentration of nitrobenzene, and this velocity, expressed in molecules per unit of surface, is the same for zinc as for lead. This fact and the low temperature coefficient found show that the velocity is a velocity of diffusion.

As in the case of zinc, the variation of the reaction velocity at concentrations of nitrobenzene above the critical value is attributed to the adsorption of molecules of lead acetate on the surface of the metal, and it is shown that the average life of a molecule of zinc acetate on the surface of zinc is four times that of a molecule of lead acetate on lead.

Addition of water causes first a diminution and then an increase of velocity of the reaction, and possible explanations of these effects are discussed. G. M. B.

**Comparison of the Theory of Explosion Waves with Recent Experiments.** E. JOUGUET (*Compt. rend.*, 1925, **181**, 546—548).—Laffitte (Thesis, Paris, 1925) has recently been able to produce



spherical combustion waves having the velocity of plane explosion waves. This is apparently in contradiction with the author's theory ("Mécanique des Explosifs," Doin, Paris, 1917, 364). The theory was only a first approximation and it is re-discussed in the light of Laffitte's work.

R. A. M.

**Pressures Developed in Closed Vessels by the Combustion of Explosives.**

E. BURLLOT (*Mém. Poudres*, 1924, **21**, 403—410).—A comparison is made between the values obtained for the pressures developed by the combustion of explosives in closed vessels, measured (i) by the acceleration of a freely-moving piston, and (ii) by the deformation of "crushers." The higher results are given by (i), from which it is concluded that the frictional forces tending to diminish the acceleration of the piston are negligible, and that the pressures measured in this way correspond satisfactorily with those actually developed in the bomb.

N. H. H.

**Experimental Determination of the Force and Co-volume of Explosives.** E. BURLLOT (*Mém. Poudres*, 1924, **21**, 411—490; cf. this vol., ii, 558).—The values of the force,  $f$ , and the co-volume,  $\alpha$ , obtained from the equation  $p/\Delta = \alpha p + f$  do not agree with those obtained from the two equations  $f = P_0 V_0 T/273$ , and  $\alpha = \alpha' + V_0/1000$ . The reason is held to lie in the difficulty of interpreting the determinations of the pressure ( $p$ ), the specific volume ( $V_0$ ), and the temperature of combustion ( $T$ ). The two methods of determining  $f$  and  $\alpha$ , namely, (i) measurement of the pressures developed in the bomb, and (ii) analysis of the gases and solid residues formed, are critically examined and compared. For this the data obtained from numerous experiments of the author are utilised. It is concluded that, practically,  $\alpha$  may be calculated by means of the expression  $\alpha = \alpha' + V_0/1000$ , and that as regards  $f$  an agreement between the calculation based on the pressures measured by a freely-moving piston, corrected for cooling, and that based on the laws of the specific heats of gases at high temperatures and pressures depends on a readjustment of these laws.

N. H. H.

**Nature of the Constant of Mass Action.** R. D. KLEEMAN (*Physical Rev.*, 1924, [ii], **23**, 307—308).—Van't Hoff's assumption that the molecules formed in the reacting chamber in his process can be removed so rapidly that no dissociation takes place is inadmissible unless the process is carried out infinitely slowly, when the constant of mass action is a function, not only of the temperature, but also of the volume of the mixture and the masses of the constituents. The existence of catalytic action by contact can be deduced.

A. A. E.

**Laws of Unimolecular Reactions (Fermentations; Catalytic Reactions).** L. AMBARD (*J. Chim. phys.*, 1925, **22**, 402—412).—A general theory of catalytic action, more comprehensive than the classical theory, is developed from experiments on catalysis by amylolytic enzymes. Univalent anions link, by adsorption, the enzyme to the substance to be transformed, in this case starch paste or glycogen. When the concentrations of starch and enzyme

are constant, and that of the anion, from sodium chloride, varies,  $\phi$ , the amount of substance transformed in unit time, is proportional to the concentration of sodium chloride (when this is small), then increases less rapidly, and finally decreases. The maximum values of  $\phi$  differ with the various chlorides, bromides, and iodides studied. In the absence of an electrolyte, no fermentation occurs and  $\phi$  thus expresses the proportion of the enzyme activated by the anion. Further, with fixed concentration of the substrate,  $\phi$  is proportional to the concentration of the enzyme only when the concentration of the univalent anion is constant.  $\phi$  is proportional to the concentration of the substrate between concentrations of glycogen from 5% to 10%. Outside these limits, the law of mass action fails, and other factors, besides the number of collisions (the only factor embraced by the kinetic theory), and the concentration of catalyst and anions, intervene. These are (1) the number of collisions between catalyst and substance which can be utilised, and (2) adsorption of the enzyme, which is a function of the concentration of substance to be transformed when concentrations of enzyme and anions are constant. The hydrolysis of sucrose is also discussed.

L. S. T.

**Oxidation in Sea Water.** H. W. HARVEY (*J. Marine Biol. Assoc.*, 1925, **13**, 953—969).—"Deep water" from the English Channel contains a catalyst which increases the rate of oxidation of easily oxidisable substances such as pyrogallol and quinol. The decomposition of hydrogen peroxide is also catalysed by deep water. Both effects are inhibited by cyanide and by glycine. It is suggested that the catalysts are organic compounds of iron and that the inactivity of surface water is due to the presence of oxidisable organic matter. When these substances are oxidised by hydrogen peroxide the surface water becomes more active.

P. E.

**Secondary Kinetic Salt Effect in the Case of Hydroxyl Ion Catalysis.** J. N. BRÖNSTED and C. V. KING (*J. Amer. Chem. Soc.*, 1925, **47**, 2523—2531).—The decomposition of nitrosotriacetone-amine catalysed by hydroxyl ions shows a negative primary salt effect (cf. A., 1924, ii, 331, 745). In piperidine-piperidinium ion and phosphate buffers the reaction shows a considerable secondary salt effect, positive in the first, and negative in the second case. An apparatus for determining the velocity of a reaction accompanied by the evolution of a gas is described.

W. T.

**Mechanism of Oxidation Processes. IX.** H. WIELAND (*Annalen*, 1925, **445**, 181—201; cf. A., 1924, i, 1172).—I. [With H. HAUSSMANN.]—Mode of Action of Catalase.—Whilst hydrogen peroxide is to be expected as a primary product in biological oxidation processes brought about by catalases, its presence in the living cell could not be demonstrated by experiments in which the enzyme was rendered suddenly inactive by treatment with 4*N*-sulphuric acid, or hydrocyanic acid, or by cooling in liquid air, the last-named procedure being applied both to freshly-gathered leaves

and to a newly-killed 14-days-old dog (cf. Macleod and Gordon, A., 1922, i, 1095; 1923, i, 125; *J. Path. Bact.*, 1925, 28, 155). Whilst the dilute acid extract of fresh leaves gives with titanium-sulphuric acid reagent the same coloration as hydrogen peroxide, this is derived from an unidentified substance which is not a peroxide. The following experiments on the deactivation of catalase were carried out with liver catalase prepared according to the method of Batelli and Stern (*Ergeb. d. Physiol.*, 1910, 10, 544), except that filtration of the extract was replaced by centrifuging and decantation (cf. Morgulis, *ibid.*, 1924, 23, 320). The standard for comparison was a clear solution obtained by extracting 0.004 g. of the crude enzyme with cold water and diluting to 100 c.c., 1 c.c. of which solution was further diluted to 100 c.c.; this volume, then containing 0.0188 mg. of dissolved material, was used to catalyse the decomposition of 5 c.c. of neutral 0.1M-hydrogen peroxide solution at 0°, the unimolecular reaction (cf. Senter, A., 1903, ii, 661; 1905, ii, 377; 1911, ii, 995; Waentig and Steche, A., 1911, i, 759; 1912, ii, 839) being followed by titration at intervals with 0.005N-potassium permanganate in presence of 2N-sulphuric acid. The addition of 2 c.c. of 0.001N-hydrocyanic acid reduces the activity of the catalase to one-sixth of its original value. Aëration of the deactivated solution, either in a vacuum through a capillary tube or at the ordinary pressure, resulted in a still further decrease in activity of the enzyme, and the fresh catalyst was deactivated by drawing air, hydrogen, nitrogen, or carbon dioxide through the solution (cf. Waentig and Steche, A., 1912, ii, 839; 1914, i, 605; Michaelis and Pechstein, A., 1913, i, 1008), by keeping the solution in a water-pump vacuum, or by mechanical agitation (cf. Abderhalden and Guggenheim, A., 1908, i, 237). Catalase deactivated by vacuum is not reactivated on subsequent aëration. Deactivation by inert gases and by agitation is ascribed to reduction of active surface by coagulation, whilst under reduced pressure the skin of gas (air) previously surrounding each particle is removed. The observedly great activity and sensitiveness of the catalase examined is ascribed to its freedom from protective colloids. Deactivation is also effected by increased pressure (of supernatant gas), but is reversible up to an excess pressure of 600 mm. of mercury, and is ascribed to the blocking of the active surface by reversible adsorption. Reactivation is considerably accelerated by diluting the pressure-deactivated solution with gas-free water, which allows the adsorption equilibrium to be established in one phase. A similar reactivation of catalase deactivated by hydrocyanic acid can be effected by dilution, indicating that this poisoning is also due to adsorption. Methylcarbylamine behaves similarly to hydrocyanic acid, its deactivating effect being of about the same order. Deactivation by carbon monoxide is of about the same order as that of indifferent gases (cf. Senter, A., 1905, ii, 377). A similar series of experiments on the deactivation of colloidal ferric hydroxide by hydrocyanic acid indicated that this also is purely an adsorption phenomenon, a result contrary to Warburg's view that the poisoning of enzymes by hydrocyanic acid is due to labile complexes formed

between the poison and the iron present in the surface of colloidal enzyme particles.

II. [With H. LÖVENSKIÖLD.]—Mode of Reaction of Hydrogen Peroxide.—Oxidation of  $\alpha\beta$ -dihydroxybutyric acid (cf. Riiber, A., 1908, i, 639) in neutral (ammonium salt) aqueous alcoholic solution with hydrogen peroxide affords acetaldehyde, whilst crotonic acid yields  $\alpha\beta$ -dihydroxybutyric acid (*silver* salt, white flocks) when treated with aqueous hydrogen peroxide at  $40^\circ$ . The latter oxidation indicates the fission of the hydrogen peroxide into two hydroxyl groups, which become attached directly to the unsaturated carbon atoms.

F. G. W.

### Polymerisation of Acetylene under the Action of $\alpha$ -Particles.

W. MUND and W. KOCH (*Bull. Soc. Chim. Belg.*, 1925, **34**, 241—255).—The polymerisation of acetylene to a solid polymeride under the influence of radium emanation previously observed (cf. this vol., i, 625) has been studied quantitatively. A detailed description of the apparatus and the experimental procedure is given, whereby the velocity of polymerisation of acetylene containing approximately  $5 \times 10^{-5}\%$  of radium emanation at  $0^\circ$  and 700 mm. is measured. Allowing for the effect of the radium-A and radium-C in equilibrium with the emanation and for the absorption by the walls of the containing globe, it was found that each  $\alpha$ -particle emitted by the emanation, and having a range of 3.94 cm. in air at  $0^\circ$  and 760 mm., caused a disappearance of  $4.38 \times 10^6$  mols. of acetylene, and produced in the gas  $2.13 \times 10^5$  ions. Most of the molecules disappearing from the gaseous phase are assumed to become polymerised, but some may be absorbed by the polymeride, which is known to absorb considerable quantities of oxygen.

J. W. B.

**Catalytic Transference of Hydrogen as the Basis of the Chemistry of Decomposition Processes.** A. J. KLUYVER and H. J. L. DONKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 605—618).—On the assumption that the breaking down of sugar by fermentation is the result of a number of coupled dehydrogenation and hydrogenation reactions, along with intramolecular changes and condensation reactions (cf. this vol., i, 1215), the probable mechanism of these reactions is discussed. Activation of the hydrogen atoms in the substrate is brought about by the affinity of the protoplasm for hydrogen, which thus loses part of its affinity for the substrate residue. The latter becomes to a certain extent unsaturated, and a rearrangement takes place consisting in a transference of hydrogen from one part of the molecule to another, succeeded by a splitting up into acids and aldehydes of small mol. wt., and, in some cases, by partial recondensation of the products. There is an optimum degree of affinity, since if the latter is too small there will be no activation of hydrogen, if too great the hydrogen will be bound by the protoplasm. The affinity of the protoplasm for oxygen may also give rise to hydrogen activation, owing to the action on the hydroxyl group. Not only the fermentation of sugars, but all the chemical reactions brought

about by aërobic respiratory processes and anaërobic fermentation processes, appear capable of explanation by the catalytic transference of hydrogen under the influence of the protoplasm of the organisms. The difference between aërobic and anaërobic processes, therefore, is apparently not fundamental, but one of degree only. It is not necessary to ascribe the intermediate steps in any complete fermentation process to the agency of separate enzymes, but simply to manifestations of a definite degree of affinity of the protoplasm for the hydrogen of the various intermediate products. The affinity for hydrogen of the protoplasm of a given organism must vary to a certain extent with the hydrogen-ion concentration of the protoplasm.

M. S. B.

**Aluminium Oxide as a Condensing Agent and the Rôle of Carriers in Catalysis.** K. W. ROSENMUND and A. JOITHE.—(See i, 1403.)

**Catalysis by Alumina of the Reaction between Ethyl Alcohol and Ammonia.** G. W. DORRELL (*J. Chem. Soc.*, 1925, 127, 2399—2407).—Ammonia and ethyl alcohol vapour in known concentrations were carried by a stream of nitrogen over alumina. The effects of varying the temperature of the reaction, the speed of the gases, and the ratio of alcohol to ammonia on the proportion of ammonia aminated were observed. The optimum temperature is about 300°. The amination of ammonia is small when the reacting gases travel slowly, but increases as the time of contact decreases. This fact is traced to the decomposition of ethylamine into ethylene and ammonia when passed slowly over alumina. The amination of ammonia per mol. of alcohol decreases in the presence of excess of alcohol probably on account of the formation of secondary and tertiary amines. Ammonia is readily absorbed by alumina at 344°, but no decomposition into its elements could be detected.

E. E. W.

**Oxidation of Dihydroxyacetone and Glyceraldehyde in Phosphate Solutions and Acceleration of Oxidation by Heavy Metals.** F. WIND (*Biochem. Z.*, 1925, 159, 58—67).—The rate of oxidation of dihydroxyacetone and glyceraldehyde by molecular oxygen in the presence of phosphate is 26—27 times that of lævulose (cf. Meyerhof and Matsuoka, A., 1924, i, 1045). The oxidation of lævulose is accelerated by cupric and ferrous salts, is inhibited by potassium pyrophosphate and cyanide in the presence of cupric salts, but is accelerated by potassium pyrophosphate in the presence of ferrous salts. The oxidation of dihydroxyacetone is accelerated by 0.001*N*-copper (125%), ferrous iron (61%), and manganese (63%), and is inhibited by 0.001*N*-potassium cyanide (40%).

E. C. S.

**Composition of Reduced Nickel as a Catalyst.** B. KUBOTA and K. YOSHIKAWA (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1925, 3, 223—232).—Reduced nickel used as a catalyst contains numerous unstable hydrides which may coexist. They may be classified into three groups, (a) hydrides capable of effecting hydrogenation of the aromatic nucleus, (b) hydrides reducing ethylenic

compounds, (c) hydrides capable of reducing groups such as the nitro group. When benzene containing thiophen is passed over the catalyst a limiting amount of nickel sulphide is formed and no further hydrogenation of the nucleus occurs. The percentage of nickel thus converted is a measure of the percentage capable of affecting the aromatic nucleus. The catalyst retains its activity towards ethylene compounds. Ethyl sulphide is now passed over and an additional amount of nickel sulphide is formed, reaching a limit when hydrogenation (b) ceases. Hydrogen sulphide is now passed over and the final percentage of nickel existing as sulphide is a measure of the percentage entering into the reduction of nitrobenzene. If nitrobenzene is reduced at  $180^{\circ}$  with a catalyst poisoned by thiophen, a theoretical yield of aniline is obtained, whereas only 38% is obtained from the unpoisoned catalyst.

A table shows the percentages of nickel reduced at various temperatures effective in the three classes of reactions, and hydrides the presence of which would account for the percentage of nickel effective in the reduction of nitrobenzene. R. A. M.

**Catalytic Formation of Methane from Carbon Monoxide and Hydrogen. I.** K. M. CHAKRAVARTY and J. C. GHOSH (*J. Indian Chem. Soc.*, 1925, 2, 150—156).—A sugar charcoal-nickel (73 : 27) catalyst for the reaction  $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ , prepared by the carbonisation of a mixture of solutions of sucrose and nickel acetate under prescribed conditions, retains its activity undiminished for months when the theoretical ratio of hydrogen and carbon monoxide is used. The critical space velocity (c.c. of gas per c.c. of catalyst material per min.) below which no carbon monoxide is found in the outflow gases is large and increases considerably with temperature. This catalyst entirely suppresses the reaction  $2\text{CO} = \text{C} + \text{CO}_2$  and prevents the deposition of carbon on the nickel surface. Ceria acts as a promoter for this catalyst, e.g., at  $355^{\circ}$  the critical space velocity is 3.5 without ceria, whilst with ceria it is greater than 4.4. The presence of carbon dioxide in the outflow gases is due mainly to the reaction  $2\text{CO} + 2\text{H}_2 = \text{CO}_2 + \text{CH}_4$ , and partly to the reaction  $\text{C} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$ , the latter being suppressed at high space velocities. J. W. B.

**Catalytic Formation of Methane from Carbon Monoxide and Hydrogen. II. Production of Fuel Gases Rich in Methane.** K. M. CHAKRAVARTY and J. C. GHOSH (*J. Indian Chem. Soc.*, 1925, 2, 157—164).—The application of the sugar charcoal-nickel catalyst (cf. preceding abstract) in pumice to the production of methane in accordance with the equations  $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$  and  $2\text{CO} + 2\text{H}_2 = \text{CO}_2 + \text{CH}_4$  from mixtures of hydrogen and carbon monoxide (1 : 1) has been studied; its efficiency is small unless a promoter is employed. Ceria (cf. Medsforth, T., 1923, 123, 1452) is without influence in promoting the second reaction, but vanadic acid is very efficient, its activity rapidly increasing with rise in temperature. The activity of this catalyst remains steady for months if the reaction temperature be maintained below  $500^{\circ}$ , and at  $400^{\circ}$  the exothermic reactions involved maintain the temperature

of the catalyst without external heating. Ferric oxide is also an efficient promoter, but the substitution of coconut charcoal for sugar charcoal yields a catalyst which, although possessing initial high activity at low temperatures, does not remain steady and has a small temperature coefficient. Examination of the composition of the incoming and effluent gases shows that equivalent quantities of methane and carbon dioxide are produced by the second reaction, the excess of methane found resulting from the first reaction, which is favoured by a high space volume. The calorific value of the resulting gas is slightly lower than that of carburetted water-gas, the large volume of carbon dioxide produced acting as a diluent.

J. W. B.

**Activity of Contact Substances. II. Catalytic Synthesis of Water by Metals of the Iron Group and their Binary Alloys with One Another and with the Platinum Metals, in so far as they are Catalytically Active at the Ordinary Temperature.**

H. REMY and H. GÖNNINGEN (*Z. anorg. Chem.*, 1925, **148**, 279—292; cf. this vol., ii, 563).—An extension of previous work. Iron, cobalt, nickel, their binary alloys with one another and with ruthenium and osmium, and also rhodium-cobalt alloys possess no catalytic activity at the ordinary temperature against a hydrogen-oxygen mixture. As previously noticed (*loc. cit.*), the activities of the various catalysts are markedly influenced by previous treatment with hydrogen or oxygen. Rhodium-nickel alloys are only active catalytically after previous treatment with hydrogen and rhodium-iron and iridium-iron alloys after oxygen treatment. Data are given for the relative catalytic activities of the various active alloys against a mixture of 2 vols. of hydrogen and 1 vol. of oxygen systematically diluted with hydrogen, oxygen, or nitrogen. The following numbers represent the relative catalytic efficiencies of the various alloys etc. against a mixture of 2 vols. of hydrogen and 1 vol. of oxygen after previous exposure to hydrogen, the figures in parentheses representing the corresponding activities after exposure to oxygen: rhodium-iron 0 (24); rhodium-nickel 111 (0); palladium-iron 77 (95); palladium-cobalt 87 (71); palladium-nickel 118 (71); iridium-iron 0 (71); iridium-cobalt 65 (31); iridium-nickel 118 (71); platinum-iron 91 (111); platinum-cobalt 111 (65); platinum-nickel 105 (74); platinum 118 (115). The remarkable dependence of the catalytic efficiency on the previous treatment with oxygen or hydrogen is readily seen; iron alloys, which are the least active after exposure to hydrogen, are the most efficient after exposure to oxygen. It is remarkable that an iron-iridium alloy, previously exposed to hydrogen, possesses an activity about 40% of that of platinum against a gas mixture of the composition ( $2\text{H}_2, \text{O}_2, 6\text{N}_2$ ). The alloy is otherwise inactive as a catalyst.

J. S. C.

**Effect of X-Rays on the Platinum Catalyst in the Contact Sulphuric Acid Reaction.** G. L. CLARK, P. C. MCGRATH, and M. C. JOHNSON (*Proc. Nat. Acad. Sci.*, 1925, **11**, 646—651).—Preliminary investigations have shown that X-rays do not activate

the platinum catalyst in the oxidation of sulphur dioxide when it is exposed to the radiation in dry air. When exposed in a moist atmosphere containing 0.013 part of water per 1 part of dry air, it was activated and an increase in conversion obtained over the first period of use. The activity then fell to a minimum and finally returned to its normal value before irradiation. Subsequent irradiation gave less activation and a slower return to the normal. The decreased effect of X-rays after the first exposure is regarded as being due to the building up of a film of sulphuric acid which is not easily ionised by the radiation. A. E. M.

**Gaseous Catalysis by Means of Metals of the Platinum Group.** L. DUPARC, P. WENGER, and C. URFER (*Helv. Chim. Acta*, 1925, 8, 609—631; cf. Wenger and Urfer, A., 1918, ii, 230).—The relative efficiency of rhodium and platinum as catalysts is studied in the cases of the oxidation of sulphur dioxide and ammonia, and the reduction of carbon monoxide, carbon dioxide, nitric oxide, and nitrous oxide, and the effects of the alteration of conditions have been observed. In the catalytic oxidation of ammonia, using platinum-black as a catalyst, the best yields are obtained when the concentration of the catalyst is 3%. Above 700°, the yields are considerably reduced, and in this region at a given temperature the yield is inversely proportional to the concentration of the catalyst. At 520°, the yields are not altered appreciably by a variation in the rate of passing the gases between the limits of 10 and 60 litres per hr., the yield increasing with increasing concentration of the catalyst. A rhodium-black catalyst is much more reactive than platinum, and consequently a much lower concentration of catalyst must be employed. At a rate of 45 litres per hr. the yields are almost as large with a rhodium catalyst concentration of 0.1% (optimum) as with a 3% platinum catalyst. When the former is employed, the heat of reaction is sufficient to maintain the catalyst in a state of incandescence, whereas external heat must be continually applied in the case of the platinum catalyst. Data relevant to the theory of catalytic action are discussed and a theory of the mechanism is deduced in each case. In the catalytic oxidation of sulphur dioxide the intermediate is the oxide  $\text{Rh}_2\text{O}_3$ :— $\text{Rh}_2\text{O}_3 + 3\text{SO}_2 = 3\text{SO}_3 + 2\text{Rh}$ ;  $4\text{Rh} + 3\text{O}_2 = 2\text{Rh}_2\text{O}_3$ , since the reaction which proceeds slowly below 600° reaches its maximum efficiency at this temperature, at which the rhodium-black most rapidly absorbs oxygen, whereas at 650° and above, when the dissociation of the rhodium oxide is appreciable, the yields of sulphur trioxide decrease owing to the difficulty with which the metal oxide is reformed. A similar mechanism applies to the case of platinum, the maximum absorption of oxygen and the maximum yield of sulphur trioxide coinciding at 400° and diminishing at 500° and above. In the case of the oxidation of ammonia, maximum yields are obtained at 560° and consequently the oxide of the catalyst cannot be the intermediate in this case. The ammonia reduces the catalyst oxide to yield the metal and water, and the former then reacts with the ammonia to form



its hydride and highly reactive nascent nitrogen, which immediately combines with oxygen to form nitrogen peroxide, which with excess of ammonia yields a mixture of ammonium nitrite and nitrate. With a 0.1% rhodium catalyst and the (theoretical) mixture of 2 vols. of ammonia and 3.5 vols. of oxygen, the rhodium is not oxidised, but immediately takes up the hydrogen from the ammonia and the nascent nitrogen is completely oxidised to nitrogen peroxide. With a 5% rhodium catalyst, carbon monoxide mixed with an equal volume of hydrogen is reduced in accordance with the equation  $3\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} + \text{CO}_2 + \text{C}$  when a slow current of the mixed gases is passed, and in accordance with the equation  $3\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} + 2\text{CO}$  when a rapid stream is employed. With a mixture of 1 vol. of carbon monoxide and 3 vols. of hydrogen, a theoretical yield of methane is produced in accordance with the equation  $\text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$ . Reduction of carbon dioxide is difficult, the yields being only 20–25%. In the case of nitric oxide, the catalyst becomes incandescent at  $320^\circ$ , and quantitative reduction in accordance with the equation  $2\text{NO} + 5\text{H}_2 = 2\text{NH}_3 + 2\text{H}_2\text{O}$  occurs with a concentration of catalyst between 5% and 0.5%. No reduction occurs if the gases be passed at a rate of less than 9 litres per hr., and the reaction is too violent when it exceeds 45 litres per hr., but with a sufficiently high rate raising the temperature above  $320^\circ$  does not influence the yield. With nitrous oxide, when a mixture of 1 vol. of nitrous oxide and 4 vols. of hydrogen is passed at a rate of 40 litres per hr. the catalyst becomes incandescent at  $330^\circ$ , reduction being quantitative in accordance with the equation  $\text{N}_2\text{O} + \text{H}_2 = \text{N}_2 + \text{H}_2\text{O}$ ; no trace of ammonia is produced.

J. W. B.

**Decomposition of Carbon Monoxide in the Corona due to Alternating Electric Fields.** I. M. CRESPI and R. W. LUNT (*J. Chem. Soc.*, 1925, **127**, 2052–2057).—The behaviour of carbon monoxide in the corona due to alternating electric fields of frequency 250 has been investigated. It decomposes yielding a solid substance containing carbon and oxygen and a gaseous mixture of carbon monoxide and dioxide of approximately constant composition. The composition of the solid is independent of the electrical potential and varies solely with the initial pressure of the carbon monoxide. The solid is a dark brown, hygroscopic powder, having an acid reaction in aqueous solution; it is readily soluble in alcohol and sparingly soluble in ether.

E. E. W.

**Anode Phenomena in the Electrolysis of Potassium Ethyl Malonate.** J. B. ROBERTSON (*J. Chem. Soc.*, 1925, **127**, 2057–2067; cf. this vol., ii, 312).—The formation of ethyl succinate on electrolysis of potassium ethyl malonate is shown to be an oxidation reaction. It takes place only when the anode is of suitable material and when its potential exceeds 2.3–2.4 volts referred to the normal hydrogen electrode standard. Grey platinum and smooth platinum anodes both favour the occurrence of synthesis, but platinised platinum and gold anodes do not. Anodes of all four materials used cause what appears to be complete oxidation of a portion of

the electrolyte. The extent of this oxidation is small with platinised platinum and still smaller with gold, but is more considerable with smooth platinum and grey platinum.

E. E. W.

**Photochemical Union of Hydrogen and Chlorine.** R. G. W. NORRISH (*J. Chem. Soc.*, 1925, **127**, 2316—2334).—The rate of combination of hydrogen and chlorine is uninfluenced by desiccation down to a water-vapour pressure of  $10^{-4}$  mm. It approaches zero between  $10^{-4}$  and  $10^{-7}$  mm. (Coehn and Jung, this vol., ii, 142). It is shown that at  $10^{-4}$  mm. the surface of the reaction vessel under the conditions of experiment was no longer completely saturated with water molecules. The photochemical dissociation of chlorine molecules occurs only at the water film covering the walls of the vessel, and the reaction spreads outwards into the gas phase by "Nernst chains," its rate being constant so long as the surface of the vessel is saturated with water molecules, but decreasing when it becomes unsaturated. The anti-catalytic effect of hydrogen and oxygen (this vol., ii, 572) is explained on the basis of this hypothesis, which is further extended to account for the observed photochemical induction period. Ammonia formed from traces of nitrogenous impurities is assumed preferentially to combine with the water film, and to require removal by photochemical reaction with the chlorine before the primary reaction can occur. Quantitative observations on the effect of the addition of known quantities of ammonia on the induction period have been made, and it is shown that its duration can be calculated from the expression  $(1-b/P)apv/s$ , where  $p$  and  $P$  are the pressures of ammonia and chlorine,  $v$  and  $s$  the volume and surface of the reaction vessel respectively, and  $a$  and  $b$  are constants; the expression is in agreement with the hypothesis proposed.

E. E. W.

**Photochemical Reaction between Bromine and Tartaric Acid in Aqueous Solution.** I. J. C. GHOSH and J. MUKHERJEE (*J. Indian Chem. Soc.*, 1925, **2**, 165—178).—The photochemical reaction between bromine and tartaric acid in aqueous solution (resulting in the formation of hydrobromic acid, carbon dioxide, and aldehydotartronic acid) has been studied for blue light (450—490  $\mu$ ). The velocity of the dark reaction is negligible, but with light of an incident intensity of 5400 ergs per  $\text{cm}^2$  per sec. there is a period of induction of 120—150 mins. No induction period is observed when the reaction mixture is exposed to an intense light source. The rate of disappearance of the bromine is at first slow, reaches a maximum, and then continually falls, the velocity constants in the last portion of the curve being those of a unimolecular reaction. The velocity constant depends only on the intensity of the light and is independent of its state of polarisation. The temperature coefficient of the reaction is between 1.7 and 2.0. A photochemical after-effect was observed when the reaction mixture was exposed to intense sunlight for 5 mins. and then kept in the dark at  $30^\circ$ , the reaction proceeding at a velocity much greater than that observed in the ordinary photochemical reaction at the same temperature, but ceasing at the end of 1 hr. Hence an intermediate

compound of bromine and tartaric acid, in which the bromine is available for iodometric titration, must be formed initially, and this decomposes in the dark with a velocity great in comparison with that of the initial photochemical reaction. By a mathematical analysis of the reaction, it is shown that when the pressure  $p$  of the acceptor molecules (osmotic pressure) is constant (tartaric acid in excess) the curve plotted between  $1/k$  and  $1/p$  should be a straight line, and this is the case when the initial concentration of the bromine is 0.0147*N*, but it is not so for higher concentrations of bromine. For an infinite concentration of tartaric acid, the velocity constants of the reaction will be independent of the concentration of the photoactive component, bromine, the life period of the activated bromine molecules being less for higher initial concentrations of this component than for lower, the diminution of the velocity coefficient with increase in the initial concentration of the bromine being due to this cause. The application of Einstein's law of photochemical equivalence is discussed. J. W. B.

**Photochemical Studies. V. Actinoscopic Reactions.** A. REYCHLER (*Bull. Soc. chim. Belg.*, 1925, **34**, 236—241).—The action of light in effecting the liberation of iodine from a solution of potassium iodide in the presence of potassium dichromate and eosin (cf. Straub, A., 1920, i, 896) has been investigated. The presence of both the potassium dichromate and the eosin is necessary in order that the liberation of iodine may proceed with an appreciable velocity, the latter increasing with increasing intensity of the light. No reaction occurs in the dark. Since the same amount of iodine is liberated in an atmosphere of carbon dioxide as in air, atmospheric oxidation plays no part in the reaction. J. W. B.

**Formation of Active Hydrogen in the Creepage Corona Discharge.** F. O. ANDEREGG and W. N. HERR (*J. Amer. Chem. Soc.*, 1925, **47**, 2429—2431).—Glass wool in the discharge space tends to increase the yield of active hydrogen. The tube exhibits fatigue effects which may be removed by discharging in nitrogen. A trace of air admitted and then swept out produced a similar result, probably due to an adsorbed film of gases on the glass, since traces of nitrogen or oxygen admitted with the hydrogen were without effect. Disuse of the tube allows it to recover very slowly from fatigue. Earthenware, flint, or platinum in the discharge space gave no appreciable yield of active hydrogen; they may promote decomposition of the active form. W. T.

**Effect of Ultra-violet Light on Dried Hydrogen and Oxygen.** H. B. BAKER and (MISS) M. CARLTON (*J. Chem. Soc.*, 1925, **127**, 1990—1991).—The work of Coehn and Tramm indicated that the mixture of hydrogen and oxygen dried to the point at which no explosion took place, but only slow combination on heating, would combine as readily in the dried as in the undried condition, under the action of ultra-violet light.

The work has been repeated with six pairs of quartz tubes filled with the gaseous mixture produced by the electrolysis of very

pure barium hydroxide, one of each pair containing some distilled phosphorus pentoxide. In every case, whether the drying lasted 8 weeks or 2 weeks, there was a difference in the rate of union of the dried and the wet gases. After drying for 7 weeks and 8 weeks, respectively, the dried gas gave no measurable contraction after  $6\frac{1}{4}$  hrs.' and 5 hrs.' exposure to the light from a quartz mercury lamp, the comparative wet tubes showing a considerable amount of union with the same exposure. No ozone was produced in either the wet or the dry gas. E. E. W.

**Decomposition of Hydrogen Peroxide.** W. P. DAVEY (*Science*, 1925, **61**, 388—389).—Ditman's statement (this vol., ii, 51) on the decomposition of hydrogen peroxide by a single electrical conductor the ends of which are immersed in solutions of hydrogen peroxide and colloidal platinum, respectively, cannot be substantiated when precautions are taken to prevent contamination of the hydrogen peroxide by any agent tending to decompose it. A. A. E.

**Mercury and Ionised Helium.** S. C. LIND and D. C. BARDWELL (*Science*, 1925, **61**, 344—345).—No evidence could be obtained of the formation of a compound of helium and mercury when the helium was ionised by means of radon. The result, however, is not necessarily at variance with those obtained using an electrical discharge (cf. Manley, this vol., ii, 57, 314, 696; Boomer, *ibid.*, ii, 144), since electron bombardment frequently produces chemically active resonance states, which are not known to be produced by  $\alpha$ -particles. A. A. E.

**Explosions with Alkali Metals.** H. STAUDINGER (*Z. Elektrochem.*, 1925, **31**, 549—551).—When an alkali metal is brought into contact with bromine or with a halogenated hydrocarbon, little or no immediate reaction takes place; but the system explodes when subjected to a minimal mechanical impact, which may be measured. Thus with chloroform the requisite priming energy is 1.5 kg. metre for lithium, 0.6 for sodium, 0.02 for potassium, and 0.0007 for sodium-potassium alloy. This latter is in general by far the most sensitive form of alkali metal. The results with various halogen compounds indicate that the limit of priming energy has no connexion with the energy of reaction. Sodium-potassium is found to explode similarly with silver halides, solid carbon dioxide, mercuric oxide, ammonium nitrate, and organic nitro compounds, and the priming energies have been measured. It is suggested that a layer of a labile unpolymerised molecular compound of alkali metal with the other substance, comparable with the primary labile peroxides of organic compounds, is first formed. This protects the metal from immediate attack, but is susceptible to explosive decomposition, which is then imparted to the whole system. W. A. C.

**Lithium. V. Alkali Polybromides and Polychlorides.** G. F. HÜTTIG and O. SCHLIESSMANN (*Z. anorg. Chem.*, 1925, **148**, 87—92; cf. Hüttig and Krajewski, this vol., ii, 296; Hüttig and Keller, this vol., ii, 963).—Alkali bromides were heated with excess of bromine in a bomb tube at 500—700° and the tube was cooled to the temper-

ature of liquid air. The tube was then opened, inserted in a special apparatus, evacuated, and the bromine vapour-pressure curve determined. No polybromide of lithium was found; rubidium formed a tribromide which decomposed between  $30^{\circ}$  and  $90^{\circ}$ , and ammonium formed a tribromide which was already partly decomposed at  $0^{\circ}$ . Lithium, potassium, caesium, and calcium do not form polychlorides. A. G.

**Complex Salts of Stannous Iodide with Rubidium and Caesium Iodides.** V. AUGER and T. KARANTASSIS (*Compt. rend.*, 1925, **181**, 665—666).—The double salt,  $\text{RbSnI}_3$ , is obtained as yellow needles by cooling the pale-yellow liquid obtained when stannous iodide is added to excess of a solution of rubidium iodide acidified with hydriodic acid. Cubic crystals of  $\text{RbSnI}_5$  are obtained when excess of stannous iodide is used. The corresponding caesium salts are prepared similarly. The dry salts are fairly stable; they oxidise in the air, partly to rubidium (or caesium) iodostannate.

S. K. T.

**Systematic Doctrine of Affinity. XXXVI. Ammoniates of Cupric Halides.** W. BILTZ [with H. BRÖHAN and W. WEIN] (*Z. anorg. Chem.*, 1925, **148**, 207—216; cf. this vol., ii, 1183).—Corresponding data are tabulated. The compounds investigated were:  $\text{CuCl}_2 \cdot 10\text{NH}_3$ ;  $\text{CuCl}_2 \cdot 6\text{NH}_3$ ;  $\text{CuCl}_2 \cdot 5\text{NH}_3$ ;  $\text{CuCl}_2 \cdot 3\frac{1}{3}\text{NH}_3$ ;  $\text{CuCl}_2 \cdot 2\text{NH}_3$ ;  $\text{CuBr}_2 \cdot 10\text{NH}_3$ ;  $\text{CuBr}_2 \cdot 6\text{NH}_3$ ;  $\text{CuBr}_2 \cdot 5\text{NH}_3$ ;  $\text{CuBr}_2 \cdot 3\frac{1}{3}\text{NH}_3$ ;  $\text{CuBr}_2 \cdot 2\text{NH}_3$ ;  $\text{CuI}_2 \cdot 10\text{NH}_3$ ;  $\text{CuI}_2 \cdot 6\text{NH}_3$ ;  $\text{CuI}_2 \cdot 5\text{NH}_3$ ;  $\text{CuI}_2 \cdot 3\frac{1}{3}\text{NH}_3$ . Heats of solution of some of these compounds and of the pure halides in hydrochloric acid solutions are recorded.

J. S. C.

**Higher Oxides of Silver. I.  $\text{Ag}_2\text{O}_3$ .** F. JIRSA [with J. JELINEK] (*Z. anorg. Chem.*, 1925, **148**, 130—140).—The decomposition of the substance  $2\text{Ag}_2\text{O}_3 \cdot \text{Ag}_2\text{O}_2 \cdot \text{AgNO}_3$  (cf. this vol., ii, 314), obtained by the anodic oxidation of silver nitrate to silver nitrate, pure silver peroxide,  $\text{Ag}_2\text{O}_2$ , and oxygen, was followed by measuring the oxygen evolved; at  $64.3^{\circ}$  the higher oxide was half decomposed in about 1 hr. and at  $77.6^{\circ}$  in about 4 hrs. A summary of the literature on the higher oxides of silver is included. A. G.

**Systematic Doctrine of Affinity. XXXV. Ammoniates of Aurous Halides.** W. BILTZ [with W. WEIN] (*Z. anorg. Chem.*, 1925, **148**, 192—206; cf. this vol., ii, 1183).—Corresponding data for the following aurous halide ammoniates are recorded:  $\text{AuCl} \cdot 6\text{NH}_3$ ;  $\text{AuCl} \cdot 2\text{NH}_3$ ;  $\text{AuCl} \cdot \text{NH}_3$ ;  $\text{AuBr} \cdot 6\text{NH}_3$ ;  $\text{AuBr} \cdot 4\text{NH}_3$ ;  $\text{AuBr} \cdot 3\text{NH}_3$ ;  $\text{AuBr} \cdot 2\text{NH}_3$ ;  $\text{AuBr} \cdot \text{NH}_3$ ;  $\text{AuI} \cdot 6\text{NH}_3$ ;  $\text{AuI} \cdot 3\text{NH}_3$ ;  $\text{AuI} \cdot 2\text{NH}_3$ ;  $\text{AuI} \cdot \text{NH}_3$ . The existence of  $\text{AuCl} \cdot 12\text{NH}_3$ , and of  $\text{AuI} \cdot 8\text{NH}_3$  is demonstrated. Heats of solution of the pure halides and of the lower ammoniates in 5% potassium cyanide solution are recorded.

J. S. C.

**Compounds of Gold with Carbon Monoxide.** W. MANCHOT and H. GALL (*Ber.*, 1925, **58**, [B], 2175—2178).—Compounds of carbon monoxide with the halides of all the metals of the eighth

and of related metals of the first group of the periodic system have been described with the exceptions of cobalt, nickel, palladium, and gold. Anhydrous auric chloride combines with carbon monoxide at about  $95^{\circ}$ , giving the *product*,  $\text{AuCl}_2\text{CO}$ . Very considerable reduction of auric chloride occurs simultaneously, but this can be avoided to some extent by mixing the carbon monoxide with about 10% of chlorine. The new product is extraordinarily sensitive towards moisture. Replacement of auric chloride by aurous chloride or caesium chloroaurate brings no advantage. The bromides of gold do not yield volatile compounds with carbon monoxide.

H. W.

**Vaterite and  $\mu$ -Calcium Carbonate.** R. E. GIBSON, R. W. G. WYCKOFF, and H. E. MERWIN (*Amer. J. Sci.*, 1925, **10**, 325—333).—The material originally obtained by Vater by diffusion of calcium chloride (containing barium chloride) into potassium carbonate and named vaterite-*A*, when examined by the X-ray powder method, proved to be calcite. A second form (vaterite-*B*) obtained by Heide on crystallising colloidal calcium carbonate at  $5^{\circ}$ , was found by similar means to be identical with the  $\mu$ -calcium carbonate of Bütschli, Spannenberg, and Rinne. The latter substance was prepared by slowly dropping solutions of calcium chloride and potassium carbonate into water (with stirring) at  $60^{\circ}$ , but better by slowly dropping a 0.1*M*-solution of calcium chloride into stirred solutions of potassium carbonate (ranging from 10 to 50 g. per 700 c.c.) maintained at  $60^{\circ}$ .

A. COUSEN.

**New Peroxide of Barium.** (MISS) M. CARLTON (*J. Chem. Soc.*, 1925, **127**, 2180—2184).—When excess of hydrogen peroxide is added to a solution of barium hydroxide at temperatures below  $20^{\circ}$ , the hydrate  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$  first formed changes in appearance, forming a granular precipitate which turns buff-coloured on keeping. This substance is a cream-coloured, non-crystalline powder. It does not contain hydrogen peroxide, for this substance cannot be extracted with ether or liberated by heat. The solid substance decolorises potassium permanganate more rapidly than the oxide  $\text{BaO}_2$ ; it liberates iodine from potassium iodide and bromine from potassium bromide in the presence of dilute nitric acid. It reacts with sulphur, but does not form sulphur dioxide. The substance was analysed by heating at  $500$ — $600^{\circ}$  in a current of nitrogen, and by titrating the substance dissolved in dilute nitric acid with potassium permanganate. It is concluded that the new substance has the formula  $\text{BaO}_3$ .

E. E. W.

**Systematic Doctrine of Affinity. XXXIII. Ammoniates of Beryllium Halides.** W. BILTZ and C. MESSERKNECHT (*Z. anorg. Chem.*, 1925, **148**, 157—169; cf. this vol., ii, 1191).—The existence of the following compounds has been demonstrated, the values of the heat of dissociation and of the total heat of formation, as calculated from tensimetric data and the values of the heats of solution of the pure halides and of the lower amines in hydrochloric acid being tabulated:  $\text{BeCl}_2 \cdot 12\text{NH}_3$ ;  $\text{BeCl}_2 \cdot 6\text{NH}_3$ ;  $\text{BeCl}_2 \cdot 4\text{NH}_3$ ;  $\text{BeCl}_2 \cdot 2\text{NH}_3$ ;  $\text{BeBr}_2 \cdot 10\text{NH}_3$ ;  $\text{BeBr}_2 \cdot 6\text{NH}_3$ ;

$\text{BeBr}_2, 4\text{NH}_3$ ;  $\text{BeI}_2, 13\text{NH}_3$ ;  $\text{BeI}_2, 6\text{NH}_3$ ;  $\text{BeI}_2, 4\text{NH}_3$ . The lower ammoniates are stable compounds, dissociating only at relatively high temperatures, the dissociation being always accompanied by the formation of varying amounts of the corresponding ammonium halide.

J. S. C.

**Analytical-synthetic Researches on Zincite.** E. DITTLER (*Z. anorg. Chem.*, 1925, **148**, 332—344).—Analytical and synthetical experiments are described with the object of determining the cause of the red colour in zincite. The conversion of zinc ore into zincite is a metamorphic change produced by carbon dioxide under pressure. Under suitable temperature conditions, it is considered that the equilibrium  $3\text{MnO} + \text{CO}_2 \rightleftharpoons \text{Mn}_3\text{O}_4 + \text{CO}$  is set up, and that the higher manganese oxide separates almost completely from the molten zinc oxide, leaving traces of manganites, which confer the characteristic colour to the mineral. Natural zincite melts at  $1670 \pm 10^\circ$ ; increase in the manganous and ferrous oxide contents rapidly depresses the m. p. to  $1550^\circ$ .

S. K. T.

**Systematic Doctrine of Affinity. XXXIV. Ammoniates of Cadmium and Mercury Halides.** W. BILTZ and C. MAU (*Z. anorg. Chem.*, 1925, **148**, 170—191; cf. this vol., ii, 1191).—The following cadmium compounds have been investigated and the corresponding data as for the iron-group metal compounds calculated and tabulated:  $\text{CdCl}_2, 10\text{NH}_3$ ;  $\text{CdCl}_2, 6\text{NH}_3$ ;  $\text{CdCl}_2, 4\text{NH}_3$ ;  $\text{CdCl}_2, 2\text{NH}_3$ ;  $\text{CdCl}_2, \text{NH}_3$ ;  $\text{CdBr}_2, 12\text{NH}_3$ ;  $\text{CdBr}_2, 6\text{NH}_3$ ;  $\text{CdBr}_2, 2\text{NH}_3$ ;  $\text{CdBr}_2, \text{NH}_3$ ;  $\text{CdI}_2, 6\text{NH}_3$ ;  $\text{CdI}_2, 2\text{NH}_3$ . Some evidence was also obtained for the existence of  $\text{CdCl}_2, 5\text{NH}_3$ . From the values of  $d_4^{25}$ , the molecular volumes of some of these compounds are calculated.

Similar data are given for the following mercuric compounds:  $\text{HgCl}_2, 9.5\text{NH}_3$ ;  $\text{HgCl}_2, 8\text{NH}_3$ ;  $\text{HgCl}_2, 2\text{NH}_3$ ;  $\text{HgBr}_2, 8\text{NH}_3$ ;  $\text{HgBr}_2, 2\text{NH}_3$ ;  $\text{HgI}_2, 6\text{NH}_3$ ;  $\text{HgI}_2, 2\text{NH}_3$ ;  $\text{HgI}_2, 4/3\text{NH}_3$ . Some evidence for the existence of  $\text{HgI}_2, 12\text{NH}_3$  was obtained.

Of the mercurous compounds, the existence of  $\text{HgCl}, \text{NH}_3$  and  $\text{HgBr}, \text{NH}_3$  is definitely established, the approximate heats of formation being calculated, whilst some indication for the existence of  $\text{HgCl}, 5\text{NH}_3$  and  $\text{HgBr}, 4\text{NH}_3$  was obtained.

J. S. C.

**Amides of Mercurous Salts.** F. FEIGL and A. SUCHARIPA (*Z. anal. Chem.*, 1925, **67**, 134—140).—The action of ammonia on mercurous chloride is usually represented by the equation  $\text{Hg}_2\text{Cl}_2 + 2\text{NH}_3 = \text{NH}_4\text{Cl} + \text{HgNH}_2\text{Cl} + \text{Hg}$ . That this is not a true representation of the reaction is shown by the fact that the black product yields less mercuric chloride when treated with hydrochloric acid than corresponds with half the mercury in the mercurous chloride used. The quantity of mercury dissolved by acid increases with the age of the precipitate to a maximum of about 47.5% when the reactions are carried out at  $20^\circ$ , but only 16% is dissolved if the reactions are conducted at  $100^\circ$ , showing that an amide of mercurous chloride is first formed and that this decomposes reversibly into mercuric amidochloride and metallic mercury. The reaction therefore takes place in two stages, viz.: (1)  $\text{Hg}_2\text{Cl}_2 + 2\text{NH}_3 \rightarrow \text{NH}_2\text{Hg}_2\text{Cl} +$

$\text{NH}_4\text{Cl}$  and (2)  $\text{NH}_2\text{Hg}_2\text{Cl} \rightleftharpoons \text{NH}_2\text{HgCl} + \text{Hg}$ . Mercurous amido-chloride is formed by heating an intimate mixture of the mercuric compound with metallic mercury.

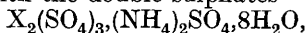
A. R. P.

**Composition of a Precipitated Aluminium Hydroxide.** J. SHIDEI (*Mem. Coll. Sci. Kyōtō*, 1925, 9, 43—73).—Precipitated aluminium hydroxide has been alleged by a number of investigators to form a definite hydrate when kept for a long time under water. Measurements have been made of the vapour tension of precipitated alumina (kept for 17 months under water), the composition varying from  $\text{Al}_2\text{O}_3 \cdot 5.639\text{H}_2\text{O}$  to  $\text{Al}_2\text{O}_3 \cdot 2.544\text{H}_2\text{O}$ . Mündells' differential manometer was used, giving an accuracy of 0.01 mm. The rate of dehydration at constant temperature of a number of samples of the hydrated oxide was also observed. All measurements were made at  $30^\circ$ , and it was found that the dehydration in a vacuum of the former hydroxide is continuous, without any sudden change in its velocity, until the composition has been reduced to  $\text{Al}_2\text{O}_3 \cdot 2.494\text{H}_2\text{O}$ . Further hydration would be extremely slow. The pressure of the aqueous vapour from the hydroxide in a vacuum increases rapidly at first and then gradually, taking a long time to reach equilibrium.

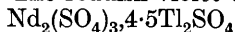
The vapour tensions decrease continuously with the diminution in the water content of the substance. It was concluded that the precipitated hydroxide which had been kept under water for 17 months was not a definite hydrate, but remained as an oxide absorbing water.

L. L. B.

**Sulphates of Neodymium and Thallous Thallium.** F. ZAMBONINI and V. CAGLIOTI (*Atti R. Accad. Lincei*, 1925, [vi], 2, 153—158; cf. this vol., ii, 222, 579).—The  $25^\circ$  isotherm for the system  $\text{Nd}_2(\text{SO}_4)_3\text{--Tl}_2\text{SO}_4$  indicates the existence of the compounds  $\text{Nd}_2(\text{SO}_4)_3 \cdot 4.5\text{Tl}_2\text{SO}_4$ ,  $\text{Nd}_2(\text{SO}_4)_3 \cdot \text{Tl}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ , and  $\text{Nd}_2(\text{SO}_4)_3 \cdot \text{Tl}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$ . The last is in equilibrium with a solution containing 3.8% of neodymium sulphate and 0.26% of thallous sulphate, and forms minute, violet crystals. The second compound is in equilibrium with solutions containing 3.78—0.30% of neodymium sulphate and 0.28—3.0% of thallous sulphate. It is isomorphous with the double sulphates



where  $\text{X} = \text{La}, \text{Ce}, \text{Di}$ . The reddish-violet compound



is in equilibrium with solutions containing 0.26—0.19% of neodymium sulphate and 3.85—4.70% of thallous sulphate.

F. G. T.

**Behaviour of Zirconium Phosphate towards Acids and Bases.** J. H. DE BOER and A. E. VAN ARKEL (*Z. anorg. Chem.*, 1925, 148, 84—86).—Zirconium phosphate is dissolved by oxalic acid, and by concentrated sulphuric and phosphoric acids; unlike hydrofluoric acid (this vol., ii, 705), these acids dissolve only the freshly precipitated or moist phosphate, and the solutions are less stable. The oxalic acid solution is decomposed by heating



or by the addition of alcohol or mineral acids, and zirconium phosphate is reprecipitated from the sulphuric or phosphoric acid solutions by dilution. Zirconium phosphate is converted into the hydroxide by alkalis, but the action is only superficial; complete dissolution may be brought about by the addition of a substance capable of dissolving the hydroxide in alkaline solution. Such substances are the aliphatic oxy-acids (*e.g.*, tartaric, malic, and lactic acids), alcohols with at least two hydroxyl groups on neighbouring carbon atoms (*e.g.*, glycerol, dextrose, sucrose, pyrocatechol, and pyrogallol), and hydrogen peroxide. The solution in hydrogen peroxide precipitates the hydroxide when heated and the per-zirconate by addition of alcohol. From the other solutions the hydroxide is obtained by partial neutralisation with acid, preferably after previous precipitation of the phosphoric acid with barium chloride. Hafnium phosphate behaves similarly, but the solutions are less stable; by this means the two metals can be readily separated. A. G.

**Formula of Cerium Hydride.** E. J. WEEKS (*Chem. News*, 1925, **131**, 245—246).—Theoretical reasons are given to show that cerium hydride formed by heating the metal in a current of hydrogen is a mixture of  $\text{Ce}_2\text{H}_2$  and  $\text{CeH}_4$ . A. R. P.

**Ionium. I. Recovery of Ionium from Carnotite. II. Adsorption of Ionium-Thorium by Barium Sulphate. III. Ionium-Thorium Ratio in Carnotite.** G. D. KAMMER and A. SILVERMAN (*J. Amer. Chem. Soc.*, 1925, **47**, 2514—2522).—The direct precipitation of ionium from an acid solution of carnotite ore is impracticable on a large scale. With large quantities of ore, precipitation with oxalic acid is unsuccessful; precipitation with hydrofluoric acid gives good results, but the precipitate is bulky and difficult to handle. Ionium is strongly adsorbed by barium sulphate, 1 g. of barium sulphate adsorbing 16% of its own weight of thorium sulphate (thorium is an isotope of ionium). Radium-barium sulphate obtained in the production of radium contains considerable ionium, which can be recovered either by fusing or by boiling the sulphates with sodium carbonate. In the commercial treatment of low-grade carnotite, most of the ionium remains in the ore residue; this can be rendered soluble by heating with sulphuric acid. Ionium can be extracted from high-grade carnotite (containing more than 15% of uranium oxide) with hydrochloric acid. The radioactive substance adsorbed by barium sulphate in addition to radium is chiefly ionium, accompanied by a small amount of actinium, and not solely actinium, as often assumed. The average Colorado carnotite contains ionium-thorium in the ratio 1 : 15.8. W. T.

**Action of Gaseous Ammonia on Phosphorus Chlorides.** H. PERPÉROT (*Compt. rend.*, 1925, **181**, 662—664).—From a study of the solid *products*,  $\text{PCl}_n \cdot 2n\text{NH}_3$ , obtained by mixing solutions of pentachloride, trichloride, or oxychloride of phosphorus in carbon tetrachloride with similar solutions of ammonia, it is concluded

that the primary action of gaseous ammonia on these chlorides proceeds according to the general equation:  $\text{PCl}_n + 2n\text{NH}_3 = \text{PCl}_n, 2n\text{NH}_3 = \text{P}(\text{NH}_2)_n + n\text{NH}_4\text{Cl}$ .  
S. K. T.

**Reduction of Inorganic Halides. IV. Tantalum Pentachloride.** O. RUFF and F. THOMAS (*Z. anorg. Chem.*, 1925, **148**, 1—18; cf. A., 1921, ii, 508; 1923, ii, 868).—Tantalum pentachloride is reduced to lower chlorides when heated with red phosphorus, tin, magnesium, lead, zinc, or aluminium, but is not reduced by sulphur, antimony, arsenic, bismuth, or mercury. Reduction by aluminium was more fully investigated, the reaction mixture being heated at 300° in an evacuated bomb tube. At this temperature complete reduction to metallic tantalum did not occur, even with excess of aluminium. A chloride of the composition  $\text{TaCl}_4$  was obtained when somewhat less than the calculated amount of aluminium for reduction to this stage was taken, and the aluminium chloride and excess of tantalum pentachloride were distilled off at 250°. It is uncertain whether this is a compound of quadrivalent tantalum or whether it is a complex of tri- and penta-chlorides. On further heating, more pentachloride is lost and the residue becomes progressively richer in tantalum. Thus at 350—400° the trichloride is obtained and at 600° the dichloride, these being definite compounds, and at 680—700° the proportion of tantalum is still higher and the product is pyrophoric. The dichloride dissolves in water with evolution of hydrogen and formation of an oxychloride of tervalent tantalum, and is thus distinguished from the trichloride, which dissolves without evolution of gas. In alkaline solutions, both chlorides are oxidised to the quinquevalent state with evolution of hydrogen, the measurement of which is a convenient method of determining the state of oxidation of the tantalum. When the pentachloride, prepared by chlorinating the pentoxide, is sublimed in a vacuum at 500° an *oxychloride*,  $\text{TaO}_2\text{Cl}$ , is obtained.  
A. G.

**Reduction of Inorganic Halides. V. Derivatives of Tantalum Trichloride.** O. RUFF and F. THOMAS (*Z. anorg. Chem.*, 1925, **148**, 19—24; cf. preceding abstract).—When a tantalum trichloride solution is evaporated under reduced pressure with hydrochloric acid a crystalline salt is obtained which is formulated as  $\text{Ta}_3^{\text{III}}\text{Cl}_7\text{O}, 3\text{H}_2\text{O}$ . Lindner and Feit (A., 1924, ii, 768) proposed the formula  $(\text{HTa}_3^{\text{III}}\text{Cl}_7, \text{H}_2\text{O}), 3\text{H}_2\text{O}$ , believing it to contain bivalent tantalum on the basis of valency determinations by oxidation with permanganate and reduction of silver. Both these methods are, however, untrustworthy, and measurements of the hydrogen evolved when the substance is oxidised to the quinquevalent state in alkaline solution (see preceding abstract) show that the tantalum is tervalent. Only 3 mols. of water are lost when it is heated, and the evolution of hydrochloric acid on further heating is ascribed to traces of water having been retained. The formulæ of the derivatives described by Lindner and Feit require similar modification.  
A. G.

**Bismuth Trihydride and Silver Bismuthide.** E. J. WEEKS and J. G. F. DRUCE (*Nature*, 1925, **116**, 710).—When heated in a vacuum, bismuth dihydride decomposes thus:  $3\text{Bi}_2\text{H}_2 = 4\text{Bi} + 2\text{BiH}_3$ ; when heated in hydrogen, the reaction is  $2\text{Bi}_2\text{H}_2 + \text{H}_2 = 2\text{BiH}_3 + 2\text{Bi}$ . The bismuth trihydride was detected by interaction with silver nitrate solution, whereby a black precipitate of silver bismuthide is produced:  $\text{BiH}_3 + 3\text{AgNO}_3 \rightleftharpoons 3\text{HNO}_3 + \text{BiAg}_3$ .  
A. A. E.

**Effect of Vacuum and of Heat on the Neutral and Basic Bismuth Nitrates. Determination of Water of Constitution and of Nitric Acid in these Salts.** PICON (*Compt. rend.*, 1925, **181**, 516—518).—A glass T-tube was connected with a mercury pump; in one arm was placed phosphorus pentoxide, and in the other, one of the bismuth nitrates which were to be dehydrated. After evacuation, the T-piece was sealed. In order to minimise loss of nitric acid, the arm containing the neutral salt was cooled to  $-80^\circ$  during evacuation. The nitric acid was determined by Dumas' method, and by titration with ferrous salts, which alone among volumetric methods gave consistent results. The neutral nitrate yielded the compound  $\text{Bi}_2(\text{NO}_3)_6 \cdot 3\text{H}_2\text{O}$ , which retained its water after 6 months' drying. The nitrate,  $\text{Bi}(\text{OH})_2\text{NO}_3$ , gave the compound  $12(\text{BiO}, \text{NO}_3) \cdot 5\text{H}_2\text{O}$ . Another nitrate,  $18(\text{BiO}, \text{NO}_3) \cdot \text{Bi}_2\text{O}_3 \cdot 7\text{H}_2\text{O}$ , yielded the compound  $18(\text{BiO}, \text{NO}_3) \cdot \text{Bi}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ .

The salt  $10(\text{BiO}, \text{NO}_3) \cdot \text{Bi}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$  lost 4 mols. of water.

The same salts (with the exception of the neutral nitrate which decomposed) were heated at  $100^\circ$  for 10 days. Salts containing 6, 2.45, and 4.87% of water lost 3.64, 0.5, and 2.85%, respectively, leaving products agreeing well with those obtained by vacuum desiccation. The neutral nitrate cannot be completely dehydrated by phosphorus pentoxide without decomposing, and the effect of heat on this salt is complex.

R. A. M.

**Acid Nature of some Derivatives of Sulphur, Selenium, and Tellurium.** D. D. KARVE (*J. Indian Chem. Soc.*, 1925, **2**, 128—141; cf. this vol., ii, 633).—The Hantzsch criteria for pseudo-acids, viz., comparison of the absorption spectra of the acid, its salts and esters in various solvents, the velocity of reaction with ethyl diazoacetate, the velocity of inversion of sucrose in concentrated solution, and the action of the indicator, dimethylaminoazobenzene, have been used to investigate the acid properties of several derivatives of sulphur, selenium, and tellurium. The main conclusions are as follows: methyl- and ethyl-sulphuric acids are true acids  $[\text{RO} \cdot \text{SO}_3]\text{H}$  in dilute aqueous solution, but react as pseudo-acids,  $\text{RO} \cdot \text{SO}_2 \cdot \text{OH}$ , in dilute alcoholic and concentrated ethereal solutions. Selenious acid in the pure condition and in relatively concentrated alcoholic solutions, is an associated pseudo-acid, aqueous solutions containing a large proportion of the pseudo-acid and only a very small percentage of the hydrate of the true (monobasic) acid. Selenic acid (98%) is a true acid,  $[\text{HSeO}_4]\text{H}$ , and in water and alcohol forms the true oxonium salt,  $[\text{HSeO}_4] \cdot \text{H}_2\text{OR}$  ( $\text{R} = \text{H}$  or  $\text{Et}$ ),

salt formation increasing with dilution. Benzenesulphinic acid is a pseudo-acid in the solid state, in alcoholic solution (50 mols.), and in more concentrated ethereal solution, but in aqueous solution it is present as a true acid. Ethylsulphinic acid is a weaker acid than the phenyl derivative (but is still stronger than sulphurous acid) and in 12.5 mols. of alcohol and 4.5 mols. of ether exists entirely as the pseudo-acid. Ethylseleninic acid is present as a pseudo-acid even in aqueous solution. Tellurous acid is a very weak pseudo-acid and its salts can be titrated directly with strong acids. All three telluric acids (cf. Mylius, A., 1901, ii, 550) were investigated. Ordinary telluric acid is inactive towards ethyl diazoacetate and the indicator, and therefore possesses the formula  $\text{Te}(\text{OH})_6$ ; *allotelluric acid* is a true acid, but pure telluric acid,  $\text{H}_2\text{TeO}_4$ , is represented as a pseudo-acid of the constitution  $(\text{OH})_2\text{Te} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$ .

J. W. B.

**Constitution of the Thionic Acids.** I. VOGEL (*J. Chem. Soc.*, 1925, 127, 2248—2249).—The following formulæ are proposed for the thionic acid: dithionic acid,  $\text{OH}\cdot\text{SO}_2\cdot\text{SO}_2\cdot\text{OH}$ ; trithionic acid,  $\text{S}:(\text{SO}_2\cdot\text{OH})_2$ ; tetrathionic acid,  $\text{S}:\text{S}:(\text{SO}_2\cdot\text{OH})_2$ ; pentathionic acid,  $\text{S}:\text{S}:\text{S}:(\text{SO}_2\cdot\text{OH})_2$ . These formulæ explain the formation of tri-, tetra-, and penta-thionic acids from sulphur sesquioxide (this vol., ii, 890) in various circumstances, the liberation of two atoms of sulphur from pentathionates by bromine and by mercuric cyanide, the conversion of tetrathionates into pentathionates by acidified thiosulphate solution, and other reactions and properties of these acids.

E. E. W.

**Polythionates. I. Decomposition of Polythionates in Aqueous Solution.** A. KURTENACKER and M. KAUFMANN (*Z. anorg. Chem.*, 1925, 148, 43—57).—The decomposition of aqueous solutions of polythionates has been followed by the analytical methods previously described (this vol., ii, 239, 434). Potassium trithionate decomposes according to the equations:  $\text{S}_3\text{O}_6'' + \text{H}_2\text{O} = \text{S}_2\text{O}_3'' + \text{SO}_4'' + 2\text{H}^+$  and  $\text{S}_2\text{O}_3'' + \text{S}_3\text{O}_6'' + \text{H}^+ = \text{S}_4\text{O}_6'' + \text{SO}_3\text{H}'$ . Sulphur is not precipitated and only a little pentathionate is formed; this occurs at a later stage of the reaction and probably according to the equation:  $5\text{S}_2\text{O}_3'' + 6\text{H}^+ = 2\text{S}_5\text{O}_6'' + 3\text{H}_2\text{O}$ . In acid solution, decomposition is much more rapid and a third reaction takes place, namely, the decomposition of thiosulphuric acid:  $\text{S}_2\text{O}_3'' + \text{H}^+ = \text{HSO}_3' + \text{S}$ . Both the tetra- and penta-thionate are much more stable than the trithionate. The pentathionate decomposes according to the equation  $\text{S}_5\text{O}_6'' = \text{S}_4\text{O}_6'' + \text{S}$ , and the mixture of thionates resulting from this reversible reaction is, as shown by Debus (T., 1888, 53, 278), highly stable. The tetrathionate also tends to form this stable mixture, and the necessary sulphur is obtained by the decomposition of a part of the tetrathionate to trithionate:  $\text{S}_4\text{O}_6'' = \text{S}_3\text{O}_6'' + \text{S}$ . Tri- and penta-thionate do not react to form tetrathionate,  $\text{S}_3\text{O}_6'' + \text{S}_5\text{O}_6'' = 2\text{S}_4\text{O}_6''$ , even in acid solution, but trithionate, or its decomposition products, accelerates the decomposition of pentathionate to tetrathionate and sulphur.

A. G.

**Polythionates. II. Influence of Thiosulphate and Sulphite on the Stability of Polythionates.** A. KURTENACKER and M. KAUFMANN (*Z. anorg. Chem.*, 1925, **148**, 225—234; cf. preceding abstract).—The decomposition of aqueous solutions of the alkali trithionates is only slightly influenced by the presence of sulphites or thiosulphates. Addition of thiosulphate to tetra- or pentathionate solutions results in an increased rate of decomposition, the effect being catalytic in that the thiosulphate concentration remains unaltered. The experimental data in the case of tetrathionate solutions are in excellent agreement with the following reaction schemes: (i)  $\text{S}_2\text{O}_3'' \rightleftharpoons \text{SO}_3'' + \text{S}$ ; (ii)  $\text{S}_4\text{O}_6'' + \text{S} \rightleftharpoons \text{S}_5\text{O}_6''$ ; (iii)  $\text{SO}_3'' + \text{S}_4\text{O}_6'' = \text{S}_3\text{O}_6'' + \text{S}_2\text{O}_3''$ , the reaction products being mainly tri- and penta-thionate. The catalytic action of thiosulphate in the decomposition of pentathionate solutions is likewise due to its tendency to lose sulphur according to scheme (i) above. The accelerating action of sulphites is due to the formation of thiosulphate according to the equations:  $\text{S}_4\text{O}_6'' + \text{SO}_3'' \rightleftharpoons \text{S}_3\text{O}_6'' + \text{S}_2\text{O}_3''$ ;  $\text{S}_5\text{O}_6'' + \text{SO}_3'' \rightleftharpoons \text{S}_4\text{O}_6'' + \text{S}_2\text{O}_3''$ . J. S. C.

**Polythionates. III. Action of Hydrogen Sulphide on Polythionates.** A. KURTENACKER and M. KAUFMANN (*Z. anorg. Chem.*, 1925, **148**, 256—264; cf. preceding abstract).—The course of the extremely slow reaction between hydrogen sulphide and trithionate is represented satisfactorily by the equations  $\text{S}_3\text{O}_6'' + \text{H}_2\text{S} = 2\text{S}_2\text{O}_3'' + 2\text{H}^+$ ;  $\text{S}_2\text{O}_3'' + 2\text{H}_2\text{S} + 2\text{H}^+ = 3\text{H}_2\text{O} + 4\text{S}$ . The rate of reaction is retarded in presence of acid. The rate of the more rapid reaction between hydrogen sulphide and tetrathionate also decreases with increasing acidity. In neutral solution, the course of the reaction is represented by the equations:  $\text{S}_4\text{O}_6'' + \text{H}_2\text{S} = 2\text{S}_2\text{O}_3'' + \text{S} + 2\text{H}^+$ ;  $\text{S}_2\text{O}_3'' + 2\text{H}_2\text{S} + 2\text{H}^+ = 3\text{H}_2\text{O} + 4\text{S}$ ;  $5\text{S}_2\text{O}_3'' + 6\text{H}^+ = 2\text{S}_5\text{O}_6'' + 3\text{H}_2\text{O}$ . The presence of small quantities of trithionate is ascribed to the action between thiosulphate and undecomposed tetrathionate (*loc. cit.*). In acid solution, only the first and third of the above reactions occur, sulphur and pentathionate being the principal reaction products. J. S. C.

**Polythionates. IV. Action of Alkali on Polythionates.** A. KURTENACKER and M. KAUFMANN (*Z. anorg. Chem.*, 1925, **148**, 369—381).—Potassium trithionate is decomposed fairly rapidly by concentrated alkali solutions:  $2\text{S}_3\text{O}_6'' + 6\text{OH}' = \text{S}_2\text{O}_3'' + 4\text{SO}_3'' + 3\text{H}_2\text{O}$  (Fordos and Gélis, *J. pr. Chem.*, 1850, **50**, 86). The decomposition is slower in the case of dilute alkali and probably follows the equation  $\text{S}_3\text{O}_6'' + 2\text{OH}' = \text{S}_2\text{O}_3'' + \text{SO}_4'' + \text{H}_2\text{O}$  (cf. Foerster and Hornig, A., 1923, ii, 23). Tetrathionates are decomposed by dilute alkali at the ordinary temperature according to the equation: (a)  $4\text{S}_4\text{O}_6'' + 6\text{OH}' = 5\text{S}_2\text{O}_3'' + 2\text{S}_3\text{O}_6'' + 3\text{H}_2\text{O}$  (Thatcher, A., 1904, ii, 395). Pentathionate solutions are decomposed slowly by cold dilute alkalis. The primary reaction is:  $\text{S}_5\text{O}_6'' \rightleftharpoons \text{S} + \text{S}_4\text{O}_6''$ ; the tetrathionate then probably decomposes thus: (b)  $2\text{S}_4\text{O}_6'' + 6\text{OH}' = 3\text{S}_2\text{O}_3'' + 2\text{SO}_3'' + 3\text{H}_2\text{O}$ ; (c)  $2\text{S}_4\text{O}_6'' + 2\text{SO}_3'' = 2\text{S}_3\text{O}_6'' + 2\text{S}_2\text{O}_3$ , *i.e.*, according to (a) above. The sulphur, which redissolves, may react with some of the sulphite produced in (b):  $\text{S} +$

$\text{SO}_3'' = \text{S}_2\text{O}_3''$ , or, more probably, with excess of alkali:  $4\text{S} + 6\text{OH}' = 2\text{S}'' + \text{S}_2\text{O}_3'' + 3\text{H}_2\text{O}$ , the sulphide then reacting with the trithionate formed in (b):  $\text{S}_3\text{O}_6'' + \text{S}'' = 2\text{S}_2\text{O}_3''$ . The net reaction producing thiosulphate, besides (b), is:  $2\text{S}_5\text{O}_6'' + 6\text{OH}' = 5\text{S}_2\text{O}_3'' + 3\text{H}_2\text{O}$ . Boiling, concentrated alkali decomposes pentathionates with formation of sulphide, since the former also decomposes the trithionate. The analytical methods of Riesenfeld and Feld (A., 1922, ii, 45) are modified; they give approximately correct results, although the indefinite end-points and the formation of sulphide in the case of pentathionates are drawbacks. S. K. T.

**Selenium as Chloride Carrier.** O. and C. A. SILBERRAD (*J. Chem. Soc.*, 1925, 127, 2449—2450).—In addition to acting catalytically as a chlorine carrier in the chlorination of toluene by sulphuryl chloride (cf. this vol., i, 1137), selenium also acts similarly in the direct chlorination of toluene by chlorine both in the presence and absence of light. Just as with sulphuryl chloride, it accelerates substitution in the nucleus and decreases it in the side-chain.

E. E. W.

**Reduction of Tungstates.** V. I. SPITZIN (*Z. anorg. Chem.*, 1925, 148, 69—83).—Tungstates may be reduced to constant weight by hydrogen at 650—700°, and it is shown quantitatively that the products from the ditungstate,  $\text{Na}_2\text{W}_2\text{O}_7$ , paratungstate,  $\text{Na}_{10}\text{W}_{12}\text{O}_{41}$ , tetratungstate,  $\text{Na}_2\text{W}_4\text{O}_{13}$ , and pentatungstate,  $\text{Na}_2\text{W}_5\text{O}_{16}$ , are, in every case, mixtures of sodium tungstate,  $\text{Na}_2\text{WO}_4$ , and tungsten. Above 700° a further loss in weight takes place, and at 900° each of the above acid tungstates and also sodium tungstate are reduced to tungsten. The various tungsten bronzes are also reduced to sodium tungstate and tungsten at 650—700°. The blue bronze,  $\text{Na}_2\text{W}_5\text{O}_{15}$ , is reduced successively to the violet,  $\text{Na}_2\text{W}_4\text{O}_{12}$ , the red,  $\text{Na}_2\text{W}_3\text{O}_9$ , and the yellow bronzes,  $\text{Na}_2\text{W}_2\text{O}_6$ ; this reduction takes place comparatively slowly at 550° and rapidly at 650°, but at no temperature does reduction cease at any intermediate stage. The formation of bronzes by the reduction of acid tungstates is believed to take place according to equations of the type:  $\text{Na}_2\text{W}_4\text{O}_{13} + \text{H}_2 = \text{Na}_2\text{W}_4\text{O}_{12} + \text{H}_2\text{O}$ ;  $\text{Na}_2\text{W}_4\text{O}_{12} + 3\text{H}_2 = \text{Na}_2\text{W}_3\text{O}_9 + \text{W} + 3\text{H}_2\text{O}$ . In this case, the molecule of bronze could never contain more atoms of tungsten than that of the tungstate from which it was prepared. This, however, is sometimes the case, but this is ascribed to impurities in the tungstate; thus sodium tetratungstate yields a blue bronze, but the metatungstate,  $\text{Na}_2\text{W}_4\text{O}_{13} \cdot 10\text{H}_2\text{O}$ , which can be purified by crystallisation from water, yields the violet bronze. A. G.

**Systematic Doctrine of Affinity. XXXII. Higher Ammoniates of Halides of the Iron Group.** W. BILTZ [with E. RAHLFS] (*Z. anorg. Chem.*, 1925, 148, 145—151).—The existence of the following compounds has been demonstrated:  $\text{MnCl}_2 \cdot 12\text{NH}_3$ ;  $\text{MnCl}_2 \cdot 10\text{NH}_3$ ;  $\text{FeCl}_2 \cdot 10\text{NH}_3$ ;  $\text{CoCl}_2 \cdot 10\text{NH}_3$ ;  $\text{MnBr}_2 \cdot 10\text{NH}_3$ . From tensimetric and thermal data the values of the heat of dissociation, the total heat of formation, and the temper-

ature at which  $p_{\text{NH}_3}=100$  mm. have been calculated and are tabulated. These numbers are considered in relation to the corresponding data for the corresponding hexammine derivatives (A., 1915, ii, 465; 1920, ii, 318). The properties of cobaltous decamminechloride differ from those described by Clark, Quick, and Harkins (A., 1921, ii, 116). J. S. C.

**Action of Sodium Chloride on Ferrous Metals.** R. GIRARD (*Compt. rend.*, 1925, **181**, 552—555).—Plates of cast iron or steel were immersed in air-free or aerated solutions of sodium chloride. Steel suffered corrosion in both cases, whilst cast iron was affected only in air-free solutions, and in aerated solutions was partially protected by a coating of adhering ferric substances. [Cf. B., 1925, 961.] R. A. M.

**Various States of Beryllium Oxide.** H. COPAUX and C. MATIGNON (*Compt. rend.*, 1925, **181**, 550—552).—The loss of weight of basic beryllium carbonate has been determined at different temperatures. The decomposition is practically complete at 500—550°, but further small decreases in weight occur at higher temperatures. The oxide prepared by calcination has  $d^{775}$  2.876,  $d^{875}$  2.926, and  $d^{1100}$  3.010. The oxide obtained at 800° is much more readily soluble in hydrofluoric acid than is the product obtained at 1100°. The heat of solution of the former product in hydrofluoric acid is 22.06 cal. (mean) and for the more strongly heated oxide it is 22.28 cal. Although the small difference is in the sense opposite to that expected on theoretical grounds, it is considered that it may be real. Basic beryllium carbonate requires heating to about 1000° before a definite state is attained. R. A. M.

**Reaction between Ferric Sulphate and Alkali.** A. KRAUSE (*Z. anorg. Chem.*, 1925, **148**, 265—278).—Experiments in which varying amounts of alkali (sodium hydroxide, potassium hydroxide, ammonia, sodium carbonate, potassium carbonate, sodium hydrogen carbonate, and aniline) were added to a fixed volume of ferric sulphate solution, show that the value of the ratio  $[\text{Fe}_2\text{O}_3]/[\text{SO}_3]$  of the precipitate obtained is related to the  $p_{\text{H}}$  value of the resulting solution by an equation of an exponential type, a sulphate-free precipitate being obtained only when this  $p_{\text{H}}$  value exceeds 7.7. On adding the theoretical quantities of sodium hydroxide, ammonia, and sodium carbonate, the values of the  $[\text{Fe}_2\text{O}_3]/[\text{SO}_3]$  ratio are 24.0, 11.1, and 8.8, respectively. The anomalous behaviour of ammonia, which in the more acid solutions functions as a strong base, is discussed. J. S. C.

**Potentiometric Indication in the Action of Halogens on Ferrocyanides.** C. DEL FRESNO (*Anal. Fis. Quím.*, 1925, **23**, 427—437).—The oxidation of ferrocyanides to ferricyanides in solution by chlorine and by bromine can be followed potentiometrically. Owing to the instability of aqueous solutions of chlorine and bromine, the method is not of practical importance. In the case of iodine, oxidation is complete only in the presence of an excess of the halogen. G. W. R.

**Oxidation of Complex Sulphites of Tervalent Cobalt.**

G. SCAGLIARINI and G. TARTARINI (*Atti R. Accad. Lincei*, 1925, [vi], 2, 191—194).—By oxidising, by means of a current of air, a solution containing the complex salt,  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{SO}_3)_3(\text{H}_2\text{O})_3]$ , the sulphite radicals may be oxidised to sulphate groups. It is suggested that the oxidation is progressive, giving the anions,  $[\text{Co}(\text{SO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_3]'''$ ,  $[\text{Co}(\text{SO}_3)(\text{SO}_4)_2(\text{H}_2\text{O})_3]'''$ , and  $[\text{Co}(\text{SO}_4)_3(\text{H}_2\text{O})_3]'''$ .

The first and last stages of this process have been realised by the preparation of *hexamminecobaltic triaquodisulphitosulphatocobaltate*,  $[\text{Co}(\text{NH}_3)_6][\text{Co}(\text{SO}_3)_2(\text{SO}_4)(\text{H}_2\text{O})_3]$ , and of *triquotriamminecobaltic triaquotrisulphatocobaltate*,  $[\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3][\text{Co}(\text{SO}_4)_3(\text{OH}_2)_3]$ . The former is obtained as golden-yellow crystals by the atmospheric oxidation of a solution of ammonium carbonate in a solution of cobalt sulphite saturated with sulphur dioxide. From concentrated solutions, the second salt is deposited. F. G. T.

**Compound of Rhodium with Carbon Monoxide.**

W. MANCHOT and J. KÖNIG (*Ber.*, 1925, 58, [B], 2173—2174).—Hydrated rhodium chloride is converted by carbon monoxide preferably at 140° into the compound,  $\text{Rh}_2\text{OCl}_2 \cdot 3\text{CO}$ , m. p. 125.5°, decomp. 300°. Anhydrous rhodium chloride does not appear to react with carbon monoxide. H. W.

**Synthesis of Cristobalite in the Wet Way.**

R. WEIL (*Compt. rend.*, 1925, 181, 423—424).—Precipitated silica was heated for 200 hrs. at 650—750° in a steel tube with water containing a little sodium silicate. A mixture of quartz and cristobalite in varying proportions was obtained, lower concentration giving a greater proportion of the latter. Below 650°, no cristobalite was formed. The crystals were about 0.05—0.1 mm. in length; the transition point was about 250°. E. B. L.

**Preparation of Pure Metallic Titanium, Zirconium, Hafnium, and Thorium.**

A. E. VAN ARKEL and J. H. DE BOER (*Z. anorg. Chem.*, 1925, 148, 345—350).—By passing the metal chloride vapour mixed with nitrogen, or carbon monoxide, etc., over a heated tungsten filament all the possible nitrides, carbides, sulphides, selenides, and phosphides of the above metals were prepared. The pure metals are formed as thick layers on the filament when the vapours of the iodides of these metals are used unmixed with other gases. Zirconium thus prepared is soft and ductile, but has the same space-lattice as ordinary zirconium; hafnium is denser, melts at a higher temperature, and has a higher electron emission than zirconium. Thorium and titanium are ductile. The pure metals obtained by Weisz's method (D.R.-P. 314791) may contain nitride, carbide, and oxide. The "metals" obtained by Fischvoigt and Koref (*Z. tech. Phys.*, 1925, 6, 296) probably consist of nitrides, carbides, or suboxides, owing to the use of impure hydrogen. S. K. T.

**Direct Reading Spectrophotometer.**

C. W. KEUFFEL (*J. Opt. Soc. Amer.*, 1925, 11, 403—410).—A direct-reading spectrophotometer.



meter combining a constant deviation spectrometer with its wavelength scale, and a direct-reading rotating disc photometer with its photometric scale, are described. The method of adjustment is described, and the probable precision of measurement discussed.

A. E. M.

**Constricted Mercury Arc as a Source of Light for Photochemical Work.** G. S. FORBES and G. R. HARRISON (*J. Amer. Chem. Soc.*, 1925, **47**, 2449—2454).—The intensity, steadiness, economy, convenience, efficiency, and life of the water-cooled, constricted-column, mercury-vapour lamp run at atmospheric pressure are discussed in comparison and contrast with the standard vertical sealed electrode commercial lamp. The only disadvantage of the constricted lamp is its more rapid deterioration, but this is not serious, as the design of the lamp is such that it can be emptied, cleaned, and refitted in a very short time.

W. T.

**Methods of Studying the Chemical Effects of Electric Sparks on Gases at Low Pressures.** P. JOLIBOIS (*Compt. rend.*, 1925, **181**, 608—610).—A simple apparatus is described with which measurements may be made of the pressure changes caused by the passage of sparks, of known energy content, through gases maintained at low temperatures.

F. G. T.

**Non-polarisable Electrodes for Physiological Purposes.** H. C. STEVENS and E. KARRER (*J. Opt. Soc. Amer.*, 1925, **11**, 423—426).—A zinc-zinc sulphate electrode specially adapted for use in nerve-stimulating experiments is described. The cell possesses the advantages of being non-polarisable, preventing undue diffusion of the stimulating current, stimulating symmetrically around a nerve, and being capable of application to a nerve without the necessity of severing the end. A simple modification for stimulating small muscle areas is described.

A. E. M.

**Automatic Recorder for Measuring Size-frequency Distribution of Grains.** R. H. LAMBERT and E. P. WIGHTMAN (*J. Opt. Soc. Amer.*, 1925, **11**, 393—402).—A simple automatic photographic method for determining the weight or size distribution of particles in a sedimenting liquid has been developed. The principle consists in the photographing of the liquid in the capillary of the sedimentation tube. The error in the Ostwald-Hahn-Kelley sedimentation process has been shown to be the lag in the flow of liquid in the capillary due to its viscosity and a method for its correction has been developed. By the method of calibration other sources of error are eliminated.

A. E. M.

**Gas Circulating Apparatus.** A. R. PEARSON and J. S. G. THOMAS (*J. Chem. Soc.*, 1925, **127**, 2450—2451).—Gas is circulated through a closed system by an oscillating column of mercury combined with an arrangement of glass valves acting as in a force pump. The principle of the hot air engine is utilised to keep the mercury oscillating in a U-tube, the closed end of which is connected with a glass bulb heated by a burner.

E. E. W.

**Fat-free Mercury Valve with Porous Glass Plates.** A. STOCK (*Ber.*, 1925, **58**, [B], 2058—2060).—A new type of valve is described in the two arms of which glass plates pervious to gases but impervious to mercury are sealed. The trouble arising from the sticking of the glass floats in the otherwise similarly-constructed gas valve (cf. Stock and Priess, A., 1915, ii, 339) is thus avoided.

H. W.

**Purification of Phosphoric Oxide.** H. WHITAKER (*J. Chem. Soc.*, 1925, **127**, 2219—2221; cf. T., 1922, **121**, 692).—An improved apparatus is described for purifying phosphoric oxide by distillation in a current of oxygen. The improvements facilitate the introduction of phosphoric oxide into the retort tube, and the collection of the sublimate in a storage bottle, whereby transference from the receiver is avoided.

E. E. W.

**Liquid Hydrogen Sulphide as a Source of Laboratory Supply of the Gas.** C. J. MOORE (*Ind. Eng. Chem.*, 1925, **17**, 1223).—The use of liquid hydrogen sulphide in cylinders for laboratory purposes is cheaper and more convenient than production of the gas in a generator. A gasometer is used in place of a reducing valve. No danger exists of the development of excessive pressure through dissociation. [Cf. *B.*, 1925, 917.]

C. I.

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### Mineralogical Chemistry.

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**Helium in Earth Gases of Petrol Sources.** J. CLAY (*Proc. K. Akad. Wetensch. Amsterdam*, 1925, **28**, 529—530).—The helium content of a number of samples of petroleum gas from different parts of India varies from 0.0006% to 0.0033%. The gases were first carefully freed from hydrogen by burning with a large excess of oxygen in a Drehschmidt capillary tube; the oxygen was removed by pyrogallol, the carbon dioxide by potassium hydroxide, and the remaining gases by coconut charcoal at the temperature of liquid air. The final residue, measured in a MacLeod gauge and tested spectroscopically, was found to be helium. M. S. B.

**Siliceous Matter in Quaternary Clays.** A. DEMOLON (*Compt. rend.*, 1925, **181**, 673—675).—Investigation of the loss of water on heating, base exchange, and adsorption of lime by quaternary clays, indicates that the aluminosilicates are the most important constituents of these clays and that they are to be classed as zeolitic silicates with a kaolinic nucleus as distinguished from true kaolinite. (Cf. *ibid.*, 1925, **180**, 1518.) S. K. T.

**Composition of the Ash Evolved from the Volcano Acatenango in Guatemala on June 12th, 1925.** A. GUTBIER and H. BRINTZINGER [with W. BUBAM] (*Z. anorg. Chem.*, 1925, **148**, 141—144).—Analysis gave the following results: Si, 28.37; P, 0.04; Ti, 0.29; F, trace; Cu, trace; Al, 10.51; Fe, 4.22; Ca, 4.56; Sr, 0.06; Mg, 0.48; K, 0.69; Na, 3.84%. The composition is

deduced to be:  $\text{SiO}_2$ , 60.45;  $\text{P}_2\text{O}_5$ , 0.09;  $\text{TiO}_2$ , 0.48; F, trace;  $\text{CuO}$ , trace;  $\text{Al}_2\text{O}_3$ , 19.72;  $\text{FeO} + \text{Fe}_2\text{O}_3$ , 6.02;  $\text{CaO}$ , 6.38;  $\text{SrO}$ , 0.07;  $\text{MgO}$ , 0.79;  $\text{K}_2\text{O}$ , 0.83;  $\text{Na}_2\text{O}$ , 5.17%. It is thus similar to the dust evolved from Santa Maria in Guatemala in 1902 (*U.S. Bull.*, 1903, **228**, 273), and is notably poor in phosphates and potassium.  
A. G.

**Buttgenbachite, a New Mineral.** A. SCHOEP (*Compt. rend.*, 1925, **181**, 421—423).—The mineral consists of sky-blue crystals found in the Belgian Congo. Its physical properties are described; its chemical composition is: water 17.34,  $\text{CuO}$  71.56, Cl 6.02,  $\text{N}_2\text{O}_5$  5.40%, corresponding with the formula  

$$18\text{CuO}, 3\text{Cl}, \text{N}_2\text{O}_5, 19\text{H}_2\text{O}.$$
E. B. L.

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## Analytical Chemistry.

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**Continuous Reading Hydrogen-ion Meter.** K. G. GOODE (*J. Amer. Chem. Soc.*, 1925, **47**, 2483—2488; cf. A., 1922, ii, 307).—To avoid the use of a telescope and scale for titration work, a device is described which, by making use of the three-electrode vacuum tube as a voltmeter, and as a direct current amplifier, serves to indicate on the scale of milliammeter the potential between any two electrodes ordinarily used in electrochemical work. This device does not draw an appreciable current from the source to be measured and is continuous and automatic in its action. W. T.

**Highly Sensitive Congo Paper.** F. W. HORST (*Z. angew. Chem.*, 1925, **38**, 947).—In preparing highly sensitive Congo paper the last traces of foreign dyes must be eliminated, the dye solution must contain no fixed alkali, and the dyeing of the paper must be clean and uniform. The commercial dye is dissolved in hot water, the solution filtered, and the dye reprecipitated by careful addition of pure sodium chloride. The purified dye is again dissolved in water and the dye acid precipitated by addition of dilute hydrochloric acid. After decantation and filtration, the dye acid is dissolved in hot water containing ammonia, and the paper drawn several times through the dilute solution (1—1.5 g. per litre) and finally washed off with cold distilled water. Congo paper so prepared gives a distinct blue colour with a 1/3000 *N*-mineral acid.

W. T. K. B.

**Evaluation of Chlorates.** E. C. WAGNER (*Ind. Eng. Chem.*, 1925, **17**, 1183—1186; cf. A., 1924, ii, 563).—The methods compared were: Bunsen's evolution method (improved by the use of a new receiver obviating the need of transferring the liquid before titration); Ditz's iodometric method; Kolb and Davidson's iodometric method; the ferrous sulphate excess method; reduction to chloride by ignition with ammonium chloride; reduction to chloride by evaporation with hydrochloric acid; reduction to chloride by sulphurous acid, and precipitation as silver chloride.

All the methods investigated gave accurate results, with the

exception of that of Kolb and Davidson, the results from which were consistently about 0.4% too high. L. L. B.

**Reduction of Chloric Acid and Chlorates by Ferrous Sulphate.** C. O. HARVEY (*Analyst*, 1925, **50**, 538—543).—Reduction of chloric acid and chlorates in the presence of ferrous sulphate is most complete in acid solution in the presence of potassium iodide. By determining the liberated iodine volumetrically at 45°, a completeness of reaction of 99.2% of theory may be obtained, which is reduced to 97.2% in the absence of potassium iodide. Using a gravimetric determination at 100°, 96.8% is obtained in neutral solution, rising to 98.9% in acid solution at the same temperature. [Cf. *B.*, 1925, 988.] D. G. H.

**Determination of Hypiodite and Iodate, Hypobromite and Bromate, and Bromate and Iodate in the Presence of Each Other.** E. SCHULEK (*Z. anal. Chem.*, 1925, **67**, 142—147).—The solution containing hypiodite and iodate is treated with phenol to destroy the hypiodite and, after saturation with carbon dioxide, potassium iodide is added, followed by an excess of 10% sulphuric acid; the liberated iodine, which corresponds with the iodate present, is titrated with thiosulphate. In a second portion, the two acids are determined together iodometrically in the usual way. A similar procedure serves for the determination of hypobromite and bromate in the same solution. For the determination of bromate and iodate in mixtures, the sum of the two acids is ascertained by measuring the iodine liberated from potassium iodide by a portion of the mixture, reducing a second portion to bromide and iodide by boiling with sulphur dioxide and determining the iodide formed by the method previously described (this vol., ii, 712). A. R. P.

**Presence of Iodate in Surface Waters.** C. F. HICKETHIER and A. JACOBUCCI (*Z. anal. Chem.*, 1925, **67**, 129—134).—The surface waters of the northern part of the province of Santa Fé, Argentine Republic, contain traces of iodate (0.13—0.38 part per million), indicating that this region is the remains of an inland sea of the tertiary period. Iodates interfere in Trommsdorf's test (zinc iodide-starch paper) for nitrites, but not in those of Ilosva and Rodillon (neutral-red). A. R. P.

**Use of Hydrazine Sulphate in Iodometry.** E. CATTELAÏN (*J. Pharm. Chim.*, 1925, [viii], **2**, 387—391).—Hydrazine sulphate is a more satisfactory standard for iodometry than sodium thiosulphate, as it is anhydrous and readily purified and yields stable aqueous solutions. In the presence of sodium acetate iodine oxidises it quantitatively with evolution of nitrogen if a large excess is used. The excess is then titrated with thiosulphate. A. R. P.

**Electrometric Titration of Fluorides.** W. D. TREADWELL and A. KÖHL (*Helv. Chim. Acta*, 1925, **8**, 500—507).—The method of Greeff (*A.*, 1913, ii, 975), based on the production of the compound  $\text{Na}_3\text{FeF}_6$  using potassium thiocyanate as indicator, is not suitable for the determination of small quantities of fluorides. By using a potentiometric end-point in the titration, quantities of

fluorine as small as 5 mg. can be determined to 0.5 mg. The solution is neutralised, saturated with sodium chloride, diluted with an equal volume of ethyl alcohol, and titrated with 0.03*N*-ferric chloride solution containing 1% of ferrous chloride, using a platinised platinum electrode and silver chloride electrode for comparison, the solution being stirred throughout the titration by means of a rapid stream of carbon dioxide. The end-point is determined graphically from the observed readings of a millivoltmeter. Using a microburette small quantities may be determined to 0.1 mg. The use of chromous, vanadous, zirconium, or aluminium salts in place of iron for the titration does not give so satisfactory a method.

G. M. B.

**Qualitative Test for Oxygen.** H. SCHMALFUSS and H. WERNER (*J. pr. Chem.*, 1925, [ii], **111**, 62—64; cf. this vol., ii, 238).—Nitric oxide, prepared by dropping saturated aqueous sodium nitrite into a solution of ferrous sulphate in concentrated hydrochloric acid, and purified by shaking with a solution of pyrogallol (2.5 g.) in aqueous potassium hydroxide (100 c.c.; *d* 1.05), is drawn into a wide-necked bottle containing water (1 c.c.) from which the air has previously been evacuated at 20—30°, and on the inside of the wall of which has been placed a drop of a solution of diphenylamine (1 g.) in sulphuric acid (75 c.c.) and water (25 c.c.), a small piece of filter-paper being held on the wall by the latter solution. The inlet tube of the bottle has connexions for barometer, filter-pump, nitric oxide, and the gas to be tested. The pressure of the nitric oxide in the bottle should not be more than 400 mm., and the filter-paper should not assume a blue colour in less than 2 mins. The gas under test is then admitted, the presence of oxygen being evidenced by the development of the usual blue coloration on the filter-paper. A dilute acetic acid solution of  $\alpha$ -naphthylamine and sulphanilic acid may be substituted for the above diphenylamine solution.

F. G. W.

**Determination of Molecular Oxygen in Aqueous Solution in the Presence of Nitrous Acid.** G. ALSTERBERG (*Biochem. Z.*, 1925, **159**, 36—47).—Nitrous acid, which causes considerable errors in the determination of dissolved oxygen by Winkler's method, may be removed by sodium azide. When present in a concentration of <0.0001% (as when dealing with biological material) a sufficient quantity of azide is added to the sulphuric acid solution of the manganese hydroxide precipitate. If nitrous acid is present in greater concentration, the azide is added in a concentration of 0.5% simultaneously with the alkaline potassium iodide solution at the commencement of the determination.

E. C. S.

**Ozone [Determination and Solubility].** H. VON WARTENBERG and G. VON PODJASKI (*Z. anorg. Chem.*, 1925, **148**, 391—396).—Dilute ozonised air may be analysed with an accuracy of 5—10% by rapidly bubbling a large volume through a small quantity of potassium iodide solution, the liberated iodine being titrated with sodium arsenite solution. Colorimetric comparison of the iodide solution with standards is unsatisfactory. Ozone

dissolves in many organic liquids in accordance with Henry's law to form fairly stable solutions. The solubility in such liquids is much higher than in water (cf. Fischer and Tropsch, A., 1917, ii, 463).  
S. K. T.

**Separation of Selenium and Tellurium.** V. LENHER and C. H. KAO (*J. Amer. Chem. Soc.*, 1925, 47, 2454—2461).—Hydroxylamine hydrochloride can be employed for the separation of selenium and tellurium in hydrochloric, tartaric, or citric acid solution. The optimal concentration of hydrochloric acid is 17% (*d* 1.085). Hydroxylamine sulphate is less satisfactory. Hydrazine hydrochloride and the sulphate tend to cause precipitation of tellurium with the selenium; this can be avoided in the method of Pellini (A., 1903, ii, 752) by proper control of temperature. The procedure of the separation by the above methods is simple, but is complicated when oxalic acid is used. Lactic acid is unsuitable.  
W. T.

**Sensitive Reaction for Nitrate.** F. L. HAHN and G. JAEGER (*Ber.*, 1925, 58, [B], 2335—2340).—Nitrate is reduced in aqueous solution by metallic lead in the presence of lead salts to nitrite which can be detected by the diazo reagent ( $\alpha$ -naphthylamine and sulphanilic acid). The sensitiveness of the test is unfortunately diminished by the impossibility of effecting a quantitative reduction of nitrate to nitrite, partly because the latter is itself further reduced by the lead reagent but mainly because the nitrate is reduced to other products. The proportion of nitrate converted into nitrite diminishes with decreasing concentration of nitrate. The test is somewhat more sensitive than the diphenylamine reaction but is specific and more trustworthy. Large quantities of foreign substances markedly diminish the yield of nitrite. Ammonium salts, free acids, and the salts of many heavy metals completely inhibit the test, which must then be performed on the "sodium carbonate extract." If nitrite is present it may be removed by carbamide and sulphuric acid or by evaporation with ammonium chloride; larger amounts are preferably removed by 2 : 4-diamino-6-hydroxypyrimidine. The determination of somewhat greater quantities of nitrate is complicated not only by the presence of foreign substances but also by the individual behaviour of different specimens of the lead reagent. The method is therefore applicable only to cases such as the determination of nitrate in potable water. The final colorimetric comparison must be made with solutions obtained by simultaneous reduction of standard nitrate solutions and not with standard nitrite solutions.

The "lead reagent" is prepared by heating lead formate, obtained by adding formic acid to a concentrated aqueous solution of lead acetate, until the surface assumes a uniformly grey colour. Directions for the preparation and preservation of the "diazo reagent" in the solid state or in solution are given.  
H. W.

**Contradictions and Errors in Analytical Chemistry. VI. Ferrous Sulphate Test for Nitrate and Nitrite and the Diphenylamine Reaction.** F. L. HAHN and G. JAEGER (*Ber.*, 1925, 58, [B], 2340—2343; cf. this vol., ii, 69).—The sensitiveness



of the "ring test" for nitrate has frequently been underestimated (cf. Faurholt, A., 1923, ii, 179) but, in the absence of chlorides, 0.1 mg. potassium nitrate in 1 c.c. of solution can be detected with certainty if a mixture of the solution and a little concentrated ferrous sulphate solution is floated on sulphuric acid. In the presence of small amounts of chloride the ring loses its typical appearance, whilst with larger quantities a coloured zone appears even in the absence of nitrate. The effect is due to ferric chloride and can be obviated by addition of phosphoric acid. Small amounts of nitrate can thus be detected in the presence of much chloride or considerable quantities of bromide. Nitrite if present to the extent of 10 mg. per litre gives a distinct brown coloration if the solution is treated with a drop of concentrated ferrous sulphate solution; confusion with the colour of ferric salts is avoided by the use of phosphoric acid for acidification. A rapid qualitative method for the detection of nitrate sensitive to 0.1  $\mu\text{g.}/\text{c.c.}$ , is afforded by moistening a granule of diphenylamine with a few drops of water and gradually adding a few c.c. of concentrated sulphuric acid. The solution under investigation is mixed with an equal volume of concentrated sulphuric acid (and a drop of hydrochloric acid if chlorides are absent) and poured on to the diphenylamine solution. A distinct blue zone is observed, since the concentration of sulphuric acid favourable to the development of the colour is automatically attained at some position between the layers. The diphenylamine test depends greatly on some ill-defined property of the concentrated sulphuric acid. H. W.

**Colour Reactions of Nitrous and Nitric Acids.** L. EKKERT (*Pharm. Zentr.*, 1925, 66, 733—734).—Addition of resorcinol and concentrated hydrochloric acid to a solution of a nitrite produces an immediate saffron-yellow coloration, becoming first brownish-red and then a dark mulberry-red. After keeping for 20 mins., the solution becomes dark green if poured into an excess of sodium hydroxide; on shaking this solution with acetone, the latter becomes violet-red with a fiery-red fluorescence. If a large excess of resorcinol is used in the test and the alkali is added after 10 mins., the solution becomes blue, then green; dilution with water produces a violet colour with red fluorescence. Under the same conditions, nitrates produce only a very pale yellow coloration; on heating, however, similar colour changes to those produced by nitrites ensue, but more slowly. A. R. P.

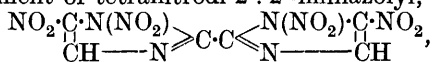
**Remarkable Behaviour of Alkali Sulphate in the Kjeldahlisation of the Nitroanilines.** B. M. MARGOSCHES and E. SCHEINOST [with M. FRISCHER] (*Ber.*, 1925, 58, [B], 2233—2237; cf. A., 1923, ii, 785).—When heated with sulphuric acid and potassium sulphate, *m*-nitroaniline alone of the three isomerides gives ammonia quantitatively. The effect of the addition of varying amounts of sodium, potassium, or lithium sulphate in the kjeldahlisation of *o*- and *p*-nitroaniline under otherwise standard conditions is described in detail. In general, the percentage of nitrogen converted into ammonia increases in an irregular manner as the quantity of alkali

sulphate increases, but lithium sulphate causes at first a diminution in the percentage converted. In no case is the theoretical value attained. Borax has approximately the same action as sodium sulphate. The behaviour of *o*-nitroacetanilide resembles that of *o*-nitroaniline; whereas *p*-nitroacetanilide and *p*-nitroaniline behave differently. Addition of mercuric oxide in the kjeldahlisation of *p*-nitroaniline in the presence of potassium sulphate causes low results, whereas accurate values are obtained by use of copper oxide (0.1—0.5 g.). Molybdic acid is more effective than vanadic, tungstic, or titanio acid in the kjeldahlisation of nitroanilines.

H. W.

### Determination of Nitroamino and Nitroimino Groups.

K. LEHMSTEDT and O. ZUMSTEIN (*Ber.*, 1925, 58, [B], 2024—2027).—Treatment of tetranitrodi-2 : 2'-iminazoly],



with boiling ferrous chloride and hydrochloric acid or with mercury and concentrated sulphuric acid causes quantitative conversion of the two *N*-nitro groups into nitric oxide, whereas the *C*-nitro groups remain unaffected. Similarly, 2-nitroaminopyridine is quantitatively reduced by ferrous chloride to nitric oxide and 2-aminopyridine; with sulphuric acid and mercury, low results for the *N*-nitro group are obtained owing to the very rapid isomerisation of the compound to the nuclear-substituted nitro-2-aminopyridine. Both methods give satisfactory results with trinitrodi-2 : 2'-iminazoly] and 5-nitro-2-nitroaminopyridine. The ferrous chloride method appears to be more generally applicable than the Lunge process, whereas the isolation of the non-volatile products is generally less difficult from the sulphuric acid solution. H. W.

### Use of Liquid Amalgams in Volumetric Analysis. III.

#### Determination of Phosphorus by Means of Lead Amalgam.

K. SOMEYA (*Z. anorg. Chem.*, 1925, 148, 58—64; cf. this vol., ii, 904).—The molybdenum in ammonium phosphomolybdate is rapidly and quantitatively reduced to the tervalent state by lead amalgam in the closed reductor previously described; by subsequently titrating with permanganate, according to the usual procedure, phosphorus may be accurately determined. The accuracy of the method was proved with pure disodium hydrogen phosphate and with a standard sample of iron. A. G.

#### Use of Phenolphthalein as an Indicator for the Determination of Phosphoric Acid by Titration of Ammonium Phosphomolybdate.

P. NYSENS (*Bull. Soc. chim. Belge*, 1925, 34, 232—236).—The errors in the titration of ammonium phosphomolybdate with potassium hydroxide, using phenolphthalein as an indicator, are due to the following causes : (1) 2 mols. of ammonium hydroxide react neutral to phenolphthalein when 0.972 mol. of sulphuric acid is added, the error, therefore, being —1.4% of the ammonia present; (2) diammonium hydrogen phosphate has an

acid reaction towards this indicator, corresponding with an error of  $-1.70\%$  of the phosphoric acid present. Both errors are therefore in the same sense, but since the 24 mols. of molybdic acid ( $\text{MoO}_3$ ) present may be titrated exactly in the presence of this indicator, the error is reduced to  $-0.13\%$ , *i.e.*, within the errors of titration, and hence the volumetric results agree with those obtained gravimetrically by the conversion of the phosphomolybdate into pyrophosphate.

J. W. B.

**Rapid Determination of Phosphates.** R. F. LE GUYON and R. M. MAY (*Bull. Soc. chim.*, 1925, [iv], **37**, 1291—1293).—The phosphate is precipitated from solution, which may contain chlorides, by silver nitrate in presence of a slight excess of sodium acetate. The precipitate is then dissolved in concentrated nitric acid and the silver content of the solution determined by titration with ammonium thiocyanate.

S. K. T.

**Ammonium Oxalate as a Reagent for Distinguishing Sodium from Potassium Salts.** J. MEYERFELD (*Z. anal. Chem.*, 1925, **67**, 150—151).—The solubility of potassium oxalate is about 40 g. and of sodium oxalate 3.2 g. per 100 c.c. of cold water, and sodium oxalate is even less soluble in a saturated solution of ammonium oxalate. Addition of the latter to a saturated solution of a sodium salt gives an immediate crystalline precipitate, whereas potassium salts have no action. The test will distinguish more than 10% of sodium in a potassium salt preparation if the dry salt mixture is added to a saturated ammonium oxalate solution.

A. R. P.

**Analysis of Lithium Minerals.** A. GUNTZ and F. BENOIT (*Bull. Soc. chim.*, 1925, [iv], **37**, 1294—1297).—The silica in lithium ores may be accurately determined by fusing with alkali, and boiling the water extract with ammonium carbonate solution. The precipitate is united with that obtained by boiling the filtrate with zinc oxide until all ammonia is expelled. The precipitates are then dissolved in hydrochloric acid and treated as usual. Calcination with calcium oxide is essential for the accurate determination of the water. Lithium is determined by treating the mineral with a mixture of sulphuric and hydrofluoric acids, calcining the residue at dull red heat, extracting with slightly ammoniacal dilute hydrogen peroxide solution, and boiling for 10 mins. After filtration, the solution is evaporated to dryness with a little ammonium oxalate, ignited, dissolved in water, and precipitated with an ammoniacal ammonium fluoride solution. Lithium fluoride separates and is weighed after ignition. When phosphates are present the first residue is dissolved in boiling, very dilute, hydrochloric acid and excess of litharge is added. The filtrate, after removal of lead as sulphate, is treated as before.

S. K. T.

**Detection of Calcium in the Presence of Barium and Strontium.** G. G. LONGINESCU and G. CHABORSKI (*Bul. Soc. Romăna Stiinte*, 1924, **27**, 9—11).—The solution of the chlorides

of the metals is treated with ammonia and ammonium carbonate and a portion of the precipitate is boiled with a 25% solution of ammonium sulphate, which converts the calcium into a soluble double sulphate, leaving the barium and most of the strontium insoluble. The filtrate is tested for calcium with ammonium oxalate. All the strontium remains insoluble if no calcium is present, so that any oxalate precipitate is a sure indication of calcium. Barium and strontium may be detected in another portion of the carbonate precipitate by means of potassium dichromate and calcium sulphate, respectively.

A. R. P.

### Electrometric Studies of the Precipitation of Hydroxides.

**I. Precipitation of Magnesium, Manganous, Ferrous, Cobalt, Nickel, and Thorium Hydroxides by Use of the Hydrogen Electrode.** H. T. S. BRITTON (*J. Chem. Soc.*, 1925, 127, 2110—2120).—The reactions between sodium hydroxide and solutions of magnesium, bivalent manganese and iron, cobalt, nickel, and thorium salts have been studied electrometrically. In every case the precipitated hydroxide contained an appreciable proportion of the acid radical. The following  $p_H$  values were required in order that precipitation might take place: magnesium, 10.61; manganese, 8.85; cobalt, 6.92; nickel, 6.81; ferrous iron, 5.77; thorium, 3.57. These values are peculiar to the various hydroxides and are independent of both the anion and the precipitant. They are only slightly influenced in dilute solutions by changes in the concentration of the metallic salts, and are shown to depend on the solubility products of the various hydroxides. The non-precipitation of magnesium and manganous hydroxides by ammonium hydroxide in the presence of ammonium salts is discussed in the light of these results.

E. E. W.

### Electrometric Studies of the Precipitation of Hydroxides.

**II. Precipitation of the Hydroxides of Zinc, Chromium, Beryllium, Aluminium, Bivalent Tin, and Zirconium by the Use of the Hydrogen Electrode, and their alleged Amphoteric Nature.** H. T. S. BRITTON (*J. Chem. Soc.*, 1925, 127, 2120—2141).—Salts of the above metals are precipitated at the following  $p_H$  values: aluminium, 4.14; beryllium, 5.69; zinc, 5.20; chromium, 5.34, and zirconium, 2.79 (opalescent at 1.86) when titrated with sodium hydroxide. The electrometric titration curves indicate that, in the case of stannous and zirconium salts, colloidal dispersed basic salts are first formed and these are coagulated on the addition of further alkali. Zirconium chloride and sulphate solutions are shown to consist of highly dispersed basic particles and free acid, and no evidence could be found for the existence of the "zirconyl" radical. New light is thrown on the nature of the characteristic soluble basic salts of beryllium, chromium, and zirconium. Among the bases studied, aluminium hydroxide is the only one which is definitely amphoteric. It shows a well-marked inflection of the titration curve corresponding with the formation of the compound  $\text{NaAlO}_2$ . The hydrogen-ion concentration at

which zinc hydroxide (actually basic sulphate) is precipitated is not in accord with existing solubility product data. Werner's view of the difference between green and violet chromic salts is rejected, the explanation preferred involving hydrolysis and a change in the chromium hydroxide probably akin to that produced by ageing.

E. E. W.

### Electrometric Studies of the Precipitation of Hydroxides.

#### III. Precipitation in the Cerite Group of Rare Earths and of Yttrium Hydroxide by Use of the Hydrogen Electrode.

H. T. S. BRITTON (*J. Chem. Soc.*, 1925, **127**, 2142—2147).—Hydrogen electrode titrations of several of rare-earth salts with sodium hydroxide show that the hydroxides (really basic salts) are precipitated when the solutions ( $0.0114M$ — $0.0133M$ ) attain the following  $p_H$  values: samarium, 6.83; yttrium, 6.78; neodymium, 7.02 (chloride), 7.00 (nitrate); praseodymium, 7.05; tervalent cerium, 7.41; lanthanum, 8.35. The precipitation  $p_H$  values thus lie below those of magnesium and manganous hydroxides and above those of zinc. The values for samarium, yttrium, neodymium, and praseodymium lie so close together that the separation of these hydroxides by fractional precipitation is not possible. The great difference between the hydrogen-ion concentration necessary for the precipitation of thorium hydroxide and those required in the case of the rare earths accounts for some of the processes which are used to effect their separation. Ammonium chloride, if present in sufficient quantity, prevents the precipitation of lanthanum and cerous hydroxides.

E. E. W.

#### Electrometric Studies of the Precipitation of the Hydroxides. IV. Precipitation of Mercuric, Cadmium, Lead, Silver, Cupric, Uronic, and Ferric Hydroxides by the Use of the Oxygen Electrode.

H. T. S. BRITTON (*J. Chem. Soc.*, 1925, **127**, 2148—2159).—The interaction between sodium hydroxide and salt solutions of certain metals has been followed by means of the oxygen electrode, the hydrogen electrode being inapplicable. The results are expressed in terms of hydrogen-ion concentrations and are believed to be accurate to within  $0.5 p_H$  unit except in the case of silver nitrate solution. The metals examined in this and previous papers are precipitated in the following order at approximately the hydrogen-ion concentrations given: magnesium,  $10^{-11}$ ; silver, bivalent manganese, lanthanum, and bivalent mercury,  $10^{-9}$ ; cerium, cobalt, nickel, cadmium, praseodymium, neodymium, and yttrium,  $10^{-8}$ ; samarium, ferrous iron (?), and lead (?),  $10^{-7}$ ; zinc, beryllium, copper, and chromium,  $10^{-6}$ ; aluminium,  $10^{-5}$ ; tervalent uranium and thorium,  $10^{-4}$ ; bivalent tin, zirconium, and ferric iron,  $10^{-3}$ . Basic precipitates, probably containing definite basic salts, were obtained from solutions of mercuric chloride, copper sulphate, cadmium sulphate, and lead nitrate. The precipitate obtained from uranium nitrate solution was the hydroxide containing a little nitrate and not sodium diuranate. The changes in colour observed on titrating both uranic and ferric salts are regarded as being due

to the presence of colloidal basic particles which are coagulated on the addition of further alkali. E. E. W.

**Determination of Small Amounts of Lead in Animal Tissues.** R. NAKASEKO and I. NAKANO (*Kyōtō Med. J.*, 1925, 22, (8)).—Organic matter is destroyed by heating with concentrated nitric acid and may afterwards be treated with concentrated sulphuric acid and mercuric oxide with additions of hydrogen peroxide, or by ignition at high temperature. The residue is dissolved in dilute acid, the lead precipitated as sulphide, re-dissolved, precipitated as chromate, and the chromate determined by liberation of iodine from iodides and titration with sodium thiosulphate. 0.005 Mg. of lead per 1 c.c. of solution may be detected by this method, phosphates in the sulphide, and chromic salts and excess of ammonium salts in the chromate interfering. Electrolytic determination of minute amounts of lead is conducted by electrolysis in a platinum vessel which itself acts as cathode. Dilute nitric acid acts as electrolyte and a current of 0.05 ampere at 0.5 volt is passed for 5–10 hrs., the lead peroxide is dissolved from the platinum wire acting as anode, and the iodine liberated from potassium iodide is titrated by means of 0.001N-sodium thiosulphate. Phosphates, magnesium, and ammonium salts interfere with the determination.

L. F. H.

**Determination of Metals Dissolved in Mercury. Rapid Method of Purifying Mercury.** A. S. RUSSELL and D. C. EVANS (*J. Chem. Soc.*, 1925, 127, 2221–2230; cf. this vol., ii, 406).—Rapid methods of determining metals in mercury and of freeing mercury from dissolved metals have been worked out on the basis of the following facts. All metals more electropositive than mercury, except cobalt, pass rapidly into solution as sulphates without the accompaniment of mercury when amalgams of them are shaken with potassium permanganate or certain other oxidising agents in dilute sulphuric acid. The point at which the last trace of the metal in the mercury has gone into solution is shown by the breaking of the surface of the mercury into bubbles. The order in which the metals pass into solution is: zinc, manganese, cadmium, thallium, tin, lead, copper, chromium and iron, bismuth and cobalt. This order is definite and independent of the oxidising agent and acid employed, but is different from that of the electrode potentials in the free state. Permanganate is reduced by all the metals mentioned except zinc and iron to the extent of 100% of the theoretical quantity. 100% efficiency is obtained with all the metals except iron when ferric sulphate is the oxidising agent.

E. E. W.

**Volumetric Determination of Mercuric Iodide, Mercuric Chloride, and Some Other Mercury Compounds.** S. ELLMAN (*Amer. J. Pharm.*, 1925, 97, 672–674).—Gravimetrically, mercuric iodide may be determined by solution in potassium iodide solution, and precipitation as sulphide with hydrogen sulphide; volumetrically, by treating this precipitate with standard iodine solution to

convert it into iodide and sulphur, and subsequent titration of the excess of iodine with thiosulphate. These methods should be carried out in neutral or slightly acid solution, and the volumetric one may be applied to mercuric chloride and various solutions of mercury salts. [Cf. *B.*, 1925, 989.] B. F.

**Volumetric Determination of Iron by Jellinek and Winoogradov's Method.** H. ASMUS (*Oesterr. Chem.-Ztg.*, 1925, **28**, 168—169; cf., *A.*, 1923, ii, 871).—For the determination of small amounts of iron by titration with thiosulphate, the solution containing the iron as ferric chloride is heated to boiling in a flask through which a current of carbon dioxide is passed and thiosulphate nearly equal to that required completely to reduce the ferric salt is added rapidly, followed by the remainder drop by drop until the blue colour of the methylene-blue-magenta indicator becomes red. A preliminary colorimetric test is made to determine the approximate amount of iron present. [Cf. *B.*, Dec. 24th.] A. R. P.

**Detection of Iron, Chromium, and Manganese without the Use of Nitric Acid.** G. G. LONGINESCU and E. PETRESCU (*Bul. Soc. Romăna Stiinte*, 1924, **27**, 13—15).—The ammonia-ammonium sulphide precipitate of group III metals is dissolved in hot 4% hydrochloric acid and the insoluble sulphides are filtered off. The filtrate is tested for iron in the usual way and then treated with 2 c.c. of saturated ferric chloride solution, followed by an excess of sodium hydroxide solution to dissolve zinc and aluminium, leaving a granular precipitate of ferrosferric hydroxide containing manganese and chromium hydroxides. The precipitate is tested for chromium and manganese by the hypochlorite method of Chaborski (*A.*, 1924, ii, 278). A. R. P.

**Separation of Iron from Mercury.** G. SPACU (*Z. anal. Chem.*, 1925, **67**, 147—150).—The dilute solution of the two metals is treated with an excess of ammonium thiocyanate, and pyridine is added slowly until the red colour changes to yellowish-brown. A further few drops of pyridine are added and the solution is heated to boiling, whereby the iron is quantitatively precipitated as ferric hydroxide. The mercury is recovered from the solution by precipitation with hydrogen sulphide. [Cf. *B.*, Dec. 24th.] A. R. P.

**Determination of Nickel as Dioxide.** L. MOSER and W. MAXYMOWICZ (*Z. anal. Chem.*, 1925, **67**, 140—142).—Vaubel's method of determining nickel as the dioxide (*A.*, 1922, ii, 875) is shown to be worthless. Calcination of nickel nitrate at 280—330° for 30 mins. yields a black powder which contains only 2.3% of peroxide oxygen, whereas nickel dioxide should contain 17.64%. A. R. P.

**Determination of Molybdenum as Trioxide after Precipitation as Trisulphide.** W. HARTMANN (*Z. anal. Chem.*, 1925, **67**, 152—155).—In order to obtain molybdenum trisulphide in a form which filters readily, the alkaline molybdate solution is treated with freshly prepared ammonium polysulphide solution and the

mixture acidified with dilute sulphuric acid. The precipitate is collected, washed, and roasted gently to obtain the trioxide, which may contain traces of ferric oxide, silica, zinc oxide, copper oxide, and vanadium pentoxide. After weighing, it is dissolved in ammonia; zinc and copper are removed from the solution by addition of colourless ammonium sulphide, and vanadium is determined by distillation of the filtrate, after expelling ammonia by boiling with sodium hydroxide, with hydrochloric acid and potassium bromide. The sum of the impurities is deducted from the weight of crude oxide. [Cf. *B.*, Dec. 24th.] A. R. P.

**Chemical Examination of Basic Eruptive Rocks.** I. A. ATHANASIU (*Bul. Soc. Romăna Stiinte*, 1924, **27**, 17—36).—Basic eruptive rocks usually contain up to 3% or sometimes more of titanium dioxide and this introduces complications in the usual analysis when the mass obtained by fusion of the rock sample with alkali carbonate is evaporated with hydrochloric acid. On this account, it is preferable to use sulphuric acid for the evaporation as the silica is thus dehydrated more efficiently, whilst the titanium remains in solution. A further advantage claimed for this method is that the barium and zirconium are eliminated with the silica as insoluble sulphates. Titanium is separated from the filtered solution by hydrolysis in the presence of sodium sulphite; in the presence of phosphoric acid, the precipitate is contaminated with this compound and the titanium must then be determined volumetrically or colorimetrically. The other constituents of the rock are determined by the usual methods in the filtrate from the titanium. A. R. P.

**Separation of Zirconium from Iron.** P. WENGER and M. MÜLLER (*Helv. Chim. Acta*, 1925, **8**, 512—513).—When a mixture of ferric and zirconium oxides is fused for 2 hrs. in an open crucible with sodium carbonate and subsequently extracted with water, ignited, and again extracted with concentrated hydrochloric acid at 100°, the separation of iron from zirconium is not quantitative as claimed by Wunder and Jeanneret (*A.*, 1912, ii, 96), since some sodium zirconate is produced (cf. *A.*, 1920, ii, 57), but with careful working the proportion of this does not exceed 0.5%, so that the method is valuable in technical analysis or where the ratio of iron to zirconium is large. G. M. B.

**Separation and Determination of Bismuth.** A. GIRARD and E. FOURNEAU (*Compt. rend.*, 1925, **181**, 610—611).—Bismuth iodide gives with tetra-acetylammonium hydroxide (and other bases) strongly coloured complexes which are readily soluble in organic solvents; this property may be used for the determination of small amounts of bismuth, e.g., in tissue. After destruction of organic matter by treatment with sulphuric and nitric acids, the residue is dissolved in a solution containing iodine, and this is shaken with a benzene solution of tetra-acetylammonium hydroxide, imparting to the benzene a deep red colour which is compared with standard colorations. In the presence of ferric salts the liberation of iodine is prevented by the addition of a reagent containing formic acid,



sodium formate, potassium iodide, and sodium sulphite. 0.0003 G. of bismuth may be characterised by this method. L. F. H.

**Reaction between Bismuth Sulphide and Hydrochloric Acid.** S. RAMACHANDRAN (*Chem. News*, 1925, **131**, 294—295).—Freshly precipitated bismuth sulphide begins to evolve hydrogen sulphide in 1:1 hydrochloric acid at 30°, and in 1:16 acid at 85°; it dissolves readily in 1:5 acid at 100°. A. R. P.

**Proof of the Formation of Gold From Mercury.** H. STAMM-REICH (*Z. anorg. Chem.*, 1925, **148**, 93—96).—The presence of gold in mercury is detected by distilling off the bulk of the mercury under reduced pressure and examining the last drop. When mercury containing metals of relatively low m. p., such as lead, bismuth, zinc, cadmium, and sodium, is distilled, a quantitative separation is obtained in one operation. The last drop remaining from the distillation of gold-containing mercury is treated with nitric acid and the dissolution observed with a microscope. A spherical crystal aggregate remains, the weight of which can be calculated from its size, and by this method  $1 \times 10^{-6}$  mg. of gold in 1 kg. of mercury can be detected. When a base metal (*e.g.*, copper or iron) has been used for one pole of the discharge, this, or its oxide, remains as a skeleton after the dissolution of the mercury; this slowly crumbles, leaving the gold as small flakes. This may be avoided by shaking the mercury with mercuric chloride or by dissolving it in aqua regia and reducing with hydrazine sulphate. When mercury is bombarded with electrons from a cathode it may contain tungsten; this is removed by shaking with sodium hydroxide solution in the presence of air. A. G.

**Spectrographic Detection of Traces of Gold.** P. JOLIBOIS and R. BOSSUET (*Bull. Soc. chim.*, 1925, [iv], **37**, 1297—1304).—The detection of traces of gold in minerals by an examination of the arc and spark spectra is described. The most suitable line in the latter case is that of wave-length 2428.1 Å. About 10<sup>-4</sup>% of gold may be detected. Solutions are treated with mercury or bismuth salts, precipitated with hydrogen sulphide and the gold detected in the precipitate; or else they may be electrolysed with bismuth cathodes, the spark spectra of which reveal the presence of any gold. Minerals are reduced, pure silver being added to increase the size of the metallic button, of which the arc spectrum is observed. A control must be performed on the litharge used in the reduction; a method is described for partly removing any gold it may contain. S. K. T.

**Complex Base of Osmium.** [Detection of Osmium.] L. TSCHUGAEV [with E. FRITZMANN].—(See i, 1395.)

**Fehling's Reagent.** G. PÉGURIER (*Ann. Chim. Analyt.*, 1925, **7**, 289—291).—The reagent, of which 10 c.c. are equivalent to 0.05 g. of dextrose, is made by mixing 45 c.c. of a solution of 150 g. of tartaric acid in 450 c.c. of water and 25 c.c. of a solution containing

52.5 g. of pure crystals of copper sulphate in 250 c.c. of water to which a few drops of concentrated sulphuric acid have been added, with enough sodium hydroxide solution (French Codex strength) to make up to 150 c.c. The mixture is stable for several months if kept in a yellow flask with paraffined rubber stopper. D. G. H.

**Detection of Pentoses in Plant Glucosides.** P. THOMAS and R. IMAS (*Compt. rend. Soc. Biol.*, **92**, 300; from *Chem. Zentr.*, 1925, **11**, 77).—By means of the reaction previously described (cf. this vol., ii, 604) pentose has been found in the hydrolysed alcoholic extract of the seeds of *Vicia angustifolia* (in agreement with von Bertrand and Weisweiller, cf. A., 1911, i, 15), but not in the seeds of *Vicia faba*, *V. sativa*, and *V. narbonensis*. A glucoside containing pentose was also found in the dried wings of the fruit of *V. angustifolia*. Primeverose gives the reaction. Investigations on convulvin, rhamnose, rhodose, and digitalin show that methyl- and ethyl-pentoses do not give the reaction in the form characteristic for pentose, nor do various glucosides such as salicin, amygdalin, etc.

A. C.

**Determination of  $\alpha$ -Cellulose.** C. G. SCHWALBE (*Papierfabr.*, 1925, **23**, 697—705; cf. this vol., ii, 720).—The usual methods for the determination of  $\alpha$ -cellulose give results which may vary by several % when carried out by different laboratories. This may be due to variations in the ordinary temperature, in the time of treatment with sodium hydroxide, and in the wetting of the fibre. The individual fibres of a sample differ in the ease with which they are wetted, and it is possible that the addition of a wetting agent, e.g., Turkey red oil, would be advantageous. Three new methods for the determination are described and have been tested in a number of laboratories, but none of them is completely satisfactory.

A. G.

**Identification of Drugs Containing Tannins.** A. H. WARE (*Pharm. J.*, 1925, **115**, 131—135).—Aromadendrin, when dissolved in 90% alcohol, zinc or magnesium and strong hydrochloric acid being added, gives a pink colour which intensifies to red, and then fades. If neutralised with alkali, the red solution becomes yellow. An extract, e.g., a kino or a cutch, is first rubbed into a paste with water, and the residue from an ethereal extract tested as above. If 5 c.c. of an aqueous extract are boiled with 10—12 drops of dilute acetic acid and 5 c.c. of 0.25% iron ammonium citrate, the liquid cooled and filtered, and 1 g. of ammonium chloride added, only pyrogallol-tannins are precipitated (from logwood, however, hæmatoxylin is precipitated). If 5 c.c. of extract are boiled with 1.5 g. of sodium dihydrogen phosphate, filtered, and the filtrate boiled with ferric citrate solution, gallotannins give a violet solution or a precipitate, ellagitannins a greenish-black precipitate, and hamamelitannins a brown solution or precipitate. If the extract is heated with a little sodium nitrite, ellagitannins give a green colour, other tannins a brown, or reddish-brown.

Extensive tables for the identification of kinos are given. B. F.

**Colour Reaction for Lactic Acid.** F. KUTTER (*Pharm. Zentr.*, 1925, **66**, 753).—The reaction described by Ekkert (this vol., ii, 1007) has been published by Brauer (A., 1920, ii, 517).

**[Determination of] Ethyl Phthalate.** III. J. A. HANDY and L. F. HOYT (*J. Amer. Pharm. Assoc.*, 1925, **14**, 219—229).—The Eilles test, employing pyrogallol, is untrustworthy, and the use of other phenols instead of pyrogallol is of no advantage. The Utz test and the Handy and Hoyt test may give positive reactions with controls; in the Andrew test, maximum fluorescence may not be produced. Dilution of an ethyl-alcoholic solution with water or 10% sulphuric acid before extraction with petroleum yields identical results, but in practice the former is preferable.

#### CHEMICAL ABSTRACTS.

**Detection and Determination of Small Amounts of Acetone.** C. BÜLOW (*Science*, 1925, **61**, 344).—The formation of acetone-2 : 4-dinitrophenylhydrazone, which is insoluble in cold water, may be used for the determination of 0.03% of acetone in urine.

A. A. E.

**Determination of Vanillin, Piperonal, and Coumarin.** L. G. RADCLIFFE and E. H. SHARPLES (*Perf. Ess. Oil Rec.*, 1924, **15**, 396—402, 437—439; 1925, **16**, 20—23, 51—54, 87—92, 156—162, 197—199, 271, 353—355, 387—390).—Many methods of determining these substances, when alone or in the presence of one another, have been examined, and are critically reviewed. A bibliography of the literature is given. The following methods are recommended: piperonal may be determined by reaction with excess of phenylhydrazine, and titration of the latter with hydrochloric acid, using methyl-orange as external indicator, the results being 100—101% of the theoretical. Piperonal-vanillin mixtures may be determined by conversion into a mixture of *p*-nitrophenylhydrazones, and extraction of the vanillin compound from ethereal solution by aqueous sodium hydroxide. Coumarin may be determined by boiling it with sodium sulphite to convert it into sodium dihydrocoumaric acid  $\beta$ -sulphonate and titrating the excess of sulphite with iodine. [Cf. B., Dec. 24th.]

B. F.

**Determination of Hydroxymethylfurfuraldehyde, and Fiehe's Reaction.** E. TROJE (*Z. Ver. Deut. Zucker-Ind.*, 1925, [828], 635—752).—Crude hydroxymethylfurfuraldehyde, obtained as a syrup by heating sucrose in an autoclave with a dilute solution of oxalic acid (cf. Middendorp, *ibid.*, 1924, [814]), is purified by distillation, in small quantities, under greatly reduced pressure (b. p. 141—142°/2 mm.). The substance crystallises in the receiver, which is cooled to about  $-8^{\circ}$ , and the crystals, after removal of adherent oil by means of a centrifuge and by pressing on a porous plate and between filter-papers, melt at  $32.3^{\circ}$ . The compound suffers partial decomposition on distillation at 2 mm. and when kept. Attempts to synthesise it by the methods of Tiemann and Reimer and of Gattermann failed owing to its instability. Like furfur-

aldehyde, however, the hydroxymethyl derivative yields a variety of coloured condensation products with phenols, amines, etc. Hydroxymethylfurfuraldehyde may be determined colorimetrically by mixing its dilute aqueous solution with 10% hydrochloric acid and a few drops of dilute ethereal resorcinol and observing the time taken for the gradually deepening red coloration to attain the intensity of specified standard solutions containing magenta and methyl-orange. This method involves a correction for temperature. A gravimetric method, in which the hydroxymethylfurfuraldehyde solution is mixed with a large excess of a solution of phloroglucinol in hydrochloric acid and the resultant phloroglucide dried and weighed, gives varying results owing to the difference in the constitution of the phloroglucide according to the method of precipitation and drying. In the titrimetric method, the aldehyde is oxidised with a measured excess of iodine in alkaline solution, and the unchanged iodine is determined, after acidification, by titration with thiosulphate (1 mg. of hydroxymethylfurfuraldehyde uses, on an average, 0.1478 c.c. of 0.1*N*-iodine). Lævulose is oxidised, under the conditions specified, beyond the formation of a monobasic acid. Fiehe's colour reaction (with resorcinol) for synthetic invert-sugar and other methods of detecting the adulteration of honey and presence of artificial honey are critically reviewed. Inversion of sucrose in the cold or with invertase yields invert-sugar containing no more, and even less, hydroxymethylfurfuraldehyde than natural honey, whereas inversion with strong acids or by heating leads to values considerably higher than those for natural honey. [Cf. *B.*, Dec. 24th.] W. T. K. B.

**Determination of Amino-acids formed by Hydrolysis of Proteins. I. Determination in Groups.** E. CHERBULIEZ and R. WAHL (*Helv. Chim. Acta*, 1925, 8, 571—582).—A new method for the proximate analysis of an amino-acid mixture is described. After hydrolysis and determination of the free ammonia by distillation with magnesia, the hexone bases and cystine are removed, as usual, with phosphotungstic acid. The remaining amino-acids are then separated as benzoylamino-acids by three successive benzoylations. The process is made more complete by evaporating the mother-liquors to recover a further small proportion of benzoylamino-acids and by determining a trace that is volatilised in this evaporation. A residue in the benzoylation which is insoluble in alkalis is shown to contain mixed anhydrides of benzoic and benzoylamino-acids. These are split at once by the action of sodium ethoxide in alcoholic solution and the acids are added to the main fraction. The nitrogen is then determined by Kjeldahl's method in each fraction. Results are quoted for an analysis of casein in which 97.45% of the nitrogen present is allocated to ammonia and amino-acids, and of ovalbumin, for which the figure is 91.35% as compared with 51% which had hitherto been accounted for. G. M. B.

**Tests for Cystine and Cysteine.** M. X. SULLIVAN (*Abstr. Bact.*, 1925, 9, 37).—Of the amino-acids, sulphur and sulphydryl

compounds examined, cysteine is the only substance that gives a red colour with sodium  $\beta$ -naphthaquinone-4-sulphonate in the presence of alkali and a reducing agent, *e.g.*, sodium sulphite. Cystine gives the reaction slowly owing to gradual reduction to cysteine. Reduction of cystine to cysteine may also be effected by sodium cyanide.

A. A. E.

**Spectrophotometric Identification of Dyes. III. Basic Violets of the Triphenylmethane Group.** W. C. HOLMES (*Ind. Eng. Chem.*, 1925, **17**, 918—919).—A spectrophotometric examination of commercial samples of methyl-violet, crystal-violet, ethyl-violet, benzyl-violet, and gentian-violet has been made with a view to their differentiation. [Cf. *B.*, 1922, 839.]

A. D.

**Highly Sensitive Physical Method for Detecting Proteins in a Solution.** P. L. DU NOUY (*Science*, 1925, **61**, 472).—A comparison of the surface tensions of a solution containing sodium oleate (1 in  $6 \times 10^5$ ) and egg-albumin (1 in  $5 \times 10^7$ ) and one containing sodium oleate alone (1 in  $6 \times 10^5$ ) shows that at these dilutions egg-albumin will prevent the lowering of the surface tension of water by sodium oleate.

A. A. E.

**Jaffe's Reaction for Creatinine. III. 2:6-Dinitrophenol.** I. GREENWALD (*J. Amer. Chem. Soc.*, 1925, **47**, 2620).—No red colour is obtained when 2:6-dinitrophenol reacts with creatinine and sodium hydroxide (cf. Greenwald and Gross, *A.*, 1924, ii, 508).

J. W. B.

**Spectrophotometric Determination of Fluorescent Substances in Solution.** R. FABRE (*Bull. Soc. chim.*, 1925, [iv], **37**, 1304—1310).—The method previously described (cf. this vol., ii, 260) is applied to the determination of quinine, quinidine, and fluorescein in solution (cf. this vol., i, 609).

S. K. T.

**Analysis of Xanthate.** W. HIRSCHKIND (*Eng. Min. J. Press*, 1925, **119**, 968—970).—Sulphide is detected with sodium nitroprusside in a 1% cold aqueous solution, and thiocarbonate by a red or brown colour of the precipitate yielded by lead acetate in a 2% solution. The available xanthate is determined in the nitrate obtained after the addition of barium chloride; in one aliquot part free alkali is determined, and in another the proportion of an added excess of acid which is not required for the liberation of unstable xanthic acid.

CHEMICAL ABSTRACTS.

**Reactions of Glycyrrhizin.** P. BERTOLO (*Giorn. Chim. Ind. Appl.*, 1925, **7**, 404—405).—Mercury, silver, and cadmium salts of glycyrrhizic acid were prepared; the last may be separated from the accompanying glycyrramin by washing with distilled water; decomposition by means of hydrogen sulphide and recrystallisation yields the pure acid. Pure glycyrrhizin gives an immediate violet coloration in presence of sulphuric acid and aromatic hydroxy-aldehydes owing to its glucosidic nature. With dextrose and sulphuric acid, or with sulphuric acid alone, the coloration appears more slowly, indicating the additional formation of phenolic substances through the action of the acid.

G. L. R.

## ERRATA.

## VOL. 126 (ABSTRACTS, 1924).

Page Line  
i, 273 26 for "KERNER" read "KIRNER."

## VOL. 128 (ABSTRACTS, 1925).

- i, 30 9\* ,, " *$\alpha$ -cyano- $\beta$ -salicylpropionic acid*" read " *$\alpha$ -cyano- $\beta$ -salicylpropionic acid*," and for " *$\alpha$ -cyano- $\beta$ -m-tolylpropionic acid*" read " *$\alpha$ -cyano- $\beta$ -m-hydroxyphenylpropionic acid*."
- i, 298 14—15 ,, "*ethyl 3-aldehydo-5-methylindole-2-carboxylate*" read "*3-aldehydo-5-methylindole-2-carboxylic acid*."
- i, 495 26 ,, "*dipropylallylammonium iodide*" read "*dipropyldiallylammonium iodide*."
- i, 510 26\* ,, "MÜLLER" read "MILLER."
- i, 743 6\* Insert author's name, "S. THURLOW."
- i, 759 7, 9, 18 and 20 for "*Mercuralis*" read "*Mercurialis*."
- i, 830 16 and 18 for "*Columba*" read "*Calumba*."
- i, 881 23 for "*Glatfield*" read "*Glatfeld*."
- i, 890 7\* ,, "N. ETSSLIN" read "H. ENSSLIN."
- i, 943 26 ,, "*hexahydrocadaline*" read "*hexahydrocadalene*."
- i, 954 15\* ,, "Nöhreu" read "Nöhren."
- i, 971 2\* ,, "*Ketonor-7-demethylo- $\psi$ -corydaline*" read "*Keto-7-demethylo- $\psi$ -corydaline*."
- i, 1010 33 ,, "*Biochem. J.*" read "*Biochem. Z.*"
- ii, 23 7\* ,, "JOUNEAUX" read "JOUNIAUX."
- ii, 59 3 ,, "GETMAN" read "GERMANN."
- ii, 65 18\* ,, "C. MÜLLER" read "E. MÜLLER."
- ii, 195 4 ,, "ADAMS" read "ADAM."
- ii, 257 5 ,, "SKOBELZYN" read "SKOBELTZYN."
- ii, 279 17 ,, "SCHENK" read "SCHENCK."
- ii, 382 1\* { for "Maximum . . . 18 hours," read "The lowering of the
- ii, 383 1, 2 { adsorptive power of silica by decreasing the water content, noted by other observers, was confirmed."
- ii, 763 10\* for "I. MASSOW" read "I. MASSON."
- ii, 888 22 ,, "*Thiosulphites*" read "*Thiosulphates*."
- ii, 936 18\* ,, "READ" read "REED."
- ii, 942 6 ,, "WEISENBERG" read "WEISSENBERG."
- ii, 1166 14 ,, "PUTTEN" read "PATTEN."

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## ERRATUM.

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Page	Line	
2997	3*	col. ii insert "[with <i>Frederick J. Corby</i> , <i>Oliver C. Elvins</i> , <i>Eveline Jones</i> , <i>Richard E. Kellett</i> , and <i>Cyril J. A. Taylor</i> ].'

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\* From bottom.